Fabrication of Functionalised Biomimetic Silica Shell – Magnetic Core Particles and Their Applications in Heavy Metal Ion and Fine Mineral Particle Recovery

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Doctor of Philosophy

in Chemical Engineering

by

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Statement of Originality

I hereby certify that the work embodied in the thesis is my own work, conducted under normal supervision.

The thesis contains published scholarly work of which I am a co-author. For each such work a written statement, endorsed by the other authors and my supervisor, attesting to my contribution to the joint work has been included at the beginning of the corresponding chapters. The thesis contains no material which has been accepted, or is being examined, for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to the final version of my thesis being made available worldwide when deposited in the University's Digital Repository, subject to the provisions of the Copyright Act 1968 and any approved embargo.

Emily Hyde

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Roberto Moreno-Atanasio

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iron particles

Abstract

In our energy conscious world, magnetic separation provides a facile, low energy technique offering low operating costs, high yield and ease of operation. For non-magnetic materials, their specific adsorption onto magnetic carrier particles allows those materials to be separated via the application of magnetic fields. Magnetic core – silica shell particles are ideally posed as magnetic carrier particles combining the magnetism offered by the core with an easily functionalised silica shell which provides adsorption selectivity. However, the fabrication of magnetic core-shell carrier particles reported in the literature often involve high temperatures, long reaction times, harsh reaction conditions and/or complex, multi-step methodologies, and, therefore, prove difficult to effectively scale up.

Biomimetic silication, utilising the branched, polyamine, polyethyleneimine (PEI), as a scaffolding/silication directing molecule, was identified as a promising avenue for silica shell fabrication. In addition, a novel facile method of silica particle synthesis (NaOH-silica synthesis), requiring only two reactants, trimethoxymethylsilane (TMOMS) and sodium hydroxide (NaOH), was developed and characterised in this work.

Functionalisation of the silica shell material is vital to achieve selective adsorption. The PEI-directed silication method, focused on in this work, introduces intrinsic amine (for PEI-silica) and amine/thiol functionalisations (for PEI-thiol silica) with the silane reactants, TMOMS and 3-mercaptopropyltrimethoxysilane (3mPTMOS), respectively. Control of the surface charge of NaOH-silica particles was achieved via the rapid electrostatic adsorption and acidic desorption of the PEI. In addition, a technique for the more permanent, covalent surface modification of the PEI-thiol silica particles utilised the thiol surface groups to covalently attach various surface modifiers to the particle surface. Successful surface modification was confirmed by Fourier transfer infrared (FTIR) spectroscopy and zeta potential measurements. The results from these studies convey rapid, reliable techniques for reversible and irreversible silica surface functionalisation.

PEI-silica particle synthesis was adapted for coating micron-sized magnetic carbonyl iron cores, to develop the magnetic core-shell carrier particles. The PEI-silica coated carbonyl iron particles were characterized via scanning electron microscopy (SEM), energy dispersive x-ray (EDX) spectroscopy and FTIR spectroscopy. Varying the fabrication method and silane concentration successfully tuned the shell characteristics. Methods using sonication produced smooth, more evenly distributed coatings with a tendency towards multicore particles. In contrast, raspberry-like coatings were produced via slow reactant addition, one- and two-pot methods. The PEI-silica coating methodology was

scaled up by factors of 10 and 50 to investigate the effect of increased reaction size on the core-shell particles produced. The scaled reactions were found to retain similar morphological features and core coverage to the small reaction size. Moreover, thiol/amine functionalised raspberry-like and smooth coatings were produced by applying the coating methods for PEI-thiol silica shell synthesis.

Utilising the PEI-silica shell - magnetic core particles as magnetic carrier particles, the adsorption at pH 6.0 and magnetic recovery of the heavy metal ion, Cu (II), was demonstrated using UV-visible spectroscopy and SEM/EDX. To determine the viability of recycling the core-shell magnetic carrier particles, acid desorption in 1 mM HCl and re-adsorption of Cu(II) was also demonstrated. The raspberry-like PEI-silica shell morphology exhibited superior performance overall, when compared with smooth shell morphology, achieving a maximum adsorption capacity of $160 \pm 10 \text{ mg Cu(II)}$ per g coreshell particles. For both PEI-silica coating morphologies, Cu(II) adsorption showed good agreement with both the Langmuir and Freundlich adsorption models.

The use of the PEI-silica shell – magnetic core carrier particles for fine particle magnetic separation was demonstrated in this study using SEM/EDX for characterisation. A large range of different target materials were investigated including fine clays (talc, montmorillonite and kaolin) and metal/metalloid oxides (quartz and TiO₂). Control over the incubation pH was observed as paramount to the successful adsorption and subsequent magnetic separation of the target fine particles. Desorption was achieved via vigorous mixing and incubation in 3.00 mM NaOH, demonstrating the potential for carrier particle reusability. PEI-thiol silica and PEI-silica coated carbonyl iron carrier particles were also used for the successful adsorption and magnetic separation of Au nanoparticles (diameter 10 ± 2 nm). The PEI-thiol silica coated particles proved slightly more effective than the PEI-silica coated particles, due to their dual amine/thiol surface functionalisation.

In conclusion, this thesis project pioneered the development of a biomimetic silica shell fabrication method for the production of functionalised magnetic core-shell carrier particles with proven applicability in the removal of heavy metal ion and fine particle species from solution.

List of Publications

A complete list of publications related to this thesis is provided below and these manuscripts have been published in peer reviewed journals and conference proceedings.

- **Hyde, E.D.E.R.**, Moreno-Atanasio, R., Neville, F. (2017). Fabrication of magnetic core PEI-silica shell particles. *Materials Research Bulletin*, *96* (3), 222-232.
- **Hyde, E.D.E.R.**, Seyfaee, A., Neville, F., Moreno-Atanasio, R. (2016). Colloidal silica particle synthesis and future industrial manufacturing pathways: a review. *Industrial & Engineering Chemistry Research*, *55* (33), 8891-8913.
- Hyde, E.D.E.R., Seyfaee, A., Moreno-Atanasio, R., Aubin, J. Neville, F. (2015, September 27-October 1). *Covalent surface modification of biomimetic silica particles*. Paper presented at the Asia Pacific Conference of Chemical Engineering Congress 2015: APPChE 2015, incorporating CHEMECA 2015 (pp 918-928), Melbourne, Australia.
- **Hyde, E.D.E.**, Moreno-Atanasio, R., Millner, P.A., Neville, F. (2015). Surface charge control through the reversible adsorption of a biomimetic polymer on silica particles. *The Journal of Physical Chemistry B, 119* (4), 1726-1735.

Other publications related to the PhD study, but not included in this thesis. These manuscripts have been published in peer reviewed journals and conference proceedings.

- Neville, F., Dixon, L., **Hyde, E.D.E.R.** (2016). A comparative study of hydrophobic silica particle synthesis. *Advances Powder Technology*, 27 (6), 2317-2323.
- Neville, F., Dixon, L., Hyde, E.D.E.R. (2015, September 27-October 1). Comparison of facile synthesis routes for hydrophobic silica particles. Paper presented at the Asia Pacific Conference of Chemical Engineering Congress 2015: APPChE 2015, incorporating CHEMECA 2015 (pp. 1699-1710), Melbourne, Australia.
- Seyfaee, A., Hyde, E.D.E.R., Aubin, J., Moreno-Atanasio, R., Neville, F. (2015, September 27-October 1). Investigation of polymeric nuclei and their role in biomimetic silication: effect of physical conditions. Paper presented at the Asia Pacific Conference of Chemical Engineering Congress 2015: APPChE 2015, incorporating CHEMECA 2015 (pp. 2081-2092), Melbourne, Australia.

Nomenclature

а	particle radius	m
A _H	Hamaker constant	J
A _λ	absorbance at a particular wavelength	-
b	path length	cm
с	concentration	М
C _e	concentration of the adsorbate at equilibrium	mg L⁻¹
C ₀	initial concentration	mg L⁻¹
Ct	concentration remaining unadsorbed in solution at	mg L⁻¹
	adsorption time t	
dB/dx	magnetic field gradient	T m ⁻¹
d _H	hydrodynamic particle diameter	m
D	translational diffusion coefficient	m ² s ⁻¹
E_{vdW}	van der Waals interaction energy	J
f(ka)	Henry's function	m kg V ⁻² s ⁻²
Fm	magnetic force on a particle	Ν
h	the shortest separation distance between particle	m
	surfaces	
Н	magnetic field strength	т
H _c	coercivity	A m ⁻¹
k	Boltzmann constant	J K ⁻¹
Ka	acid dissociation constant	mol dm ⁻³
K _f	Freundlich dimensionless empirical constant	-
K∟	Langmuir constant	L mg⁻¹
m	mass of the adsorbent	g
M_R	remanence	A m ⁻¹
Ms	saturation magnetisation	A m ⁻¹
n	Freundlich dimensionless empirical constant	-
Qe	adsorption capacity at equilibrium	mg g⁻¹
Q _m	maximum adsorption capacity	mg g⁻¹
т	temperature	К
T _B	blocking temperature	К
T _c	Currie temperature	К
UE	electrophoretic mobility	m² V ⁻¹ s ⁻¹
V	volume of adsorbate	L
Vp	volume of the particle	m³

X	a non-hydrolysable organic radical	-
У	an integer $(1 \ge y \ge 4)$	-
α	molar absorptivity coefficient	M ⁻¹ cm ⁻¹
ε ₀	vacuum permittivity	F m⁻¹
٤ _R	relative permittivity or dielectric constant of the medium	-
η	viscosity	kg s ⁻¹ m ⁻¹
μ	magnetic permeability	N A ⁻¹
σζ	electrokinetic surface charge density	mC m ⁻²
Х	magnetic susceptibility	-
Xf	magnetic susceptibility of the fluid	-
Хр	magnetic susceptibility of the particle	-
Ψζ	zeta potential	V

List of abbreviations

3mPTMOS	3-mercaptopropyltrimethoxysilane
4-ATP	4-aminothiophenol
AOT	sodium bis(2-ethylhexyl) sulfosuccinate
APTS	3-aminopropyltriethoxysilane
ASP	adsorption saturation plateau
ATR	attenuated total reflectance (crystal)
ATR-FTIR	attenuated total reflectance – Fourier transfer infrared
	(spectrometer)
BSE	backscattered electrons
C18TMS	octadecyltrimethoxysilane
СТАВ	cetyltrimethylammonium ammonium bromide
DLS	dynamic light scattering
DMT	Derjaguin-Muller-Toporov (model)
EAF	electric arc furnace
EDL	electrical double layer
EDTA	ethylenediaminetetraacetic acid
EDX	energy dispersive x-ray (spectroscopy)
FEGSEM	field emission gun scanning electron microscope
FTIR	Fourier transfer infrared (spectroscopy)
Gly-gly buffer	glycylglycine buffer
JKR	Johnson-Kendall-Roberts (model)
HGMS	high gradient magnetic separators
LCPAs	long chain polyamines
LGMS	low gradient magnetic separators
MES	2-N-morpholinoethanesulfonic acid
MUA	mercaptoundecanoic acid
NMR	nuclear magnetic resonance
OTMS	octyltrimethoxysilane
PB	phosphate buffer
PEG	polyethylene glycol
PEI	polyethylenimine
PLAr	poly-L-arginine
PLL	poly-L-lysine
PTM	post-translation modification
PZC	point of zero charge

RAFT	reversible addition-fragmentation chain transfer
SDV	silica deposition vesicle
SE	secondary electrons
SEM	scanning electron microscopy
TBOS	tetrabutoxysilane
ТЕМ	transmittance electron microscopy
TEOS	tetraethoxysilane
ТЕРА	tetraethylenepentamine
TMOS	tetramethoxysilane
TMOMS	trimethoxymethylsilane
ТО	double layered structure
ТОТ	triple layered structure
ТРМ	3-methacryloxypropyltrimethoxysilane
UV-vis	ultraviolet-visible light (spectroscopy)
VDW	van der Waals (forces)
VTMS	vinyltrimethoxysilane
W/O	water in oil (emulsion)

CHAPTER ONE

Introduction

1.1 Introduction

Biomimetic silica synthesis has carved out an enviable position as an environmentally sound alternative to other silica particle synthesis pathways currently available, as its synthesis is able to be conducted under mild reaction conditions (Lechner and Becker, 2015; Sumper and Brunner, 2006). In addition, the entrapment of biomimetic molecules, used as catalysts in the biomimetic silication process, and the selection of a silane reactant allows for silica particles to be synthesised with inbuilt functionalisations (Luckarift *et al.*, 2006; Neville *et al.*, 2009; 2013a; Rutledge and Wright, 2008), thus avoiding long, complex, multi-step post-synthesis surface modification techniques (Anbia *et al.*, 2015; Boa *et al.*, 2017; Li *et al.*, 2013a; Roto *et al.*, 2016; Wang *et al.*, 2015c; Zhang *et al.*, 2012a). More specifically, the use of the biomimetic polyamine, polyethylenimine (PEI), as a silication directing/scaffolding agent for silica particle synthesis, produces PEI-silica particles with inherent amine surface groups (Neville *et al.*, 2009; 2013a). However, despite the advantages of biomimetic silication, little work has been done to adapt biomimetic synthesis techniques for coating.

The work of this project aims to address the gap in the current literature by expanding upon the existing biomimetic silication and functionalisation techniques and adapting these processes for the fabrication of core-shell particles. A magnetic core was chosen for this project. Magnetic core-shell particles are able to be collected through the application of an external magnetic field, thus allowing the core-shell particles to be used in a multitude of applications, such as, waste management and mineral recovery (Anbia *et al.*, 2015; Boa *et al.*, 2016; 2017; Gray *et al.*, 1994; Li *et al.*, 2013a; Zhang *et al.*, 2012a). To demonstrate the applicability of the biomimetic silica shell – magnetic core particles in these fields, the core-shell particles were assessed for the removal/recovery of common ion and fine particle materials.

This chapter begins with a discussion on the significance of this research project in Section 1.2. In Section 1.3 the research objectives of this thesis project are stated. Finally, in Section 1.4 the thesis structure will be outlined in Section 1.4.

1.2 Significance of research

A global issue facing human society is that of waste management in chemical and mineral processing industries (Mahapatra *et al.*, 2015; Mahmood and Malik, 2014; Moreno-Garrido *et al.*, 2015; Tang *et al.*, 2017; Taylor *et al.*, 2010; Wongsasuluk *et al.*, 2014; Yi *et al.*, 2011). For this study, pollution from heavy metal ions and fine particle materials was identified as a particular challenge as these materials evade traditional

separation methods due to their small size, large specific surface area and/or high surface energy (Anastassakis, 1999).

Many heavy metal ions are known carcinogens and toxic agents (Boa *et al.*, 2017; Dieter *et al.*, 1999; O'Donohue *et al.*, 1999; Zhou *et al.*, 2004). Heavy metal ion pollution of aqueous environments, generally as a consequence of leaked industrial waste and/or natural events (Kumari *et al.*, 2015), thus, pose significant health and environmental risks both in Australia and internationally (Mahmood and Malik, 2014; Taylor *et al.*, 2010; Wongsasuluk *et al.*, 2014; Yi *et al.*, 2011).

On the other hand, fine particles, typically created during mineral beneficiation, can elude conventional separation techniques resulting in the inefficient recovery of valuable minerals and, ultimately, their loss in the waste stream (Jiang *et al.* 2016; Tan *et al.*, 2014; Murthy *et al.*, 2011). Moreover, fine mineral particles are typically disposed of in large tailing dams. (Tang *et al.*, 2017). Issues associated with the discarding of fines in tailing dams, include the inefficient use of land and the environmental pollution risk posed in the event of dam leakage (Tang *et al.*, 2017). Reducing the volume of suspended waste disposed of in tailing dams has, therefore, become of significant industrial and environmental interest.

A third form of waste, which has become prominent as their role in the fields of electronics and optics increases (Mehdinia *et al.*, 2014; Zhao *et al.*, 2013b), are metal nanomaterials, such as, Au nanoparticles. The increase in the amount of metal nanoparticles manufactured and, consequently, finding their way into the environment as waste, has led to concerns related to their possible toxicity for humans and the ecosystem (Meisterjahn *et al.*, 2016). In the case of Au nanoparticles, several studies have brought attention to their unintentional release into the environment and related environmental toxicity (Mahapatra *et al.*, 2015; Moreno-Garrido *et al.*, 2015).

Magnetic carrier particle technology provides a means with which to deal with the ion and fine particle waste without contributing to the waste problem as a secondary pollutant (Bao *et al.*, 2017; Raitani *et al.*, 2012). Magnetic carrier particles act through specific attachment to the waste material, allowing the target material to be separated from solution through the application of an external magnetic gradient (Bao *et al.*, 2017; Raitani *et al.*, 2012). Functionalised magnetic core – silica shell particles combine the magnetism of the core with the physical/chemical stabilising influence of the silica shell (Boa *et al.*, 2017; Laurent *et al.*, 2008) and the specificity of adsorption available through tunable surface functionalisation (Bao *et al.*, 2017; Liu *et al.*, 2013; Zhang *et al.*, 2012a). However, as current core-shell particle fabrication methods involve multiple steps, complex procedures, harsh conditions, long reaction times and/or high temperatures, their viable scale up will prove difficult (Bao *et al.*, 2017; Liu *et al.*, 2013; Wang *et al.*, 2010b; Zhang *et al.*, 2012a). The biomimetic method of core-shell magnetic carrier fabrication proposed in this thesis provides a pathway to alleviate the synthesis shortcomings of previous carrier particle systems and consequently provide a novel solution to a number of the waste management problems currently confronting society.

1.3 Research objectives

The work of this thesis forms a proof of concept study, which investigates the use of biomimetic silica synthesis technology to create functionalised silica shells for a magnetic core. Furthermore, this thesis aims to demonstrate applicability of these functionalised magnetic core – silica shell particles as magnetic carrier particles through their specific, reversible adsorption to, and magnetic separation of, target materials/ions. In order to achieve this purpose, three major objectives were identified.

The first set of studies was focused on the development of a facile method of silica synthesis and functionalisation. These studies were undertaken to facilitate the specific and reversible adsorption of target materials onto the silica surface later in the project. During this phase, a simplified alternative to biomimetic PEI-silica particle synthesis was developed and novel techniques for reversible and irreversible surface modification were pioneered.

The second set of studies focused on the investigation of how to apply the biomimetic silica method, including the methods developed during the first phase of the project, to coat the magnetic carbonyl iron particles. During this phase, keeping the reaction complexity and the use of harsh reactants/reaction conditions low during fabrication, while simultaneously maintaining optimal coating quality, was prioritised. The effect of the order of addition of reactants, mixing procedure and multiple coats were systematically considered.

The third objective of the project was to determine the effectiveness of utilising the core-shell particles developed in this study as magnetic carrier particles for the reusable recovery/removal of target materials from aqueous environments. To achieve this objective, two projects were designed. The first investigated the recovery of the heavy metal ion, Cu(II), from an aqueous solution using the core-shell particles. The

second, considered the potential use of the core-shell particles for the recovery of fine particle materials, including clays, metal/metalloid oxides and gold nanoparticles.

Taken as a whole, the meeting of these objectives resulted in the production of novel magnetic carrier core-shells particles with synthesis/functionalisation advantages compared with the current literature, and with a demonstrated efficacy in heavy metal ion and fine particle recovery applications.

1.4 Thesis structure

This thesis begins with a literature review in Chapter 2 split into multiple sections. Following a brief introduction in Section 2.1, Section 2.2 opens the chapter with a comprehensive examination and critical review of the current silica synthesis processes, including fumed silica synthesis, precipitated silica synthesis, the microemulsion method synthesis, the Stöber method synthesis and biomimetic silica synthesis. Literature methods of silica surface modification, both those relying on *in situ* (in synthesis) and post-synthesis techniques, are also thoroughly surveyed in Section 2.3. In Section 2.4, current methods of magnetic core – silica shell particle fabrication are discussed alongside a brief background on the fundamental aspects of magnetic materials. Current applications of magnetic carrier particles, including their uses in fine mineral particle recovery, heavy metal ion removal and CO₂ capture, are explored in Section 2.5.

In Chapter 3, the experimental materials and methods are outlined. The characterisation techniques and instruments utilised are also described in this section.

Chapters 4 to 8 present the results of this thesis. In Chapter 4, a novel facile method of silica particle synthesis was developed and characterised. A rapid, reversible method of post-synthesis silica surface modification was also demonstrated. This surface modification technique allowed for the surface charge of the particles to be successfully tuned.

Chapter 5 explores another method of surface modification, utilising the thiol groups on the biomimetic PEI-thiol silica particles developed in the literature. In this chapter, the formation of a covalent disulfide bond attached the thiol modifier to the silica surface. The novel surface modification method presented in this chapter, thus, acted to bypass the multi-step processes for covalent surface modification found in the literature.

Chapter 6 adapted the PEI-silica and PEI-thiol silica methods of silica particle synthesis for the fabrication of a silica shell for magnetic carbonyl iron core particles. The method

for silica shell fabrication was optimised through the examination of multiple synthesis methods and reactant concentrations. In addition, the optimised shell fabrication reactions were increased in volume by factors of 10 and 50 to demonstrate their potential for feasible scale up.

Chapter 7 investigated the use of the core-shell particles developed in Chapter 6 as magnetic carrier particles for the removal of the heavy metal ion, Cu(II), from aqueous solutions. In this study, the reusability and optimisation of Cu(II) removal using the core-shell particles was explored. Moreover, as a way to elucidate the mechanism for ion adsorption, the Cu(II) adsorption onto the core-shell particles was fitted to the Langmuir and Freundlich isotherm models.

In Chapter 8, the core-shell particles were employed as magnetic carrier particles for the recovery fine particles, including clays and metal/metalloid oxides. The adsorption process was optimised through the variation in solution pH. Desorption of the target fine particles from the core-shell particles was demonstrated via incubation in high pH and vigorous vortex mixing. The adsorption and magnetic recovery of gold nanoparticles was also demonstrated.

In the concluding chapter, Chapter 9, a summary of the key findings of this work are presented. Recommendations for future work are also presented in this chapter.

CHAPTER TWO

Literature Review

Publications:

Hyde, E.D.E.R., Seyfaee, A., Neville, F., Moreno-Atanasio, R. (2016). Colloidal silica particle synthesis and future industrial manufacturing pathways: a review. *Industrial & Engineering Chemistry Research, 55* (33), 8891-8913.

Statement of Contribution

Chapter 2

Hyde, E.D.E.R., Seyfaee, A., Neville, F., Moreno-Atanasio, R. (2016). Colloidal silica particle synthesis and future industrial manufacturing pathways: a review. *Industrial & Engineering Chemistry Research*, *55* (33), 8891-8913.

By signing below, I confirm that Research Higher Degree candidate Emily D.E.R. Hyde contributed by collaborating in design of this review article. In addition, Research Higher Degree candidate Emily D.E.R. Hyde contributed by taking primarily responsibility for preparing, drafting and editing of 64 % (by word count) of the journal publication listed above and 100 % (by word count) of the publication as included in Chapter 2 of this thesis project. Dr Ahmad Seyfaee was responsible for preparing, drafting and editing 36 % (by word count) the review study. Dr Frances Neville and Dr Roberto Moreno-Atanasio contributed by collaborating in design of the review study, and by supervision and critical review.

I thereby certificate that this statement of contribution is accurate:

Emily Hyde

.....

Ahmad Seyfaee

Frances Neville

Roberto Moreno-Atanasio

2.1 Introduction

This chapter presents a summary and critique of the literature on silica particle/shell synthesis and functionalisation, as well as, the development and uses of magnetic core-shell carrier particles.

The focus of Section 2.2 is on exploring and contrasting the major silica particle synthesis routes currently utilised industrially and/or in the research stage, with particular consideration for biomimetic synthesis techniques. Section 2.3 follows with a review of the common methods of silica surface modification presented in the literature.

Section 2.4 begins with an investigation into current methods of silica shell fabrication. This is followed by a discussion on magnetism and the forces governing the magnetic separation of the core-shell particles. The selection of the magnetic core is also discussed in this section. Common applications of magnetic core-shell particles, particularly in relation to waste management, are then explored in Section 2.5.

Finally, Section 2.6 contains a summary of this literature review. This section also aims to summarise any gaps in the current understanding or available processes identified within the body of the review.

2.2 Silica synthesis

Silica, due to its accessibility and ease of recovery, has been used extensively throughout history to manufacture glass, ceramics, and silicones (Iler, 1979). Silica also forms the basis for concrete, mortar, and sandstone and has been used widely in the construction of buildings and roadways (Oertel *et al.*, 2014; Wason, 1987). More recently, colloidal silica has factored significantly in nano- and microparticle research (Bergna, 2006). For the purposes of this literature review, colloids will be defined as possessing a size between 1 nm and 1 μ m; according to Bergna (2006), particles within this size range are large enough to retain an "individual identity" (Bergna, 2006) in solution without being overtly influenced by gravitational forces. The synthesis of colloidal silica particles will be the focus of this section of the review.

In general, research interest in colloidal silica is due partially to the large number of advantageous properties it possesses, including a relatively large surface area, low toxicity, apparent biocompatibility, well established chemistry, optical transparency, relative chemical and thermal stability, and high colloidal stability in many conditions and solvents (Guerrero-Martínez, 2010; Liberman *et al.*, 2014; Wang *et al.*, 2014d).

The possible uses of colloidal silica have been expanded even further with the advent of in situ or post-synthesis surface modification (Bagwe et al., 2006; Baig and Varma, 2014; Chen et al., 2011; Liberman et al., 2014; Mugica et al., 2016; Neville et al., 2009; Qiao et al., 2016; Xie et al., 2015; Zaravadi-Poor et al., 2011; Zhong et al., 2015) (discussed further in Section 2.3) and/or the use of silica as a coating agent for various core materials (Baig and Varma, 2014; Guerrero-Martínez, 2010; González-Ruiz et al., 2015; He et al., 2015; Knopp et al., 2009; Osei-Prempeh et al., 2015; Wang et al., 2014d; Zhang et al., 2014b) (discussed further in Section 2.4). Common commercial and potential uses of colloidal silica include utilisation as drug carriers (Bitar et al., 2012; Geszke-Moritz and Moritz, 2016; Lin et al., 2015; 20 Hao et al., 2015; Kempen et al., 2015; Rajanna et al., 2015; Tang et al., 2012; Wang et al., 2016; Yang et al., 2012), biosensor supports (Bitar et al., 2012; Choi et al., 2011; Ma et al., 2012; Wang et al., 2014c; Zhao et al., 2013a), catalyst supports (Baig and Varma, 2014; Bérubé et al., 2010; Chen et al., 2011; Chermahini et al., 2015; Jin et al., 2014; Margelefsky et al., 2008; Xie et al., 2015; Yang et al., 2012), antifouling coatings (Huang et al., 2012; Lin et al., 2016; Wu et al., 2013; Zhu et al., 2014), and additives to paints/lacquers/coatings (Jensen and Saber, 2015; Jo et al., 2014; Puig et al., 2014).

Owing to the large number of uses, it is unsurprising that colloidal silica production has become a significant industry. In 2012, commercial silica production had a market

value of approximately 3.6 billion US dollars with an estimated global production rate of 2.4 million tonnes annually (Drummond *et al.*, 2014). According to a 2014 report by The Freedonia Group (2014), global demand for specialty silica was expected to continue to increase, reaching a production rate of approximately 2.9 million tonnes per year in 2018.

For most applications, the commercial marketplace requires colloidal silica to be produced cheaply and uniformly, with an ability to tailor the properties of the product. Mineral silicas, although common, are frequently contaminated with various metal ions and therefore are not suitable for use in colloidal silica applications, such as, the scientific and industrial uses mentioned previously (Rahman and Padavettan, 2012). Mineral silicas also typically exist, with a few exceptions, in the less useful, due to the diminished surface area, and, when colloidal sized, potentially hazardous to human health, crystalline form (Jaganathan and Godin, 2012; Wason, 1987). Therefore, for most applications silica produced through various chemical synthesis methods is preferred.

A number of different synthesis routes of colloidal silica have been developed. The main colloidal silica synthesis processes, both those used commercially and those still in the research phase of development, are summarised in Figure 2.1.



 Figure 2.1. Colloidal silica production methods. Reprinted with permission from Colloidal Silica Particle Synthesis and Future Industrial Manufacturing Pathways: A Review, E. D. E. R. Hyde, A. Seyfaee, F. Neville, and R. Moreno-Atanasio, Industrial & Engineering Chemistry Research, 2016, 55 (33), 8891-8913, DOI: 10.1021/acs.iecr.6b01839. Copyright 2016 American Chemical Society. For convenience, the routes of chemical synthesis of colloidal silica, presented in Figure 2.1, are categorised by the phase of the silica feedstock, that is, gaseous and liquid routes. Within these two major categories are several distinct synthesis methods. each having advantages and disadvantages in terms of production and the properties of the final product. Reviews in the literature, have focused mainly on the research aspects of developing individual silica synthesis methods, such as, microemulsion (Guerrero-Martínez et al., 2010; Malik et al., 2012; Uskokocić and Drofenik, 2005) and biomimetic synthesis (Lechner and Becker, 2015; Patwardhan, 2011; Wang et al., 2014b), and/or specific areas of application for colloidal silica (Bitar et al., 2012; Knopp et al., 2009; Liberman et al., 2014; Rahman and Padavettan, 2011; Slowing et al., 2007). In contrast to these reviews, the literature review contained within this section, focuses on exploring and contrasting the major synthesis routes currently utilised industrially and/or being developed. In addition, as it is most relevant to this project, this section of the literature review chapter will focus on the synthesis of colloidal spherical silica. Methods specific to different morphological features, for example; gels and mesoporous silica will not factor significantly in this section. The review of Singh and co-workers (Singh et al., 2014) provides a more comprehensive discussion on mesoporous silica fabrication.

2.2.1 Gaseous silica synthesis methods

A number of gaseous synthesis methods have been developed (Ferch, 2006; Mezey, 1966); however, only two have retained commercial longevity, namely the arc silica and fumed silica methods (Ferch, 2006). Of the other gaseous methods of silica production that have been attempted over the years, none appear to have a current market share (Ferch, 2006; Mezey, 1966).

The production of arc silica involves an endothermic reaction, requiring extremely high energy inputs. Due to the amount of energy required for production, the arc silica methodology has been largely abandoned (Deutsche Forschungsgemeinschaft, 1991; Ferch, 2006; Saevarsdottir and Bakken, 2010). As of 1990 arc silicas contributed less than 1% of the silica market share (Ferch, 2006). In view of the declining popularity of the arc silica method, this section will focus on fumed silica synthesis. It is important to note that "fumed silica" should not to be confused with "silica fume", which is a non-crystalline low purity silica produced as the unintentional by-product of silicon or silicon alloy production (Ferch, 2006). Silica fume is beyond the scope of this thesis.

The following sections will discuss the methodology and chemistry of the fumed silica approach (Section 2.2.1), and the properties and applications of fumed silica (Section 2.2.2).

2.2.1.1 Fumed (pyrogenic) silica synthesis

Flame aerosol processes are one of the few colloidal synthesis methods able to cope with the large throughput required to make the process viable on an industrial scale (Ferch, 2006). With production rates of up to 25 t h⁻¹ (Pratsinis, 2006), industrial plants are still employing the flame aerosol method to manufacture fumed silica along with carbon black, pigmentary titania, and alumina (Flagan and Mori, 2006; Strobel and Pratsinis, 2007; Ulrich, 1984). The method to produce fumed silica was originally developed in the early 1940s in Germany (Klopfer, 1952; Mezey, 1966; White and Duffy, 1959), where fumed silica was designed as an alternative to the widespread tire filler, carbon black. Unfortunately, industrial confidentiality has made it difficult to obtain information about current industrial practice; however, the details of a particular plant specific set up operating in the 1960s can be found in Mezey (1966).

The fumed silica synthesis technique employs volatile liquid silicon tetrachloride as the silicon feedstock (Mezey, 1966). This silicon tetrachloride feedstock can be purchased as a by-product of the polysilicon industry and/or prepared on site through the treatment of silicon carbide at high temperatures with HCI (Figure 2.2) (Mezey, 1966; Wason, 1987; White and Duffy, 1959). As HCI is a by-product of the fumed silica reaction, HCI can easily be sourced and recycled from later in the process, as can be seen in Figure 2.2.



Figure 2.2. Schematic of an industrial fumed silica production process. Reprinted with permission from Colloidal Silica Particle Synthesis and Future Industrial Manufacturing Pathways: A Review, E. D. E. R. Hyde, A. Seyfaee, F. Neville, and R. Moreno-Atanasio, Industrial & Engineering Chemistry Research, 2016, 55 (33), 8891-8913, DOI: 10.1021/acs.iecr.6b01839. Copyright 2016 American Chemical Society.

To begin the synthesis process, silicon tetrachloride is vaporised in a hydrogen and oxygen flame (Figure 2.2) at temperatures exceeding 1000 °C (generally 1100–1800 °C) (Cabot Corporation, 2011; Evonik Industries, 2015; Wacker Chemical Corporation, 2009). The reaction proceeds via condensation polymerisation and/or oxidation of the SiCl₄ feed stock (Scheme 2.1) (Boldridge, 2010; Cabot Corporation, 2011; Evonik Industries, 2015; Wason, 1987).
Scheme 2.1. Production of SiO₂ from SiCl₄ feedstock.

$$2H_{2(g)} + O_{2(g)} + SiCl_{4(g)} \xrightarrow{>1000^{\circ}C} SiO_{2(s)} + 4HCl_{(g)}$$

The silica product forms as molten silica nuclei, which grow as the reaction continues into molten, spherical, nonporous "sub-particles" (7–40 nm diameter, 2.2 g cm⁻³ density). High temperature fusion and partial sintering of these "sub-particles" result in their agglomeration into larger, mesoporous silica aggregates with a higher specific surface area (BET, 50–380 m² g⁻¹) and wider size distribution (Boldridge, 2010; Cabot Corporation, 2011; Deutsche Forschungsgemeinschaft, 1991; Evonik Industries, 2015; Leblanc, 2010; Taikum *et al.*, 2010; Wacker Chemical Corporation, 2009; Wason, 1987). Overall, the formation reaction is exothermic, so little additional fuel is needed to keep the reaction vessel at the required temperature (Pratsinis, 1998). It is important to note that a low residence time within the flame is essential to ensure only amorphous silica is produced (Wason, 1987).

Once formed, fumed silica must be extracted from the vaporous HCI by-product (Scheme 2.1). Generally, the separation is achieved first by mechanical means, *i.e.* cyclones or filters, then through the treatment of silica with water-saturated hot air to remove adsorbed HCI (Figure 2.2) (Pratsinis, 1998; Wason, 1987). As mentioned earlier, the HCI by-product may be used as a source of chlorine to produce the silicon feedstock (*i.e.* silicon tetrachloride) and the H₂ gas resulting from the silicon tetrachloride production can be used as fuel for the hydrogen flame (Figure 2.2) (Wason, 1987; White and Duffy, 1959). A vacuum de-aeration step may follow the purification phase to increase the density of the powder for ease of transportation (Figure 2.2) (Wason, 1987).

Control of particle size, size distribution, and surface area may be achieved by varying the concentration of reactants, flame temperature, and retention time (Hurd and Flower, 1987; Mezey, 1966; Vansant *et al.*, 1995). Depending on which properties are favoured for a particular application, milling can be employed to reduce aggregates to their spherical nonporous sub-particle sizes of 7–40 nm (Figure 2.2). Additives introduced during or after the flame process may be used to alter the surface properties allowing the creation of mixed metal oxides, hydrophilic silicas, and hydrophobic silicas (Evonik Industries, 2015; Wason, 1987). Pratsinis (1998) provides a thorough overview on controlling reaction conditions and additives to achieve particular desired properties in the fumed silica product.

The fumed silica methodology makes use of the pollutant by-product of the polysilicon industry, *i.e.* silicon tetrachloride (Xiao et al., 2016). So, despite the significant environmental disadvantage of its high energy consumption, the utilisation of silicon tetrachloride as the silicon source for silica production, has ensured fumed silica synthesis has remained highly attractive silica particle production pathway. With this in mind, a number of studies (Isobe and Kaneko, 1999; Park and Park, 2008) have attempted to pioneer gaseous synthesis of silica at lower temperatures achieving mixed results in terms of product size distribution and purity. The Yan et al. (2014) synthesis method was the first to demonstrate that a silica product of high purity (99.89% SiO₂), large surface area (342 m² g⁻¹), and low polydispersity (0.221) could be produced through low-temperature gaseous phase synthesis. In the study of Yan et al. (2014) the hydrolysis of vaporised silicon tetrachloride with water vapor was carried out at the relatively low temperature of 150 °C. In addition, studies have also examined the employment of the silicon tetrachloride reactant in the liquid (sol-gel) synthesis method (Moreno et al., 2016; Rahman and Padavettan, 2012; Xiao et al., 2016). However, no studies were found examining the possibility of industrialisation of this method.

2.2.1.2 Properties and applications of fumed silica

Currently, fumed silica enjoys commercial use in many industries, as a rheological control additive, polisher, flowing aid, and even as dental-filler (Boldridge, 2010; Teoh *et al.*, 2010). In particular, the high purity (>99.8 wt. % SiO₂), low moisture content, and transparency of fumed silicas make them ideal for the production of silicone rubber for medical applications and electrical wire/cable/building insulation (Brunner and Wakili, 2014; Diao *et al.*, 2011; Taikum *et al.*, 2010). Fumed silica is used as a reinforcing agent, particularly in concrete, and is also highly valued because of its fine particle size (7–40 nm "sub-particles" after milling of the aggregates) offering a high degree of reinforcement and the ability to accelerate hydration for ultrahigh performance concrete (Oertel *et al.*, 2014; Prasertsri and Rattanasom, 2012). However, because of its high cost when compared to silica produced via commercial liquid synthesis methods (*i.e.* precipitated silica), fumed silica is rarely used in the current manufacture of tyres or mechanical rubber goods (Prasertsri and Rattanasom., 2012).

The synthesis of high purity silica is highly desirable for many applications and can be achieved through high purity reactants, complete combustion, and careful handling (Leblanc, 2010). In most cases, metallic elements (*e.g.* aluminium, calcium, zinc, etc.) in trace concentrations are the only significant contaminants (Leblanc, 2010). Because

of the lack of ionic impurities, fumed silica shows favourable dielectric properties (Leblanc, 2010) which could prove useful in electronic applications.

Dispersions of fumed silica also display excellent thixotropic (shear thinning) properties due to the relatively low number of surface silanol groups (Wagner and Brünner, 1960). In static conditions, the surface silanols increase viscosity through weak hydrogen bonding interactions with the fluid. Owing to the relatively low number of silanols available for hydrogen bonding, these interactions ease within a dynamic environment, where even the strain of a light shear force can break the connection between fluid molecules and silica (Moreland, 1978).

In recent years, the bulk of research has focused on the development of fumed silica products for modern research applications, where the preparation of nanoparticle composites with a fumed silica core have been suggested for multiple applications. These applications include acting as a conductive nanomaterial for microelectronics (AI-Hussaini *et al.*, 2013), a shielding component of transparent protective films (Zhang *et al.*, 2011a) and a support for photoluminescent compounds which are utilised as molecular detection tools (Becuwe *et al.*, 2011; 2015). Currently, however, *in situ* entrapment of biological molecules has remained unachievable due to the extreme temperatures and conditions required for pyrogenic silica synthesis.

Overall, the dry synthesis of gaseous methods means that pyrogenic silicas are completely anhydrous and in possession of a relatively low number of surface silanol groups when compared with silica synthesised via liquid methods (Wagner and Brünner, 1960). While these properties are beneficial when silica is to be used as a reinforcing filler in rubber (Diao *et al.*, 2011; Hewitt, 2007), they make it difficult to disperse pyrogenic silicas in water without the aid of wetting agents or surface modifications (Iler, 1979). Silicas produced via pyrogenic methods differ from liquid-method silicas by often possessing a higher purity and consisting of pore-free primary particles (Wagner and Brünner, 1960). However, the high energy requirements and harsh reaction conditions of pyrogenic synthesis process restrict its usefulness in the current energy and environmentally conscious society; hence, recent studies on pyrogenic silica are sparse. In contrast, liquid silica synthesis methods (Section 2.2.2) have a significantly lower energy cost.

2.2.2 Liquid silica synthesis methods

A vast number of liquid synthesis methods exist with extensive literature studies dedicated to increasing the economy and the environmental sustainability of various methods (Abarkan *et al.*, 2006; Betancor and Luckarift, 2008; Canton *et al.*, 2011; Dingsøyr and Christy, 2001; Filipović *et al.*, 2009; Mihaly *et al.*, 2014; Sierra *et al.*, 2000).

Liquid silica synthesis methods produce silica through the supersaturation and resultant polymerisation of silicic acid, Si(OH)₄, to form gel networks and discrete particles, as illustrated in Figure 2.3. Although the condensation polymerisation of silicic acid occurs at neutral pH, acidic or basic conditions increase the rate of polymerisation (Matsoukis and Gulari, 1988). Generally, acidic conditions favour the production of gels (Figure 2.3). Silicas in acidic solutions possess little or no surface charge which results in flocculation/connectivity between silica particles during acidic synthesis and, consequently, gel formation (Iler, 1979). Basic conditions give silica a highly negative surface charge, which stabilises the suspension during synthesis and facilities individual particles growth under Oswald ripening (Iler, 1979) (Figure 2.3).



Figure 2.3. Schematic of the formation of silica gels and particles during liquid synthesis from silicic acid under basic or acidic reaction conditions. Reprinted with permission from Colloidal Silica Particle Synthesis and Future Industrial Manufacturing Pathways: A Review, E. D. E. R. Hyde, A. Seyfaee, F. Neville, and R. Moreno-Atanasio, Industrial & Engineering Chemistry Research, 2016, 55 (33), 8891-8913, DOI: 10.1021/acs.iecr.6b01839. Copyright 2016 American Chemical Society.

There are a number of methods to precipitate silica gel or particles, these include precipitated silica, microemulsion (Guerrero-Martínez *et al.*, 2010; Malik *et al.*, 2012; Uskokocić and Drofenik, 2005), Stöber method (Bazula *et al.*, 2014; Bogush *et al.*, 1988; Stöber *et al.*, 1968; van Helden *et al.*, 1981), and biomimetic silica syntheses (Lechner and Becker, 2015; Patwardhan, 2011; Wang *et al.*, 2014b). The precipitated silica and Stöber methods both rely on highly basic conditions to induce particle silica formation, as per Figure 2.3. Particle formation can also be facilitated in neutral or acidic conditions by use of microemulsions or certain scaffolding/silication inducing biological or biomimetic molecules (which often become entrapped during synthesis); these factors are the basis for the microemulsion and biomimetic silica synthesis methods, respectively.

Liquid synthesis methods rely on different silica sources, for example, precipitated silicas are formed from the basic sodium silicate which is neutralised in order to form

solid silica (Drummond *et al.*, 2014). Whereas, the feedstock for the Stöber, microemulsion and biomimetic methods is generally supplied by alkoxysilanes which undergo condensation polymerisation for form silicas. The Stöber method employs ammonia to create a highly basic environment under which discrete silica particles are able to form (Stöber *et al.*, 1968). The microemulsion method confines the silica polymerisation reaction within spherical droplets. The droplets act to prevent particle interlinking/gel formation (Chang and Fogler, 1996). In the case of scaffolding/silication inducing biological or biomimetic molecules, such as, those used in the biomimetic method, the molecules generally contain amine groups that are encapsulated within the silica being formed (Neville *et al.*, 2009; 2013a). These amine groups impart the silica particles being formed with a strong positive surface charge in acidic and neutral pH, therefore, stabilising the silica sol, so particles grow individually through Oswald ripening (Iler, 1979).

2.2.2.1 Precipitated silica synthesis

Precipitated silica, formed from sodium silicate, has the largest share of the global specialty silica market (Drummond *et al.*, 2014; The Freedonia Group, 2014). The precipitated silica (or neutralisation) method is expected to maintain this position and enjoy the most rapid growth in the next decade or so (Drummond *et al.*, 2014; The Freedonia Group, 2014). A number of press releases have documented the continued expansion and development of commercial precipitated silica manufacturing over the last few years (Huber Engineered Materials, 2012; PPG Industries, 2016; Evonik Industries, 2015). However, despite indications that the precipitated silica market will continue to grow in the near future, the harsh conditions required for precipitated silica synthesis is likely to hinder the continued industrial expansion of this technology as more environmentally friendly synthesis alternatives are cultivated.

The "precipitated silica" synthesis method is based on the neutralisation of a soluble silicate with an acid. The neutralisation reaction generates a silicic acid concentration greater than the solubility limit of silica, leading to its polymerisation and precipitation out of solution (Drummond *et al.*, 2014). Commercial precipitated silica is generally produced in a batch or semi batch process from sodium silicate and sulfuric acid, as per Scheme 2.2 (Drummond *et al.*, 2014).

Scheme 2.2. Precipitated silica synthesis from the neutralisation reaction of sodium silicate and sulfuric acid.

 $Na_2O \cdot 2.6SiO_2 + H_2SO_4 \rightarrow 2.6SiO_2 + Na_2SO_4 + H_2O$

To a preheated aqueous solution of sodium silicate, sulfuric acid is added to achieve the desired pH (usually pH 8–10) (Okel, 2012). While maintaining the required pH, simultaneous, or alternating, additions of sodium sulfate and sulfuric acid are added to the mixture. To ensure the formation of discrete particles, instead of a gel, intermittent stirring is used throughout the reaction. Preheating of the mixture and control of the level of supersaturation also helps prevent gel networks from forming. After the reaction is complete, the precipitate is filtered, washed, dried, and milled to the size range appropriate for the product's application (Drummond *et al.*, 2014).

The chemical properties of the precipitated silica, such as, its porosity and average particle size, are most influenced by variations in pH, reaction temperature, reactant concentration, and stirring rate (Drummond *et al.*, 2014; Filipović *et al.*, 2009; Shapiro and Kolthoff, 1940; Sierra and Guth, 1999; Sierra *et al.*, 2000; Wason, 1987). The physical characteristics of precipitated silica are generally 30–800 m² g⁻¹ BET surface area, 2–20 nm average primary particle size, 1.9–2.1 g cm⁻³ density of primary particles, and >30 nm mean pore diameter (Brinkmann *et al.*, 2006; Vansant *et al.*, 1995). Precipitated silicas are slightly less pure than pyrogenic silicas (Section 2.1.1) having a SiO₂ content by weight of 98–99% (Chevallier and Pratt, 2002) compared with >99.8% for fumed silica (Cabot Corporation, 2011; Evonik Industries, 2015; Wason, 1987). Nevertheless, the lower energy consumption and production costs, when compared with gaseous silica processes (Section 2.2.1), results in precipitated silicas being utilised in many colloidal silica applications. The precipitated silica method, however, offers only scarce control over particle properties making it difficult to tailor the silica product for specific purposes.

The particulars of current operating procedures are difficult to obtain due to confidentiality issues (Drummond *et al.*, 2014). However, patent literature reveals that existing processes generally operate at pH 8–10 (basic conditions), have a residence time of 60 to 240 min and a reaction temperature range of 60 °C to greater than 170 °C (Chevallier and Prat, 2002; Drummond *et al.*, 2014; Esch *et al.*, 1996; Okel, 2012; Stenzel *et al.*, 2009; Wason, 1987). Ranges of reactant concentration, stirrer rate, and feed rate were not available publicly through patents. Continuous processes have been

developed (Donnet *et al.*, 1981; Hagar and Gallis, 2011), but are difficult to viably scale up because of the loss in associated yield (Drummond *et al.*, 2014).

Precipitated silicas are currently used in a wide variety of applications, which include, acting as: reinforcing agents for rubber manufacture (Idrus *et al.*, 2011; Pattanawanidchai *et al.*, 2014; Prasertsri and Rattanasom, 2012; Wason, 1987), catalytic supports (Kim *et al.*, 2004; Sun *et al.*, 2013), flow regulators (Müller *et al.*, 2008) and adsorbents (Faramawy *et al.*, 2016).

Tailoring the properties of precipitated silica for particular applications has been the subject of large number of the ongoing research studies into the precipitated silica product (Jesionowski and Krysztafkiewicz, 2001; Liu *et al.*, 2008b; Pattanawanidchai *et al.*, 2014; Rahman and Padavettan, 2012; Schaefer *et al.*, 2012; Zhang *et al.*, 2010; 2012b). Of particular interest in the literature is adapting the properties of precipitated silica in an effort to better enhance the mechanical and thermal properties of rubber products (Liu *et al.*, 2008b; Pattanawanidchai *et al.*, 2014; Schaefer *et al.*, 2012; Zhang *et al.*, 2012; Did et *al.*, 2008b; Pattanawanidchai *et al.*, 2014; Schaefer *et al.*, 2012; Zhang *et al.*, 2010; 2012b). There are also a number of recent studies aimed at expanding the uses of precipitated silica even further through surface modification for CO₂ carbon capture technology (Goeppert *et al.*, 2010; Osei-Prempeh *et al.*, 2015), catalysis and antibacterial applications (Quang *et al.*, 2011). Improving control over pore size and size distribution of precipitated silica during the synthesis and drying stages has been studied in recent years (Zhang *et al.*, 2016).

The precipitated silica method is highly cost-effective and with continued improvements, has even approached the purity obtained by the fumed silica synthesis route (Drummond *et al.*, 2014). However, ultimately methods that offer greater control over the product properties and milder reaction conditions are likely to eventually supersede the current industrial monopoly enjoyed by the precipitated silica synthesis process.

2.2.2.2 Microemulsion method synthesis

Microemulsions are thermodynamically stable dispersions of two or more immiscible phases (Guerrero-Martínez *et al.*, 2010). To decrease the interfacial energy, the dispersed phase may form spherical droplets. To stabilise these emulsions, surfactants are added which assemble at the interface of the droplets and continuous phase, forming micelles, which further lower the interfacial energy (Guerrero-Martínez *et al.*, 2010).

In the production of colloidal silica, often a surfactant-stabilised water-in-oil (W/O) microemulsion, also referred to as a reverse microemulsion, is used (Guerrero-Martínez *et al.*, 2010). By conducting the nucleation and growth of silica within the aqueous droplets, the silica product can be templated by the size and shape of the droplet. The microemulsion environment also acts to sterically stabilise the growing silica inhibiting cross-particle polymerisation (*i.e.* irreversible particle coagulation) and gel formation (Chang and Fogler, 1996). This enables the generation of much smaller silica particles than are usually able to be produced from other liquid synthesis methods (Chang and Fogler, 1996). Overall, the microemulsion method offers a large degree of control to be exercised over important properties of the synthesised silica, such as, the degree of aggregation, size, shape, particle size distribution, and porosity (Abarkan *et al.*, 2006; Mihaly *et al.*, 2014; Miyake *et al.*, 2007).

In 1978, 1–10 µm diameter silica particles were prepared by the reaction of aqueous sodium silicate and ammonium sulfate at the interface of a water-in-benzene emulsion, using a non-ionic surfactant for stabilisation (Nakahara *et al.*, 1978). Yamauchi *et al.* (1989) produced nanometer sized (14–71 nm) silica by the addition of the alkoxysilane, tetraethoxysilane (TEOS), to a W/O microemulsion of an anionic surfactant, isooctane and aqueous ammonia liquid. In a process similar to the Stöber method (to be discussed in Section 2.2.2.3), the TEOS, within the water droplets, was catalysed by ammonia to hydrolyse and polymerise into silica. Interestingly it was found that the size of the silica produced exceeded the size of the aqueous droplets (6–8 nm diameter water droplets vs 14-71 nm diameter silica particles). The authors (Yamauchi *et al.*, 1989) suggested this may be the result of adjacent droplets coalescing during the early stages of silica formation.

Osseo-Asare and Arriagada have conducted extensive work to characterise and model synthesis of silica from TEOS in W/O microemulsion systems stabilised by non-ionic surfactants (Arriagada and Osseo-Asare, 1992; 1999a; 1999b; Osseo-Asare and Arriagada, 1990; 1999). Spherical silica with a size range of 50–70 nm and a narrow size distribution (below 8.5 % standard deviation from the particle mean diameter) were produced from a system of non-ionic surfactant/ammonium hydroxide/cyclohexane (Osseo-Asare and Arriagada, 1990). The same procedure using an anionic surfactant, sodium bis(2-ethylhexyl) sulfosuccinate (AOT), was found to produce only highly polydisperse particle distributions or gels (Arriagada and Osseo-Asare, 1995).

Increasing the molar ratio of alcohol to water was demonstrated to decrease particle size from 1.5 to 0.1 µm (Esquena *et al.*, 1997). A very high or very low water-to-

surfactant molar ratio caused microemulsion instability, resulting in a bimodal size distribution or particle flocculation, respectively (Arriagada and Osseo-Asare, 1992). The diameters of synthesised silica could be further influenced by the ammonia concentration, with higher ammonia concentrations limiting the minimum achievable mean particle diameter even with increased water/surfactant ratio (Arriagada and Osseo-Asare, 1999b). An emulsion of the immiscible phases: aqueous nitric acid and TEOS, was found to produce large spherical silica particles with an average diameter of 10 µm (Kawaguchi and Ono, 1990).

Chattopadhyay and Gupta (2003) pioneered a microemulsion method which makes use of a supercritical antisolvent to synthesise nanosized silica. This method utilises supercritical CO₂ as both reactant and antisolvent with the aim of reducing the reaction time of the microemulsion process. A W/O microemulsion of aqueous sodium silicate, an oil phase of *n*-heptane or isooctane and an anionic surfactant was prepared (Chattopadhyay and Gupta, 2003). The microemulsion was then injected into the supercritical CO₂ at 35 °C, whereupon the solvent was extracted, and the exposed surface of the aqueous droplets reacted with the CO₂ producing nanosized silica within the size range of 20–800 nm depending on the reactant concentrations (Chattopadhyay and Gupta, 2003). This process has consequently been used in the development of silica coating procedures (Guo *et al.*, 2016; Thakur and Gupta, 2005) and silica–polymer composite synthesis (Wang *et al.*, 2014d).

More recent work has focused on developing pre-existing microemulsion synthesis methods for specific uses (Liu *et al.*, 2015d; Miyake *et al.*, 2007; Nooney *et al.*, 2015; Ren *et al.*, 2015). For example, a significant number of drug molecules are unstable in the highly basic conditions employed by most colloidal silica synthesis techniques (Yamauchi *et al.*, 1989). Through the addition of fluoride to the microemulsion system, the condensation of monomeric silica species proceeded within acidic conditions (as low as pH 1.07) facilitating drug molecule entrapment (Finnie *et al.*, 2007; Reetz *et al.*, 1996).

Analogous to the W/O emulsions, oil in ionic liquid microemulsions have also received some attention (Zhao *et al.*, 2008). These microemulsions have the ability to template and produce hollow silica spheres (Zhao *et al.*, 2008), which are of particular importance as molecular (*e.g.* drugs, dyes, and inks) transportation systems (Bao *et al.*, 2016a; Zhao *et al.*, 2008). Recently, uniform hollow silica spheres have also been prepared using a W/O microemulsion.

Mesoporous colloidal silica templated through microemulsions has received a great deal of research attention (Kobler *et al.*, 2008; Lv *et al.*, 2016; Ma *et al.*, 2013; Miyake *et al.*, 2007; Möller *et al.*, 2007). For example, one method of microemulsion mesoporous silica preparation utilises the hydrophobic silica source tetrabutoxysilane (TBOS), which is mechanically dispersed in a highly basic aqueous phase using a cationic surfactant, such as, cetyltrimethylammonium ammonium bromide (CTAB) (Huo *et al.*, 1997; Miyake *et al.*, 2002; 2007). As the TBOS is hydrolysed the organic dispersed phase of the microemulsion is composed of TBOS and butane, from which mesoporous silica is polymerised (Miyake *et al.*, 2007). The microemulsion synthesis method has also being adapted for the creation of core–shell particles with the silica as the shell or core depending on the application (Chung *et al.*, 2011; Fernandes *et al.*, 2013; Grasset *et al.*, 2006; Jiang *et al.*, 2012; Lian *et al.*, 2012; Nooney *et al.*, 2015; Wang *et al.*, 2011a; Zhang *et al.*, 2006; 2014b) (Section 2.4).

The microemulsion method provides significant control over particle size, morphology, and dispersity. However, the oil phase of the microemulsion method poses difficulties environmentally and for entrapment of temperature/pH – sensitive biological molecules.

2.2.2.3 Stöber method synthesis

In 1968, Stöber *et al.* (1968) developed a robust method of silica production, hereby known as the Stöber method, which allowed the controlled synthesis of spherical, monodisperse, nano- to micrometer size silica particles. The Stöber method of synthesis is based on the hydrolysis and condensation polymerisation of alkoxysilanes, detailed in Schemes 2.3 and 2.4, respectively (Matsoukas and Gulari, 1988; van Blaaderen and Kentgens, 1992).

Scheme 2.3. Hydrolysis of alkoxysilanes.

$$\begin{array}{c} | \\ -Si - OR + H_2 O \rightleftharpoons -Si - OH + ROH \\ | \\ \end{array}$$

Scheme 2.4. Condensation polymerisation of alkoxysilanes.

$$\begin{array}{c|c} I & I & I \\ -Si-OH + HO - Si- \rightleftharpoons & -Si-O - Si- + H_2O \\ I & I & I \end{array}$$

In this method, a combination of a short-chained alkanol and water is used as the medium, and the reaction is performed in the presence of the basic catalyst, ammonia (Bogush *et al.*, 1988; Stöber *et al.*, 1968). Since the invention of the Stöber method of synthesis, the reaction conditions and their effect on particle properties have been thoroughly researched (Bazula *et al.*, 2014; Bogush *et al.*, 1988; Ibrahim *et al.*, 2010; Plumeré *et al.*, 2012; van Blaaderen and Kentgens, 1992; van Helden *et al.*, 1981; Wang *et al.*, 2010b).

Stöber *et al.* (1968) demonstrated the synthesis of silica particles with mean diameters ranging between 0.05 and 2 μ m. The first step of the method involved obtaining the required concentration of dissolved ammonia within the alcoholic medium. This was achieved either by bubbling ammonia through the medium at 0 °C or by the addition of a saturated ammonium hydroxide solution to the mixture. To the reaction mixture, the alkoxysilane (commonly TEOS) was added and agitation was used throughout the reaction. Typically, clouding of the reactant mixture was observed within 1–5 min of the reaction beginning, indicating silica particle formation had started. A total reaction time of 120 min was used for all experiments (Stöber *et al.*, 1968).

The alkyl chain lengths of the alcoholic media and tetraalkoxysilane branches were systematically studied for their effect on particle size and reaction rate (Stöber *et al.*, 1968). Faster reaction rates were observed for reactions preformed in a medium of short chained alcohols, with methanol producing the fastest reaction and the slowest of the studied reactions was being performed in butanol. However, the reactions preformed in short chained alcohol media tended to produce wider particle size distributions when compared with reactions performed in alcohols with longer chain

lengths (Stöber *et al.*, 1968). A similar trend was observed when comparing the chain lengths of the tetraalkoxysilane reactant used. By increasing the alkyl-chain length of the alkoxysilane used, the condensation polymerisation reaction rate became slower and the silica produced decreased in size (Stöber *et al.*, 1968).

Van Helden *et al.* (1981) characterised Stöber silica via dynamic light scattering (DLS) and transmittance electron microscopy (TEM) demonstrating the high sphericity, low polydispersity, and large size range available through this technique.

Bogush *et al.* (1988) further developed the Stöber method by exploring the effect of temperature within the range of 9–55 °C. A distinct decrease in mean particle size was observed with increasing temperature. Higher reaction temperatures also increased the monodispersity of the silica produced. At room temperature, high concentrations of TEOS were found to produce particles with wide size distributions, however, synthesis at high temperature was found to mitigate that effect, producing silica particles with narrow size distributions even with high concentrations of TEOS.

Bogush *et al.* (1988) worked to define the reactant concentration ranges required to produce monodisperse silica. Bogush *et al.* (1988) systematically studied the effect of reagent concentrations (*i.e.* the concentration of water, ammonia, and TEOS) within the mixture on particle size and particle distribution. Keeping the TEOS concentration constant, variations in water and ammonia concentration revealed that a maximum particle size, of around 800 nm, could be obtained at a water concentration of 7 M and ammonia concentration of 2 M (Bogush *et al.*, 1988).

The van Blaaderen group (1992) studied the effect of chemical microstructure on morphology using a combination of techniques, including ²⁹Si nuclear magnetic resonance (NMR) spectroscopy, TEM, and DLS.

There have been continued efforts over recent years to further improve synthesis efficiency and control over material properties (Plumeré *et al.*, 2012; Wang *et al.*, 2010b). Wang *et al.* (2010b) examined systems with a high TEOS concentration (0.22–1.24 M) and low ammonia concentration (0.81 M) in order to produce silica particles within a 30–1000 nm size range. Ibrahim *et al.* (2010) investigated the effect of TEOS and NH₃ concentrations on the nucleation and growth processes of the Stöber synthesis. The authors (Ibrahim *et al.*, 2010) observed that increasing the TEOS or NH₃ concentration resulted in a shorter nucleation period and a faster growth rate, both increases produced silica particles with a larger average particle size. In addition, Plumeré *et al.* (2012) varied the reaction conditions (such as, reagent concentration

and temperature) in order to optimise the size, dispersity, porosity, and aggregation behaviour of Stöber silica for post-synthesis surface modification.

A number of modified Stöber synthesis methods have been developed for particular purposes (Bazula et al., 2014; Lee et al., 2007; Takeda et al., 2013), of which a few examples will be presented here. Bazula et al. (2014) produced microporous silica in an effort to improve the surface area characteristics of the silica product. In the modified method, micropores were generated in the nonporous Stöber silica after synthesis, through alternating steps of washing in water and incubation in alcohol (Bazula et al., 2014). Functionalisation of the silica surface during synthesis was possible through the co-precipitation of a traditional alkoxysilane (i.e. TEOS) with other alkoxysilanes 3-mercaptopropyltrimethoxysilane (e.g. (3mPTMOS), vinyltriethyloxysilane or 3-aminopropyltriethoxysilane). The additional alkoxysilane possessing a desired functional group alongside hydrolysable and polymerisable alkoxysilane branches (Ashik and Wan Daud, 2016; Bai et al., 2016; Barrera et al., 2016; Lee et al., 2007; Takeda et al., 2013). The co-precipitation method will be discussed further in Section 2.3.1.2. The Stöber process has also been adapted for coating purposes (Mine et al., 2003; Kobayshi et al., 2005), as will be discussed in Section 2.4.1.

In 2001, Dingsøyr and Christy (2001) determined that the ammonia catalyst used in the Stöber method of silica production could be replaced with sodium hydroxide (NaOH). The basic catalyst, whether it be a product of the NH₃/H₂O equilibrium (such as, in the original Stöber method) or directly supplied NaOH (Dingsøyr and Christy, 2001) acts by increasing the concentration of hydroxyl groups, driving the hydrolysis and condensation reactions forward, and promoting silica fabrication (van Blaaderen and Kentgens, 1992). However, both the Stöber method and Dingsøyr-Christy method require the use of harsh chemicals and an organic solvent which may become a safety and environmental concern for the commercial scale up.

Khan *et al.* (2004) successfully demonstrated the Stöber method synthesis of uniform silica colloids in laboratory-scale continuous microfluidic chemical reactors in an effort to showcase the favourable operation of microfluidic devices. Apart from this laboratory scale study, there is a considerable lack of significant literature exploring scale up of the Stöber process. It is likely that the advantages of enhanced size control and increased monodispersity afforded by the Stöber method, when compared to the leading precipitated silica production route (Section 2.2.2.1), are not enough to offset the cost of using the alkoxysilane reactant in place of the naturally abundant sodium

silicate feedstock. In addition, although the Stöber method does not require the high temperatures of the precipitated silica method the reaction still requires highly basic conditions and/or an organic solvent.

2.2.2.4 Biomimetic sol-gel synthesis

Biomimetic sol-gel synthesis methods are silication techniques inspired by the mechanisms certain biological organisms employ to create elaborate silica structures for the purposes of protection and structural stability (Morse, 1999; Simpson, 1984).

Biological silica synthesis (biosilication) in organisms, such as, diatoms and siliceous sponges, outstrips current synthetic silica production methods by possessing superior control over silica structure/patterning and the ability to rapidly produce silica in mild reaction conditions (Lechner and Becker, 2015; Sumper and Brunner, 2006). To achieve these advantages in silication, biological organisms use a number of silica-inducing biomolecules whose clever chemical structures, honed over millennia of evolution, control and promote silica formation *in vivo* (Patwardhan, 2011; Sumper and Brunner, 2006). Learning from these biomolecules and their silication mechanisms has allowed material scientists to develop new biomimetic silica synthesis methods (Lechner and Backer, 2015).

2.2.2.4.1 Biosilication

The mechanisms of biosilication (the formation of biological silica) have received significant research attention, especially those employed by diatoms and siliceous marine sponges (Brunner *et al.*, 2009; Durkin *et al.*, 2009; Kröger *et al.*, 1999; 2000; 2001; 2002; Kröger, 2007; Perry *et al.*, 2003; Poulsen *et al.*, 2003; Poulsen and Kröger, 2004; Richthammer *et al.*, 2011; Scheffel *et al.*, 2011; Sumper and Brunner, 2006; Sumper *et al.*, 2003; Wang *et al.*, 2013b; Wenzl *et al.*, 2008).

In this section, the key biomolecules and mechanism involved in their biosilication, as it is currently understood, will be discussed as a background to the *in vitro* biomimetic processes they have inspired. A number of additional biomolecules which influenced the morphology of the precipitated silica but do not possess intrinsic silication activity themselves will also be touched upon. However, a detailed discussion of the mechanistic features of these morphological molecules is outside the scope of the current review. For a more detailed discussion on morphology please see the reviews

by Lechner and Becker (2015), Lopez *et al.* (2005), Patwardhan (2011), and Sumper and Brunner (2006).

Diatoms are unicellular organisms capable of synthesising elaborate species-specific biosilica cell walls with ornate microscale structures and nanoscale patterning. Synthesis of cell walls are performed within the highly controlled acidic environment of a specialised silica deposition vesicle (SDV) (Kröger *et al.*, 2000; Poulsen *et al.*, 2013; Hildebrand *et al.*, 2009a; 2009b; Wang *et al.*, 2013b). As the SDV itself has so far eluded isolation (Kröger and Poulsen, 2008), biosilica chemical extraction techniques (Brunner *et al.*, 2009; Kröger *et al.*, 1999; 2000; 2001; 2002; Poulsen *et al.*, 2003; Poulsen and Kröger, 2004; Richthammer *et al.*, 2011; Wenzl *et al.*, 2008) and intracellular analysis of the diatom genome (Durkin *et al.*, 2009; Scheffel *et al.*, 2011) have been utilised to determine the mechanism of diatom biosilication. So far, these techniques have identified a number of organic molecules that become entrapped during synthesis and are believed to be responsible for the growth and arrangement of these intricate biological structures, including long chain polyamines (LCPAs), specialised proteins (silaffins, silacidins and cinguliums), and saccharides (*e.g.* chitin).

In vitro activity of LCPAs in physiologically relevant conditions (pH 5.5) was dependent on the presence of a multivalent anionic species (Sumper et al., 2003). A phase separation model was proposed as the mechanism of LCPA mediated silication (Sumper, 2002; Sumper and Brunner, 2006). In the proposed model, the amphiphilic character of the LCPAs and the ionic/H-bonding cross-linking role of the multivalent anionic species allowed multiple LCPA molecules to assemble into amine-anion-rich microdroplets (Knecht et al., 2005; Lutz et al., 2005; Sumper et al., 2003). In fact, the ability to form a supramolecular amine-rich microphase appears to be vital for silica precipitating activity in all soluble organic diatom biomolecules discovered so far (Kröger et al., 2000; 2002; Poulsen and Kröger, 2004; Sumper et al., 2003; Sumper, and Brunner, 2006; Wenzl et al., 2008). The role of multivalent anions is generally assumed by phosphate in *in vitro* tests (Sumper et al., 2003; Sumper, and Brunner, 2006). In vivo, the multivalent anions component is believed to be fulfilled by anionic polypeptides called silacidins (Richthammer et al., 2011; Wenzl et al., 2008), heavily phosphorylated saccharide species (Hedrich et al., 2013), and/or Type-2 silaffins (Poulsen et al., 2003; Poulsen and Kröger 2004). Once supramolecular micelles are assembled, silicic acid polymerisation is induced at the amine-rich aqueous interface of the micelle where the cationic amine groups electrostatically attract silicic acid mono/oligo-mers and uncharged amine groups act as acid-base catalyst polymerisation (Belton et al., 2008; Kröger et al., 1999; 2000; Lechner and Becker,

2015). Additionally, selection of the LCPAs within a particular diatom species appears to play a role in biosilica nanopatterning *in vivo* (Bernecker *et al.*, 2010; Sumper and Brunner, 2006; Sumper, 2002; 2004a).

Recent studies indicate that the anionic components within the medium may have a role beyond ionic cross-linking during aggregation, that is, these anionic components may assist in inducing silication (Richthammer *et al.*, 2011; Wallace *et al.*, 2009; Wang *et al.*, 2013b; 2015c). In particular, Wallace *et al.* (2009) demonstrated how an NH_3^+/COO^- -terminated surface induced silica nucleation where NH_3^+ only surfaces did not.

Silaffins (so named due to their affinity to silica) are polypeptides rich in lysine and serine residues with a high degree of post-translation modification (PTM) (Kröger, 2007; Sumper and Brunner, 2006). Unlike the LCPAs which are found ubiquitously in diatom cell walls, so far only nine silaffin proteins have been identified in two diatom species (Kröger and Poulsen, 2008; Pamirsky and Golokhvast, 2013). Of the silaffins identified, only three native silaffin proteins, silaffin-1A₁, silaffin-1A₂, and silaffin-1B (denoted Type-1 silaffins), are able to directly mediate *in vitro* formation of spherical silica in acidic conditions (Kröger, 2007; Lechner and Becker, 2015; Sumper and Kröger, 2004b).

Type-1 silaffins are believed to employ a mechanism similar to LCPAs for the mediation of silica formation (Sumper and Brunner, 2006). However, unlike LCPAs, the specialised zwitterionic structure of these silaffins allows the assembly of multimolecular aggregation (with a reported 700 molecules per aggregate) required for silication activity without anionic additives (Kröger *et al.*, 2002; Sumper and Brunner, 2006). The zwitterionic character of these silaffins is supplied through the high degree of modification made to the polypeptide backbone of the molecule, with positively charged polyamine groups attached to the lysine residues and negatively charged phosphorylation of the serine residues (Kröger *et al.*, 2002; Lechner and Becker, 2012; Sumper and Brunner, 2006).

A number of other biomolecules have been identified which do not possess the ability to precipitate silica without additional additives, including Type-2 silaffins (Kröger and Poulsen, 2008; Pamirsky and Golokhvast, 2013; Poulsen *et al.*, 2003; Poulsen and Kröger, 2004), saccharides (Brunner *et al.*, 2009; Lechner and Becker, 2015; Spinde *et al.*, 2011), and other proteins species (Lechner and Becker, 2015; Scheffel *et al.*, 2011). These biomolecules are believed to provide a cross-linking role and/or impart

some degree of morphological control on the deposited silica, which results in the elaborate nanopatterning observed *in vivo* (Lechner and Becker, 2015).

Sponges are the other major biosilica producing organism. Two classes of sponges, demosponges and hexactinellids, form needle-like silica structures, known as spicules, for defence and structural support (Shimizu *et al.*, 1998; Werner *et al.*, 2015). In both classes of sponge, the vesicles of specialised sclerocyte cells produce an axial protein filament onto which the formation and deposition of a soft gel-like biosilica is facilitated by specialised biomolecules (Shimizu *et al.*, 1998). A dehydration process follows, causing the biosilica to solidify and shrink into the characteristic spicule morphology (Wang *et al.*, 2011b; Werner *et al.*, 2015). In addition to LCPAs (detailed earlier in relation to diatoms) (Kröger, 2007; Matsunaga *et al.*, 2007), sponges possess a number of other silication specific biomolecules including the enzymatic catalysts (silicateins) and silicatein interacting proteins (silintaphins).

Silicatein (so named as they are silica proteins) isoforms have been identified in siliceous sponge species (Belikov *et al.*, 2005; Funayama *et al.*, 2005; Krasko *et al.*, 2000; Müller *et al.*, 2008; Pozzolini *et al.*, 2004; Shimizu *et al.*, 1998). *In vitro*, silicatein is able to mediate the hydrolysis and polycondensation of low concentrations of silica precursors (*e.g.* orthosilicates, TEOS) under mild reaction conditions (near neutral pH and ambient temperatures), producing soft gelatinous silica nanospheres (Cha *et al.*, 1999). However, in contrast to the previous biomolecules discussed, silicateins mediate polycondensation of silicic acid through enzymatic catalysis. A descriptive mechanism for this catalytic polymerisation has been proposed by Schröder and co-workers (Schröder *et al.*, 2012; Wang *et al.*, 2012). Moreover, silicateins are believed to self-assemble *in vivo* providing some degree of structural guidance for silica deposition (Müller *et al.*, 2007; Wang *et al.*, 2011b). This proposed role has been backed up by *in vitro* evidence (Schloßmacher *et al.*, 2011).

Two silica-interacting proteins, denoted silintaphin-1 and silintaphin-2, have been identified in spicules of *S. Domuncula* species of sponge and are believed to assist in the assembly of silicateins (Wang *et al.*, 2012). Silintaphin-1 has also been shown to significantly enhance the polymerisation ability of silicatein *in vitro* (Müller *et al.*, 2014; Schloβmacher *et al.*, 2011).

2.2.2.4.2 Biomimetic silication

Bioextracts (*i.e.* molecules obtained directly from biological sources) pose difficulties in their extraction, availability and purification, and are therefore not ideal for probing the

mechanistic features of biosilication or the manufacture silica on a large scale (Patwardhan, 2011). As discussed in the previous subsection, biomolecule extracts, such as, Type-1 silaffins, native LCPAs, and silicateins, possess silication activity *in vitro* when exposed to a silicic acid source (generally hydrolysed TEOS or tetramethoxysilane (TMOS)) under acidic/neutral pH and ambient temperatures (Cha *et al.*, 1999; Kröger *et al.*, 1999; 2000; 2001; 2002; Sumper *et al.*, 2003; Sumper and Brunner, 2006; Zhou *et al.*, 1999).

By utilising knowledge on how bioextracts promote and control silication *in vivo* and *in vitro* a number of bioextract mimics (biomimetic) molecules have been developed for synthetic silication (Neville *et al.*, 2011a; Patwardhan, 2011). These synthetic equivalents, or approximates, allow for the advantages of the biosilication to be retained while circumventing the difficulties associated with the extraction of the original biomolecules. For instance, a system of polyethylenimine (PEI) and phosphate buffer (PB) is used as a Type-1 silaffin mimic. The silaffin and PEI structures are shown in Figure 2.4. In the PEI/PB system the PEI acts to mimic the long-chained polyamine chains substituents of the silaffin molecule, while the phosphate ions in the biomimetic PEI/PB system play a similar role to the phosphorylate modifications of the silaffin molecule (Figure 2.4) (Neville *et al.*, 2011a).



Figure 2.4. (A) The chemical structure of the silaffin peptide, which contains polyaminated hydrocarbon chains. (B) The chemical structure of a similarly structured biomimetic molecule: branched, polyethyleneimine (PEI). Reprinted (adapted) with permission from Fabrication and Activity of Silicate Nanoparticles and Nanosilicate-Entrapped Enzymes Using Polyethyleneimine As a Biomimetic Polymer, F. Neville, M. J. F. Broderick, T. Gibson, and P. A. Millner, Langmuir, 2011, 27 (1), 279-285, DOI: 10.1021/la1033492. Copyright 2010 American Chemical Society.

Biomimetic molecules developed for the purpose of silicic acid polycondensation include the R5 peptide (Brott *et al.*, 2001; Knecht and Wright, 2003; Naik *et al.*, 2003; Rodriguez *et al.*, 2004) – a synthetic peptide possessing the amino acid sequence of one of the repeat units of the silaffin-1 precursor (Kröger *et al.*, 1999); various cationic polypeptides/peptides (*e.g.* poly-L-lysine (PLL), poly-L-arginine (PLAr), poly-L-ornithine) (Coradin *et al.*, 2002a; 2002b; Hu *et al.*, 2015; Krasko *et al.*, 2000; McKenna *et al.*, 2004; Patwardhan *et al.*, 2003; 2006; Tomczak *et al.*, 2005; Wang *et al.*, 2013b; 2014b; Wieneke *et al.*, 2011); co-polypeptides (Han *et al.*, 2015; Jan *et al.*, 2005); a number of synthetic polyamines (*e.g.* PEI, poly(allylamine hydrochloride), polyallylamine) (Bernecker *et al.*, 2010; Brunner *et al.*, 2002a; 2002b; Li *et al.*, 2003; Yuan *et al.*, 2005; Yuan *et al.*, 2005; Yuan *et al.*, 2006; Tomczak *et al.*, 2002; Suo2c; 2002d; Yuan and Jin, 2005; Yuan *et al.*, 2006); surfactants (Coradin *et al.*, 2002a); short-chained

alkylamines (Belton *et al.*, 2008; Noll *et al.*, 2002); and amine-terminated dendrimers (*e.g.* polypropylenimine and polyamidoamine) (Knecht and Wright, 2004; Knecht *et al.*, 2005).

Typically, an anionic counterion is required to be present for silication activity, which is believed to assist in cross-linking (Lutz *et al.*, 2005) and/or surface charge neutralisation for particle growth through aggregation (Knecht *et al.*, 2005; Neville *et al.*, 2013a). In addition, a number of silicatein mimics, including co-polypeptides (*e.g.* cysteine-lysine) (Cha *et al.*, 2000) and enzymes (lysozyme, specific members of the cathepsin L family) (Ki *et al.*, 2014; Song *et al.*, 2014) are capable of both the hydrolysis and condensation alkoxysilanes (Cha *et al.*, 2000).

Similar to in vitro experiments using biosilication molecules, the majority of these biomimetic molecules produce spherical silicas (Brunner et al., 2004; Cha et al., 2000; Han et al., 2015; Knetch and Wright, 2003; Knetch et al., 2004; 2005; Kröger et al., 1999; McKenna et al., 2004; Naik et al., 2003; Neville et al., 2013a; Noll et al., 2002; Patwardhan et al., 2002c; 2002d; 2003; Wang et al., 2014b). The biomimetic silication mechanism also generally appears reminiscent of native biosilication whereby aminerich multimolecular aggregates are formed through crosslinking with an intrinsic anionic element or separate multivalent anionic species introduced as an additive (Brunner et al., 2004; Han et al., 2015; Hu et al., 2015; McKenna et al., 2004; Yang, 2013). These assembles then act as morphological templates and silication promotors. The primary particles formed though the templating action of the biomimetic aggregates in some conditions produce larger (micrometer sized) particles through flocculation facilitated by the presence of electrolytes in solution (Lechner and Brunner, 2015). Therefore, control over product particle size and distribution can be exercised through careful selection of the chemistry and relative concentrations of the cationic and anionic components of the template, as well as, the presence of additive electrolytes which may promote flocculation (Brunner et al., 2004; Han et al., 2015; Hu et al., 2015; McKenna et al., 2004; Rodriguez et al., 2004; Yang, 2013).

Although *in vitro* silication techniques have not yet fully achieved the high degree structural control observed in biological silicas (Yi *et al.*, 2012), a number of robust techniques have been developed which are able to induce the production of a variety of nonspherical ordered silica morphologies (Brott *et al.*, 2001; Cha *et al.*, 2000; Huang *et al.*, 2014; Jin *et al.*, 2005; Naik *et al.*, 2003; Patwardhan *et al.*, 2002c; 2003; 2006; Pires *et al.*, 2014; Pouget *et al.*, 2007; Rodriguez *et al.*, 2004; Shi *et al.*, 2013; Tomczak *et al.*, 2005; Yu *et al.*, 2014; Yuan *et al.*, 2005; 2006; 2012; Wang *et al.*, 2014b; 2015c).

As an example, in basic pH, lysozyme mediated silication under sonication could be used to produce hollow silica nanospheres (Shiomi *et al.*, 2005; 2007). Hollow silica nanospheres have significant applications in drug delivery and as general molecular cargo carriers (Tan *et al.*, 2014; Zhu *et al.*, 2011). Hollow nanospheres were also synthesised through the templating effect of multimolecular assembles of block copeptides or polyamine micelles (Belton *et al.*, 2008; Bernecker *et al.*, 2010; Jan *et al.*, 2005).

As the template is entrapped during synthesis, the surface chemistry of the silica product can be tailored through selection of the anionic/cationic components of the molecular template, as will be discussed further in Section 2.3.1.3 (Hu et al., 2015). In addition, the mild reaction conditions available through biomimetic silica synthesis are also an advantage in molecular encapsulation studies. In contrast to previous silica methods (Gill and Ballesteros, 1998; 2000; Luckarift et al., 2004), biomimetic synthesis allows for the effective in situ entrapment of temperature and/or pH sensitive molecules without significant losses in activity (Chen et al., 2015; Choi et al., 2011; Cui et al., 2016; Jin and Yuan, 2007; Jo et al., 2014; Kawachi et al., 2014; Kuan et al., 2010; 2013; Lai et al., 2010; Lechner and Becker, 2012; Li et al., 2015; Luckarift et al., 2004; Marner et al., 2009; Müller et al., 2013; Neville et al., 2009; 2011a; Neville and Seyfaee, 2013b; Poulsen et al., 2007; Sheppard et al., 2012; Song et al., 2014; Zhu et al., 2013). The silica casing can act as a carrier, protector, and/or capture device for the entrapped molecule, enhancing the stability of the molecule and aiding the recovery of the molecules from solution (Jo et al., 2014; Kawachi et al., 2014; Kuan et al., 2010; Marner et al., 2009; Poulsen et all., 2007; Sheppard et al., 2012). This encapsulation technique has potential applications in a variety of fields including drug delivery, imaging, enzymatic catalysis, antifouling, and environmental clean-up (Chen et al., 2015; Forsyth et al., 2013; Hamade et al., 1998; Lechner and Becker, 2015; Luckarift et al., 2006).

2.2.2.4.3 Silica source and potential industrialisation

Many of the published biomimetic procedures utilise the alkoxysilanes, TEOS or TMOS, as the silica source. However, there are number of issues associated with these common precursors. For instance, TMOS is a toxic compound, whereas the nontoxic TEOS has a low reactivity and often requires comparatively long reaction times (Kolesar *et al.*, 1989; Müller *et al.*, 2013; Neville *et al.*, 2009). Neville *et al.* (2009; 2011a; 2013a) developed a PEI-mediated silication technique utilising acid hydrolysed

trimethoxymethylsilane (TMOMS). TMOMS is a nontoxic alkoxysilane possessing a relatively high silication activity (Neville *et al.*, 2009). This method (also known as the PEI-silica method) has been shown to produce spherical silica (Neville *et al.*, 2013a; Neville and Seyfaee, 2013b). Fabrication of silica functionalised with thiol groups is also possible using the modified Neville *et al.* (2009) synthesis method as will be discussed in Section 2.3.1.2. The nucleation/growth mechanism and reactant concentration dependence of the PEI-TMOMS silica production has been thoroughly explored through *in situ* experiments (Neville and Seyfaee, 2013b; Seyfaee *et al.*, 2014; 2015a; 2015b).

Limited effort to industrialise biomimetic processes has been made so far. In 2011, He *et al.* (2011) published a bench scale study demonstrating microfluidic synthesis of PEI-mediated silica from a hydrolysed TMOS silica source. He *et al.* (2011) reported particle size and distribution could be precisely tuned through deliberate variations in reaction conditions. It was observed that the microfluidic unit enhanced silica yield and narrowed particle distribution when compared with batch processes at the same scale (He *et al.*, 2011).

Three factors contributing to the struggle of scaling up the biomimetic methods may be the cost, availability, and toxicity of the reactants. As discussed, a significant number of synthetic biomimetic molecules have been reported on in the literature, thus the selection of the most appropriate mediator for scale up may be made easier by the shear amount of options available. However, just as important to the scale up feasibility is the selection of the silicon source, and here there is considerably less choice. None of the alkoxysilane sources currently investigated (TEOS, TMOS, or TMOMS) are able to be naturally sourced. Moreover, these alkoxysilanes do not provide an accurate model of the reactivity held by naturally available sodium silicate, which is relatively cheaply and abundantly available, and therefore the most favourable choice of silica precursor for potential industrial scale up (Coradin *et al.*, 2002a).

Biomimetically induced precipitation of sodium silicate has been reported on only a few occasions. PLL and PLAr induced the unorganised gelation of dilute sodium silicate (Coradin *et al.*, 2002b). Utilising arginine-derived surfactants as the silication-mediator, Coradin and coworkers produced an interconnected network comprising meso-to-macroporous silica from sodium silicate (Coradin *et al.*, 2002a). A silica precipitate was also obtained from a lysozyme/bovine serum albumin/sodium silicate solution at neutral pH (Coradin *et al.*, 2003).

In contrast, Annenkov *et al.* (2015) mimicked the *in vivo* concentrating effect of biological desiccating agents through increasing the gravity during synthesis (centrifugation), allowing the synthesis of a bimodal distribution of silica nanospheres from a sodium silicate and poly(acrylic acid) solution. In 2015, non-purified lysozyme sourced directly from egg shells was also found to induce the rapid precipitation of sodium silicate (Chen *et al.*, 2015). However, the morphology of the resultant silica was not reported.

Overall, biomimetic silication offers a number of advantages when compared with other silica synthesis techniques, including mild reaction conditions, an aqueous solvent, the ability to tune surface properties, and the capacity to successfully entrap and protect a number of sensitive biological molecules. Additionally, the dual templating and silication inducing nature of the biomimetic catalysts present materials scientists with an unprecedented degree of control over precipitated silica morphology and size distribution. This morphological control is clearly demonstrated by the intricate nano-and microscale structures produced by *in vivo* biosilication (Wang *et al.*, 2013b).

However, despite these favourable characteristics, demonstrating the commercial feasibility of biomimetic methods, especially in comparison to precipitated silica synthesis, still poses an obstacle to scale up. In addition, insufficient understanding of biosilication mechanisms means biomimetic methods have yet to fully realise the potential in morphological and rate control successfully demonstrated by *in vivo* biosilication.

2.2.3 Conclusions

For the majority of applications of silica, the physical and chemical attributes of the material are paramount for performance. Colloidal silica produced via different methods may possess variations in hydration, purity, the number of surface silanol groups, and porosity, which can have a significant impact on their appropriateness for particular applications. For each application, the method of silica production is chosen as a result of a trade-off between cost, environmental imprint, availability, and suitability of the silica properties. So, while one method may be appropriate for the production of silica for laboratory scale projects, another may be more appropriate for a particular commercial application.

The range of different silica properties available through different synthesis procedures is the reason multiple methods of silica production are still relevant and in use. Current synthesis techniques encompass both gaseous and liquid media. Gaseous synthesis techniques are unique in their ability to produce silica colloids of a very high purity. However, as continuous improvements bring the liquid synthesised silicas closer to achieving the same or better measures of purity, this advantage diminishes. In addition, liquid method syntheses require less energy and have a larger capacity for modifications to produce silica with application specific properties. Hence liquid synthesis methods have a greater proportion of the current scientific literature devoted to their study and improvement.

Of the liquid synthesis techniques, only precipitated silica has made the leap to commercial production as it has the lowest production costs. However, the Stöber, biomimetic sol-gel, and microemulsion methods continue to be studied in detail and used widely in the development of novel silica technologies. Most promising is the biomimetic sol-gel method which combines mild reaction conditions with a high degree of morphological control. However financial feasibility is still a major obstacle to successful scale up.

Despite the extensive research into colloidal silica synthesis, the area still requires continued scientific attention. Optimisation of current methods to increase cost effectiveness, and decrease energy and material wastage, is essential maintain to commercial techniques in the current market and launch laboratory methods into industrial scale production. Continued pioneering of novel synthesis techniques will be necessary to increase the environmental sustainability of silica production in a more environmentally conscious society and to cater to new markets for the colloidal silica product, such as, the manufacture of medicinal and catalytic supports.

2.3 Silica surface modification

Functionalisation of the silica surface through surface modification has been extensively studied in the literature, especially in an effort to increase suspension stability (Bagwe *et al.*, 2006; Jal *et al.*, 2004; Philipse and Vrij, 1989; Vansant *et al.*, 1995). Surface modification of the silica surfaces allows the stability of the silica bulk material to be coupled with the reactivity of the additional surface groups.

Common methods of silica surface modification can be broken into several categories, which are summarised in Figure 2.5.



Figure 2.5. Method of silica surface modification.

For most silica materials, the exposed surface groups are limited to siloxanes (\equiv Si-O-Si \equiv) and silanols (\equiv Si-OH) which are relatively stable (Jal *et al.*, 2004). Due to the relative inertness of silica post-synthesis, *in situ* modification techniques are very popular. By introducing modifiers, changing the silane reactant or changing the encapsulated catalyst used, silica particles/gels may be synthesised with intrinsic functionalisations. *In situ* techniques will be described in Section 2.3.1.

The stability of the silica surface means that post-synthesis modification is generally limited to one of two options:

- Post-synthesis conditioning the silica surface to allow for covalent bonds to be formed between the modifier and silica surface (discussed in Section 2.3.2.1);
- Physical adsorption of a modifier, *e.g.* by electrostatic adsorption where the modifier is positively charged and therefore adsorbs to the negatively charged silica surface at an appropriate pH (discussed in Section 2.3.2.2).

2.3.1 *In situ* methods of silica surface functionalisation

Variation in the reactants or introduction of new additives during silica synthesis may result in functionalisation of the silica surface *in situ*. As would be expected, the individual protocols are largely dependent on the method of silica synthesis and the modifying compound added. Overall three different cases of *in situ* surface functionalisation are discussed in the literature. These are summarised in Table 2.1.

Method of in situ	Synthesis	Alterations to the synthesis methods
functionalisation	methods	
Mixed metal oxides	Pyrogenic	Doping the feed with the appropriate
method	techniques (Wason, 1987)	hydrolysis
	Sol-gel (Stöber) synthesis (Akurati <i>et al.</i> , 2006; Aizawa <i>et al.</i> , 1994)	Doping the feed with the appropriate metal alkoxides before synthesis
Co-precipitation method	Biomimetic sol-gel synthesis / Sol-gel (Stöber) synthesis (Chiu <i>et al.</i> , 2014; Lee <i>et al.</i> , 2007; Meng <i>et al.</i> , 2009; Neville <i>et al.</i> 2009).	Using a functionalised alkoxysilane (<i>e.g.</i> 3mPTMOS)
Biomimetic entrapment method	Biomimetic sol-gel synthesis (Luckarift <i>et al.,</i> 2006; Neville <i>et al.,</i> 2009; Rutledge and Wright, 2008).	Silica synthesised by this method often possesses additional surface groups due to the entrapment of the scaffolding proteins/enzymes/polymers catalysts during synthesis

Table 2.1. A summary of the methods of *in situ* silica particle functionalisation and how the synthesis methods they pertain to are adapted to enact surface modification.

2.3.1.1 Mixed metal oxides method

Pyrogenic silicas (silicas synthesised by gaseous methods) are polymerised from gaseous or vaporous silane molecules in a high temperature process (Iler, 1979) (detailed discussion in Section 2.2.1). In many cases the surface properties of the pyrogenic silica are modified to improve the suitability of the silica particles for their end use. In the case of fumed silica, modifications to the surface properties of silica produced can be made by one of two methods: interaction with the silanol group (as will be discussed in Section 2.3.2) or through alteration of the flame synthesis process (Wason, 1987). As presented in Table 2.1, alteration of the flame processes generally aims to convert the pure silica particles to a mixed metal oxide by introducing various doping oxides during the flame hydrolysis process (Wason, 1987).

Similarly, the creation of mixed metal oxides via the sol-gel route involves the doping of the reactant mixture with the required metal alkoxide (compounds similar in structure to alkoxysilanes, but with the silane central Si atom replaced by the appropriate metal atom) (Akurati *et al.*, 2006). The doping metal alkoxide can then be polymerised with the alkoxysilane to produce the modified silica. Originally, some issues associated with the difference in polymerisation rates between alkoxysilanes and the doped metal alkoxides were identified (Aizawa *et al.*, 1991). However, by optimising reaction conditions (for example, conducting hydrolysis in acid conditions to synthesise TiO₂-SiO₂ particles) these problems were overcome (Miller *et al.*, 1994). A number of commercially important mixed metal oxide particles have been identified over the years (Akurati *et al.*, 2006), those of current prominence are summarised in Table 2.2 along with their advantageous properties and current/possible applications.

Table 2.2. A summary of the types of functionalised mixed metal oxide particles, their applications and the advantageous properties provided by the mixed metal oxide functionalisation for specific applications.

Mixed metal	Applications	Advantageous properties
oxides		
TiO ₂ -SiO ₂ (Akurati <i>et al.</i> , 2004; Chen <i>et al.</i> , 2012; Elia <i>et al.</i> , 2011)	Catalysis (Dagan <i>et al.</i> , 1995; Srinivasan <i>et al.</i> , 1994; Stark <i>et al.</i> , 2002)	TiO ₂ catalytic activity High thermal stability High mechanical stability High specific surface area
	Protective coatings for stainless steels (Atik and Zarzycki, 1994; Park <i>et al.,</i> 2007)	Provides protection against oxidation and chemical attack (<i>e.g.</i> from H ₂ SO ₄)
SnO ₂ -SiO ₂ (Akurati <i>et al.</i> , 2006; Cardoso <i>et</i> <i>al.</i> , 2004)	Catalysis (Xie <i>et al.</i> , 2012)	SnO ₂ catalytic activity Stability against aggregation (pure SnO ₂ particles have a tendency aggregate) High thermal stability High mechanical stability High specific surface area
	Electrochemical sensors (Canevari <i>et al.</i> , 2011; Popova <i>et al.</i> , 2004; Tricoli <i>et al.</i> , 2008; Yuan <i>et al.</i> , 2011)	SnO ₂ semiconducting properties Stability against aggregation (pure SnO ₂ particles have a tendency aggregate) High thermal stability, Increased sensitivity as a gas sensor
Al ₂ O ₃ -SiO ₂ (Chen <i>et al.</i> , 2016)	Production of aqueous dispersions in the paper, textile coatings and synthetic fibres industries (Evonik Industries, 1967)	Strong thickening properties

2.3.1.2 Co-precipitation method

The Stöber method employs the polymerisation of an alkoxysilane or silane precursor, usually TMOS or TEOS, in an ethanol/water medium with an ammonium catalyst (discussed in Section 2.2.2.3). During hydrolysis, the methoxy/ethoxy groups of TMOS/TEOS form hydroxyl groups, converting the alkoxysilane to silicic acid which then undergoes polymerisation to form silica. Although TMOS and TEOS are by far the

most common precursors, other alkoxysilanes can also be employed as reactants to achieve silica particles. Lee *et al.* (2007) pioneered a one step process whereby one alkoxy branch of the silane precursor was replaced by the desired organic surface group. These modified alkoxysilanes were hydrolysed and polymerised within an ammonium/water/ethanol system as per the traditional Stöber process and resulted in the production of monodisperse, spherical particles intrinsically modified with the desired surface groups, this known as the co-precipitation method. In Table 2.3, the different reactant alkoxysilanes tested by Lee and coworkers (2007), and the surface groups they added to the surface are summarised.

Table 2.3. A summary of the alkoxysilanes used for *in situ* co-precipitation synthesisand the surface functional groups the alkoxysilanes introduce to the silica surface (in
addition to silanol and siloxanes).

Alkoxysilane reactant	Additional surface functional	
	groups on resultant particles	
3-Mercaptopropyltrimethoxysilane (3mPTMOS)	Thiol groups (-SH)	
O SI SH		
Vinyltrimethoxysilane (VTMS)	Vinyl groups (-C=C)	
Octyltrimethoxysilane (OTMS)	Long chained alkyl groups (- C_8H_{17})	

Lee et al. (2007) demonstrated the in situ functionalisation of the silica surface with non-polar groups, including vinyl and long alkyl chain functional groups, via the co-

precipitation method (Table 2.3). These functional groups can be used to increase the hydrophobicity of the surface, preventing the wetting of the silica particles which may produce undesirable agglomeration in silica powders (Song *et al.*, 2014). The reduction of water adsorption is particularly important when silica is used in the production of rubber (Song *et al.*, 2014). Lee *et al.* (2007), also introduced thiol surface groups, via the co-precipitation of 3mPTMOS, which facilitated silica particle/surface interaction with a number of new materials, including metal ions and metal surfaces (Boa *et al.*, 2017; Neville *et al.* (2007) demonstrating the production of silica particles functionalised with various long chained alkyl groups, aromatic and cycloalkyl groups via the Stöber co-precipitation method. Other studies have used the co-precipitation method with the appropriate alkoxysilane to synthesis silica particles functionalised with polyethylene glycol (PEG) (Oh *et al.*, 2009), phenylurea (Gorbachuk *et al.*, 2011) and hexadecane (Xu *et al.*, 2011).

Neville *et al.* (2009) developed the co-functionalisation method for biomimetic synthesis to produce thiol functionalised biomimetic silica particles. Similarly, to the Lee *et al.* (2007) method, Neville *et al.* (2009) replaced the TMOMS silica precursor with 3mPTMOS. However, instead of the ammonia catalyst and ethanol/water medium used by Lee and coworkers (2007), the biomimetic co-functionalisation was performed in an aqueous medium using PEI/PB as a silication mediator. Therefore, Neville *et al.* (2009) combined the advantages of the biomimetic method, as discussed in Section 2.2.2.4, with the co-precipitation method of functionalisation.

However, not all types of functional groups are able to be attached to the silica surface via the co-precipitation method. For example, other studies (Chiu *et al.*, 2014; Meng *et al.*, 2009) have shown that the direct precipitation of 3-aminopropyltriethoxysilane (APTS), in an attempt to produce amine functionalised silica particles, is not possible using a straight forward co-precipitation approach. However, mixed co-precipitation of APTS with TEOS (Takeda *et al.*, 2013), 3mPTMOS (Chiu *et al.*, 2014) or vinyltriethoxysilane (VTMS) (Nair and Pavithran, 2009) leading to amine, thiol/amine and vinyl/amine co-functionalised silica particles, respectively, has been achieved. APTS can also be polymerised onto an existing silica surface as a post-synthesis modification (Bao *et al.*, 2016b; Tang *et al.*, 2013) (Section 2.3.1).

The co-precipitation has been employed for the synthesis of functionalised silica coatings (Ashik and Wan Daud, 2016; Bai *et al.*, 2016). For example, Ashik and Wan Daud (2016) employed Stöber method co-precipitation with the silane,

octadecyltrimethoxysilane (C18TMS), in order to produce a silica coating functionalised with long chain alkyl surface groups. This surface functionalisation acted to sterically stabilise the silica coated metal oxide nanoparticles in solution. The use of co-precipitation for coating will be more extensively discussed in Section 2.4.1.

2.3.1.3 Biomimetic entrapment method

The third case of *in situ* surface modification is a consequence of the biomimetic method of synthesis, denoted the entrapment method (Luckarift *et al.*, 2006; Neville *et al.*, 2009). Biomimetic silica synthesis methods rely on protein or biomimetic polymers scaffolds to promote silication and direct the morphology/size of the synthesised silica (Luckarift *et al.*, 2006). As these scaffolds/enzymes are entrapped within the particles during synthesis it naturally results in the scaffold/enzyme being present both within the silica and on the silica surface (Rutledge and Wright, 2008).

Although, often just a by-product of the biomimetic synthesis technique (Section 2.2.2.4), in some cases the presence of the scaffolding/enzymatic material on the surface can be a major advantage. One example of this is lysozyme, which is an enzyme used as a scaffolding catalyst for silica formation. Once entrapped as part of the synthesis process, lysozyme can also provide the silica surface with antibacterial activity (Luckarift *et al.*, 2004).

Entrapped scaffold molecules can also functionalise the surface. For example, using PEI as a scaffolding catalyst results in the precipitation of positively charged silica particles functionalised with amine groups (Neville *et al.*, 2010; 2013a). Amine functionalisation via the entrapment method is of particular significance, as amine functionalisation alone is difficult to achieve through the co-precipitation method, as discussed in Section 2.3.1.2 (Chiu *et al.*, 2014; Meng *et al.*, 2009).

Overall, the three *in situ* modification methods discussed in Section 2.3.1 are advantageous in that they do not require additional steps in order to vary surface properties. Conducting surface modifications during the synthesis period may result in a simplified process (by having only the one combined functionalisation and synthesis step instead of two separate procedures), reduce equipment costs and lessen production time (Lee *et al.*, 2007). Alternative grafting methods which use silane coupling agents (discussed in Section 2.3.2.1) are also likely to result in low surface coverage when compared with *in situ* methods of silica functionalisation due to steric repulsion during the grafting process (Lee *et al.*, 2007).

On the other hand, the amount of the modifying chemical required may be increased when employing *in situ* methods due to the modifying species being found within the bulk of silica as well as on the silica surface. This excess of material may pose a significant cost increase when using expensive modifying compounds. *In situ* techniques are also constrained by the method of silica synthesis chosen. Depending on the required surface groups, it may be impossible to achieve the required modification with an *in situ* surface modification method, as the required modifying compound may prevent the hydrolysis/polymerisation of silica under the conditions of the synthesis method chosen.

2.3.2 Post-synthesis methods of surface modification

2.3.2.1 Modification via covalent attachment

One form of post-synthesis surface modification is via covalent attachment of the modified group (modifier). Chemical bonding through covalent attachment of surface modifier offers an irreversible mode of attachment (Jal *et al.*, 2004). Whether this lack of reversibility is an advantage or disadvantage depends largely on the application.

The relative chemical inertness of silica makes covalent attachment difficult. Due to this, covalent attachment to the silica surface generally requires surface activation or specific modifying functional groups (Jal *et al.*, 2004). Cassidy and Yager's (1971) extensive review on the origins of silica surface modification concluded that the most common form of silica surface modification is through the use of a covalent siloxane linkage mechanism. The covalent siloxane mechanism employs a silane coupling agent of the general formula $X_{(4-y)}$ Si (OR)_y where OR groups are alkoxy branches with the ability to undergo hydrolysis, X is a non-hydrolysable organic radical and y is an integer $1 \ge y \ge 4$ (Philipse and Vrij, 1989). Upon acid or base hydrolysis, where the OR groups are converted to silanols, the silane coupling agent will undergo a condensation polymerisation with the exposed silanol groups on the surface of silica. The covalently bonded coupling agent then allows the reaction between an organic group and the surface organic radical, X (Philipse and Vrij, 1989). Through this organic radical, the covalent siloxane linkage mechanism provides a robust method to adhere organic materials to the silica surface.

The use of alkoxysilanes with the required surface modifying group already attached in the *X* position to modify the silica surface in one step is also popular (Bigui *et al.*, 2013; Hernández *et al.*, 2004; Jal *et al.*, 2004; Lin *et al.*, 2001). A specific example of this

method is the work of Hernández *et al.* (2004) where 3mPTMOS was reacted with silica particles made via the sol-gel route within an alcohol/aqueous medium. The result was thiol modified particles with the ability to adsorb metal ions in solution.

However, for bulky or long X groups (e.g. OTMS), this one step alkoxysilane modifying technique resulted in low coverage, due to the steric hindrance of the X branch of the alkoxysilane (Jal et al., 2004). In these cases, it is more efficient to covalently bond the relatively small silane coupling agent to the silica surface and build the required surface groups on the exposed X groups via a single- or multi-step reaction (Jal et al., 2004). For example, literature studies (Li and Benicewicz, 2005; 2008; Ma et al., 2014) have focused on combining the silane coupling agents with a reversible additionfragmentation chain transfer (RAFT) agent in the interest of covalently anchoring polymers to the silica surface. Here the silane coupling agent was modified to convert the X group to a RAFT agent. Once attached, the RAFT agent is able to initiate the polymerisation of monomers directly onto pre-prepared silica surface (Li and Benicewicz, 2005). This 'graft from' approach of polymer attachment vastly improves upon the 'graft to' approach, which requires alkoxysilanes with X groups of fully formed polymers to approach and attach to the surface. The 'graft to' technique results in relatively low coverage due to the steric hindrance provided by previously attached chains (Ma et al., 2014).

Despite the large body of work in this area (Bigui *et al.*, 2013; Hernández *et al.*, 2004; Jal *et al.*, 2004; Lin *et al.*, 2001; Ma *et al.*, 2014), little literature focuses on the postsynthesis covalent modification of biomimetic silica particles. As biomimetic synthesis techniques often encapsulate the scaffolding catalyst resulting in other surface groups being present in addition to the silanol (Section 2.3.1.3), the effectiveness of the traditional covalent modification techniques may require reassessment for biomimetic silicas.

2.3.2.2 Modification via physical adsorption

The second method of post-synthesis modification is physical adsorption. Silica surfaces are generally negatively charged (at pH above the pK_a) and hydrophilic due to the presence of silanol and siloxane surface groups (Jal *et al.*, 2004). Physical forces, such as, electrostatic, van der Waals, hydrogen bonding or hydrophilic-hydrophobic equilibrium forces, allow molecules to be attracted to, or repelled, from the silica surface (Siwińska-Stefańska *et al.*, 2008). One of the strongest forms of physical

adsorption is driven by the electrostatic forces of oppositely charged surfaces and molecules, which causes electrostatic adsorption (Siwińska-Stefańska *et al.*, 2008).

Electrostatic adsorption of surface modifiers onto a surface is a reversible process that allows the modifying agent to be attached and stripped from the surface by simple changes in the solution pH or salt concentration. As discussed in Section 2.3, whether the reversibility of this form of surface modification is an advantage or not is dependent on the application. Many cationic compounds have been attached to the silica surface via this mechanism, including natural latex polymer (Siwińska-Stefańska *et al.*, 2008), amine surfaces (Li *et al.*, 2013b) and PEI (Lindquist and Stratton, 1976). The most relevant to this thesis is PEI adsorption and, as such, PEI adsorption will be the focus of the rest of Section 2.3.2.

Polyethyleneimine (PEI) is a synthetic cationic polymer and has been used successfully in the past to modify silica surfaces (Bharali *et al.*, 2005; Figeys and Aebersold, 1997; Erim *et al.*, 1995; Lindquist and Stratton, 1976; Mészáros *et al.*, 2002; Towns and Regnier, 1990; Xia *et al.*, 2009). However, a direct and comprehensive study of the surface charge shifts caused by PEI modification of silica particles had not been published prior to the work in this thesis (Chapter 4).

Lindquist and Stratton (1976) adsorbed PEI polymers onto Ludox AM colloidal silica particles to investigate the stabilising effect of PEI adsorption. The complex formed between the remaining PEI in the supernatant and the cupric ion was used to spectroscopically determine the amount of PEI adsorbed on silica colloidal particles (Kindler and Swanson, 1971). In Lindquist and Stratton's (1976) study, the effect of variations in PEI molecular weights, salt concentration and pH during incubation, on the amount of PEI adsorbed was investigated. The amount of PEI adsorbed by weight decreased only slightly with increased molecular weight of the PEI molecule suggesting the configuration of adsorbed PEI on the surface was mostly flat, but with some segments extended into solution. At low pH, more tertiary amine groups on the PEI molecule are ionised leading to greater steric repulsion between PEI branches. Thus, at low pH the PEI molecule size is larger than at high pH resulting in a smaller amount of PEI adsorption on the silica surface. High salt concentration (0.10 M NaCl), during PEI adsorption was found to somewhat negate the sizing effect by screening the charge between ionised PEI branches. However, even with a high salt concentration, the PEI adsorption was still dependent on pH (Lindquist and Stratton, 1976).

PEI adsorption has been successfully employed to neutralise the negative surface charge of the silica surface in silica lined capillaries to improve the performance of

capillary electrophoresis analysis of proteins (Erim *et al.*, 1995; Figeys and Aebersold, 1997; Towns and Regnier, 1990). Work by Erim *et al.* (1995) and Towns and Regnier (1990) investigated the electrostatic adsorption of PEI polymer onto the internal silica surface of the capillary. In both studies, a similar procedure was used, involving the activation of the silica surface by pre-flushing the capillary with a basic sodium hydroxide solution, followed by incubation of the PEI solution within the capillary for one hour, before repeated flushing with water (Erim *et al.*, 1995; Towns and Regnier, 1990). Erim *et al.* (1995) found the PEI capillary coating to be stable for a pH range of 3-11. Figeys and Aebersold (1997), on the other hand, used two different types of silane coupling agent followed by crosslinking to covalently attach the PEI to the interior silica surface of the capillary. After cross-linking, the PEI coating was observed to remain stable at neutral pH for at least a month; however, Figeys and Aebersold, (1997) did not report on the effect of changing the solution pH on the PEI coating's stability.

Silica or silica coated nanoparticles have enjoyed widespread success as drug delivery agents mainly due to their low toxicity and potential biodegradability (Borm et al., 2006; Finnie et al., 2009; Xia et al., 2009). One major obstacle for effective drug delivery via inorganic nanoparticle carriers is the ability for the carriers to pass through cell barriers. Drug delivery systems produced using a silica support process the flexibility of the silica surface chemistry which allows the surface modified with different functionalities depending on their target cell or tissue (Bharali et al., 2005; Bonoiu et al., 2009; Ghosh et al., 2008; McBain et al., 2007; Xia et al. 2009). For example, the negative surface charge of nucleic acid means effective delivery necessitates the positive modification of the carrier silica particle's surface charge, therefore allowing the silica carrier particle to bind to DNA and siRNA (Xia et al., 2009). Xia et al. (2009) studied the effectiveness of PEI (with molecular weights between 0.6 to 25 kDa) modified mesoporous silica particles as a drug delivery agent. PEI modified particles were found to possess a high binding effectiveness and a high rate of cellular uptake making them promising candidates for an enhanced drug delivery system (Xia et al., 2009). During particle characterisation, Xia et al. (2009) conducted a zeta potential analysis on the modified and unmodified particles at pH 7.4; however, the complete zeta potential curve of the PEI modified particles was not reported.
2.3.3 Conclusions

Control over the surface chemistry of silica can have a significant effect on the applicability and performance of silica and silica coated particles. Surface modification acts to introduce strategic functional groups which can be used to tune the surface chemistry of the silica. Two broad categories were used to classify the methods of silica surface modification in this chapter, within synthesis modification (*in situ* methods) and post-synthesis modification.

In situ modification utilises 'in reaction' conditions to introduce the desired functional groups. *In situ* modifications can be categorised as mixed metal oxide, co-precipitation and biomimetic entrapment methods. As *in situ* methods are performed during synthesis, their suitability is highly dependent on the silica synthesis technique employed. Pyrogenic synthesised silica may be modified by doping it with key metal alkoxides during the flame synthesis process resulting the production of a mixed metal oxide. Although some mixed metal oxides have come to commercial significance over the years, the prohibitively high energy and economic cost of the pyrogenic synthesis process decreases the current attractiveness of this modification method in comparison to new techniques. Co-precipitation introduces functional groups to Stöber and biomimetically synthesised silicas through the selection of alkoxysilanes substituted with the target functional group. This allows the modification to be made during the polymerisation of the alkoxysilane. However, only certain substitutes will allow the alkoxysilane to undergo polymerisation, significantly restricting the types of functionalisation possible using this method.

In situ modification can also be made through the entrapment of molecules during silica synthesis. This method of modification is particularly pertinent to biomimetic silica synthesis methods where bioinspired molecules are used as scaffolds or enzymes to induce silication. The entrapment method is also limited by the molecules that possess scaffolding or silication inductive properties. In addition, in the case of the entrapment method the modifications are incidental so require no further forethought.

Overall, *in situ* modification simplifies the chemical functionalisation of silica by conducting modification and synthesis in a single step. This may cut down on the reaction time and reaction equipment necessary. Moreover, *in situ* modification results in better overall coverage of the silica surface when compared with post-synthesis methods. However, to their detriment, *in situ* methods often require higher amounts of the chemical modifier and are restricted by the method of silica fabrication being used.

Post-synthesis modification through covalent attachment of the chemical modifier offers an irreversible stable functionalisation of the silica surface. Due to the chemical stability of the silica surface post-synthesis modification reactions generally require conditioning of the surface prior to the covalent attachment of the desired surface group. Silane coupling agents are alkoxysilanes possessing at least one non-hydrolysable organic radical branch. Once the alkoxysilane is polymerised onto the surface of the silica, the surface modifying group may be attached via reaction with the organic radical branches. Modification through silane coupling agents is a multi-step, complex process, which may result in low surface coverage, especially in comparison with *in situ* methods of modification. In its favour, however, post-synthesis modification offers the ability to robustly attach an extensive range of functionalities, including polymers and bulky functional groups.

Finally, physical adsorption via electrostatic attraction offers another pathway for silica surface modification. This technique is separate to the previously discussed methods as it is reversible in nature which can advantageous or disadvantageous dependent on the application. Modification through the physical adsorption of PEI onto the silica surface has received attention due to its applications in the fields of medicine and analytical chemistry.

Although, many studies have been conducted on surface modification of the silica surface, a technique that offers robust and high coverage functionalisation without limiting the modifications available or requiring multi-step complex reaction procedures has yet to be reported upon. Overall, however, surface modification offers a degree of tunability to silica surfaces enhancing and expanding their application thus making the process attractive to a large number of fields. In particular, surface modification allows silica to be tuned for selective interaction with target materials allowing it to be used for separation processes, as in the case of magnetic separation using carrier magnetic core-silica shell particles (Sections 2.4 and 2.5).

2.4 Silica shell – magnetic core particles

Core-shell particles seamlessly combine the advantageous properties of the core and the shell materials into a single entity (Esmaeilpour *et al.*, 2016; Gawande *et al.*, 2015; Kalantari *et al.*, 2013; Melnyk *et al.*, 2016; Roto *et al.*, 2016; Zhang *et al.*, 2012a). Thus, core-shell particles are significantly more flexible and tunable than their single material counterparts. In the literature, an extensive spectrum of different core-shell combinations have been developed. In the interest of brevity, this literature review will restrict itself to the development of silica coated magnetic core particles.

Magnetic core-silica shell particles have garnered much recent research attention (Esmaeilpour *et al.*, 2016; Gawande *et al.*, 2015; Kalantari *et al.*, 2013; Melnyk *et al.*, 2016; Roto *et al.*, 2016; Zhang *et al.*, 2012a), especially given their ability to combine the magnetism afforded by their magnetic core with the advantageous properties of their silica shell, including the ability to be functionalised, physical/chemical stability and biocompatibility (Jal *et al.*, 2004; Roto *et al.*, 2016; Zhang *et al.*, 2012a). These combined properties allow magnetic core-silica shell particles to be utilised in catalysis, environmental clean-up, magnetorheology, adsorption and biomedical applications (Dutz *et al.*, 2009; Esmaeili-Shahri *et al.*, 2015; Gawande *et al.*, 2015; Gutiérrez *et al.*, 2015; Liu *et al.*, 2015c; Roto *et al.*, 2016).

The development of the magnetic core-shell particles to act as carrier particles for the separation of fine particles and heavy metal ions is limited by two main factors: the adsorption capacity of the shell and the magnetic separation potential provided by the magnetic core. Silica coating fabrication and functionalisation techniques are discussed in Section 2.4.1. To determine the magnetic separation potential of the magnetic core, a background understanding of the magnetism is required, thus, Section 2.4.2 of the literature review will give a short introduction to magnetism and magnetic materials as a background. A discussion on the magnetic collection methods and devices follows in Section 2.4.2.1. In Section 2.4.3, the selection of magnetic core material is discussed.

2.4.1 Silica shell fabrication and functionalisation

Silica is a highly popular coating material for core-shell particles. As a robust inorganic coating, silica provides protection to the material core by enhancing the stability of the particle in high temperature conditions, extremes of pH and organic solvents (Bao *et al.*, 2017; Laurent *et al.*, 2008). In addition, silica coatings provide an easily functionalised surface and stability against particle aggregation (Bao *et al.*, 2017; Laurent *et al.*, 2017; Laurent *et al.*, 2017; Material aggregation (Bao *et al.*, 2017; Laurent *et al.*, 2008). These advantages offered by silica make it an ideal shell material

for a wide variety of cores. In the literature, silica has been coupled with extensive range of core materials, including gold (Liz-Marzán *et al.*, 1996; Mine *et al.*, 2003; Riberio *et al.*, 2017), platinum (Joo *et al.*, 2009), silver (Kobayashi *et al.*, 2005) and organic drugs (Wang *et al.*, 2017). Of particular interest for this study is the combination of a silica shell with a magnetic core material (Roto *et al.*, 2016; Sacanna *et al.*, 2012; Vogt *et al.*, 2010; Wang *et al.*, 2015a).

Many studies have been dedicated to the development of silica shell fabrication techniques, most commonly utilising techniques adapted from the Stöber (Section 2.2.2.3) or the microemulsion methods of silica synthesis (Section 2.2.2.2) (Roto *et al.*, 2016; Sacanna *et al.*, 2012; Vogt *et al.*, 2010; Wang *et al.*, 2015a). In addition, a number of these studies have introduced enhanced or tunable surface properties, such as, thiol or amine functionalisation; control over shell thickness; and/or control over the shell's morphological features (Bao *et al.*, 2011; Biradar *et al.*, 2011; Du *et al.*, 2009b; Kalantari *et al.*, 2013; Kobayashi *et al.*, 2005; Roto *et al.*, 2016; Stöber *et al.*, 1968; Vogt *et al.*, 2010; Wang *et al.*, 2015a).

Vogt *et al.* (2010) utilised an optimised inverse microemulsion method to produce silica shells of tunable thickness designed for biomedical applications. In this study, silica shell thickness was able to be finely adjusted by tuning of the reaction time and the concentration of the silane precursor (Vogt *et al.*, 2010). While, Sacanna *et al.* (2012) demonstrated the production of single-core hematite microcubes encapsulated in silica shells using a modified Stöber method synthesis in an oil-in-water microemulsion. The hematite microcube cores acted as nucleation sites for the oil droplet formation, promoting single-core inclusion (Sacanna *et al.*, 2012). In these experiments, the silanol, 3-methacryloxypropyltrimethoxysilane (TPM), catalysed by ammonia, was then polymerised at the oil-water interface to create the silica shell over a 1 h reaction period. Finally, the addition of azo-bis-isobutyrylnitrile at 80 °C was used to harden the core-shell particles over a 3 h period (Sacanna *et al.*, 2012).

Zhang *et al.* (2012a) produced 500 nm diameter core-shell particles for heavy metal recovery applications (Section 2.5.2). Core-shell particles were formed when clusters of multiple nanosized Fe_3O_4 particles were encapsulated by TEOS hydrolysis in alkali conditions using a modified Stöber process. An amine monomer (1,2-diaminobenzene) was also included during the fabrication reaction, resulting in an *in situ* amine surface functionalisation. The shell fabrication reaction was conducted over 4 h period and at room temperature (Zhang *et al.*, 2012a).

Li *et al.* (2013a) used a modified Stöber process, over a 3 h reaction period, to produce silica coated magnetite nanoparticles in an ammonia catalysed reaction. However, in Li and coworkers' study (2013a) the amino functionality of the silica surface was introduced post-synthesis through the copolymerisation of TEOS and APTS under Stöber synthesis conditions with another 3 h reaction.

Tang *et al.* (2013) produced functionalised mesoporous silica coated magnetite microparticles through the ammonia catalysed silication of TEOS in an ethanol/water medium using a modified Stöber process. The first silication reaction was conducted at room temperature and over 24 h. An additional 5 h ammonia catalysed silication reaction followed, in order to achieve the mesoporous silica shell. In this second reaction, TEOS and the long-chained silane, hexadecyltrimethoxysilane, were used as reactants. Following the fabrication of the silica shell, amine surface groups were introduced through a 24 h amine catalysed polymerisation APTS onto the silica surface (Tang *et al.*, 2013).

Wang and coworkers (2015a) also fabricated amine functionalised mesoporous silicamagnetite microparticles. The procedure reported in this paper used modified Stöber process with an ethanol/water medium and ammonia catalyst. The TEOS silane was added dropwise and the reaction was conducted for 12 h. Following this first coating step, dropwise additions of NH₄F and TEOS were made at 40 °C and the reaction was allowed to proceed for 20 h (Wang *et al.*, 2015a). After calcination at 550 °C, the coreshell particles were then functionalised through the polymerisation of APTS on the particle surface via a reflux reaction conducted at 120 °C over 24 h.

The procedure for core-shell particle production developed by Anbia *et al.* (2015) involved the synthesis of the silica shell for magnetite nanoparticles through an adapted microemulsion method. To form the shell, the magnetite core nanoparticles were combined with CTAB surfactant in a basic aqueous medium for 3 h with vigorous mixing. After 3 h, dropwise additions of the silica precursor, TEOS, were made to the reaction while the reaction remained heated slightly above room temperature (30-35 °C), the reaction continued to be stirred until the resulting gel product became homogeneous. Following the reaction, the particles were then heated at 135 °C in an autoclave for 48 h and then calcined at 540 °C. Two post-synthesis modification procedures were used to introduce the melamine functional groups to the surface for the core-shell particle's desired application in metal ion recovery.

Roto *et al.* (2016) developed a thiol functionalised silica shell for magnetite nanoparticles. First, a silica shell was fabricated from the silication of sodium silicate in

a slightly acidic solution at 80 °C for 3 h, using a process based on the precipitated silica method (Section 2.2.2.1). Next a layer of 3mPTMOS was polymerised onto the surface using a zeolite catalyst and toluene medium to produce a post-synthesis thiol functionalisation. The surface modification reaction proceeded under reflux for 24 h (Roto *et al.*, 2016).

In Bao and coworkers' study (2016b; 2017), functionalised magnetite core – silica shell particles were produced for the purpose of heavy metal ion recovery (Section 2.5.2). In Bao *et al.* (2016b; 2017), the silica shell was prepared by first suspending the magnetite nanoparticle cores in an ethanol:water medium and heating the suspension to ~50 °C. Under vigorous stirring and a nitrogen flow, the silane TEOS added dropwise to the suspended cores. The reaction preceded first with vigorous mixing for 5 h, then statically for another 2 h. Bao *et al.* (2016b; 2017) then functionalised the silica shell surface using one- and two-step post-synthesis modification reactions. In Bao *et al.* (2016b) modification of the core-shell particles surface proceeded through the polymerisation of APTS, for an amine functionalisation. An amine/thiol functionalisation was attained in Bao *et al.* (2017) by following the APTS reaction with a second surface modification reaction, whereby (chloromethyl)thiirane was polymerised onto the particle surface.

Unfortunately, these methods of silica shell fabrication often require an unideal combination of complex procedures, long reactions times, high temperatures and harsh conditions (Anbia *et al.*, 2015; Bao *et al.*, 2016b; 2017; Li *et al.*, 2013a; Roto *et al.*, 2016; Sacanna *et al.*, 2012; Tang *et al.*, 2013; Vogt *et al.*, 2010; Wang *et al.*, 2015a; Zhang *et al.*, 2012a). The disadvantages of current procedures drive the continuing development of more facile, environmentally attractive and economically feasible silica coating synthesis and functionalisation methods.

2.4.2 Magnetism

As discussed in Section 2.4.1, silica shells are commonly combined with magnetic core materials (Roto *et al.*, 2016; Sacanna *et al.*, 2012; Vogt *et al.*, 2010; Wang *et al.*, 2015a). In this section, a summary on magnetism and magnetic materials is given as a background for the discussion of magnetic core particles in Section 2.4.3.

Magnetic materials, that is, materials that show a response to an external magnetic field, can be classified into seven distinct categories: diamagnets, paramagnets, ferromagnets, ferrimagnets, antiferromagnets, helimagnets and superparamagnets (Jiles, 1998).

The atoms within a ferromagnetic material (*e.g.* iron, cobalt, nickel) possess unpaired electrons, which give the atom a net magnetic moment (Figure 2.6) (Issa *et al.*, 2013; Jiles, 1998). In the bulk material, adjacent atoms within a certain area form a "magnetic domain" wherein the magnetic moments of the atoms are aligned. Within the bulk material, the alignment of domains is randomly distributed resulting in a net magnetic moment of zero. However, with the application of an external magnetic field, the domains become aligned along the direction of the applied field and the material acquires its own net magnetic moment. These materials have large magnetic susceptibilities and, thus, respond strongly to the application of a magnetic field. Ferromagnets also retain some residual magnetic moment after the removal of the external magnetic field.



Figure 2.6. Schematic of the relative magnitude and directionality of the electron magnetic moments in the different types of magnetic materials: ferromagnets, paramagnets, antiferromagnets and ferrimagnets.

Paramagnetic materials (such as, lithium and magnesium) also possess unpaired electrons; however, there are no magnetic domains in paramagnets, so the magnetic moments of the unpaired electrons are randomly orientated (Figure 2.6) (Issa *et al.*, 2013; Jiles, 1998). Paramagnetic materials show a weak response to a magnetic field and, unlike ferromagnetic materials, retain no residual magnetic moment once the field is removed. Diamagnetic materials (such as, gold, silver and silica) possess no

unpaired electrons and, therefore, no net magnetic moment (Issa *et al.*, 2013; Jiles, 1998). In response to an applied magnetic field, diamagnets experience a small repulsive force due to realignment of electron orbits within the diamagnetic structure.

Antiferromagnetic materials (such as, hematite and NiO) are ionic compounds or alloys where the magnetic moments of elements occupying adjacent lattice sites are equal and opposite (Figure 2.6) (Jiles, 1998). The magnetic moments of the atoms cancel out resulting in a net magnetic moment of zero. In the presence of a magnetic field this results in similar magnetic behaviour to paramagnets, with antiferromagnets showing a weak response to the applied field and no residual magnetism once the field is removed. Likewise, helimagnetism resembles paramagnetism and arises from competing ferromagnetic and antiferromagnetic interactions (Jiles, 1998).

Conversely, as a bulk material, ferrimagnets (e.g. Fe₃O₄) are effectively indistinguishable from ferromagnetic materials (Issa *et al.*, 2013; Jiles, 1998). However, structurally ferrimagnets are ionic compounds where the atoms occupying neighbouring sites have opposite but unequal magnetic moments (Figure 2.6), resulting in a non-zero net magnetic moment overall. Ferrimagnets also possess domains, similar to ferromagnets, allowing them to retain a residual magnetic moment after interacting with a magnetic field. However, the residual magnetic moment for ferrimagnets tends to be much smaller than for ferromagnets.

There is a lower limit on the magnetic domain sizes possible for ferri/ferromagnets (~100 nm). Particles sized below this limit are composed of a single magnetic domain (Issa *et al.*, 2013). These nanosized ferri/ferromagnets display a unique form of magnetism known as superparamagnetism, provided the temperature is above a certain critical limit known as the blocking temperature, T_B (K). Superparamagnetic particles respond strongly to applied magnetic fields. However, like paramagnetic materials, they retain no residual magnetism after the magnetic field is removed (Issa *et al.*, 2013).

There are a few key measures important for the classification of magnetic materials. The related properties of magnetic susceptibility, χ , and permeability, μ (N A⁻¹), quantify the magnitude and direction (*i.e.* whether the material is attracted or repulsed) by which the material responds to an external magnetic field. For ferro- and ferrimagnetic materials, permeability of the material is influenced by hysteresis (*i.e.* the magnetic history of the material) (Jiles, 1998).

For materials where a residual magnetic field remains after the external magnetic field is removed (*i.e.* ferromagnets or ferrimagnets) the coercivity, H_c (A m⁻¹), saturation

magnetisation, M_S (A m⁻¹), and remanence, M_R (A m⁻¹), are also important properties. For ferro- or ferrimagnets, exposure to a magnetic field results in the magnetic moments of multiple domains becoming aligned. These domains remain aligned even after the external magnetic field is removed resulting in a residual magnetic field known as the remanent magnetisation or remanence. However, the amount of induced magnetisation possible for a particular sample is limited. The magnetism applied by an external magnetic field that facilities the alignment of all domains within a particular material, is known as the material's saturation magnetisation. (Jiles, 1998). The coercivity of a material is a measurement of the magnetic field (in the reverse direction) required to bring the remanence magnetic moment of the material back to zero after magnetic saturation.

Based on their coercivity, magnetic materials can be classified as being hard or soft. For hard ferro/ferrimagnets, coercivity is low which make them ideal for permanent magnet application. However, for more temporary magnets, soft magnets are preferred due to their relatively small coercivity. (Jiles, 1998).

Temperature can also influence the magnetic properties displayed by a material. For example, ferromagnetic materials heated beyond a certain threshold temperature, known as their Currie temperature, T_c (K), will become paramagnetic (Jiles, 1998). However, for room temperature separation operations, temperature influences are generally not significant.

2.4.2.1 Magnetic collection

Advantages of magnetic separation include low energy consumption, low operating costs, high yield and ease of operation (Raitani *et al.*, 2012). In addition, magnetic separation is particularly suited to fine particle, molecular or ion separation where traditional methods may prove ineffective or difficult (Broomberg *et al.*, 1999). For non-magnetic materials, magnetic additives, known as magnetic carrier particles, can be introduced (Moffart *et al.*, 1994). These magnetic carrier particles adsorb or interact with the non-magnetic materials imparting them with magnetism, therefore allowing non-magnetic materials to be separated using magnetic separation techniques.

Magnetic carrier technologies have been considered since the early 1900s and continue to be of significance today (Moffart *et al.*, 1994; Broomberg *et al.*, 1999) (Section 2.5). Magnetic cores in a core-shell arrangement, as opposed to pure magnetic particles, significantly broaden the range of applications by stabilising the

magnetic cores and tailoring particle surface interactions (Hua *et al.*, 2012; Ngomsik *et al.*, 2005; Zou *et al.*, 2016). For magnetic carriers, a coated magnetic core may allow for more selective interactions with a broader range of fine particles, molecules or ions. Moreover, coating the magnetic core material will often increase the chemical stability of the magnetic core, expanding the range of environments the particles can be used in and allowing for desorption and reuse of the carrier particles (Bao *et al.*, 2017; Laurent *et al.*, 2008). Magnetic cores have also been utilised in medicinal, catalysis and biosensor fields (Moffart *et al.*, 1994); however, these applications are outside the scope of this study.

The objective of this project was the development of magnetic carrier particles (coreshell particles) for selective separation and recovery of targeted fine particles, molecules and ions. Hence, the collection of the magnetic carrier particle via an external magnetic field is of the upmost importance. In order to collect magnetic particles, the magnetic force, in competition with the other prevailing forces (including gravitational, hydrodynamic and interparticle forces), must attract the magnetic carrier particle to towards a magnetic source for collection (Moffart *et al.*, 1994).

Considering a system where magnetic particles are suspended within a liquid medium and a magnetic field is generated around a magnetised wire, the magnetic force on a particle, F_m (N), can be calculated by Equation 2.1 (Moffart *et al.*, 1994),

$$F_m = V_p \left(\chi_p - \chi_f\right) H \frac{dB}{dx}$$
 2.1

where V_p (m³) is the volume of the particle, the magnetic susceptibilities of the particle and fluid are given by χ_p and χ_f respectively, the magnetic field strength is H (T) and the magnetic field gradient is given by dB/dx (T m⁻¹).

Magnetocollection is possible with a positive net magnetic force and in systems where the particle is more magnetically susceptible then the fluid medium (Equation 2.2). Under these conditions the particle, is attracted towards the magnetic source (Moffart *et al.*, 1994),

$$\frac{dB}{dx} \gg 0 \text{ and } (\chi_p - \chi_f) > 0$$
 2.2

From Equation 2.1, the key driving forces for magnetic collection of particles can be determined. Firstly, it is the difference between the magnetic susceptibilities of the fluid medium and particle that allows collection. For most processes, the medium will be diamagnetic (such as, for water and ethanol mediums), resulting in a very small (practically negligible), negative fluid magnetic susceptibility. Therefore, the particles must possess a high magnetic susceptibility for effective collection. An interesting consequence of the phenomena encapsulated in Equation 2.2, is that particle collection can also be enforced using a magnetic collection medium with non-magnetic particles (Friedman and Yellen, 2005). However, for industrial scale operations the cost efficiency of non-magnetic mediums (e.g. water and organic fluids) is too large an advantage for such a system to compete.

The attraction of the particle for collection is mainly dependent on the size of the particle (V) and its magnetic susceptibility (χ_p), these properties are discussed in Section 2.4.3. These factors also significantly influence the type and efficiency of the magnetic collection device employed. The magnetic field strength and magnetic field gradient are also important aspects in determining the force felt by the particles for collection. These factors will be discussed in relation to the different collection devices in this section.

An additional factor that may impact the magnetic collection is magnetic flocculation. When the magnetic susceptibility of the particle and fluid are dissimilar, a magnetic field gradient is present around the particles, due to this the particles are attracted to each other, which may result in particle flocculation (Moffart *et al.*, 1994; Sacanna *et al.*, 2012). Moreover, ferro/ferrimagnets experience residual magnetism after a magnetic field is applied, which may also introduce instability. Magnetic flocculation is an advantage for magnetocollection as it increases the speed of sedimentation and thus can decrease the required vessel volume, offsetting capital costs and ongoing running cost of the filtration equipment (Moffart *et al.*, 1994). However, magnetic flocculation before collection can be a disadvantage due to the reduction in available surface area for interaction with the species targeted for removal (Moffart *et al.*, 1994).

Problem with magnetic flocculation may be somewhat alleviated by selecting a magnetic core with high saturation magnetisation and low coercivity (Moffart *et al.*, 1994; Sacanna *et al.*, 2012). This facilitates selective magnetisation, so particles are magnetised when they need to be separated, but do not retain significant magnetisation following the removal of the external magnetic field. In this way, selective magnetisation could eliminate/reduce problems associated with undesirable

magnetic flocculation. In the case of coated magnetic particles, coatings, such as, silica shells, may further prevent/reduce flocculation by creating steric or/and electrostatic repulsion forces between particles (Ashtiani *et al.*, 2015; Kciuk *et al.*, 2009; Liu *et al.*, 2011).

The devices used to collect or separate particles based on magnetism are called magnetic separators. Conventional separators can be divided into two types, both in widespread commercial use. The first are low gradient magnetic separators (LGMS), including drum separators, which utilise a permanent magnet for separation (Moffart *et al.*, 1994; Svoboda, 2004). The second type are high gradient magnetic separators (HGMS). HGMS units are fitted with electromagnets, advanced ceramic permanent magnets or superconducting magnets allowing for separation of particles of low magnetic susceptibilities (Moffart *et al.*, 1994; Svoboda, 2004).

Another possible way to classify magnetic separators is based on whether they possess an open or enclosed field. Open field separators are more common for LGMS and utilise an external magnetic field (Moffart *et al.*, 1994). In contrast, enclosed field separators, common for HGMS, employ magnetic coils and ferromagnetic packing around the coils in order to entrap the magnetic carrier particles (Moffart *et al.*, 1994). The magnetic particles can then be collected from the packing by removing the magnetic field and flushing the system. Despite the operational advantages of open field separators, they have been difficult to fabricate for HGMS units (Moffart *et al.*, 1994).

The selection of magnetic separation is unit is almost wholly dependent on the magnetism of the material to be separation. Therefore, in the case of carrier particle technology, the selection of magnetic core material is vital for operation.

2.4.3 Magnetic cores

The objective of this project was the development of core-shell particles to act as magnetic carriers for separation of fine particles and molecules. Hence, the performance of the magnetic carrier particles for magnetic collection is of the upmost importance (Section 2.4.2). From Equation 2.1, it can be derived that the magnetic susceptibility and volume of the particles pose the most significant effect on the magnetic force experienced by the particle during collection. Therefore, when selecting a magnetic core, its size and magnetic susceptibility are major factors. In addition, the accessibility, affordability, ease of coating and stability of the coated core should also

be factored into the selection process. In Section 2.4.3.1 the size of the magnetic core will be discussed, followed by the magnetic material of the core in Section 2.4.3.2.

2.4.3.1 Core size

Typically, core-shell particle size and thus the core size itself can be selected based on the desired properties of the final core-shell product. Nanosized magnetic core-shell particles (1-100 nm diameter) dominate current literature studies for applications in medicinal, biological and electronics fields (Issa *et al.*, 2013). Nanosized magnetic core-shell particles are attractive due to unique features accessible at the high surface area to volume ratio of 1-100 nm sized particles and the superparamagnetic behaviour of magnetic cores less than 100 nm in diameter (Issa *et al.*, 2013; Wang *et al.*, 2009). However, magnetic particles below the size of 10 nm are not ideal for separation applications. On this small scale, the nanoparticle's magnetic energy induced by an applied magnetic field is larger than the thermal energy, resulting in the nanoparticle suspension behaving as a paramagnetic material (Nguyen, 2012). Referred to as ferrofluids, these nanoparticle suspensions will not settle even under extremely high magnetic field gradients (Nguyen, 2012).

Superparamagnetic behaviour arises in nanosized (usually 10-100 nm) ferro- or ferrimagnets where their small size restricts them to possessing only one magnetic domain (Section 2.4.2). These nanosized magnetic cores therefore possess high magnetic moments when exposed to a magnetic field without retaining any residual magnetism once the external field is removed (Jiles, 1998). For separation purposes, this is an advantage, as the particles can interact with a magnetic field without remanent magnetisation causing aggregation once the field is removed (Issa *et al.*, 2013). Aggregation of magnetic core-shell particles, while advantageous during magnetic collection as it increases the speed of collection by inducing more rapid settlement (Section 2.4.2), is not ideal for adsorption/desorption processes due to the reduced core-shell surface area.

The magnetic separation of nanosized magnetic carriers, due to their small magnetic volume, requires a considerable magnetic field gradient for effective collection (Equation 2.1) (Teste *et al.*, 2011). In fact, due to the high magnetic field required for their collection, very few devices have been developed to cope with nanosized particles (Teste *et al.*, 2011). In contrast, micron sized particles (0.1-10 μ m) have a vast range of HGMS devices commercially available for separation making them a more attractive option as commercial magnetic carrier particles (Tang *et al.*, 2017; Teste *et al.*, 2011).

The application of magnetic core-shell particles for separation will be discussed in detail in Section 2.5.

The micron sized magnetic cores due to their larger size are often ferro- or ferromagnetic materials, meaning their remanent magnetism may cause unwanted magnetoflocculation. However, this loss of particle colloidal stability can be compensated by the introduction of a coating which implements repulsion between particles electrostatically and/or sterically (Issa *et al.*, 2013). Utilisation of soft magnetic materials (possessing a low coercivity) as a magnetic core material also results in the remanent magnetism being easy to remove after magnetic collection (Ashtiani *et al.*, 2015).

Micron sized carbonyl iron and magnetite cores have been successfully used in the literature for mineral separation and heavy metal ion recovery applications (Abou El-Reash, 2016; Funes *et al.*, 2014; Gray *et al.*, 1994; Gutha *et al.*, 2017; Zhang *et al.*, 2012b). For example, Gray *et al.* (1994) utilised micron sized silane coated magnetite particles (<38 μ m) for recovery of gold. Micron sized carbonyl iron particles both bare and with a MnO_x coating were used successfully for the removal of Mn ions (Funes *et al.*, 2014). However, as will be discussed in more detail in Sections 2.5.1 and 2.5.2, recent investigation of coated micron sized cores for ion and mineral separation applications has limited, especially compared to that of nano sized cores.

In addition to separation applications (Section 2.5), micron sized magnetic core-shell particles have been developed as the active component of magnetorheological fluids (Ashtiani *et al.*, 2015; Bae *et al.*, 2017; Jung *et al.*, 2016). Magnetorheological fluids are intelligent suspensions of magnetically responsive materials where the mechanical properties of the fluid can be controlled by the application or absence of a magnetic field (Jung *et al.*, 2016). Micron sized magnetic particles have also proved to have applications in MRI cell labelling (Taylor *et al.*, 2014). However, in comparison with the nanosized counterparts, micron sized core-shell particles have been somewhat neglected in the literature in recent years, despite their advantages.

2.4.3.2 Core material

Industrial magnetic separators (Section 2.4.2.1) are able to achieve effective separation of material possessing paramagnetic magnetism. Thus, when employing magnetic carriers, the goal is to increase the magnetic properties of the non-magnetic material target to the point where its response to magnetic flux approaches that of a

paramagnetic material. To achieve efficient magnetic separation, ferro- or ferrimagnetic carrier materials are often utilised due to their extremely strong magnetic response (Broomberg *et al.*, 1999).

Commonly used ferro or ferri-magnetic core materials for core-shell fabrication, include magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃) and carbonyl iron (Fe) (Arias *et al.*, 2007; Chomoucka *et al.*, 2010).

Magnetite (Fe₃O₄) is used widely as a magnetic core material due to its availability, ease of synthesis and biocompatibility (Ashtiani *et al.*, 2015). Magnetite particles can be fabricated using the facile co-precipitation method of synthesis which allows control of particle size from micron sized down to the nanoscale (Lee *et al.*, 2008; Wang *et al.*, 2010a). When nanosized, magnetite particles are superparamagnetic, and thus retain no residual magnetism. Therefore, the nanosized magnetite can be removed through magnetic means without needing to be subsequently demagnetised in order to prevent the unwanted magnetic flocculation of the particles.

On the other hand, micron sized magnetite possesses a low coercivity, which allows it to be easily demagnetised. The ability to be easily demagnetised is advantageous in carrier particle applications where it limits unwanted particle aggregation following magnetic separation (Ashtiani *et al.*, 2015). However, micron sized magnetite particles possess several properties that reduce their suitability for use as a magnetic carrier material, including their tendency toward rapid oxidation and aggregation in solution (Bao *et al.*, 2017). Various inorganic coatings, including the fabrication of a silica shell, have been found to enhance their chemical stability and protect against rapid oxidation of the core material (Bao *et al.*, 2017; Laurent *et al.*, 2008).

Carbonyl iron is a form of elemental Fe fabricated through the thermal decomposition of pentacarbonyl iron (Chomoucka *et al.*, 2010). The resulting composition of carbonyl iron is 97 wt.% Fe and 3 wt.% C, O and N (Funes *et al.*, 2014). Carbonyl iron has a typical particle size of 0.5-10 µm particle diameter, however, nanosized particles can also be created by incorporating polymers, as surfactants/catalysts, into the decomposition reaction (Huber, 2005). As a magnetic material, carbonyl iron particle sizes larger than a single ferromagnetic domain. These properties make carbonyl iron particles easy to magnetise and demagnetise through the application and removal of external magnetic fields (Ashtiani *et al.*, 2015). These properties allow for the carbonyl iron particles to be used as temporary magnets, a feature which has been exploited thoroughly in the development of magnetorheological fluids (Ashtiani *et al.*, 2015). The

disadvantage of the carbonyl iron material is its high density, which results in fast particle sedimentation. However, recent studies have shown that coating and/or functionalisation of the carbonyl iron surface can significantly improve the suspension stability (Ashtiani *et al.*, 2015; Kciuk *et al.*, 2009; Liu *et al.*, 2011).

Carbonyl iron has enjoyed widespread use in magnetorheology both in its coated and uncoated forms (Ashtiani *et al.*, 2015; Kciuk *et al.*, 2009; Liu *et al.*, 2011). In addition, coated carbonyl iron has also featured in a number of studies investigating magnetic drug delivery (Arias *et al.*, 2007; Chomoucka *et al.*, 2010; Reshmi *et al.*, 2009). However, carbonyl iron has had little attention by researchers focused on the development of magnetic carrier particles. Only a few studies have focused on the use of coated carbonyl iron for magnetic separation of heavy metal ions (Funes *et al.*, 2014) and the delivery of drugs (Arias *et al.*, 2007).

2.4.4 Conclusions

Materials possess innate properties, related to the distribution and directionality of their electron spins that govern their response to an external magnetic field. Low energy consumption, low operating costs, high yield and ease of operation are just some of the advantages of separating materials through application of an external magnetic field (Raitani *et al.*, 2012). For non-magnetic materials, magnetic carrier particles can be employed. By tuning the surface of the magnetic carrier particles, the carrier particles can be made to selectively interact with the non-magnetic material of interest, allowing them to be separated by magnetic separation devices.

Core-shell particles combine the properties of multiple materials into single particles. In magnetic carrier applications, magnetic core particles can be combined with various shell materials. The selection of an appropriate shell allows the carrier particles to specifically target the desired non-magnetic materials for attachment, enhancing the selectivity of the magnetic separation overall. Silica shell coating offers a number of advantages including the ability to be functionalised, offering an increase to the physical/chemical stability of the core and biocompatibility (Jal *et al.*, 2004; Roto *et al.*, 2016; Zhang *et al.*, 2012a). Synthesis of the silica coating has previously involved adapting the Stöber method (Section 2.2.2.3) or microemulsion method of silica synthesis (Section 2.2.2.2) (Roto *et al.*, 2016; Sacanna *et al.*, 2012; Vogt *et al.*, 2010; Wang *et al.*, 2015a). However, many of these methods may be difficult to replicate when scaled up, as they often involve complex procedures and multiple steps, especially when including surface functionalisation.

For the separation process itself, the magnetic susceptibility and volume of the magnetic core, the magnetic susceptibility of the fluid, and the gradient and strength of external magnetic field, provide the driving forces for magnetic separation. Therefore, the selection of the magnetic core material and size determines the performance of the core-shell particles as magnetic carrier particles. The most common magnetic cores of carrier particles are the ferromagnetic and ferrimagnetic materials, carbonyl iron (Fe) and magnetite (Fe₃O₄), respectively. These materials respond particularly strongly to magnetic fields and retain some magnetism after the removal of the field. However, both materials possess disadvantages when uncoated. Carbonyl iron possesses a high density, making it difficult to keep the carbonyl iron particles suspended while the target materials are adsorbed. While, uncoated magnetite (Fe₃O₄) undergoes rapid oxidation and aggregation in solution (Bao *et al.*, 2017).

Size is another important factor to take into consideration when selecting a suitable magnetic material as a carrier. In the nanometer size range, magnetic particles become superparamagnetic meaning they respond strongly to magnetic field but do not retain magnetism once the magnetic field is removed. Hence superparamagnetic particles do not undergo post-magnetic separation magnetic flocculation. However, nanoparticles have a significantly smaller volume, which as can be seen in Equation 2.1 reduces the driving force felt by the particles during magnetic separation compared with larger micron sized cores.

The selection of the core-shell material can not only influence the potential applications to carrier particle technology but also determine whether the material is feasible for industrial manufacturing to be used on a larger scale. However, further work is needed to ensure silica shell synthesis and functionalisation able to be feasibly scaled up.

2.5 Applications

Magnetic carrier technologies have been in used since the 1940s when magnetite was used to electrostatically adsorb organic impurities in wastewater purification (Moffart *et al.*, 1994). In bioprocess reactors, magnetic carriers have been utilised to immobilise enzymes and biological catalysts with the aim of preventing contamination from the catalysts and for ease of reuse and reactivation (Broomberg *et al.*, 1999; Kopp *et al.*, 2015; Moffart *et al.*, 1994). Magnetic carrier technologies have also been used to separate molecules or colloidal solids (Anastassakis, 1999; 2002; Bao *et al.*, 2017; Li *et al.*, 2013a; Prakash *et al.*, 1999; Raitani *et al.*, 2017; Zhang *et al.*, 2012a). So far, magnetic carrier separation of solids has mainly focused on small scale processes (Anastassakis, 1999; 2002; Bao *et al.*, 2017; Li *et al.*, 2017; Zhang *et al.*, 2012; Shaikh *et al.*, 1999; Raitani *et al.*, 2014; Wang *et al.*, 2012; Bao *et al.*, 2017; Li *et al.*, 2013a; Prakash *et al.*, 2002; Bao *et al.*, 2017; Li *et al.*, 2013a; Prakash *et al.*, 2010a; Yuan *et al.*, 2017; Li *et al.*, 2013a; Prakash *et al.*, 2012; Bao *et al.*, 2017; Li *et al.*, 2013a; Prakash *et al.*, 1999; Raitani *et al.*, 2017; Li *et al.*, 2013a; Prakash *et al.*, 1999; Raitani *et al.*, 2017; Li *et al.*, 2013a; Prakash *et al.*, 1999; Processes (Anastassakis, 1999; 2002; Bao *et al.*, 2017; Li *et al.*, 2013a; Prakash *et al.*, 1999; Raitani *et al.*, 2017; Li *et al.*, 2013a; Prakash *et al.*, 1999; Raitani *et al.*, 2017; Zhang *et al.*, 2012a). However, if scaled up, the magnetic carrier technologies could have far reaching potential applications in the biomedical, purification and waste management industries.

This section will focus on a number of key applications of magnetic carrier separation technology. The applications which will be discussed are fine particle processing (Section 2.5.1), removal of heavy metal ions (Section 2.5.2) and CO_2 capture (Section 2.5.3).

2.5.1 Fine particle separation

Many industries produce waste in the form of suspended solids, including mineral processing, hydrometallurgy, water and wastewater treatment (Tang *et al.*, 2017). In the mineral beneficiation industry, grinding exacerbates this problem through the creation of fine and ultrafine particles (Anastassakis, 1999; 2002). These fine particles pose problems on two fronts. On the first, very fine particles are difficult to separate efficiently through conventional separation methods due to their small particle size, large specific surface area and high surface energy (Anastassakis, 1999). Secondly, waste fines require specialised handling and disposal procedures to prevent their release into the environment.

As a fine particle separation technique, magnetic separation has a number of advantages including low energy consumption, low operating costs, high yield and ease of operation (Raitani *et al.*, 2012). However, for effective separation on an industrial scale, particles must possess a magnetic susceptibility at least on par with

paramagnetic materials (~10⁻³) (Broomberg *et al.*, 1999). Magnetic susceptibility of fine particles, for the purpose of magnetic separation, can be enhanced by (i) chemical alteration of the material (usually through roasting or reduction) or (ii) through the attachment of a magnetic carrier particle (Liu and Friedlaender, 1994; Raitani *et al.*, 2012). The selective attachment of magnetic carrier particles often relies on hydrophobic interactions or electrostatic attraction (Anastassakis, 1999; 2002; Gray *et al.*, 1994; Prakash *et al.*, 1999; Raitani *et al.*, 2012; Yuan *et al.*, 2017).

As discussed above, huge quantities of super fine particles (*a.k.a.* slimes) are generated during mineral processing and are typically disposed of in large tailing dams (Tang *et al.*, 2017). Tailing dams are, unfortunately, far from an ideal disposal method, as they pose a number of significant problems. Problems with tailing dam disposal include being an inefficient use of land and posing an environmental pollution risk (Tang *et al.*, 2017). Reducing the volume of suspended waste disposed of in tailing dams has consequently become of significant industrial and environmental interest.

As drying the waste is impractical due to the extremely high energy input required, sedimentation is widely used to reduce the water content, and therefore, the overall volume, of the suspended solid waste. Unfortunately, for fine particles the rate of sedimentation is extremely low (Tang *et al.*, 2017). Therefore, flocculants are often used to aggregate particles and promote more rapid settlement. Magnetic settling methods may be used to further the increase rate of sedimentation (Tang *et al.*, 2017).

For non-magnetic solid particles (diamagnetic particles), magnetic carriers may be introduced to induce a magnetic response. Through adsorption on, or aggregation with, the suspended non-magnetic solids, magnetic carrier particles can lend their magnetic properties to the solids allowing externally applied magnetic fields to improve the rate of sedimentation.

Tang *et al.* (2017) utilised magnetic industrial waste particles, obtained from the electric arc steel manufacture process, as the magnetic carrier material. The magnetic carrier particles, referred to as electric arc furnace (EAF) dust, were characterised as micron sized (<50 μ m diameter) and were composed of mainly γ -Fe₂O₃. A suspended particle mixture of micron sized quartz and gypsum particles was chosen for separation experiments as this mixture resembles the waste produced in hydrometallurgy processing. Under the influence of a magnetic field, the EAF dust magnetic carriers were observed to remove 97.72% of the suspended solid waste. The magnetically assisted settling process provided by the EAF dust carrier particles was found to significantly accelerate the rate of settling. Furthermore, the magnetic carrier technique

reduced the volume of the sludge by 30 %. As reappropriated waste, EAF dust was found to be far more economical as a carrier particle material than magnetite particles, which are purpose made. However, the EAF dust carrier particle system did not offer any selectivity in terms of which materials were adsorbed/separated by the system (Tang *et al.*, 2017).

Selective adsorption is possible through control over adsorption pH and functionalisation of magnetic carrier particles and/or target materials (Anastassakis, 1999; 2002; Prakash *et al.*, 1999; Raitani *et al.*, 2012; Singh *et al.*, 2014; Yuan *et al.*, 2017). These controls allow carrier particles to selectively recover targeted materials alongside providing solid-liquid separation (Anastassakis, 1999; 2002; Prakash *et al.*, 1999; Raitani *et al.*, 2014; Yuan *et al.*, 1999; Raitani *et al.*, 2012; Singh *et al.*, 2014; Yuan *et al.*, 2017). The mechanism of selective attachment between magnetic carrier and target fines can be provided by covalent bond formation, electrostatic attraction and/or the hydrophobic effect (Anastassakis, 1999; 2002; Gray *et al.*, 1994; Prakash *et al.*, 1999; Raitani *et al.*, 2012; Yuan *et al.*, 2017).

Silane coated magnetite core-shell particles (19-38 μ m) were used as carrier particles (Anbia *et al.*, 2015; Bao *et al.*, 2016b; 2017; Gray *et al.*, 1994; Li *et al.*, 2013a; Zhang *et al.*, 2012a). In the presence of xanthate salt, these core-shell particles were used for the selective separation of gold microparticles (1.5-3.0 μ m) from a zircon-gold mixture (Gray *et al.*, 1994). Hydrophobic interaction was believed to be the dominating mechanism for selective adsorption of the xanthate coated gold onto the core-shell carrier particles. A recovery rate of up to 80 wt.% Au was achieved using this system. However, at low pH, electrostatic adsorption of zircon onto the carrier particles reduced the selectivity of the process (Gray *et al.*, 1994).

Anastassakis (1999) developed a selective separation method for an aqueous suspension of serpentine and magnesite fine particles ($75 \pm 25 \mu m$ diameters). Utilising a system of magnetite carrier particles ($5 \mu m$ diameter) and a surfactant additive (dodecylamine), serpentine particles were selectively adsorbed and removed by the carrier particles between pH 6 and 9 (pH controlled using acetic acid and sodium hydroxide). The presence of dodecylamine was found to be critical for successful serpentine adsorption. While magnetite and serpentine were found to be partially covered by dodecylamine in most conditions, coverage of the magnesite particles was only significant at pH=11. This lead the authors to suggest that hydrophobicity, obtained through dodecylamine surface coverage, was the driving force for magnetite-serpentine attachment and, therefore, selective serpentine separation in the key pH

range (pH 6-9). In 2002, Anastassakis (2002) was able to further develop this methodology to selectively separate quartz from a quartz/magnesite fine particle mixture using the magnetic carrier particles with dodecylamine and kerosene as additives.

Prakash *et al.* (1999) used magnetite carrier particles (10 µm) to selectively separate hematite fines from a mixture of corundum and quartz. For this system, electrostatic attraction between the targeted hematite particles and magnetite carrier particles was the suggested mechanism for selective adsorption (Prakash *et al.*, 1999). However, in order to achieve effective and selective separation of hematite, additives, such as, sodium oleate and sodium hexametaphosphate, were required alongside pH control.

To avoid discoloration and/or clogging problems that may occur upon the introduction of magnetite carrier particles to a system, Shaikh *et al.* (1994) developed magnetic surfactant additives to act as carriers. The surfactants, manganese oleate and manganese stearate, were used to coat the targeted nonmagnetic minerals, calcite and barite, allowing them to be recovered via HGMS. In addition to preventing discoloration and clogging, the authors believed the paramagnetic salt coating would adsorb more uniformly onto the targeted mineral particles than traditional magnetic particle carriers. However, the selectivity of the paramagnetic salt coating was not demonstrated by the authors, only speculated upon.

More recently, magnetite combined with an undisclosed set of 'speciality chemical' additives, was used to separate kaolin from crude mixtures of kaolin and TiO_2 (Raitani *et al.*, 2012). For all crude mixtures investigated, the combination of the magnetite carrier particles and 'speciality' additives were able to collect kaolin samples with the concentrate possessing less than 0.6% TiO_2 . The 'speciality' additives were not identified within the publication, but it was suggested that each set of 'speciality' additives was designed to selectively interact with the target material and/or the impurities to aid separation. The hydrophobic effect was suggested to govern the adsorption of the additive coated kaolin particles onto the magnetite carrier particles.

Selective recovery of iron oxides was attempted using oleate coated magnetite particles. The selective recovery was facilitated through the exploitation of the known affinity of oleate for iron oxide (Singh *et al.*, 2014). Experiments were conducted using a crude sample of slime collected from an iron ore tailings pond. Overall, using a HGMS device for magnetic separation, the oleate-magnetite carrier system was able to recover 72 % of the total Fe in the mixture and produce a concentrate consisting of 62.6 % Fe at pH 7. Experiments conducted without the oleate additive attained a lower

recovery rate (62.4 % of the total Fe) under the same magnetic separation conditions (Singh *et al.*, 2014).

Magnetite carrier particles (~2.5 µm) supplemented with surfactant additives (sodium hexametaphosphate, oleic acid and kerosene) were used to selectively separate pentlandite from a serpentine/pentlandite mixture (Yuan *et al.*, 2017). Recoveries of 92 % pentlandite were obtained when utilising the optimum operating pH of 8.8. By calculating the interaction energies between the constituents of the system at pH 8.8, it was found that the presence of surfactants was required for effective separation. The surfactants strengthened the magnetite-pentlandite interaction, in comparison to the magnetite-serpentine interaction, allowing for selective adsorption, and therefore effective separation, of the pentlandite. The calculations carried by the authors showed that, while at pH 8.8, the magnetite-pentlandite interaction was electrostatically repulsive, hydrophobic and van der Waals forces overwhelmed this repulsion allowing the magnetite interaction experienced a much larger electrostatic repulsive force, too large for it to be overcome by the other attractive interaction forces. Thus, serpentine-magnetite attachment was not energetically favourable.

In conclusion, magnetic carrier technology for the selective and non-selective separation of suspended fine particles has been around for decades. Non-selective carrier systems for magnetic settling have been shown to vastly improve the settling rate, lower the remaining solid content of the fluid and reduce the final volume of the settled sludge (Tang et al., 2017). Specific separation of target materials using magnetic carrier technology has also been developed for a number of common mineral separation problems. However, limited studies have focused on the use of core-shell magnetic carrier particles (Gray et al., 1994) which would provide robust surface functionalisations and expand the variety of surface functionalisation available. Instead, most studies utilised salts and surfactants to adjust the surface characteristics of the carrier and/or target particles to provide selectivity (Anastassakis, 1999; 2002; Prakash et al., 1999; Raitani et al., 2012; Shaikh et al., 1994; Singh et al., 2014; Yuan et al., 2017). However, these additives complicate the system and may result in secondary contamination of the concentrate. In addition, the author could find no studies addressing possibility of recyclable magnetic carriers. Recyclable carriers would help reduce contamination of the concentrate, operating costs and the environmental footprint of the technology.

2.5.2 Heavy metal ion removal

Contamination of natural waterways and water sources by heavy metal ions, such as, Cr(IV), Pb(II), Fe(III), Cu(II), Zn(II), Hg(II) and Ni(II), pose a significant toxicity risk for living organisms (Zou *et al.*, 2016). Depending on the ion, heavy metals can infiltrate the environment via a large number of potential pathways, including industrial sources, such as, mining, manufacturing and fossil fuel combustion; and natural events, including volcanic explosions and weathering (Kumari *et al.*, 2015). Many recovery methods have been proposed, such as, chemical precipitation, electrochemical treatment and ultrafiltration (Bao *et al.*, 2017; Kumari *et al.*, 2015). However, many of these methods suffer from one or more of the following disadvantages: costly operation or capital outlay, high complexity and/or resulting in secondary pollution of the concentrate (Bao *et al.*, 2017).

In comparison, adsorption has long been associated with simplicity, reliability, low cost, wide applicability and low environmental impact (Zou *et al.*, 2016). When selective ion adsorption is used in conjunction with magnetic support/carrier particles, adsorption can provide a pathway to magnetic separation. Magnetic separation, as mentioned in Section 2.5.1, boasts low energy consumption, low operating costs, high yield and limited risk of secondary contamination (Raitani *et al.*, 2012). In addition, magnetic separation has been known to reduce impurities to very low concentrations (Broomberg *et al.*, 1999). This is extremely important to water and wastewater management where even low concentrations of certain toxic heavy metal ions may cause significant damage to humans and the environment. Unlike magnetic carrier technology for fine particle separation (Section 2.5.1), where only a handful of studies have been conducted in recent years, heavy metal ion recovery through magnetic carrier technology has received extensive research attention (Bao *et al.*, 2017; Hua *et al.*, 2012; Li *et al.*, 2013a; Ngomsik *et al.*, 2005; Wang *et al.*, 2010a; Zhang *et al.*, 2012a; Zou *et al.*, 2016).

Reviews by Zou et al. (2016), Hua et al. (2012) and Ngomsik et al. (2005) have exhaustively summarised the use of core-shell magnetic carrier particles for heavy number different metal ion recovery. А large of adsorbent material coatings/functionalities have been developed for heavy metal ion recovery including montmorillonite (Kalantari et al., 2015), zeolite (Khodadadi et al., 2017), ethylenediaminetetraacetic acid (EDTA) (Liu et al., 2013), humic acid (Liu et al., 2008a), azomethine (Ojemaye et al., 2017), crosslinked chitosan (Gutha et al., 2017) and modified crosslinked chitosan (Abou El-Reash, 2016; Wu et al., 2016). However, as discussed in Section 2.4.1, silica coatings provide the additional advantage of

providing a robust inorganic shell which offers protection to the magnetic core and stability against particle aggregation (Bao *et al.*, 2017; Laurent *et al.*, 2008). Generally, silica coatings are functionalised with chemical groups able to selectively adsorb the target heavy metal ions. One of the most common mechanisms for selective adsorption of the heavy metal ions is chelation (Bao *et al.*, 2017; Li *et al.*, 2013a; Zhang *et al.*, 2012a).

Chelation is the process whereby positively charged metal ions, with large charge densities, form coordinate covalent bonds with ligand species, which are molecules possessing at least one lone pair of electrons (Lawrance, 2010). The formation of a metal ion-ligand bond is known as a Lewis acid/Lewis base reaction. The reaction proceeds through the ligand species, acting as a Lewis base, donating a lone pair of electrons to the metal ion, which acts as a Lewis acid, resulting in the formation of a complex ion (Lawrance, 2010). In particular, Schiff base ligands, which possess their lone electron pair/s on N or O atoms, are well known for their ability to reversibly bind with heavy metal ions (Moftakhar *et al.*, 2016). These ligand groups can be used to functionalise the magnetic carrier particles allowing for the adsorption of heavy metal ions (Bao *et al.*, 2017; Li *et al.*, 2013a; Zhang *et al.*, 2012a). Ligand functionalisations may also act to electrostatically stabilise the carrier particle attachment, chelation offers interaction control through pH and is available in a large variety of chemical structures (Lawrance, 2010).

Zhang *et al.* (2012a) produced 500 nm diameter amine functionalised magnetic coresilica shell particles containing multiple Fe₃O₄ nanoparticle cores per particle. These amine functionalised core-shell particles were used as carrier particles for the removal of As(III), Cu(II) and Cr(III) ions from an aqueous solution. The core-shell carrier particles developed in this study were shown to successfully remove the heavy metal ions studied. Removal of As(III) was particularly successful, with Zhang *et al.* reporting a theoretical maximum adsorption capacity of 84 ± 5 mg As(III) g⁻¹, using the Langmuir model, from the adsorption data taken at pH 6. However, regeneration of the core-shell adsorbent was not demonstrated in this study. The adsorption mechanism believed to dominate ion removal was chelation between metal ion and amine functional group. In contrast, physical adsorption only contributed a relatively small amount to the overall adsorption (~5%).

Similarly, Li *et al.* (2013a) effectively demonstrated the adsorption and separation of Cu(II) ions from an aqueous environment using amine functionalised silica coated

magnetite nanoparticles as magnetic carrier particles. Surface complexation was suggested as the dominant driving force for attachment between the amino functionalised surface and the Cu(II) ions. Electrostatic attraction was also proposed to play a small role. Li and coworkers (2013a) demonstrated the core-shell particles' capacity for regeneration. The Cu(II)-amine complex possesses negligible stability at pH~2. Therefore, by incubating the Cu(II)-core-shell particles at low pH (pH 1) the Cu(II) ions were desorbed from the amine functionalised surface and the core-shell particles regenerated. After five regeneration cycles, although the core-shell particles experienced some reduction in adsorption capacity, recoveries of up to 90 % Cu(II) were still possible. However, as discussed in Section 2.4.1, both Zhang *et al.* (2012a) and Li *et al.* (2013a) synthesised and functionalised the silica shell via procedures that required multiple steps, long reaction times and harsh conditions, which are disadvantages when considering potential scale up of the core-shell synthesis process.

Amine functionalised mesoporous silica coated magnetite microspheres were developed by Tang *et al.* (2013) (Section 2.4.1) and used in the recovery of Pb(II) and Cd(II) ions from aqueous solution. The amine functionalised silica coating was found to have a higher adsorption capacity then the mesoporous silica coating without modification, indicating the amine surface groups played a significant role in ion adsorption. Maximum adsorption capacities of 128.1 and 51.81 mg g⁻¹ for Pb(II) and Cd(II), respectively, were determined for the amine functionalised core-shell particles using the Langmuir isotherm model. Desorption was achieved through incubation in 10 mM HCl, however, a slight penalty to re-adsorption was observed over each of the six adsorption-desorption cycles investigated. The major disadvantage of this system was the long fabrication time needed to synthesise these functionalised core-shell particle, which may make it difficult to extend the technique beyond a laboratory scale (Section 2.4.1).

The melamine functionalised magnetite core – mesoporous silica shell carrier particles were observed to have a high adsorption capacity for Pb(II), Cu(II), Cr(IV) and Cd(II) ions (Anbia *et al.*, 2015). Removal efficiencies of 88 % or higher were achieved for all the ions studied at pH 4 using the melamine functionalised carrier particles. Regeneration was demonstrated through acidic desorption of the ions in 300 mM HCI. Adsorption capacities over three cycles of ion adsorption/desorption were reported, with a slight decrease in the adsorption capacity of the carrier particles recorded with reuse. In Wang *et al.* (2015a), amine functionalised mesoporous silica-magnetite microspheres were developed for the adsorption and magnetic removal of Pb(II). A Langmuir maximum adsorption capacity of 243.9 mg g⁻¹ was obtained for this system

and the result attributed to the large amount of amino surface groups available for adsorption (2.77 mmol g⁻¹). Acid treatment allowed regeneration of the amine surface over five adsorption-desorption cycles with a slight reduction in adsorption capacity with reuse. However, once again, in Anbia *et al.* (2015) and Wang *et al.* (2015a), the preparation of the core-shell carrier particles involved an unideal combination of multiple steps, long reaction times and, for Anbia *et al.* (2015), high temperatures (Section 2.4.1).

Bao and coworkers (2017) demonstrated the effective recovery of Hg(II) and Pb(II) ions from wastewater utilising silica coated magnetite nanoparticles functionalised with amine and thiol surface groups. These surface functional groups resulted in both N and S interaction sites on the surface of the core-shell particles. It was suggested amine sites interacted with the ions through chelation, while the thiol sites were believed to adsorb the ions through a cation exchange mechanism. Equilibrium adsorption was reached within 120 mins. Langmuir calculated maximum adsorption capacities of 355 and 292 mg g⁻¹ were determined from the adsorption data of Hg(II) (at pH 5-6) and Pb(II) (at pH 6-7), respectively (Bao *et al.*, 2017). Reusability of the magnetic carrier particles was also demonstrated with acidic ion desorption. A penalty to adsorption capacity was observed over each of the five cycles, however, overall the adsorption rates remained above 93 %. However, as with the methods discussed previously in this section, the methodology of the carrier particle synthesis and functionalisation involves multiple and complex steps which will make it difficult to produce the carrier particles in large quantities (Section 2.4.1).

Overall, amine functionalised silica shell – magnetic core particles have been shown to provide stable, high capacity carrier particles for heavy metal ion adsorption (Bao *et al.*, 2017; Li *et al.*, 2013a; Wang *et al.*, 2010a; Zhang *et al.*, 2012a). Chelation between the amine and metal ion was believed to be the main driving force for adsorption (Bao *et al.*, 2017; Li *et al.*, 2013a; Zhang *et al.*, 2012a). For Cu(II) adsorption, the dependence of the Cu(II)-amine complex stability on pH allowed for the desorption on Cu(II) and therefore for the regeneration and reuse of the core-shell particles over multiple cycles (Li *et al.*, 2013a). Acidic desorption was subsequently demonstrated for other ions in later studies (Anbia *et al.*, 2015; Bao *et al.*, 2017). In addition, developing particles with both amine and thiol functionalisation allowed for increased interaction sites and greater adsorption capacities without significant sacrifices to reusability (Bao *et al.*, 2017). However, the complex processes, long reaction times and/or harsh conditions employed during core-shell fabrication/functionalisation may pose a significant obstacle to process scale up (Bao *et al.*, 2017; Li *et al.*, 2013a; Wang *et al.*, 2010a; Zhang *et al.*,

2012a). Hence, the development of a facile and economically sound means of fabricating the functionalised core-shell carrier particles for heavy metal ion recovery is necessary.

2.5.3 CO₂ capture

Since the advent of the industrial revolution, fossil fuel combustion has contributed to a continually rising concentration of CO₂ in the atmosphere (ESRL, 2015; Li *et al.*, 2017). Atmospheric CO₂ is currently ~40 % higher than in the pre-industrial revolution era (ESRL, 2015; Li *et al.*, 2017). This increase in the atmospheric CO₂ has contributed to a number of serious environmental issues, including rising sea temperatures and levels, melting ice caps and an increase in the frequency of erratic weather events worldwide (Stocker *et al.*, 2013). As fossil fuels continue to dominate the world's energy production, devices for the capture and storage of CO₂ are of significant research interest. These devices will help to prevent further rises in atmospheric CO₂ and hopefully forestall its continued ill-effects (Bonenfant *et al.*, 2003; Dutcher *et al.*, 2015; Li *et al.*, 2017).

The adsorption of CO_2 onto amines is well established in the literature (Bonenfant *et al.*, 2003; Dutcher *et al.*, 2015). The CO_2 -amine interaction usually results in formation of a carbonate or bicarbonate, as shown in Schemes 2.5 and 2.6, respectively (Bonenfant *et al.*, 2003; Dutcher *et al.*, 2015). The amine- CO_2 interaction is known to be reversible. Heating the CO_2 -rich amine will drive the equilibrium of the reaction (Schemes 2.5 and 2.6) towards the reactants, desorbing the CO_2 (Dutcher *et al.*, 2015). This desorption reaction allows for the regeneration of the amine sorbents, reducing waste and overhead costs. Bonenfant *et al.* (2003) determined that sorbent compounds containing multiple amine groups and those with tertiary amines displayed superior CO_2 adsorption and regeneration capabilities.

Scheme 2.5. Carbonate formation through the amine – CO₂ reaction.

 $2R_1R_2NH + CO_2 \rightleftharpoons (R_1R_2NH_2^+)(R_1R_2NCOO^-)$

Scheme 2.6. Bicarbonate formation through the amine – CO₂ reaction.

$$R_1R_2NH + CO_2 + H_2O \rightleftharpoons (R_1R_2NH_2^+)(HCO_3^-)$$

A number of non-amine based technologies, such as those utilising cryogenics, alkali metal ceramics and metal oxides for adsorption, have also been investigated for CO_2 capture, some offering exceptionally high stability or adsorption capacities (Alcántar-Vázquez *et al.*, 2013; Bhatta *et al.*, 2015; Dey *et al.*, 2017; Memon *et al.*, 2017, Safdarnejad *et al.*, 2015). However, in spite of these advances, amine based technologies remain the most developed and economically feasible option currently available (Dutcher *et al.*, 2015).

Current CO₂ capture technologies can be categorised based on when in the lifecycle the CO₂ is captured. In post-combustion technologies, the CO₂ is collected from the emitted gas. Post-synthesis technologies receive the majority of the research attention as they can be adapted for existing plants, which results in significantly lower capital costs (Dutcher *et al.*, 2015; Khakharia *et al.*, 2013). In a typical post-combustion amine scrubbing unit, the exhaust gas containing CO₂ is passed through an aqueous amine solution where the CO₂ is captured. The CO₂-rich amine is then sent to the stripper where it is heated, and the CO₂ desorbed, allowing the aqueous amine to be reused. This process has been utilised for over 60 years and is currently considered the most economically feasible technique for CO₂ removal available (Dutcher *et al.*, 2015; Rochelle, 2009). However, issues associated with this technique include, the loss of amines through thermal degradation and evaporation, and the potential poisoning of the CO₂ capture unit from SO_x and NO_x gases also found in post-combustion flue gas (Dutcher *et al.*, 2015; Khakharia *et al.*, 2013; Mertens *et al.*, 2012; Nguyen *et al.*, 2011).

Amine losses through evaporation are not only an issue of reusability, but also a serious environmental concern (IEAGHG, 2010; Khakharia *et al.*, 2013). Although, water washers and demisters have been fitted to scrubbing units in an attempt to contain the amines, vaporised amine aerosols were found to easily escape these traps (Mertens *et al.*, 2012). An alternative technology, which reduces amine losses to evaporation, is the use of solid sorbents. Moreover, solid sorbents have further advantages over liquid amines including greater stability, higher resistance to pollutants, higher CO₂ capacity and a reduction in the energy needed for heat regeneration (Dutcher *et al.*, 2015). These solid sorbent technologies are promising but still require further development in order to challenge the economic viability of established liquid amine technologies.

Dutcher *et al.* (2015) categorised amine based solid sorbents on the basis of their preparation. Sorbents of Class I are prepared by *in situ* co-precipitation or entrapment of the amine molecules into the solid. Sorbents classified as Class II are prepared by

chemically grafting the molecule containing the amine functionalisation onto the surface of the solid support. While, Class III sorbents also had the amine attached to the solid support post-synthesis in this class the amine group was polymerised onto the surface.

There are advantages and disadvantages to each class of solid sorbent. For example, Class I sorbents were found to consistently produce the highest CO₂ adsorption capacity (Dutcher *et al.*, 2015). However, when compared with the grafting methods (Classes II and III), Class I sorbents were found to experience more losses due to the evaporation of the entrapped amines, especially where smaller amine molecules were entrapped (Dutcher *et al.*, 2015). It was found that the stability issues associated with the escape of entrapped amines could be allayed by the use of larger amine molecules, such as, polyethylenimine (PEI) and tetraethylenepentamine (TEPA), for entrapment (Dutcher *et al.*, 2015). Advancements in solid sorbent technology are well covered by Dutcher *et al.* (2015), in the interest of brevity this literature review will provide only a few key highlights.

Wang *et al.* (2014e) prepared a 3-dimensional mesoporous silica structure impregnated with PEI via incubation and evaporation. The author's observed a PEI loading of up to 80 wt.%. At 75 °C and 1 bar CO₂, the PEI-mesoporous silica solid sorbent was observed to possess an equilibrium CO₂ capacity of 4.5 mmol g⁻¹. A slightly higher adsorption capacity of 4.7 mmol g⁻¹, at the same temperature/pressure, was measured for PEI impregnated-mesoporous carbon (Wang *et al.*, 2014e). This was also the highest CO₂ capacity for a solid sorbent identified in Dutcher and coworkers' (2015) review. The results of Wang and coworkers' (2014e) study demonstrate the high CO₂ capacity available using entrapped PEI solid sorbents.

Li *et al.* (2017) prepared polymer grafted magnetite nanoparticles for CO_2 capture. The magnetite core provided the additional advantage of magnetic responsivity allowing for a low energy method to move, place and recover the solids. Of the amine-heavy polymers examined in this study, the PEI-grafted magnetite was observed to possess the highest capacity and selectivity for CO_2 capture. Moreover, the PEI-grafted magnetite sorbent particles were found to perform well even at the elevated temperatures (40-80 °C) necessary for post-combustion CO_2 capture. The highest CO_2 adsorption was observed for particles with 16 wt.% PEI loading, which were recorded to have CO_2 adsorption capacity of 18.8 mg g⁻¹ at 60 °C. The PEI-grafted magnetite adsorption/desorption cycles.

Aside from Li and coworkers' study (2017), and despite the advantages of magnetic separation, limited work has been published investigating the possibility of CO₂ capture via amine modified magnetic core-shell particles. PEI has been identified as a clear forerunner in the search for high capacity and selective amine functionalisation for solid supports. Although, silica supports with PEI surface modification have been investigated, those investigation, to the author's knowledge have been focused on PEI attached through polymer grafting and adsorption (Li *et al.*, 2017; Wang *et al.*, 2014e). Class I PEI-silica supports, such as, those possible through the biomimetic synthesis process (Neville *et al.*, 2009), are likely to impart increased amine stability as the PEI will be entrapped within the silica structure.

2.5.4 Conclusions

Development of magnetic carrier particles for the separation of non-magnetic materials has led to applications in a number of fields, chief among them being the selective separation of fine particles, removal of toxic heavy metal ions and capture of CO₂ gas. As a separation technique, magnetic separation has the advantages of low energy consumption, low operating costs, high yield and ease of operation (Raitani *et al.*, 2012). Magnetic carrier technology acts by selectively (or non-selectively) attaching to the non-magnetic materials allowing them to be separated via robust magnetic separation techniques. However, improvements in the selectivity, efficiency, recyclability and ease of carrier particle synthesis, drive the invention of novel magnetic carrier technologies to recover target fine particles, molecules and ions.

2.6 Conclusions

In this review, the current methods of colloidal silica synthesis were discussed in Section 2.2. It was concluded, that while established high temperature gaseous synthesis methods continue to fall out of favour in our energy conscious society, liquid synthesis methods have become the current industrial leaders. The precipitated silica method provides the majority share of commercially produced specialty silicas with its economic advantages predicted to ensure continued growth in the near future. The biomimetic method and microemulsion methods of synthesis provide a superior level of surface chemistry and morphological control when compared to current industrial silica synthesis. Due to these advantages, the development of biomimetic and microemulsion methods form the bulk of current silica synthesis research. Movement toward more tailor-made products and ecologically friendly production methods will likely provide incentive for biomimetic methods, in particular, to take more of a market share. However, the lack of procedures to viably scale up the biomimetic and microemulsion methods still form a significant gap in the literature.

Functionalisation of the silica surface is necessary to facilitate selective interaction of the silica surface with target materials. Section 2.3 discussed the developments in silica surface modification, namely those provided through the adaption of during-synthesis conditions or post-synthesis procedures. Review of the literature found that although a significant number of silica functionalisation methods have been reported upon, no one method has yet produced a robust, high coverage surface modification process without the modifications available being limited or requiring a complex multi-step procedure.

Section 2.4 examined the construction of the core-shell particles. Core-shell particles have been used for a variety of applications due to the versatility of their properties which combine that of the core and shell materials into a single entity. Silica shell fabrication techniques were generally found to be adaptions of the Stöber and microemulsion methods of silication. However, many of the silica coating methods presented in the literature required complex methodologies, harsh conditions, long reaction times and/or high temperatures, especially when the silica surface was functionalised. Selection of the magnetic core material and size was found to be important for effective magnetic collection of the core-shell particles.

Magnetic core-shell particles can be used as magnetic carrier particles, which act by selectively attaching to target materials, facilitating the magnetic separation of non-magnetic materials. As a separation technique, magnetic separation has a number of

advantages including relatively low energy consumption, small operating costs, high yields and lack of process complexity (Raitani *et al.*, 2012). Section 2.5 provided an overview of current industrial and laboratory-based magnetic separation techniques based on magnetic carrier particles for the recovery of mineral fines, heavy metal ions and CO₂ gas. Improvements to selectivity, separation efficiency and recyclability drive the scientific research in these fields forward. In addition, simplification of the core-shell fabrication process will be necessary for effective large-scale operation of these separation techniques.

CHAPTER THREE

Materials and Methods

3.1 Introduction

This chapter gives the chemical materials and methodology used within this PhD project. Section 3.2 describes the chemical materials, preparation of buffers and basic equipment used for experiments. In Sections 3.3, 3.4 and 3.5, the methods for silica particle synthesis, silica particle surface modification and silica shell fabrication are described. Section 3.6 outlines the methods for adsorption-desorption of Cu(II) ions, fine particle powders and Au nanoparticles onto the core-shell particle surface. The characterisation techniques used in this project are introduced and discussed in Section 3.7, alongside their corresponding methods of sample preparation.

3.2 Materials

3.2.1 Chemical materials

All chemical materials were used without further purification except where noted. Ultrapurified water (18.2 m Ω cm) was used to make all solutions and for washing of particles and glassware, except where specified. Reactions/incubations were performed at room temperature (293-298 K) and atmospheric pressure unless otherwise stipulated.

The following materials were purchased from Sigma-Aldrich: trimethoxymethylsilane (TMOMS), 3-mercaptopropyltrimethoxysilane (3mPTMOS), hydrochloric acid (HCI), sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), branched 25 kDa polyethyleneimine (PEI), mercaptoundecanoic acid (MUA), 4-aminothiophenol (4-ATP), ethanol, methanol, carbonyl iron (\geq 97 % Fe basis), copper(II) sulfate (\geq 99 % CuSO₄), glycylglycine (\geq 99 %), talc (powder, <10 µm), montmorillonite (K10, powder), kaolin (hydrated aluminium silicate, Bolus), quartz (powder, \leq 230 mesh) titanium(IV) oxide (nanopowder, ~21 nm particle size, \geq 99.5 % trace metal basis) and gold nanoparticles (10 nm diameter, stabilised suspension in 0.1 mM phosphate buffer saline, reactant free). Analytical grade di-sodium hydrogen orthophosphate (anhydrous granular, Na₂HPO₄.2H₂O) and sodium dihydrogen orthophosphate (dihydrate, NaH₂PO₄.2H₂O) were purchased from Chem-supply. Succinic acid (99+%) was purchased from Lancaster Chemicals.

3.2.2 Buffer preparation

500 mM phosphate buffer (PB) solutions were prepared as stock solutions. 500 mM $Na_2HPO_4.2H_2O$ and 500 mM NaH_2PO_4 solutions were prepared separately by accurately weighing and dissolving the solids $Na_2HPO_4.2H_2O$ and NaH_2PO_4 in water. PB was made

by combining the $Na_2HPO_4.2H_2O$ and NaH_2PO_4 solutions in such a ratio that the desired pH was reached. PB solutions were prepared at pH 6.0, 7.4 and 8.0 at 298 K.

Succinic acid buffer was prepared by dissolving solid succinic acid in water to a concentration of 500 mM (with an initial pH of ~1.7). The pH was then adjusted through dropwise additions of 1.00 M NaOH to the desired pH of 4.0 at 298 K.

Glycylglycine (gly-gly) buffer (pH 10.0) was prepared from solid gly-gly. A 500 mM glygly solution was prepared by accurately weighing the gly-gly solid and dissolving it in water (with an initial pH of ~5.3). 1.00 mM NaOH was used to adjust the pH to 10.0 at 298 K.

3.2.3 General equipment

In this subsection, the general equipment and instruments used in this project are outlined.

1.000 mL experiments were typically performed in 1.5 mL polypropylene graduated microtubes purchased from Interpath Services. While larger experiments were conducted in 15 mL or 50 mL high clarity polypropylene conical tubes purchased from Falcon. Stock solutions were prepared and stored in the 15 mL or 50 mL high clarity polypropylene conical tubes from Falcon or glass bottles.

Three Effendorf Research Plus volume-adjustable pipettes, in the sizes 2-20, 20-200 and 100-1000 μ L, were used to accurately measure volumes. A Shimadzu UniBloc AUW120D was used for weight measurements.

Vortex mixing was performed with the either the IKA MS3 Basic Vortex Mixer or the LLG labware Vortexer LLG-uni*TEXER* with universal attachment to carry multiple microtubes and conical tubes. The speed of vortex mixing used in each instance are specified in the experimental methods within this chapter.

The ultrasonic bath used was the Unisonics Australia - ULTRASONIC CLEANER. During ultrasonication, the temperature of the bath was monitored with a liquid in glass thermometer and maintained at room temperature (298 K) through small additions of ice as necessary.

Centrifugation of the 1.5 mL polypropylene graduated microtubes was performed using the Eppendorf 5418 Centrifuge. The speed and time length of centrifugation are specified the experimental methods within this chapter.
For characterisation, the following instruments were utilised: Cressington 208 Carbon Coater, Zeiss Sigma field emission gun scanning electron microscope (FEGSEM), Spectrum Two (PerkinElmer) attenuated total reflectance – Fourier transfer infrared spectrometer (ATR-FTIR) instrument, Malvern ZetasizerNano ZS and Shimadzu UV-1800 UV-visible spectrometer. The sample preparation and characterisation techniques used with these instruments are described in Section 3.7.

3.3 Silica particle synthesis

3.3.1 PEI-silica particle synthesis

The first stage of the project involved the fabrication of PEI-TMOMS silica particles, which were synthesised as per the method outlined in Neville *et al.* (2009) and reiterated briefly here. Prior to particle synthesis, 1.00 M of TMOMS was hydrolysed in 1.00 mM HCI for 15 min. For synthesis, typically, 100 mM hydrolysed TMOMS, 2.50 mg mL⁻¹ polyethylenimine (PEI) and 29.0 mM PB were combined in a 1.000 mL reaction tube via vortex mixing (5 s at 3000 rpm). The reaction proceeded for 30 min with no further mixing. The reaction was stopped through centrifugation (1 min at 14000 rpm) and the removal of the reactants with the supernatant. This process was followed by two washing cycles. In some experiments, the concentration of hydrolysed TMOMS used in the synthesis was varied. In Chapter 4, for example, PEI-silica particles were synthesised with 200 mM hydrolysed TMOMS to achieve a more accurate comparison to the NaOH-silica particles (Section 3.3.2).

3.3.2 NaOH-silica particle synthesis

In order to simplify the PEI-silica synthesis method (Section 3.3.1), while retaining the advantageous of having an aqueous reaction medium at room temperature (293-298 K) and atmospheric pressure, a new silica synthesis method was developed as part of this project. This novel method of silica synthesis was denoted NaOH-silica particle synthesis.

Trimethoxymethylsilane (TMOMS) was used as the silica precursor. Prior to reaction, 1.00 M TMOMS was hydrolysed in 1.00 mM HCl for 15 min. In a typical 1.000 mL reaction, 200 mM hydrolysed TMOMS and 25.0 mM NaOH were combined through a brief period of vortex mixing (5 s at 3000 rpm). The synthesis reaction proceeded with no further mixing for 30 min. The 200 mM hydrolysed TMOMS concentration was used

in NaOH-silica synthesis as it was found that TMOMS concentrations of 100 mM or less were not able to produce particles within the 30 min reaction period (Neville *et al.*, 2016).

To stop the reaction the solid matter precipitated during the reaction was 'spun down' using centrifugation (1 min at 4000 rpm). The supernatant, containing the residual reactants and by-products, was removed. To wash the synthesised particles, the particles were resuspended in 1.000 mL water though ultrasonication and centrifuged to remove the washing fraction. The washing process was conducted at least twice for every particle synthesis reaction.

For Chapter 4, the average yield of NaOH-silica particles (and PEI-silica particles, method outlined Section 3.3.1, for comparison) was calculated using a sample set of no less than five 1.000 mL reactions. Particles were synthesised in 1.5 mL polypropylene graduated microtubes of known mass and desiccated for more than 72 h before the final mass measurements were taken. The yield was defined as the mass of silica particles per mL of reaction. The percentage yield was calculated as the weight percent of hydrolysed TMOMS consumed in the reaction.

3.3.3 PEI-thiol silica particle synthesis

A second method of silica particle fabrication from the literature (Neville *et al.*, 2009), known as PEI-thiol silica particle synthesis, was also used in this project. PEI-thiol silica particle synthesis follows the PEI-silica particle synthesis methodology outlined in Section 3.3.1. However, to produce PEI-thiol silica particles, the silica precursor, TMOMS, was replaced with 3-mercaptopropyltrimethoxysilane (3mPTMOS), giving the particles a thiol functionalisation, see Table 3.1.

Table 3.1. The chemical structures of the silane precursors used to produce silicaparticles. Trimethoxymethylsilane (TMOMS) was used to produce PEI-silica andNaOH-silica particles, while, 3-mercaptopropyltrimethoxysilane (3mPTMOS) was usedin the synthesis of PEI-thiol silica particles.



3.4 Modification of the silica surface

Post-synthesis modification of the silica particle surface was explored using two types of attachment. The first utilised electrostatic attraction between the modifier and the silica surface to reversibly modify the NaOH-silica surface (Section 3.4.1). The second utilised the formation of a covalent disulfide bond between PEI-thiol silica surface and modifier to introduce an irreversible surface modification (Section 3.4.2).

3.4.1 Electrostatic modification of NaOH-silica particles with PEI

The NaOH-silica particles were prepared using the methodology described in Section 3.3.2. Prior to modification, synthesised NaOH-silica particles were stored in 0.100 mL water at 276 K for up to a week. A stock solution of 1.00 mM PEI was also prepared.

Typically, PEI was adsorbed by resuspending the NaOH-silica particles from one 1.00 mL reaction (approximately 9 mg) in 145 mM pH 7.4 PB and 0.200 mM PEI to a final volume of 1.000 mL. The suspended particles were incubated with PEI for 1 h, throughout the incubation period, vortex mixing (5 s at 3000 rpm) at 15 min intervals was used to retain the particles in suspension. The modification reaction was stopped after the 1 h incubation time by centrifugation (30 s at 14000 rpm) and any unattached PEI removed with the supernatant. The modified particles were washed an additional two times with water to remove any remaining unbound PEI. Incubation PEI concentrations from 0 to 0.500 mM and incubation times between 10 to 120 min were also investigated.

PEI was desorbed from the NaOH-silica particle surface by suspending the PEI-modified NaOH-silica particles in 2.00 mM HCI. The particles were incubated for 1 h with vortex mixing (5 s at 3000 rpm) at 15 min intervals. After incubation in acid, the particles were

centrifuged as above and the supernatant was removed. The particles were washed twice with water.

3.4.2 Covalent modification of PEI-thiol silica particles

Covalent surface modifications were made by reacting thiol modifiers with the thiol surface groups of the PEI-thiol silica particles. PEI-thiol silica particles were synthesised as per Section 3.3.3. Prior to modification, PEI-thiol silica particles were stored in 0.100 mL water at 3.0 °C. The thiol modifiers used were mercaptoundecanoic acid (MUA) and 4-aminothiophenol (4-ATP). Stock solutions of 10.0 mM MUA and 10.0 mM 4-ATP in water were prepared daily for modification reactions.

Initially, approximately 3 mg PEI-thiol silica particles were suspended in PB (pH 8.0). To the resuspended particles, the thiol modifier (MUA or 4-ATP) was added, so that the final reaction concentrations were 5.00 mM thiol modifier, ~3 mg mL⁻¹ PEI-thiol silica particles and 100 mM PB, and the final reaction volume was 1.000 mL. The modification reaction was carried out for 48 h at room temperature (293-298 K) with periodic vortex mixing (5 s at 3000 rpm) to avoid particle settling. Centrifugation (30 s at 14000 rpm) stopped the reaction and the particles were washed twice with water. A control was performed for the MUA modification utilising PEI-silica particles instead of PEI-thiol silica particles to ensure disulfide bond formation was the mechanism for modification.

Due to the low solubility of MUA in water, MUA modifications were also performed in an ethanol medium. For this experiment, a stock solution of 20.0 mM MUA in ethanol was prepared. The same procedure was carried out as before, however, the PB solution used for particle resuspension was replaced with ethanol and the stock solution of MUA in ethanol was used as the thiol modifier. The final concentration of the MUA modifier in the reaction mixture was also changed to 10.0 mM. After the modification reaction, particles were first washed twice with ethanol and then once with water.

3.5 Silica shell synthesis

The magnetic separation process is detailed in Section 3.5.1. Seven different coating fabrication methods and four different reactant concentrations were used for coating; these methods and concentrations are outlined in Section 3.5.2. The two most successful coating methods were scaled up as per Section 3.5.2.5. In Section 3.5.3, the procedure for PEI-thiol silica shell synthesis and scale up methodology was detailed.

3.5.1 Magnetic separation

To trial the magnetic separation method, the magnetic separation of the magnetic core particles from the core-free silica was tested. PEI-silica particles were synthesized as per Section 3.3.1. In a polypropylene microcentrifuge tube, the PEI-silica particles (~9 mg mL⁻¹) were suspended with carbonyl iron (~5 mg mL⁻¹) in a 9:1 water:methanol medium, with a total volume of 1.00 mL, using vortex mixing (5 s at 3000 rpm) and ultrasonication. After the suspended PEI-silica and carbonyl iron core particles were thoroughly mixed, a permanent neodymium magnet was placed against the outside of the polypropylene microcentrifuge tube, attracting the magnetic carbonyl iron core species. The non-magnetic supernatant was removed using a glass pipette whilst the magnet was still in place against the outside of the reaction tube. The magnetically separated particles were subsequently washed thrice through resuspension in ~1 mL water and magnetic separation.

3.5.2 PEI-silica shell synthesis

In this study seven coating methods were trialled. The procedures for each method are detailed below. For all coating methods reactions, the final concentration of reactants was 5.0 ± 0.3 mg mL⁻¹ carbonyl iron (Fe) particles, 1:9 methanol:H₂O, 100 mM PB, 2.50 mg mL⁻¹ PEI and a TMOMS concentration of 50, 100, 200 or 300 mM. A reaction volume of 1.000 mL was used for all experiments. In the methods requiring pre-hydrolysed TMOMS, 1.00 M TMOMS was incubated in 1.00 mM HCI for 15 min immediately preceding the synthesis reaction. Also for all methods, after reactants were added, synthesis was conducted at room temperature (293-298 K) for 30 min. During the reaction time, the reaction tubes were upended at 5 min intervals to prevent settling of the carbonyl iron cores.

After the coating reactions were complete, magnetic separation was used to separate the coated magnetic particles from the nonmagnetic by-product and unused reactants. As in Section 3.5.1, the magnetic separation was carried out by placing a neodymium permanent magnet next to the reaction tube. Once the magnetic particles were drawn to the magnet, the supernatant was removed. The coated magnetic particles were subsequently washed thrice through resuspension in ~1 mL water and repeating the magnetic separation process as above.

The coating methods investigated can be split into the categories of 'two pot', 'sonication', 'all in one' and 'slow addition' methods and are detailed in the subsections below.

3.5.2.1 Two pot methods (Methods A and B)

In Method A, carbonyl iron particles suspended in methanol were combined with hydrolysed TMOMS and half the amount of PB by vortex mixing (5 s at 3000 rpm). In a separate vessel, PEI was combined with the other half of the PB (vortex mixing for 5 s at 3000 rpm). Both tubes were incubated separately for 15 min, then combined (through vortex mixing for 5 s at 3000 rpm) for a 30 min reaction. Method B followed the same sequence as Method A, however, in Method B the carbonyl iron was combined with the PEI and half the PB, and in a separate tube the TMOMS was combined with the other half of the PB.

3.5.2.2 Sonication methods (Methods C and D)

The sonication methods are one pot synthesis techniques in which the vortex mixing was substituted with ultrasonication. In Method C, neat (non-hydrolysed) TMOMS was combined with dry carbonyl iron particles, the mixture was then sonicated for 5 min. Immediately after ultrasonication PEI was added to the mixture, followed by another 5 min of ultrasonication. Then PB and methanol were added and sonicated for a final 5 min, followed by a 30 min reaction period. Method D follows Method C, but with the timing of PEI and TMOMS additions switched. Thus, in Method D, PEI was added before the first period of ultrasonication and the TMOMS before the second period of ultrasonication.

3.5.2.3 All in one method (Method E)

The all in one method is also a one pot technique. In this method, the carbonyl iron suspended in methanol was added first, followed by all other reactants added in quick succession (PB, PEI, hydrolysed TMOMS) and then combined through vortex mixing (5 s at 3000 rpm) followed by the 30 min reaction.

3.5.2.4 Slow addition methods (Methods F and G)

The slow addition methods are one pot techniques were one reactant is added gradually. In Method F, carbonyl iron particles suspended in methanol were combined first with PEI and PB. The hydrolysed TMOMS was then added in even fractions at 1 min intervals over a 10 min period. After each fraction of TMOMS was added, the reaction tube was upended to incite mixing. After the 10 min period, reactants were thoroughly combined through vortex mixing (5 s at 3000 rpm) and the reaction left to proceed for 30 min.

Method G used the same methodology as Method F, however, in Method G the suspended carbonyl iron particles were first mixed with TMOMS and PB, and the PEI was added via slow additions over a 10 min period.

3.5.2.5 Scale up

Methods D (Section 3.5.2.2) and G (Section 3.5.2.4) at 100 mM and 200 mM TMOMS, respectively, were scaled up by a factor of 10 and 50. These methods were selected as they seemed to provide the most effective coating methods. The reactant concentrations used were the same as detailed in Section 3.5.2, however, the overall reaction volumes were 10.000 mL and 50.000 mL for the scale up.

3.5.3 PEI-thiol silica shell synthesis

The methods for PEI-thiol silica shell synthesis followed the same procedures as Methods D and G used for PEI-silica shell fabrication (Section 3.5.2), however, in this method the silane used for the shell fabrication was changed to 3mPTMOS. Using the silane 3mPTMOS (as in Section 3.3.3) produced a silica shell with a thiol functionalisation. As in Section 3.5.2, the final reactant concentrations were 5.0 ± 0.3 mg mL⁻¹ carbonyl iron particles, 1:9 methanol:H₂O, 100 mM PB and 2.50 mg mL⁻¹ PEI and final reaction volume was 1.000 mL. However, only a 100 mM (for Method D) and 200 mM (for Method G) 3mPTMOS concentration were considered for these experiments as these were the most successful coating methods and silane concentrations for the PEI-silica shell fabrication experiments (Chapter 6). The sonication and slow addition methods used for PEI-thiol silica shell synthesis were the same as detailed in Sections 3.5.2.2 and 3.5.2.4, except that the TMOMS reactant was replaced with 3mPTMOS.

3.5.3.1 Scale up

The PEI-thiol silica fabrication methods examined were tested for scale up potential. Here, the volume of all reactants in Methods D and G (Section 3.5.3) were scaled by a factor of 10, thus the shell fabrication procedure was conducted in 10.000 mL reaction volumes compared with the 1.000 mL reactions tested in Sections 3.5.3.

3.6 Ion and fine particle recovery using silica shell – carbonyl iron core particles

The core-shell particles synthesised using the methods outlined in Sections 3.5.2 and 3.5.3 were utilised for the ion and fine particle recovery experiments. The optimum methodology and concentrations for synthesis were taken from the results in Chapter 6. PEI-silica shell – carbonyl iron core particles were synthesised using Method D and 100 mM TMOMS; and G and 200 mM TMOMS. In the case of PEI-thiol silica shell – carbonyl iron core particles of peI-thiol silica shell – carbonyl iron core particles only Method D was used for fabrication with 100 mM 3mPTMOS. Method G was not considered for the PEI-thiol silica shell – carbonyl iron core particles as the shell produced using Method G was fairly inconsistent/uneven (Chapter 6).

All particles were synthesised in 10.000 mL tubes as per the scale up procedure (Sections 3.5.2.5 and 3.5.3.1). After synthesis, core-shell particles were dried by desiccation for at least 7 days before use in the ion adsorption (Section 3.6.1) and fine particle recovery (Section 3.6.2) including Au nanoparticle adsorption (Section 3.6.2.1) experiments detailed below. The desiccation time of at least a week was selected to ensure particles were completely dry, therefore ensuring accurate weight measurements of the dried particles were taken.

3.6.1 Cu(II) ion adsorption – desorption

In this section, the PEI-silica shell – carbonyl iron core particles were investigated as magnetic carrier particles for the removal of the heavy metal ion, Cu(II). The core-shell particles were synthesised using the methods outlined in Section 3.5.2. As discussed at the beginning of Section 3.6, the core-shell particles were dried by desiccation for at least a week before adsorption experiments, to ensure complete drying. 100 mM CuSO₄ stock solutions were prepared weekly by dissolving solid CuSO₄ in water. From a 500 mM PB (pH 6.0) stock solution prepared as per Section 3.2.2, a diluted stock solution of 160 mM PB (pH 6.0) was prepared weekly for these experiments.

Typically, 5.0 ± 0.3 mg of the dried core-shell particles were weighed out into reaction tubes. However, a range of core-shell particles masses from 1.5 to 12.0 ± 0.3 mg were also investigated. Core-shell particles were suspended through ultrasonication in 0.750 mL water. PB (pH 6.0, 160 mM) and CuSO₄ were then added to the suspended particles. Generally, the final concentrations for the adsorption experiments were 5.0 ± 0.3 mg mL⁻¹ carbonyl iron, 32.0 mM PB (pH 6.0) and 5.00 mM CuSO₄ with an overall volume of 1.000 mL. CuSO₄ concentrations between 2.50 mM and 20.0 mM were also investigated.

No buffer or MES buffer (pH 6.0) at concentrations 16.0, 32.0 and 48.0 mM was substituted for PB for some preliminary studies.

The mixture was vortex mixed at 1000 rpm over a 10 min incubation period. After incubation, magnetic separation (Section 3.5.1) was used to separate the core-shell particles and the supernatant. The supernatant collected was kept for spectroscopic characterisation described in Section 3.7.6.3.

For Cu(II) desorption, core-shell particles were washed once with water after Cu(II) adsorption. The core-shell particles were then re-suspended in 1.000 mL of 1.00 mM HCI through ultrasonication and then vortex mixed at 1000 rpm for 10 min. After desorption core-shell particles were washed twice in water before re-adsorption or characterisation.

Following the last washing step, as much as possible of the water used for washing was removed via magnetic separation. Re-adsorption followed the same procedure as adsorption process, with particles first resuspended through ultrasonication in 0.750 mL water. Resuspension was followed by the additions of 0.200 mL PB (pH 6.0, 160 mM) and 0.050 mL CuSO₄ (100 mM) and a 10 min incubation period with continuous vortex mixing at 1000 rpm.

3.6.2 Fine particle adsorption – desorption

The fine particle recovery potential of the core-shell particles developed in this thesis was investigated by studying the interaction of the PEI-silica coated carbonyl iron particles (Section 3.5.2) with various fine particle materials. The core-shell interaction with the fine particles (talc, montmorillonite, kaolin, quartz and titanium oxide (TiO₂)) were tested at pH 4.0, 7.0 and 10.0. The ability to desorb and re-adsorb the fine particles to the core-shell surface was also investigated. Moreover, in Section 3.6.2.1, the interaction of gold (Au) nanoparticles with both the PEI-silica and PEI-thiol silica coated core-shell particles was investigated due to gold's known affinity with thiol and amine functional groups.

The PEI-silica shell – carbonyl iron core particles were synthesised as outlined in Section 3.5.2 and specified at the beginning of Section 3.6. The fine particles used in this study were talc, montmorillonite, kaolin, quartz and TiO₂. The purity and original size of these fine particles, in cases where this information was provided by the manufacturer, are noted in Section 3.2.1. All samples of fine particles, excepting TiO₂ due to its already fine nature, were dry ground using a mortar and pestle before the experiments. The size of

the fine particles following grinding were not determined in this study as it was a preliminary investigation, however, further work will involve thorough characterisation of these fine particles. A bulk suspension of each fine particle material was prepared in water at a concentration of 10.0 ± 0.3 mg mL⁻¹. Bulk suspensions were prepared freshly for each set of experiments.

The buffers used in this experiment were Gly-gly buffer (pH 10.0), PB (pH 7.0) and succinic acid buffer (pH 4.0) all prepared as a 500 mM stock solution prior to experiments. Details of buffer preparation are presented in Section 3.2.2.

 3.0 ± 0.3 mg of the dried core-shell particles were weighed into reaction tubes. The coreshell particles were then re-suspended in buffer solution and water through ultrasonication. The fine particle suspensions were then added to the reaction tubes. The final concentrations were 3.0 ± 0.3 mg mL⁻¹ suspended core-shell particles, 3.0 ± 0.3 mg mL⁻¹ suspended fine particles and 100 mM buffer with a total volume of 1.000 mL. The components were then combined by vortex mixing at 2000 rpm for 5 s. To prevent settling, the reaction tubes were vortex mixed (5 s at 2000 rpm) every 2 min 30 s.

After 10 min of incubation with the fine particles, magnetic separation (Section 3.5.1) was used to remove any unattached fine particles from the supernatant and the core-shell particles washed twice with water.

To desorb the fine particles, the fine particles/core-shell particles were incubated in 3.00 mM NaOH (pH ~11.5) for 10 min with continuous vortex mixing at 2000 rpm. After incubation, magnetic separation was used to remove desorbed fine particles in the supernatant (Section 3.5.1). Core-shell particles were washed twice following desorption. The fine particle re-adsorption process followed the adsorption methodology above.

3.6.2.1 Gold adsorption and recovery

The PEI-silica shell – carbonyl iron core and PEI-thiol silica – carbonyl iron core carrier particles were synthesised using 10.000 mL Method D outlined in Sections 3.5.2.5 and 3.5.3.1 and as discussed at the beginning of Section 3.6.

The gold (Au) nanoparticles $(10.0 \pm 2.0 \text{ nm diameter})$ were purchased from Sigma Aldrich and used as purchased. According to the manufacturer (Sigma Aldrich), the Au nanoparticles were synthesised through a propriety process from Cytodiagnostics which results in the fabrication of highly spherical gold nanoparticles, without harsh reducing

agents. The gold nanoparticles were reported by the manufacturer (Sigma Aldrich) to have concentration of ~ 6.0×10^{12} particles mL⁻¹ and were suspended in 0.1 mM phosphate buffered saline.

The core-shell particle/gold nanoparticle incubation experiments were performed in 1.000 mL volumes. 3.0 ± 0.3 mg of dried core-shell particles were re-suspended in 700 µL solution of PB (pH 8.0) (Ruan *et al.*, 2015). 300 µL of the suspended Au nanoparticles were then added and the mixture was vortex mixed (5 s at 2000 rpm). The final concentrations in the incubation experiment were 3.0 ± 0.3 mg mL⁻¹ core-shell particles, 100 mM PB (pH 8.0) and ~ 1.8×10^{12} Au particles mL⁻¹.

The core-shell particles and nanoparticles were incubated for 10 min (as in Section 3.6.2) the suspension was vortex mixed (5 s at 2000 rpm) every 150 s throughout the incubation period. After incubation, the core-shell particles were separated from any unattached gold nanoparticles through magnetic separation (Section 3.5.1) and washed twice with \sim 1 mL water.

3.7 Characterisation techniques

A number of techniques were used to characterise the synthesised particles and coatings. These techniques were used to confirm that the modification reactions were successful and determine how effective the recovery of fine particle/ion species was when using the magnetic core-shell carrier particles. The characterisation techniques used in this study and discussed in this section are: scanning electron microscopy (Section 3.7.1), energy dispersive x-ray spectroscopy (Section 3.7.2), Fourier transform infrared spectroscopy (Section 3.7.3), dynamic light scattering (Section 3.7.4), zeta potential measurement (Section 3.7.5) and UV-visible light spectroscopy (Section 3.7.6).

3.7.1 Scanning electron microscopy

3.7.1.1 Background

Scanning electron microscopy (SEM) is a technique able to achieve high magnification and high resolution electron imaging of surfaces. In Figure 3.1 is a schematic of a typical SEM unit. The electron gun supplies electrons while a system of lenses accelerate and focus the beam of electrons onto the sample's surface (Lloyd, 1987). The interaction between the electron beam and the sample surface produces signals (*e.g.* scattered or emitted electrons) from which images of the sample may be derived.



Figure 3.1. Schematic of a scanning electron microscopy (SEM) unit.

The electron source and condenser govern the electron energy (*i.e.* the probe current) and ultimately the strength of emission signal. Thus, it is the probe current which places limits on the image resolution available (Lloyd, 1987). In practice, the electron energy is selected by the operator and is generally within the range of 1 to 30 keV (Lloyd, 1987).

The interaction of the incident (primary) electron beam and sample produces multiple types of signals. Different emission types can be measured depending on the information sought. The two types of emissions detected in this study were secondary electrons (SE) and backscattered electrons (BSE).

SE are emitted from the surface due to the inelastic collision of primary electrons with electrons within the sample. This collision results in the transfer sufficient energy, from the primary electrons to the sample electrons, for the sample electrons to be emitted (Harris, 2010). Detectors to the side of the sample detect the SE and feed this information to computers which convert it to a video output. For imaging focused on topographical features of the sample, SE detection is often used due to the high resolution available through this technique (Lloyd, 1987).

BSE consist of primary electrons reflected back from within the sample via a series of largely elastic scattering events (Lloyd, 1987). As they are reflected back from the

sample, the backscattered electron detector is situated close to the source of the electron beam. Originating from within the target sample, the BSE provide images with information on the composition of the sample. The volume to which the primary electrons are able to penetrate the sample before being reflected back is determined by the average atomic number of the material at that point (Lloyd, 1987). For the same electron beam, greater penetration is possible for materials with a low average atomic number (*e.g.* SiO₂) compared with materials that have a higher atomic number (*e.g.* carbonyl iron, Fe) (Lloyd, 1987). As the atomic number of the material increases, the energies of the BSE approach that of the primary electron beam. The resultant higher signal, when converted into an image, makes the higher atomic number material appear lighter in contrast to surrounding lower atomic number materials (Lloyd, 1987). This is referred to as Z-contrast and is largely absent from SE detected images due to their lack of dependence on composition (Lloyd, 1987).

3.7.1.2 Method

Particle samples were diluted to approximately 1 mg mL⁻¹ in a water medium. The suspended particle samples were placed as 10.00 μ L droplets onto an aluminium SEM stub using a micropipette. The samples were then dried via desiccation before measurement.

For the majority of samples (these cases are specified within the results chapters), carbon sputter coating was required to prevent electron build-up on the sample from negatively impacting image clarity. Carbon coating of the samples was conducted using the Cressington 208 Carbon Coater. Samples were mounted on a platform within the coating unit which was rotated and tilted back and forth during coating to ensure good coverage of the samples. The coating was set for 30 s and produced an approximately 20 nm thick carbon layer.

A Zeiss Sigma field FEGSEM was used for analysis of the samples. The SEM images were analysed for particle size using the Image Tool (UTHSCA) software.

3.7.2 Energy dispersive X-ray spectroscopy

3.7.2.1 Background

Energy dispersive x-ray (EDX) spectrometry allows for the user to qualitatively determine the elements present in different locations within a sample and a measure of the relative proportions the elements are present in.

X-ray emissions are produced by the excitation of inner shell electrons. In EDX, the incident electron beam causes inner shell electrons to be excited to a higher level (Shindo and Oikawa, 2002). The gap left in the inner shell is then filled by an electron jumping down from a high energy level. The emission of characteristic x-ray frequencies follows this process, with the resulting x-ray energy between the energy levels of the two electron shells. In this way, emitted x-rays are specific to each element and can be used to determine the elemental composition of a sample (Shindo and Oikawa, 2002). For each element, various characteristic x-rays may be emitted depending upon the two electron energy shells where electrons are moving from. For heavy elements, higher incident energy beams are able to excite a larger range of inner shell electrons therefore allowing a greater number of the element's characteristic x-ray emission lines to be emitted.

For data collection, the electron beam can be kept stationary on a particular spot for more localised elemental information. The EDX can also be used to scan over a designated area to produce a map of the relative proportions of a previously identified element as a function its location. However, the mapping processes is extremely time consuming.

3.7.2.2 Method

The Zeiss Sigma field emission gun scanning electron microscope (FEGSEM), from Section 3.7.1, was also used for EDX analysis. The EDX is coupled with the SEM system and therefore requires the same sample preparation detailed in Section 3.7.1.2.

For this thesis, EDX area and spot compositional analyses were both used. Each EDX spectrum presented in this thesis is accompanied by an SEM image of the sample being analysed in the top left corner of the spectrum. The spot/area of EDX data collection is identified in the accompanying SEM image by a white '+' or white box/circle. For each sample, at least three EDX spectra were collected.

In Chapter 6, EDX spectra were taken to determine the elemental composition of the synthesised core-shell particles. The peak heights of Si and Fe elements from EDX analysis conducted on a number of 'spots' were used to calculate a Si:Fe peak height ratio. The average Si:Fe peak height ratio for each condition was taken as an average of 'spot' compositional analyses of three different, random particles in the sample.

In Chapter 7, EDX analysis was used to qualitatively determine the presence of adsorbed Cu(II). As Cu is present within the SEM stub material used, a silicon wafer was used as the base. The silicon wafer base was stuck to the surface of the SEM stub prior to sample preparation using carbon adhesive. The sample was then prepared as per Section 3.7.2.2 upon the silicon wafer base.

In Chapter 8, EDX spectra were taken using the method outlined Section 3.7.2.2 for qualitative determination of the elemental composition.

3.7.3 Attenuated total reflectance - Fourier transform infrared spectroscopy

3.7.3.1 Background

Fourier transform infrared (FTIR) spectroscopy is a technique that can be used to identifying key functional groups within a sample and therefore assist with chemical composition analysis (Harris, 2010). Attenuated total reflectance - Fourier transform infrared (ATR-FTIR) spectroscopy utilises an attenuated total reflectance (ATR) accessory to simplify sample preparation and reduce user-to-user variation during FTIR measurements (McMahon, 2007; Somasundaran, 2006). The principles of the FTIR and ATR accessory will be briefly discussed in this section.

The vibrational energies of the bonds within a molecule generally correspond to wavelengths within the infrared region of the electromagnetic spectrum. As such, the interactions between bonded atoms mean that each molecule has its own distinct absorbance pattern within the infrared region. FTIR databases allow for the positive identification of compounds within pure samples (Harris, 2010). Quantitative analysis is also possible with pure samples. For impure samples, FTIR can also useful in identifying key chemical groups of compounds within a sample from the characteristic absorbance patterns of their bond vibrations.

A schematic of the general FTIR set up is provided in Figure 3.2. A black body light source expels infrared radiation. The directionality and energy of the IR beam entering the rest of the apparatus is controlled by an aperture opening. The IR beam is fed through

an interferometer, which splits the beam into two; allowing one half to reflect off a stationary mirror and the other off a moving mirror (McMahon, 2007). Once the two IR beams are recombined the interference pattern produced as a function of the moving mirror's position is known as an interferogram. This interferogram contains information on every infrared wavelength within the original beam and by using the mathematical technique of Fourier transformation allows the information obtained by the detector to be decoded into absorbance per wavelength (McMahon, 2007). The interferogram signal is subsequently transmitted through the sample where frequencies within the beam are absorbed to varying degrees depending on the vibrational states of the constituting bonds within the sample (McMahon, 2007).

A detector measures and digitalises the remaining interferogram signal. This signal is then transformed into the infrared absorbance by applying the Fourier transform. To make the numbers more manageable wavenumbers (1/frequency, cm⁻¹) are employed as the unit of measurement. A background subtraction is required before sample measurements to account for the absorbance made by the sample medium and/or air.



Figure 3.2. Schematic of a Fourier transform infrared (FTIR) spectrometer.

The ATR-FTIR spectroscopy technique simplifies sample preparation and reduces userto-user variation in FTIR measurements (McMahon, 2007; Somasundaran, 2006). In ATR-FTIR spectroscopy samples are pressed against the attenuated total reflectance crystal. The beam of infrared radiation is fed into the highly optically dense ATR crystal at such an angle that it undergoes complete internal reflection, as can be seen schematically in Figure 3.3 (McMahon, 2007). An evanescent wave, however, extends past the point of internal reflectance and penetrates the sample pressed against the crystal surface. The evanescent wave typically extends 0.5-5 µm into the sample (Perkin Elmer Inc., 2005). The sample absorbs energy from the evanescent wave at the frequencies corresponding to the vibrational energies of its chemical bonds (McMahon, 2007). The evanescent wave is then returned to the IR beam in its altered state and is passed through to the detector where the infrared spectrum is generated.



Figure 3.3. Schematic of an attenuated total reflectance (ATR) crystal.

3.7.3.2 Method

ATR-FTIR measurements were performed using a Spectrum Two (PerkinElmer) instrument. An air background was taken before analysing the dried particles. To increase reliability, at least three repeats were analysed of each sample type. Prior to measurement, all samples were desiccated for at least 72 h. For Chapter 4, the samples were further dried in an oven at 383 K for 24 h before measurement.

The error of the measurement was taken as the precision limit of the instrument used as given by the manufacturer, which was 4 cm⁻¹.

3.7.4 Dynamic light scattering

3.7.4.1 Background

The Malvern ZetasizerNano ZS used in this study has the ability to measure particle size, zeta potential and molecular weight (Malvern Instruments Ltd., 2004). For this report particle size and zeta potential were measured.

The instrument uses a technique known as dynamic light scattering (DLS) to measure the size of materials dispersed in liquids. Laser light is passed through a dilute sample of suspended solids causing the light to scatter, as shown in Figure 3.4.



Figure 3.4. Schematic of a dynamic light scattering (DLS) instrument.

Constructive and destructive interference of the scattered light results in the detection of bright and dark regions at the detection site. The DLS technique measures the interference pattern with respect to time which can then be used to calculate the average speed of particle movement within the sample (Malvern Instruments Ltd., 2004). The movement of particles is the result of Brownian motion which is a function of particle size. Therefore, by establishing the speed of the particles as a result of Brownian motion, the Stokes-Einstein equation, Equation 3.1, can be used to determine the average particle diameter from the measured hydrodynamic particle diameter, d_H (m) (Malvern Instruments Ltd., 2004).

$$d_H = \frac{kT}{3\pi\eta D}$$
 3.1

In Equation 3.1, k (J K⁻¹) is the Boltzmann constant, T (K) is the absolute temperature, η (kg s⁻¹ m⁻¹) is the viscosity and D (m² s⁻¹) is the translational diffusion coefficient which is the detected velocity of Brownian motion.

3.7.4.2 Method

The intensity average (hydrodynamic diameter) size distributions of synthesised particles were obtained via DLS measurements using a Malvern ZetasizerNano ZS instrument. Sample particles were suspended in water using ultrasonication and transferred to

plastic cuvette cells for measurement. The approximate particle concentration used in sample suspensions was ~0.5 g L⁻¹. For each particle type, three samples were produced, and three DLS measurements were taken for each of those samples. Hence the mean intensity average of each particle type was calculated from the average of nine DLS measurements. The error of each data point was calculated as the standard deviation of all DLS measurements of that particular sample type.

3.7.5 Zeta potential measurements

3.7.5.1 Background

Charged particles within an aqueous environment attract a veneer of oppositely charged solution ions known as an electrical double layer. When the particle is in motion, the more tightly held ions close to the particle surface will travel with the particle while the ions further from the surface will slip away. The limiting distance at which ions will still travel with the particle forms a boundary known as the slipping plane (Harris, 2010). It is the potential at the slipping plane boundary point which is defined as the zeta potential.

The Malvern Zetasizer Nano ZS instrument was used for zeta potential measurements, as in Section 3.7.4. This instrument determines the zeta potential of particles dispersed in solution by applying a potential difference across a U-shaped cuvette containing the aqueous dispersion of particles. The applied potential difference causes particles within the cuvette to move. The velocity at which the particles move, known as the particle electrophoretic mobility, is dependent on the medium of dispersion, the strength of the applied electric potential and the magnitude of charge at the particle's slipping plane (Malvern Instruments Ltd., 2004). As with DLS particle sizing (Section 3.7.4), the particle velocity (or electrophoretic mobility) was determined by detecting the fluctuation in detected scattered laser light (Malvern Instruments Ltd., 2004). Once the other dependent variables are accounted for and entered, the Henry equation, Equation 3.2, is able to convert the measured electrophoretic mobility, U_E (m² V⁻¹ s⁻¹), to zeta potential, ψ_{ζ} (V) (Malvern Instruments Ltd., 2004).

$$U_E = \frac{2\varepsilon_R \psi_\zeta f(ka)}{3\eta}$$
 3.2

In Equation 3.2, ϵ_R is the relative permittivity of the medium, η (kg s⁻¹ m⁻¹) is the viscosity and f(ka) (m kg V⁻² s⁻²) is Henry's function. For these experiments, the Smoluchowski approximation was used for f(ka) giving it a value of 1.5. This is because the particles investigated using this technique had a diameter larger than 100 nm and the electrolyte concentration used was greater than 1 mM (in this case, the electrolyte used was 10.0 mM NaNO₃ as specified in Section 3.7.5.2), which satisfy the conditions for Smoluchowski's approximation (Malvern Instruments Ltd., 2004; Misra *et al.*, 2004).

3.7.5.2 Method

Zeta potential measurements were made with a Malvern ZetaSizer Nano ZS instrument. 10.0 mM NaNO₃ was used as a base electrolyte with pH adjustments made using 1.00 M HCl or NaOH to maintain constant the ionic strength. Samples were suspended in the pH-adjusted base electrolyte at an approximate concentration of ~0.5 g L⁻¹ and transferred to a plastic U-shaped zeta potential cuvette for measurement.

For each particle type, three samples were produced. The zeta potential of each sample was then measured three times. Therefore, the reported zeta potential measurement was an average of nine zeta potential measurements (as in Section 3.7.4.2). The error for each data point was taken as whichever gave the largest value between the zeta deviation given by the ZetaSizer and the standard deviation of all measurements of a particular data set.

3.7.6 Ultraviolet-visible light spectroscopy

3.7.6.1 Background

Ground state electrons orbiting atoms can be excited into higher orbital states by the application of energy corresponding to the energy gap between the ground and excited orbitals (Harris, 2010). Irradiation by electromagnetic radiation in the ultraviolet-visible region is one way to achieve this energy jump. The specific energy requirement, and therefore the frequency of irradiation required, is dependent on the element the electron is orbiting as well as the chemical environment that atom is in (Harris, 2010). The UV-visible light (UV-vis) spectrometer takes advantage of these principles allowing for fast and reliable quantitative analysis of samples by use of a standard curve (Clark *et al.*, 1993).

A schematic of a typical double beam spectrometer, such as, the one utilised in this study (Shimadzu UV-1800) is given in Figure 3.5. Light in the UV-visible region supplied from a suitable source (*e.g.* tungsten filament or deuterium arc lamp) is fed through a grating monochromator to isolate a particular wavelength (Clark *et al.*, 1993). The beam is then split into two, with one half passed through the sample and the other through a reference sample before recombining to enter the detector. The reference allows internal compensation for system variables including absorbance of the medium or changes in source intensity.



Figure 3.5. Schematic of a double beamed ultraviolet-visible light (UV-vis) spectrometer.

In this study, UV-vis spectroscopy utilised to determine the concentration of chemical species in the supernatant following the adsorption experiments in Sections 3.4.1.1 and 3.6.1. Quartz cells were used to avoid cell absorbance at the wavelength of interest (275 nm), and a Shimadzu UV-1800 spectrophotometer was used to make the absorbance measurements.

The Cu(II)-PEI complex has a maximum absorbance peak at 275.0 nm (Wen *et al.*, 2017; Ungaro *et al.*, 2003). At this wavelength, significant absorbance is not detected for the individual PEI or Cu(II) species (Wen *et al.*, 2017; Ungaro *et al.*, 2003). Thus, the absorbance of the Cu(II)-PEI complex at 275.0 nm can be used for the quantitative determination of the PEI or Cu(II) concentrations solution by spectroscopic measurement. In Section 3.4.1.1, the PEI concentration in the supernatant was of interest so the reagent used was a known and constant amount of Cu(II). Conversely, for the characterisation of the supernatant produced in Section 3.6.1, the concentration

of Cu(II) was of significance so the reagent contained a known/constant PEI concentration.

The process to determine of PEI concentration via UV-vis spectroscopy is given in Section 3.7.6.2 and the process to determine Cu(II) concentration is presented in Section 3.7.6.3.

3.7.6.2 Determination of PEI concentration after NaOH-silica surface modification

The amount of PEI in the supernatant after electrostatic modification of the NaOH-silica particles (Section 3.4.1.1) was detected using UV-visible spectroscopy and reported on in Chapter 4.

A reagent containing 0.200 μ M copper(II) sulfate (CuSO₄) and 4.83 mM PB (pH 7.4) was used for all experiments. PB was included in the reagent to account for the influence of PB occurring in the supernatant of the electrostatic modified NaOH-silica particle experiments. Reagent blanks (containing the reagent concentration of CuSO₄ and PB) were used as the reference sample (Figure 3.5). The reagent blanks were also used for zeroing the instrument before each set of readings.

A standard curve, plotting absorbance at 275.0 nm as a function of PEI (25 kDa) concentration was created. The linear range of the standard curve was between 2.00 and 0.010 μ M PEI. The standard curve was developed by adding known concentrations (within the 2.00 and 0.010 μ M PEI linear concentration range) of PEI to the reagent solution (0.200 μ M CuSO₄ and 4.83 mM PB). After the addition of all reactants the mixture was shaken vigorously and incubated for 1 min. After 1 min, the absorbance at 275.0 nm was measured by UV-vis spectroscopy.

To determine the amount of unattached PEI after the electrostatic modification of NaOHsilica particles (Section 3.4.1.1) the supernatant was collected for sampling. The supernatant was diluted as necessary to ensure the absorbance reading of each sample was within the linear range of the standard curve, which was found to be between 0.01 and 2.00 μ M PEI. For every sample, a final concentration of 0.200 μ M copper(II) sulfate (CuSO₄) and 4.83 mM PB (pH 7.4) was used, as above. The PB added in the reagent was adjusted by first calculating the amount of PB remaining in the diluted supernatant sample and then, if required, introducing additional PB to the cell to bring the total concentration of PB up to 4.83 mM. After the diluted supernatant sample was added to the reagent, the mixture was shaken vigorously and incubated for 1 min. After 1 min, the absorbance at 275.0 nm was measured by UV-vis spectroscopy. The adsorption experiments were carried out in triplicate and the results shown are the average of the measurements, with the standard deviation given as the error bars.

Using the standard curve, the PEI concentration of the sample, c (M), could be determined from its measured absorbance at 275.0 nm, A_{λ} , by applying the Beer-Lambert law in Equation 3.3,

$$A_{\lambda} = \alpha bc \qquad \qquad \mathbf{3.3}$$

where A_{λ} is the absorbance at a particular wavelength, λ , in this case 275.0 nm, α (M⁻¹ cm⁻¹) is the wavelength dependent molar absorptivity coefficient, b (cm) is the path length, *i.e.* the width of the cell and c (M) is the concentration of the analyte.

From the measured concentration of PEI, the concentration of PEI in the supernatant could be calculated by accounting for the dilution factor. Assuming the PEI not adsorbed was found in the supernatant, the PEI adsorbed was calculated by subtracting the measured amount from the initial concentration used during incubation. The adsorption isotherm was fitted using the Boltzmann sigmoidal growth equation (Origin lab software fitting module).

3.7.6.3 Determination of Cu(II) concentration in Cu(II) adsorption experiments

The amount of Cu(II) in the supernatant after Cu(II) adsorption onto the core-shell particles (Section 3.6.1) was detected spectroscopically (Ungaro *et al.*, 2003; Wen *et al.*, 2017) and reported on in Chapter 7. As in Section 3.7.6.2, the 275.0 nm absorbance peak of the Cu(II)-PEI complex was used.

The reagent for spectroscopic measurements consisted of 0.0940 mg mL⁻¹ PEI (25 kDa) and 8.00 mM PB (pH 6.0). The PB and PEI concentrations were consistent with published literature on the spectroscopic detection of Cu(II) (Wen *et al.*, 2017). In addition, the pH of the PB used for the reagent was changed to pH 6.0, as Wen *et al.* (2017) determined this pH resulted in the highest Cu(II)-PEI absorption at 275.0 nm. Before each set of spectroscopy measurements, the reagent blank was used to zero the instrument. The regent blank was also placed in the reference slot throughout all experiments (Figure 3.5).

A standard curve was prepared which plotted the absorbance measured at 275.0 nm against Cu(II) concentration. The measurements for the standard curve were made by adding known concentrations of CuSO₄ to the reagent mixture of PEI and PB, shaking the cell thoroughly and measuring the absorbance of the mixture at 275.0 nm. As per Wen *et al.* (2017), the standard curve was linear for Cu(II) concentrations 10.0 to 400 μ M.

Following the adsorption experiments in Section 3.6.1, the core-shell particles were magnetically removed and the supernatant was diluted to fit within the absorbance limits of the standard curve and then combined with the reagent mixture of PEI and PB. The amount of PB added with the reagent was adjusted so that the final total concentration of PB in the cell was 8.00 mM. Once the reagent and supernatant were added to the cell, the cell was shaken thoroughly and the absorbance at 275.0 nm measured by the spectrometer. By applying the Beer-Lambert law (Equation 3.3), the standard curve and the absorbance measurements could be used to determine the concentration of Cu(II) in the cell. Thus, the concentration of Cu(II) in the supernatant could be calculated by taking into account the dilution factor. By assuming that all non-adsorbed Cu(II) was found in the supernatant, the amount of Cu(II) in the supernatant from the initial amount of Cu(II) added. The adsorption capacity and removal efficiency were determined as per Lo *et al.* (2012).

3.7.6.3.1 Adsorption isotherms

The relationship between the adsorbate free in solution versus that adsorbed onto the adsorbent surface at equilibrium, for a given temperature condition, is known as the adsorption isotherm (Nsami and Mbadcam, 2013). A number of adsorption isotherm models have been developed to describe the equilibrium state of adsorption systems, the most two common being the Langmuir and Freundlich isotherms.

To determine the adsorption isotherm model that best represents the adsorption of Cu(II) onto core-shell particles in Chapter 7, the adsorption results collected were plotted as per the Langmuir and Freundlich isotherm models.

The Langmuir adsorption isotherm assumes that adsorption is monolayered and occurs at specific homogeneous sites upon the adsorbent material. The Langmuir isotherm can be written in the linear form as Equation 3.4 (Huang and Shih, 2016; Nsami and Mbadcam, 2013),

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$$
 3.4

where $C_e \text{ (mg L}^{-1}\text{)}$ is the concentration of the adsorbate at equilibrium; $Q_m \text{ (mg g}^{-1}\text{)}$ is the maximum adsorption capacity corresponding to complete monolayer coverage of the adsorbent; K_L (L mg $^{-1}$) is the Langmuir constant that can be indirectly related to the adsorption energy; and $Q_e \text{ (mg g}^{-1}\text{)}$ is the mass of Cu(II) adsorbed per mass adsorbent at equilibrium. $Q_e \text{ (mg g}^{-1}\text{)}$ can be calculated using Equation 3.5 (Nsami and Mbadcam, 2013),

$$Q_e = \frac{C_0 - C_t}{m} V$$
 3.5

where C_t (mg L⁻¹) is the concentration of Cu(II) remaining in the supernatant after adsorption at adsorbate time t as measured spectroscopically (Section 3.7.6.3); C_0 (mg L⁻¹) is the initial Cu(II) concentration; m (g) is the mass of the adsorbent; and V (L) is the volume of adsorbate. As the Cu(II) adsorption experiments were expected to have reached equilibrium by the end of the incubation time (as suggested by preliminary results), the concentration at adsorption time t, C_t , is expected to be equivalent to the equilibrium concentration, C_e .

Experimental adsorption data collected from the adsorption experiments (Sections 3.6.1 and 3.7.6.3) was plotted as C_e/Q_e against C_e . From this plot, the Langmuir constants Q_m and K_L were evaluated from the gradient and intercept of the line of best fit equation (produced using Excel software) (Equation 3.4). The R² value was also evaluated using Excel software to determine how linear the experimental data plot was. An adsorption system obeying the Langmuir adsorption model will have a close to linear relationship between C_e/Q_e and C_e and a R² value close to 1 (Equation 3.4).

The Freundlich adsorption isotherm has an empirical expression that can be written as Equation 3.6 (Nsami and Mbadcam, 2013),

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e$$
 3.6

where K_f and n are dimensionless empirical constants dependent on temperature and sorbent/sorbate nature.

The Cu(II) adsorption data collected experimentally (Sections 3.6.1 and 3.7.6.3) was also plotted as ln Q_e against ln K_f. Once again, the R² value was calculated using Excel software to determine how well the experimental data fitted to the Freundlich isotherm. The empirical constants, K_f and n, were then determined from the gradient and intercept of the plotted data (Equation 3.6).

CHAPTER FOUR

Comparison of PEI modified NaOH-silica particles with PEI-silica particles

Publications:

Hyde, E.D.E., Moreno-Atanasio, R., Millner, P.A., Neville, F. (2015). Surface charge control through the reversible adsorption of a biomimetic polymer on silica particles. *The Journal of Physical Chemistry B, 119* (4), 1726-1735.

Statement of Contribution

Chapter 4

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By signing below, I confirm that Research Higher Degree candidate Emily Hyde contributed by collaborating in the experimental design and by taking primarily responsibility for all experimental and the majority of analysis work. In addition, Emily Hyde contributed by taking primary responsibility for preparing, drafting and editing of the journal publication listed above. Dr Frances Neville contributed by collaborating in the experimental design of the project and assistance with some data analysis, and by supervision and critical review. Dr Roberto Moreno-Atanasio and Prof Paul Millner contributed by collaborating in the experimental design of the project, and by supervision and critical review.

I thereby certificate that this statement of contribution is accurate:

Emily Hyde Paul Millner Frances Neville Roberto Moreno-Atanasio

4.1 Introduction

Control of the physicochemical properties of silica particles is of paramount importance to achieve full functionality for applications, such as, drug delivery and specific ion adsorption. In this chapter, a novel, facile synthesis method to produce NaOH-silica particles is presented and the NaOH-silica particles characterised. In addition, this chapter illustrates control over the physiochemical properties of the NaOH-silica particles through rapid electrostatic adsorption and acidic desorption of the branched polyamine polyethylenimine (PEI). Hence, these results demonstrate the effective adsorption – desorption cycle of electrostatically attached species that is possible through adjustment of solution pH.

In short, the results presented in this chapter convey the rapid, reversible, and reliable method of silica particle charge control. The methods detailed herein allow for the surface interactions of silica or silica coated particles to be tailored for specific applications, including applications in drug delivery, biomedical technologies, catalysis, and coatings.

4.2 NaOH-silica particle synthesis

4.2.1 Background

As discussed in detail in the literature review chapter (Section 2.2.2.3), Stöber *et al.* (1968) developed a robust method of silica production that allowed the synthesis of spherical, monodisperse, micron-size silica particles. The Stöber technique (Bogush *et al.*, 1988; Stöber *et al.*, 1968) involves the hydrolysis and condensation polymerisation of a tetraalkoxysilane (generally tetraethoxysilane (TEOS)) in a water/ethanol medium. Ammonia is used during the reaction as a basic catalyst to promote condensation and polymerisation (van Blaaderen and Kentgens, 1992). In 2001, Dingsøyr and Christy (2001) were able to substitute the ammonia catalyst with the basic salt sodium hydroxide (NaOH). However, both the Stöber and Dingsøyr and Christy synthesis methods employ harsh chemicals and an organic solvent, which may become safety and environmental concerns during potential process scale up.

The issues associated with the Stöber method have prompted a number of recent studies (Betancor and Luckarift, 2008; Canton *et al.*, 2011; He *et al.*, 2008; Kim *et al.*, 2008; Neville *et al.*, 2009; 2011a; Seyfaee *et al.*, 2014) to modify the technique by taking inspiration from biological silication processes (Section 2.2.2.4). These studies demonstrated that polybasic peptide mimics, such as, polyethylenimines, are efficient basic catalysts due to the multiple basic amine groups they contain (Neville and Millner,

2011b). The biomimetic method developed by Neville *et al.* (2009) requires the nonhazardous silane precursor, trimethoxymethylsilane (TMOMS), to hydrolysed in acid prior to synthesis. Polymerisation of the hydrolysed silane is then performed at room temperature and physiological pH buffered conditions, where a conglomeration of the biomimetic polymer, PEI, and phosphate ions become the nucleation site for silica formation (Neville and Millner, 2011b; Neville and Seyfaee, 2013b). This biomimetic modified Stöber method has been shown to produce spherical particles with a narrow size distribution (Neville *et al.*, 2009).

In this chapter, the polyamine polypeptide mimic used by Neville *et al.* (2009) was replaced by NaOH. Hence this novel silica synthesis technique requires only two chemicals, pre-hydrolysed TMOMS and the NaOH catalyst, to be reacted at room temperature within an aqueous solution. By reducing the number of chemicals required, the novel method of silica synthesis detailed in this chapter provides a lower-priced, simplified alternative to other silica particle production methods.

4.2.2 Methodology

Two types of particle synthesis were discussed in this chapter, the PEI-silica and NaOHsilica particle synthesis, a detailed description of the synthesis methods are given in Section 3.3.1 and 3.3.2.

In brief, the NaOH-silica particles were synthesised in 1.000 mL batches by combining 200 mM pre-hydrolysed TMOMS with 25.0 mM NaOH for a 30 min reaction. Particles were centrifuged (1 min at 14000 rpm) and the supernatant removed to stop the reaction. The particles were subsequently washed with water twice to remove any remaining reactants.

PEI-silica particles were also synthesised with 200 mM TMOMS using Neville and coworkers' (2009) method for comparison (Section 3.3.1). The PEI-silica particles were synthesised by combining 200 mM pre-hydrolysed TMOMS with 2.50 mg mL⁻¹ PEI and 29.0 mM phosphate buffer in a 1.000 mL reaction for a 30 min reaction. The reaction was stopped though centrifugation (1 min at 14000 rpm) and the particles washed as per the NaOH-silica particle reaction.

Silica particles were characterised through yield measurements as outlined in Section 3.3.2. DLS analysis (Section 3.7.4) was used to characterise the hydrodynamic diameter of the particles, the sample preparation for this technique is outlined in Section 3.7.4.2. SEM imaging (Section 3.7.1) was conducted using the method outlined in Section 3.7.1.2

with no carbon sputter coating of the sample required. The SEM images were analysed for particle size using the Image Tool (UTHSCA) software.

ATR-FTIR analysis (Section 3.7.3) was performed on dried particles with an air background. All samples were dried via desiccation for 72 h and oven drying at 383 K for 24 h, as per Section 3.7.3.2. Zeta potential measurements (Section 3.7.5) were made using the method outlined in Section 3.7.5.2. The electrolyte used for particle suspension was 10.0 mM NaNO₃ with pH adjustments made by 1.00 M HCl/NaOH.

4.2.3 NaOH-silica and PEI-silica particle characterisation

Silica particles were synthesised using a modified version of the Neville *et al.* (2009) method. In both NaOH-silica and PEI-silica particle synthesis reactions, the silane precursor, in these cases TMOMS, was treated to pre-reaction acid hydrolysis to increase the rate of reaction. A basic catalyst was then added to the pre-hydrolysed mixture to initiate the nucleation and growth of silica particles. In the novel synthesis presented in this chapter, NaOH was added to the reaction as the catalyst for the silica particle formation. NaOH was used in place of the PEI/phosphate buffer catalyst which was employed in the original PEI-silica method (Neville *et al.*, 2009). The advantages of the NaOH catalyst are the reduced number of reactants and the reduced cost of the NaOH species compared with the polymer synthetic catalyst PEI. For both PEI-silica and NaOH-silica synthesis reactions a set reaction time of 30 min was employed, which according to Seyfaee *et al.* (2014) allowed PEI-silica particles to grow to maturity.

The NaOH-silica particles synthesised were characterised by yield determination, DLS sizing, and SEM imaging. In Table 4.1 the average NaOH-silica particle yield and size are tabulated and compared with the properties of the PEI-silica particles synthesised using the Neville *et al.* (2009) method.

Table 4.1. Summary of the physical propeties of PEI-silica and NaOH-silica particles made with PEI/PB and NaOH, respectively. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

Physical property	PEI-silica particles	NaOH-silica particles
Mass yield (mg of silica particles formed per mL reaction)	10.0 ± 0.3	9.0 ± 0.4
Percentage yield (wt.% of hydrolysed TMOMS consumed in reaction)	52	47
Average intensity particle size (via DLS) (nm)	990 ± 30	950 ± 50
Average particle size (via SEM) (nm)	795 ± 100	685 ± 50

The mass yields of NaOH-silica and PEI-silica dried particles were obtained, as shown in Table 4.1. The low standard deviation of the yield measurements indicates that both methods produce consistent yields of particles each time. A slightly higher yield was measured for the PEI-silica particles. However, the slight advantage in particle yield via the Neville *et al.* (2009) method is offset by the expense of the PEI catalyst in contrast to the NaOH catalyst.

The higher yield measurement for the PEI-silica particles was also reflected in the percentage of reactants used in the reaction. However, in both cases approximately 50 wt.% TMOMS remained unreacted after the 30 min reaction time. Neville and Seyfaee (2013b) observed that PEI-silica particle diameter plateaued within ~15 min of reaction time. Hence, the incomplete consumption of the TMOMS silica precursor during the reactions is likely due to thermodynamic limitations of the reaction as opposed to being limited by reaction time.

The sizes of the particles were determined using a wet method and a dry method, namely DLS and SEM imaging, respectively. The NaOH-silica and PEI-silica particle

hydrodynamic diameter distributions determined via DLS are plotted in Figure 4.1, with the average size given in Table 4.1.



Figure 4.1. NaOH-silica and PEI-silica hydrodynamic particle size distributions as measured using dynamic light scattering (DLS). Adapted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

The mean hydrodynamic diameter of NaOH-silica particles, determined using DLS, was found to be 950 ± 50 nm (Table 4.1). In contrast, the PEI-silica particles reacted for the same period had a slightly higher average intensity diameter of about 990 ± 30 nm (Table 4.1), which is in good agreement with Seyfaee *et al.* (2014). The comparable standard deviation of the NaOH-silica and PEI-silica particles (Table 4.1) suggests a similarity in particle size distribution between the two methods, which is correlated by the size distribution curves given in Figure 4.1.

In Seyfaee *et al.* (2014), the TMOMS concentration and reaction time were observed to be the main contributing factors determining PEI-silica particle size. It was also observed that the catalyst (PEI/PB) concentration played only a small role in determining the equilibrium PEI-silica final particle size, but significantly influenced the time taken for the particles to reach equilibrium (Seyfaee *et al.*, 2014).

A SEM image of the NaOH-silica particles produced using the new method is presented in Figure 4.2. The average size was determined via the Image Tool software (UTHSCA) and is given in Table 4.1.



Figure 4.2. Scanning electron microscopy image of dessicator dried NaOH-silica particles. The scale bar is 1 µm. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

NaOH-silica particles were observed by SEM imaging (Figure 4.2) to be highly spherical. As expected (Bootz *et al.*, 2004), the DLS sizing technique produced average particle sizes greater than those obtained via SEM image analysis, due to differences in the wet and dry methods, respectively. A slight roughness was observed on the outside of the particles (Figure 4.2). Seyfaee *et al.* (2014) also observed a slight roughness in the PEIsilica particles and attributed this characteristic to the mechanism of particle formation. Seyfaee and coworkers suggest PEI-silica particles were formed via the aggregation of nanometre sized subparticles. This mechanism of particle formation was first proposed to explain Stöber method silica formation by Bogush and Zukoski (1991). Hence, it is likely that a similar mechanism of particle growth is followed by the novel NaOH-silica particles. The ATR-FTIR spectrum of dried NaOH-silica particles was taken against an air background with the results presented in Figure 4.3. Key transmittance peaks and their corresponding vibrational functional groups are also highlighted in Figure 4.3.



Figure 4.3. ATR-FTIR spectrum of dried NaOH-silica particles. Measurements taken with an air background. Adapted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

The ATR-FTIR spectrum of NaOH-silica particles contains peaks characteristic of polymerised silica silicon-oxygen bond vibrations and the bond vibrations of the surface hydroxyl groups, including peaks at 763, 1012 and 3500 cm⁻¹. Similar peaks were observed in PEI-silica (Neville and Seyfaee, 2013b) and PEI-thiol silica (Chapter 5). These groups are common to silica materials due to the repetition of the silicon oxide tetrahedral structure. The peaks observed at 2970, 1411 and 1271 cm⁻¹ arise from C-H vibrations of the methyl group on the TMOMS silica precursor which is incorporated into the silica structure and were also observed for PEI-silica particles (Neville and Seyfaee, 2013b).

The zeta potential of the NaOH-silica particles was taken over a range of solution pH's between 2 and 12. These results are presented as a zeta potential curve in Figure 4.4.



Figure 4.4. Zeta potential of NaOH-silica particles as a function of solution pH.
Particles were suspended in a 10.0 mM NaNO₃ base electrolyte with pH controlled by
1.00 M HCI/NaOH. Adapted with permission from 'Surface Charge Control through the
Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R.
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The zeta potential measurements of the NaOH–silica particles (Figure 4.4) correlate well with zeta potential measurements of a silica wafer measured via streaming potential (Mészáros *et al.*, 2002). The silica surface comprises of two functional groups: siloxane groups (\equiv Si-O-Si \equiv) or silanol groups (\equiv Si-OH) (Jal *et al.*, 2004). The silanol groups take on different forms dependent on the distance between similar groups, *i.e.*, isolated silanols for separated groups of silanols and vicinal silanols when the silanol groups were close enough to form hydrogen bonds with their neighbours (Jal *et al.*, 2004). Work by Ong *et al.* (1992) found one form of silanol site (isolated) to have a p K_a of 4.5 and a prevalence of 19%, while the other type occupied 81% of silanol sites (vicinal) and had a p K_a of 8.5. In agreement with these p K_a values, Figure 4.4 shows that the unmodified NaOH–silica particles became negatively charged at pH~4 and the zeta potential dropped significantly at pH~9, likely due to the loss of protons from isolated and vicinal silanol groups, respectively.

The silica particles synthesised via the proposed NaOH-silica method have been characterised based on particle size, size distribution, yield, ATR-FTIR spectrum and
zeta potential curve. Comparison with PEI-silica particles synthesised using the Neville *et al.* (2009) method has shown that the novel method of silica particle fabrication described in this chapter produced particles with similar characteristics. The similar size and yield properties are summarised in Table 4.1 and include comparable particle diameters (795 \pm 100 nm (SEM) PEI-silica particles, 685 \pm 50 nm (SEM) NaOH-silica particles) and mass yields (10.0 \pm 0.3 g mL⁻¹ PEI-silica particles, 9.0 \pm 0.4 g mL⁻¹). However, the NaOH-silica particles possess the advantages of requiring fewer reactants and possessing a simplified reaction method. The similarities in properties discussed in this work are likely to extend to the mechanism of particle formation. However, the body of further research exploring this novel NaOH-silica synthesis method.

4.3 PEI surface modification of NaOH-silica particles

4.3.1 Background

Modification of the silica surface has been extensively studied in the literature, especially in relation to increasing colloidal silica suspension stability (Avadiar and Leong, 2011; Bagwe *et al.*, 2006; Jal *et al.*, 2004; Philipse and Vrij,1989; Vansant *et al.*, 1995). The relative inertness of the silica surface means that surface modifications are made either by conditioning the surface for covalent attachment or by electrostatic adsorption at the appropriate pH (Xia *et al.*, 2009). The most common form of silica surface modification uses a covalent siloxane linkage mechanism which provides a robust method to adhere organic materials to the silica surface (Cassidy and Yager, 1971; Li and Benicewicz, 2005; Ma *et al.*, 2014). However, modification via covalent bonding is an irreversible process and could be detrimental in some applications due to the lack of flexibility.

Electrostatic adsorption is a reversible process allowing the modifying agent to be attached and stripped from the surface by changes in the solution pH or salt concentration which allows it to be a very flexible form of functionalisation. PEI is a biomimetic cationic polymer and has been used successfully to modify silica (Avadiar and Leong, 2011; Bharali *et al.*, 2005; Erim *et al.*, 1995; Lindquist and Stratton, 1976; Mészáros *et al.*, 2002; Towns and Regnier, 1990; Xia *et al.*, 2009) and other particle surfaces (Ghosh *et al.*, 2008; Kindler and Swanson, 1971; McBain *et al.*, 2007; Vakurov *et al.*, 2012). However, a direct and comprehensive study of the surface charge shifts caused by PEI modification of silica nanoparticles was not published prior to this work.

Lindquist and Stratton (1976) investigated the stabilising effect of PEI adsorption on Ludox AM colloidal silica particles. The amount of PEI remaining in the supernatant was

determined spectroscopically in order to calculate the amount of polymer adsorbed on the silica colloidal particles (Lindquist and Stratton, 1976). Mészáros *et al.* (2002) investigated the kinetics of PEI adsorption on a silica wafer surface using reflectometry to determine the amount adsorbed. The authors (Mészáros *et al.*, 2002) also briefly studied the reversal of surface charge associated with PEI adsorption and the effect of different electrolyte concentrations using zeta potential measurements. During these studies the PEI concentrate remained as the medium with no attempt to remove the supernatant from the modified surface, so the stability of the coating could not be deduced from this study (Mészáros *et al.*, 2002). There was also no attempt to expand the study of surface charge to include the ability to desorb PEI molecules nor investigate the dependency on PEI concentration (Mészáros *et al.*, 2002).

Electrostatic adsorption of PEI has been successfully employed to neutralise the negative surface charge of the silica surface in silica lined capillaries in order to improve the performance of capillary electrophoresis analysis of proteins (Erim *et al.*, 1995; Figeys and Aebersold, 1997; Towns and Regnier, 1990). Erim *et al.* (1995) found the electrostatically adsorbed PEI coating to be stable for a pH range of 3–11.

Silica or silica-coated particles have enjoyed widespread success as drug delivery agents mainly due to their low toxicity and potential biodegradability (Borm et al., 2006; Finnie et al., 2009; Xia et al., 2009). One major obstacle for effective drug delivery via inorganic nanoparticle carriers is the ability for the carriers to pass through cell barriers (Bharali et al., 2005; Xia et al., 2009). Thus, the ability to functionalise the silica surface is another highly favourable characteristic of the material and allows the silica particle drug delivery systems to be modified with different functionalities depending on their target cell or tissue (Bharali et al., 2005; Bonoiu et al., 2009; Ghosh et al., 2008; McBain et al., 2007; Xia et al., 2009). PEI functionalisation of nanoparticles provides a promising solution, by introducing positively charged amine groups to the surface, which act to protect the carrier drug against enzymatic digestion and assist in the transportation of the drug carrier into cells (Bharali et al., 2005; He et al., 2003; Kneuer et al., 2000a; 2000b). In fact, it has been proposed that with careful surface charge control silica particles may serve the dual purpose of drug and nucleic acid delivery (Torney et al., 2007). Due to the negative surface charge of nucleic acid, effective delivery of the acid necessitates the positive modification of the silica surface charge, thus allowing it bind to DNA and siRNA (Xia et al., 2009). Xia et al. (2009) studied the effectiveness of PEI (with molecular weights between 0.6 and 25 kDa) coated (via electrostatic adsorption) mesoporous silica particles as a drug delivery agent. PEI-coated particles were found to possess a high binding effectiveness and a high rate of cellular uptake making them promising candidates for an enhanced drug delivery system (Xia *et al.*, 2009).

In the present work, infrared and UV-vis spectroscopies and zeta potential measurements were used to characterise the silica particles with adsorbed and desorbed PEI. A zeta potential study on the effect of PEI concentration during adsorption on particles demonstrated the high level of surface charge control achievable with PEI adsorption. This high degree of surface charge control will allow the surface chemistry of modified particles to be precisely tailored for specific applications.

4.3.2 Methodology

The PEI modification of the NaOH-silica particle surface is discussed in detail in Section 3.4.1. In short, PEI modification was achieved through the incubation of PEI (0.010-0.500 mM) and PB (145 mM, pH 7.4) with an aqueous suspension of NaOH-silica particles in a 1.000 mL reaction and typically over a 60 min period. The reaction tubes were inverted at 15 min intervals to maintain the suspension of the NaOH-silica particles. Unattached PEI in the supernatant was removed following centrifugation (30 s at 14000 rpm) and modified particles were washed twice with water.

PEI desorption was achieved through the 60 min incubation of suspended particles in 2.00 mM HCI (pH \sim 2.6) with inversion at 15 min intervals. Following desorption particles were separated from the acidic medium via centrifugation (30 s at 14000 rpm) and washed twice with water.

PEI-modified and PEI desorbed NaOH-silica particles were characterised by ATR-FTIR (Section 3.7.3) and zeta potential measurements (Section 3.7.5). As in Section 4.2.2, ATR-FTIR measurements were taken of dried particles against an air background following the method outlined in Section 3.7.3.2. Drying of the particles was conducted through desiccation for 72 h and oven drying at 383 K for 24 h. The zeta potential measurements were also conducted as per Section 4.2.2, using a 10.0 mM NaNO₃ electrolyte solution with 1.00 M HCI/NaOH added accordingly to adjust the pH. A more detailed account of the zeta potential measurement procedure can be found in Section 3.7.5.2.

UV-vis spectroscopy (Section 3.7.6) was used to determine the amount of PEI remaining in the supernatant following adsorption. The method for spectroscopic analysis of the supernatant is given in Section 3.7.6.2 (based on Ungaro *et al.* (2003)). The amount of PEI remaining in the supernatant was then used to determine of the amount of PEI adsorbed onto the NaOH-silica particles surface (Kindler and Swanson, 1971). An adsorption isotherm was fitted to the PEI adsorption data using the Boltzmann sigmoidal growth equation (Origin lab software fitting module).

4.3.3 Results and discussion

4.3.3.1 PEI adsorption-desorption

Modification of the particle surface was conducted through the electrostatic adsorption of PEI at pH 7.4 and its desorption at pH 2.6. The surface modification with PEI was characterised using ATR-FTIR spectroscopy, UV-vis spectroscopy (for the adsorption isotherm), and zeta potential measurements. The ATR-FTIR spectra of the unmodified, PEI adsorbed, and PEI desorbed dried particles are presented in Figure 4.5. Note that the spectra are offset for clarity.



Figure 4.5. ATR-FTIR spectra of the NaOH-silica particles, unmodified, modified with 0.200 mM PEI adsorption, and unmodified by 0.200 mM PEI desorption. The data are offset for clarity. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

In the region of wavenumbers below 1400 cm⁻¹ (Figure 4.5) the ATR-FTIR spectra of modified and unmodified particles were observed to be approximately equivalent. The 1400–500 cm⁻¹ region mostly includes peaks related to the vibrational energies of silica (see Section 4.2.3) (Badertscher *et al.*, 2009; Capozzi *et al.*, 1992; Launer, 1987; Neville and Seyfaee, 2013b). Therefore, this similarity between the data was expected.

The ATR-FTIR technique penetrates several micrometres ($0.5-5.0 \mu m$) into the sample (PerkinElmer, Inc., 2005). So, the signal related to polymerised silica, which makes up the majority of each particle, produces a much stronger signal than that of the particle surface, where the PEI coating can be detected. However, a significant shift in wavenumber was detected for the broad peak signal at approximately 3450 cm⁻¹ corresponding to the O–H and N–H stretching bonds (Badertscher *et al.,* 2009). The peak shift allowed a distinction to be made between the modified and unmodified particles. The shift of this peak at approximately 3450 cm⁻¹ is more easily observed in the truncated spectra presented in Figure 4.6.



Figure 4.6. Close up of the ATR-FTIR spectra between wavelengths 3900 and 3100 cm⁻¹ of the NaOH-silica particles, unmodified, modified with 0.200 mM PEI adsorption, and unmodified by 0.200 mM PEI desorption. The data are offset for clarity. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

The ATR-FTIR peak wavenumbers for the modified, PEI adsorbed, and PEI desorbed particles, taken from Figure 4.6, are plotted in Figure 4.7, to quantify the shift in signal of the broad peak at approximately 3450 cm⁻¹.



Figure 4.7. Wavenumber of the ATR-FTIR broad signal peak at approximately 3450 cm⁻¹ for the NaOH–silica particles, unmodified, modified with 0.200 mM PEI adsorption, and unmodified by 0.200 mM PEI desorption. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

The excitation of OH and NH bond stretching occurs at 3650-3200 and 3500-3200 cm⁻¹, respectively (Badertscher *et al.*, 2009). The unmodified particles had a signal at wavenumber 3402 ± 4 cm⁻¹, which was due only to OH stretching vibrations (Figure 4.7). In contrast, the peak for the PEI adsorbed particles was at 3455 ± 4 cm⁻¹ due to the addition of the PEI amine groups, as a result the signal was due to both NH and OH stretching. Hence the ATR-FTIR spectra indicated that the adsorption of PEI was successful.

Acidic desorption of the PEI was also investigated using ATR-FTIR. The $3424 \pm 4 \text{ cm}^{-1}$ ATR-FTIR broad peak detected for the desorbed particles decreases in wavenumber

from the adsorbed particle signal (Figure 4.7). This suggests that the PEI was desorbed when the signal was compared to the unmodified particles.

In Figure 4.6, an additional, small, narrow peak at approximately 3650 cm⁻¹ was detected in the ATR-FTIR spectra taken of the particles following PEI adsorption. The PEI molecule possesses a branched, polyamine structure and contains primary, secondary and tertiary amine functional groups (Neville et al., 2011a). Primary amines are expected to produce two NH stretching signals (Badertscher *et al.*, 2009), thus the narrow peak at approximately 3650 cm⁻¹ results from NH stretching of primary amines in the PEI structure. In the spectra taken following PEI desorption (Figure 4.7), the narrow peak at approximately 3650 cm⁻¹ disappears, becoming indistinguishable from the background signal noise. These results support that PEI adsorption and desorption onto the NaOHsilica particle surface was successful using the method proposed in this chapter. Zeta measurements used further confirm successful PEI potential were to adsorption/desorption.

To further characterise the modified particles, zeta potential measurements were made. In Figure 4.8, the curves of zeta potential versus pH for the unmodified, PEI adsorbed, PEI desorbed, and re-adsorbed particles are plotted.



Figure 4.8. Zeta potential of the NaOH-silica particles, unmodified, after modification with 0.200 mM PEI adsorption, and after 0.200 mM PEI desorption, as a function of pH. Also shown is the zeta potential curve of NaOH-silica particles with 0.200 mM PEI readsorbed after one adsorption – desorption cycle. Particles were suspended in a 10.0 mM NaNO₃ base electrolyte with pH controlled by additions of 1.00 M HCl/NaOH. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

The zeta potential curve of the unmodified NaOH-silica particles was also presented in Figure 4.4 and discussed in detail in Section 4.2.3. The negative charge of the silica surface, especially at high pH is the result of the surface silanol groups (\equiv Si-OH) (Jal *et al.*, 2004). The unmodified particles zeta potential curve correlates well with the p*K*_a values of silica (4.5 and 8.5) and silica zeta potential curves present in the literature (Mészáros *et al.*, 2002; Ong *et al.*, 1992).

Published research has indicated that the point of zero charge (PZC) of PEI occurs at pH 10.8 (Lindquist and Stratton, 1976; Vakurov *et al.*, 2012). The PZC of the adsorbed particles agrees well with the value provided in the literature (Lindquist and Stratton, 1976; Vakurov *et al.*, 2012). In addition, Wang *et al.* (2013a) determined the zeta potential of a PEI microsphere as a function of pH. The zeta potential of the PEI microsphere (Wang *et al.*, 2013a) was also found to correlate well with the zeta potential of PEI adsorbed particles shown in Figure 4.8. The agreement of the observed PZC of

the PEI adsorbed particles with the literature PZC value indicates that PEI was successfully adsorbed in this work. Furthermore, this result suggests that a PEI concentration of 0.200 mM for adsorption was enough to completely mask the silica silanol groups.

The PEI adsorbed particles had a positive zeta potential at pH greater than the PZC due to amine groups on the PEI gaining a proton. At pH less than 4 there is a decrease in the zeta potential of the PEI adsorbed particles which may be linked to PEI desorption at lower pH (Lindquist and Stratton, 1976). The decrease in PEI adsorbed onto the silica surface is the result of the solution pH approaching the pK_{a1} of silica (~4.5) (Ong *et al.*, 1992), so that the negative surface charge of the silica particles lessens, becoming more neutral, and causing the electrostatic attraction between the PEI and the silica surface to diminish. A decrease in pH was also observed to increase the size of the PEI molecule as a consequence of the increase in charge density and, thus, increase the steric repulsion between adjacent branches of the PEI molecule (Lindquist and Stratton, 1976). Lindquist and Stratton (1976) proposed that a combination of these two factors leads to the decrease in amount of PEI adsorbed at pH below 4.

The mechanism of desorption takes advantage of the neutralisation of the silica surface at pH less than ~4. As the p K_{a1} of silica is ~4.5 (Ong *et al.*, 1992) decreasing the pH below 4.5 will result in the silanol surface groups retaining their proton and neutralising the silica adsorption surface. Without the electrostatic attraction between the negative silica surface and positive PEI polymer the PEI molecule is expected to desorb from the silica particles. The successful desorption of the PEI molecule with incubation in an acidic environment can be observed in Figure 4.8, where the zeta potential curve of particles with PEI desorbed parallels that of the unmodified NaOH-silica particles. The PEI desorption suggested by the ATR-FTIR results (Figures 4.5, 4.6 and 4.7) was corroborated by the zeta potential results (Figure 4.8). However, the zeta potential is the most representative of the adsorption process of these two analytical tools, since the zeta potential is measured at the particle surface while ATR-FTIR measures the composition of entire particle in the sample.

The zeta potential curve of the particles after PEI has been re-adsorbed, (after one cycle of PEI adsorption and desorption), correlated with the original PEI adsorption curve (Figure 4.8). This result suggests that the process of charge control via PEI adsorption-desorption is fully reversible.

The zeta potential data were also transformed into surface charge density using the method outlined by Delgado *et al.* (1986). The expression used to transform the zeta

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potential, ψ_{ζ} (mV), to electrokinetic surface charge density, σ_{ζ} (mC m⁻²), is given in Equation 4.1 (Delgado, 2002), and the transformed data are given in the plot in Figure 4.9,

$$\sigma_{\zeta} = \frac{\psi_{\zeta} \varepsilon_0 \varepsilon_R (1 + \kappa a)}{a}$$
 4.1

where ε_0 is the vacuum permittivity (F m⁻¹), ε_R is the relative permittivity of the medium (in this case water), κ is the Debye constant (m⁻¹), and a is the particle radius (m).



Figure 4.9. The surface charge density of the NaOH–silica particles, unmodified, after modification with 0.200 mM PEI adsorption, and after 0.200 mM PEI desorption, as a function of pH. Surface charge density was calculated from the experimental zeta potential measurements taken of the particles suspended in a 10.0 mM NaNO₃ electrolyte (pH control with 1.00 M HCI/NaOH). Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

The electrokinetic surface charge density of the particles at various solution pH values was calculated from the zeta potential data using Equation 4.1 and is given in Figure 4.9.

The unmodified and desorbed particles were expected to possess a similar surface charge density to unmodified silica surfaces. Lindquist and Stratton (1976) investigated the surface charge density of Ludox silica nanoparticles using titration. Their results were used to verify this study. Adjusting to negate the contribution of aluminium ions found in Ludox nanoparticles, the authors determined that the surface charge density of their silica particles decreased from approximately 0 to -25 mC m⁻² with increasing pH from 3.0 to 11 (Lindquist and Stratton, 1976).

In Figure 4.9, the surface charge density of the unmodified and desorbed particles was determined as approximately 0 mC m⁻² at pH below 4. At pH exceeding 4, upon the ionisation of silanol surface groups, the silica surface gained a negative charge density reaching a maximum negative charge density of -7 to -10 mC m⁻² at pH 11. Both the charge density curves presented in this chapter and those measured by Lindquist and Stratton (1976) are largely similar, despite differences in the method of determination and the type of silica particle used. This correlation supports the hypothesis that the silanol groups determine the surface charge in both the unmodified and desorbed particle systems.

The surface charge density of the PEI modified particles is strongly positive, which is also expected from the zeta potential results. In 2002, Mészáros *et al.* (2002) determined the surface charge density of silica wafer surfaces modified via PEI adsorption by both titration and transformation of the zeta potential values. A maximum positive surface charge density occurred at pH 6 with surface charge densities of 10 and 20 mC m⁻² for the titration and zeta potential transformation measurement techniques, respectively (Mészáros *et al.*, 2002). The PEI adsorbed particles from this study possessed a similar surface charge density maximum of approximately 10 mC m⁻² at pH 6–8 (Figure 4.9). The similarity in surface charge density between the literature and this study further supports the claim of successful PEI adsorption.

4.3.3.2 Effect of PEI concentration

To study the effect of PEI concentration used during adsorption, the zeta potential curves were measured for PEI concentrations between 0.010 and 0.500 mM, Figure 4.10.



Figure 4.10. Zeta potential of the modified NaOH-silica particles, incubated with different concentrations of PEI (0.500 to 0.010 mM), as a function of solution pH. The zeta potential curve of the unmodified NaOH-silica particles as a function of pH was also included for comparison. Particles were suspended in a 10.0 mM NaNO₃ base electrolyte with pH controlled by 1.00 M HCl/NaOH. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

For clarity, a reduced set of PEI concentrations is shown in Figure 4.11.



Figure 4.11. Zeta potential of the modified NaOH-silica particles, incubated with different concentrations of PEI (0.500 to 0.010 mM), as a function of solution pH. For clarity, only a few of the PEI concentrations were displayed in this figure. The zeta potential curve of the unmodified NaOH-silica particles as a function of pH was also included for comparison. Particles were suspended in a 10.0 mM NaNO₃ base electrolyte with pH controlled by 1.00 M HCI/NaOH. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

In Figures 4.10 and 4.11, PEI concentrations of 0.125 mM and larger during the incubation stage were observed to have significantly positive zeta potentials for pH values above the PEI PZC, as expected. PEI concentrations between 0.200 and 0.500 mM PEI (Figure 4.10) were observed to have similar zeta potential curves, indicating a PEI adsorption limit had been reached. In addition, for adsorbed PEI of concentrations from 0.125 to 0.500 mM, the zeta potential became less positive when the pH was less than 4. This less positive zeta potential at pH below 4 is likely to be due to the partial desorption of PEI from the silica surface at pH below the PZC of silica (~4.5) (Lindquist and Stratton, 1976; Ong *et al.*, 1992).

PEI concentrations of 0.110 mM and lower gave negative/neutral zeta potentials for pH 2-12 (Figure 4.11). However, even for the experiments with the smallest concentrations of PEI there was a clear increase in the values of zeta potential compared to the

unmodified particles between pH 5 and 10 (Figure 4.11). This suggests that, even for the smallest concentrations used, PEI was adsorbed and masked some of the free OH groups alleviating their negative charge, as shown in Figures 4.10 and 4.12. The differences observed in zeta potential measurements with concentrations are better observed in Figure 4.12, where the zeta potential versus concentration measured at different pH values is plotted.



Figure 4.12. Zeta potential of modified NaOH-silica particles at select pH values (pH 4, 7 and 11) as a function of the concentration of PEI used during adsorption. The zeta potential NaOH-silica particles following acidic desorption are also plotted as a function of their adsorption PEI concentration before desorption, the zeta potential of the desorbed particles was taken at pH 7 and are plotted for comparison. Particles were suspended in a 10.0 mM NaNO₃ base electrolyte with pH controlled by additions of 1.00 M HCl/NaOH. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

In Figure 4.12, a rapid increase in charge with a relatively small increment in concentration at around 0.100 mM was observed. These results suggest that the adsorbed PEI reaches a threshold concentration where the charge contributions of the silanol surface groups on the silica are completely masked by the PEI molecules on the

surface. As discussed earlier in this section, masking of the silanol groups above this critical PEI concentration is supported by (a) the similarities in PZC of the modified particles with PEI and (b) the correlation between the zeta potential curves of the modified particles and the zeta potentials of the PEI microsphere (Wang et al., 2013a). Thus, the zeta potential curves for PEI concentrations below this threshold amount resemble that of the unmodified silica (Mészáros et al., 2002), whereas those with PEI adsorbed at a concentration greater than the critical amount are assumed to take on the form of a PEI zeta potential curve (Wang et al., 2013a). For the cases of very low concentration (<0.100 mM) the PEI molecules are likely to be located beyond the range of the screened electrostatic potential and would not feel the attraction of the negative silica particle surface. The increase in PEI concentration will increase the probability of the PEI molecules being closer to the silica particles. In addition, this increase in PEI concentration will increase the electrostatic repulsion between PEI molecules and so PEI molecules will be more easily directed toward the silica particle. Furthermore, due to the PEI's relatively flattened structure with multiple attachment sites per molecule (Lindquist and Stratton, 1976), each silica particle should require only a small number of PEI molecules to fully cover its surface. The presence of these three factors (PEI concentration, electrostatic repulsion, and flattened PEI molecule structure) is likely to be responsible for the rapid increase in the coverage of the silica with PEI concentration. which is observed as a rapid increase in zeta potential beyond the minimum threshold concentration.

In Figure 4.12, the zeta potential data at pH 7 of particles after desorption of the different concentrations of PEI are also included. In all cases the zeta potential values of the desorbed particles return to values within the error of the unmodified particles, indicating the successful desorption and, thus, that the charge modification process is reversible.

The zeta potential results presented in Figure 4.12 can be compared with the adsorption isotherm determined by the analysis of the supernatant. The results of the adsorption isotherm are given in Figure 4.13.



Figure 4.13. Adsorption isotherm of 25 kDa PEI on the surface of NaOH-silica particles. Initial PEI concentration used during incubation is presented as a function of PEI adsorbed. The data was fitted to using a Boltzmann function. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

The adsorption isotherm, plotted in Figure 4.13, shows a rapid increase in amount of PEI adsorbed with increasing initial PEI concentration. At approximately 0.200–0.250 mM initial PEI, the amount of PEI adsorbed plateaued, suggesting a saturation PEI concentration had been reached. Beyond this point a further increase in the initial concentration of PEI does not correspond to an increase in polymer adsorption. Hence any PEI added beyond this limiting concentration remains in solution and not adsorbed.

The observed saturation PEI concentration in Figure 4.13 corresponds to the concentration at which the zeta potential of PEI adsorbed particles also plateaus (Figure 4.12), suggesting that the threshold concentration discussed earlier is equivalent to the saturation adsorption concentration. Similar work by Szilágyi *et al.* (2011; 2014) gives credence to this hypothesis. Szilágyi *et al.* (2011) observed that the changes with electrophoretic mobility (directly related to zeta potential) of latex particles with increasing PEI incubation concentration revealed a similar trend. Their results showed a region of sharp increase in mobility followed by a plateau at a certain concentration, referred to as the adsorption saturation plateau (ASP). Szilágyi *et al.* (2011) remarked that the ASP

designated the point of maximum polymer adsorption as well as the limiting concentration for maximum zeta potential.

4.3.3.3 Effect of incubation time

Optimisation of PEI adsorption conditions is important for the development of this method for possible industrial applications. In Figure 4.14, the results of a study examining the effect of incubation time on zeta potential are presented. Incubation times between 10 and 120 min were considered. Experimental evidence (Figure 4.14) suggests that 10 min is sufficient to obtain the maximum charge reversal on the silica particle surface. In contrast, Lindquist and Stratton (1976) suggested that PEI adsorption is almost complete within 15 min of PEI addition. Hence this method provides a more rapid method for silica charge reversal with no requirement for continuous stirring after the initial short mixing period.



Figure 4.14. Zeta potential of modified NaOH-silica particles incubated with 0.200 mM PEI and varying incubation times (between 10 and 120 min) as a function of pH. The zeta potential curve of the unmodified NaOH-silica particles as a function of pH was also included for comparison. Particles were suspended in a 10.0 mM NaNO₃ base electrolyte with pH controlled by 1.00 M HCl/NaOH. Reprinted with permission from 'Surface Charge Control through the Reversible Adsorption of a Biomimetic Polymer on Silica Particles, E.D.E. Hyde, R. Moreno-Atanasio, P.A. Millner, and F. Neville, *The Journal of Physical Chemistry B* 2015 *119* (4), 1726-1735, DOI: 10.1021/jp5100439.' Copyright 2014 American Chemical Society.

4.4 Conclusions

A novel and simplistic method, the NaOH-silica synthesis method, used to synthesise silica nanoparticles was found to be robust. The NaOH-silica synthesis method employed TMOMS as the silane precursor and NaOH as the catalyst. The method produced consistent particle sizes (from DLS and SEM data) and yields, while requiring fewer reactants than previously published methods. As such the NaOH-silica synthesis method reported in this chapter is a promising alternative to current silica particle synthesis techniques.

Surface modification of the silica particles, via electrostatic adsorption of the biomimetic polymer PEI and its acidic desorption, was carried out as a means to control particle surface charge. The modified and unmodified particles were characterised by ATR-FTIR spectroscopy and zeta potential measurements. ATR-FTIR spectroscopy confirmed the adsorption of PEI onto the silica surface through the increasing wavenumber of the NH/OH peak at approximately 3450 cm⁻¹ when compared with the OH peak of the unmodified particles.

Zeta potential curves for modified and unmodified particles for pH between 2 and 12 demonstrated the effect of modification of particle surface charge. Particles with adsorbed PEI had a more positive surface charge than the unmodified particles, demonstrating the successful surface charge modification by PEI adsorption, with the modification being stable at pH above ~4. With the acidic desorption of PEI, the zeta potential curve returned to the same values as the unmodified particles, indicating successful desorption.

The effect of the PEI concentration during adsorption on the zeta potential was also studied. A threshold PEI concentration was observed after which the surface charge was solely dictated by the charge characteristics of the PEI coating. The threshold PEI concentration was determined by the zeta potential curves and PEI concentration measurements made using UV-vis spectroscopy. A study aimed at optimising incubation time for PEI adsorption found that the maximum charge modification was complete after 10 min incubation time. Hence, in this chapter, a rapid, reversible, and reliable method of silica particle charge reversal has been conveyed.

CHAPTER FIVE

Covalent surface modification of PEI-thiol silica particles

Publications:

Hyde, E.D.E.R., Seyfaee, A., Moreno-Atanasio, R., Aubin, J. Neville, F. (2015). Covalent surface modification of biomimetic silica particles. In *Proceedings of Asia Pacific Conference of Chemical Engineering Congress 2015: APPChE 2015, incorporating CHEMECA 2015*, Melbourne, Australia, September 27 – October 1, 2015; Engineers Australia: Melbourne, pp 918-928.

Statement of Contribution

 $e^{i\omega_{ij}}e^{i\omega_{ij}}$

Chapter 5

Hyde, E.D.E.R., Seyfaee, A., Moreno-Atanasio, R., Aubin, J. Neville, F. (2015). Covalent surface modification of biomimetic silica particles. In *Proceedings of Asia Pacific Conference of Chemical Engineering Congress 2015: APPChE 2015, incorporating CHEMECA 2015,* Melbourne, Australia, September 27 – October 1, 2015; Engineers Australia: Melbourne, pp 918-928.

By signing below, I confirm that Research Higher Degree candidate Emily Hyde contributed by collaborating in the experimental design and taking primarily responsibility for all experimental and analysis work. In addition, Emily Hyde contributed by taking primary responsibility for preparing, drafting and editing of the peer-reviewed conference publication listed above. Dr Ahmad Seyfaee, Dr Joelle Aubin, Dr Roberto Moreno-Atanasio and Dr Frances Neville contributed by collaborating in the experimental design of the project, and by supervision and critical review.

I thereby certificate that this statement of contribution is accurate:

Emily Hyde
······
Ahmad Şeyfaee
Joelle Aubin
······
Frances Neville
Roberto Moreno-Atanasio

5.1 Introduction

Surface functionalisation allows silica particles to be specifically tailored for selective interactions, which may significantly enhance their efficiency in practical applications, such as, in drug delivery and chemical analysis (Figeys and Aebersold, 1997; Xia *et al.*, 2009). Surface modifications allow advantageous stability of the silica bulk material to be combined with the reactivity of additional functional surface groups. Modifications by covalent attachment to the silica surface are of particular interest as they possess high stability and thus the functionalised particles can be utilised under most conditions, including organic mediums and most acidic/basic solutions (Jal *et al.*, 2004). Previous methods of covalent surface modification (Bigui *et al.*, 2013; Lee *et al.*, 2007; Ma *et al.*, 2014; Philipse and Vrij, 1989; Neville *et al.*, 2009) either required multiple reaction steps, such as, the need for a separate reaction with a pre-modifying agent (Section 2.3.2) (Bigui *et al.*, 2013; Ma *et al.*, 2014; Philipse and Vrij, 1989), or the range of potential modifying compounds were severely limited, generally to only alkoxysilane compounds (Section 2.3.1) (Lee *et al.*, 2007).

In the facile process reported in this chapter, biomimetic silica particles were modified through the attachment of select functional groups via disulfide bond formation. The novel method of covalent silica surface modification, thus, aims to increase the flexibility of functionalisation by expanding the number of potential modifiers to any compound containing a thiol functional group available for attachment to the silica particle surface.

Overall, the results in this chapter clearly demonstrate a method of covalent modification to introduce key functional groups to the biomimetic silica particle surface with the intent to increase particle functionality in practical applications. Surface modifications were characterised in this chapter with ATR-FTIR spectroscopy and zeta potential measurements.

5.2 Background

A detailed review of the current literature relating to silica surface modification, including silane coupling agents, is presented in Section 2.3.2.1. In short, due to the relative inertness of the silica surface (Jal *et al.*, 2004), covalent surface modification commonly requires an intermediate stage. This immediate stage involves the pre-treatment of the silica surface via a silane coupling agent (Bigui *et al.*, 2013; Ma *et al.*, 2014; Philipse and Vrij, 1989) (Section 2.3.2.1). Treatment with the silane coupling agent facilitates the formation of a covalent link between the particle surface and modifier. However, this pre-treatment step may the increase cost and synthesis time required for functionalisation.

Methods to modify the surface of silica during synthesis, referred to here as in situ surface modifications (Section 2.3.1), are also popular in the current literature. In 2007, Lee and coworkers (2007) adapted the widespread Stöber silica synthesis method (Stöber et al., 1968) (Section 2.3.1.2) for in situ surface modification (known as the coprecipitation method). The co-precipitation method utilises alkoxysilanes where one or more of the alkoxy branches is replaced by the desired organic surface functional group (Lee et al., 2007). These alkoxysilanes are hydrolysed and polymerised as per the traditional Stöber process. The co-precipitation method therefore produces silica particles intrinsically modified with the desired surface group/s, such as mercaptopropyl vinyl functional facilitated by alkoxysilanes. or groups the 3mercaptopropyltrimethoxysilane (3mPTMOS) and vinyltrimethyoxysilane (VTMS), respectively (Lee et al., 2007).

Neville *et al.* (2009) adapted the co-precipitation technique for biomimetic silica synthesis. In the Neville *et al.* (2009) adaption, the alkoxysilane, TMOMS (trimethoxymethylsilane), was replaced with 3mPTMOS in order to produce particles with a thiol functionalisation. Particle made using this method will be referred to here as PEI-thiol silica particles. Despite having the advantage of being an all-in-one synthesis and surface modification method, which minimises complexity and reaction time, the co-precipitation method, like the silane coupling agent method, significantly restricts the type of modifications possible. The novel method of surface modification reported in this chapter utilises the exposed thiol groups on the PEI-thiol silica particle surface (synthesised using Neville and co-worker's co-precipitation technique) in order to further modify the particle surface through robust and well-established chemistry (Anfinsen and Haber, 1961; Hatahet *et al.*, 2014; Tam *et al.*, 1991; Zhang *et al.*, 2011b).

In this chapter, a novel method of covalent functionalisation is proposed. This method functionalises the PEI-thiol silica particles while bypassing the need for pre-treatment with a silane coupling agent. In the proposed method, potential modifying compounds (or modifiers) required a thiol functional group. The thiol functional group of the surface modifying compound is used to covalently attach the modifier to the thiol surface groups on the PEI-thiol silica particle surface through the formation of a disulfide bond.

The development of disulfide bond chemistry has been spearheaded by the need to form and break disulfide bonds between peptides and protein species (Anfinsen and Haber, 1961; Hatahet *et al.*, 2014; Zhang *et al.*, 2011b). However, limited publications have been made investigating the formation of a disulfide bridge between smaller molecules or on surfaces. Disulfide bond formation is an oxidation reaction (Hatahet *et al.*, 2014) and therefore requires a corresponding species in the solution to undergo a reduction reaction. Several oxidising agents have been considered for this purpose in the literature (Tam *et al.*, 1991). Commonly dissolved air, or more accurately the dissolved oxygen component of dissolved air, is used as the oxidising agent for disulfide bridge formation in an aqueous medium (Tam *et al.*, 1991). A dissolved air / oxygen oxidising agent is advantageous in that it is inexpensive, readily available and produces the benign by-product of water (Tam *et al.*, 1991). Utilising dissolved air / oxygen as the oxidant has one major disadvantage that being the slow speed of the redox reaction (Hatahet *et al.*, 2014). However, the redox reaction equilibrium is reached more quickly in neutral or slightly basic aqueous mediums (Tam *et al.*, 1991).

The compounds 11-mercaptoundecanoic acid (MUA) and 4-aminothiophenol (4-ATP) were used in this study to demonstrate the covalent functionalisation of the PEI-thiol silica particles (Table 5.1). MUA surface modification provides the silica surface with a carboxylic acid functionalisation. The 4-ATP modification introduces additional amine surface groups, while the bulky benzene group between the amine functionalisation and the silica surface acts to prevent non-specific binding on the silica surface. In previous studies, MUA and 4-ATP have been extensively utilised to modify the surfaces of various metals / metal oxides (Aslan and Pérez-Luna, 2002; Ji *et al.*, 2001; Šimšíková *et al.*, 2013) and metals / PVC films / PbS crystals (Hayes and Shannon, 1996; Sacristán *et al.*, 2000; Torimoto *et al.*, 1994), respectively.

Table 5.1. Thiol modifiers used to modify the surface of PEI-thiol silica particles.
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Carboxylic acid groups and bulky phenyl / amine groups are two functionalisations not yet able to be achieved using *in situ* co-precipitation methods of silica surface modification (Chui *et al.*, 2014; Lee *et al.*, 2007; Nair and Pavithran, 2009; Neville *et al.*, 2009). However, the work presented in this chapter demonstrates a novel process able

to modify biomimetic silica particles with these functional groups via the formation of a disulfide bond.

5.3 Methodology

Two types of biomimetic particles, PEI-silica particles and PEI-thiol silica particles, were synthesised using methods previously described by Neville *et al.* (2009; 2010), and in Sections 3.3.1 and 3.3.3, respectively.

Modifications to the surface of the silica particles were made by reacting the MUA and 4-ATP thiol modifiers (Table 5.1) with the thiol surface groups of the PEI-thiol silica particles. This modification procedure is detailed in Section 3.4.2. In short, approximately ~3 mg PEI-thiol silica particles were suspended in phosphate buffer (pH 8.0, final concentration 100 mM). After particle suspension, the thiol modifier was added with a final concentration of 5.00 mM and a final volume of 1.00 mL. Particles and modifier were reacted for 48 h at room temperature (293-298 K). Centrifugation for 30s at 14000 rpm, stopped the reaction and the particles were washed twice with ~1 mL water. A control was performed for the MUA modification utilising PEI-silica particles instead of PEI-thiol silica particles for the modification reaction. This control experiment ensured the modifier was binding specifically with the PEI-thiol silica particle's thiol functional group.

Due to the low solubility of MUA in water, MUA modifications were also performed in an ethanol medium using the same procedure as above. The final concentration of the MUA modifier in the reaction mixture was changed to 10.0 mM. Post-reaction modified particles were washed twice with ethanol and then once with water.

Modified particles were characterised using ATR-FTIR spectroscopy (Section 3.7.3) and zeta potential measurements (Section 3.7.5). ATR-FTIR measurements were made on dried particle samples (desiccated for 72 h) with an air background as described in Section 3.7.3.2. Zeta potential measurements were made as outlined in Section 3.7.5.2, where sample particles were suspended in 10.0 mM NaNO₃ base electrolyte (pH adjustments were made with 1.00 M HCl/NaOH) for zeta potential measurements.

5.4 PEI-thiol silica particle characterisation

PEI-silica and PEI-thiol silica particles were synthesised using the method reported in Neville *et al.* (2009). In the same publication, Neville *et al.* (2009) characterised the size and shape of the PEI-silica and PEI-thiol silica particles. In Neville and Seyfaee (2013b), the PEI-silica particles were also characterised based on composition using ATR-FTIR spectroscopy. However, to the authors knowledge no research characterising the composition of the PEI-thiol silica particles had been published upon prior to this study. The composition of the PEI-thiol silica particles, and their deviation from PEI-silica particles, is important as it reveals the effect of *in situ* surface modification on the biomimetic silica particles formed.

In Figure 5.1, PEI-thiol silica particles were characterised using ATR-FTIR spectroscopy. Key functional groups present in the particle sample were identified via their distinctive infrared absorbance bands and labelled in Figure 5.1.



Figure 5.1. The ATR-FTIR spectrum of PEI-thiol silica particles. Absorbance bands of key functional groups have been identified and labelled. Reused with permission from 'Hyde, E.D.E.R., Seyfaee, A., Moreno-Atanasio, R., Aubin, J. Neville, F., Covalent surface modification of biomimetic silica particles', published in the Asia Pacific Confederation of Chemical Engineering Congress 2015: APCChE 2015, incorporating CHEMECA 2015. Copyright 2015 Engineers Australia.

In Figure 5.1, the infrared absorbance bands related to Si-O, Si-OH bond vibrations were found in the PEI-thiol silica particle ATR-FTIR spectrum (approx. 3460, 1110, 1025, 930 cm⁻¹). These absorbance bands were similar to those found in the ATR-FTIR spectrum of the PEI-silica particles (Neville and Seyfaee, 2013b) and correspond to functional groups which are common to most silica particles due the repeating tetrahedral silicon oxide structure of the silica material. PEI was used as the polycationic scaffold during synthesis and remained encased within the silica particles. The entrapped PEI scaffold results in N-H and C-H/N-H₃⁺ bond vibration peaks (approx. 3460 and 2930 cm⁻¹) in the ATR-FTIR spectrum. These peaks were also observed in the PEI-silica particle spectrum (Neville and Seyfaee, 2013b). The ~2930 cm⁻¹ peak is larger in PEI-thiol silica than its corresponding peak in PEI-silica samples (Neville and Seyfaee, 2013b), this is due to the combined absorbance from the C-H/N-H₃⁺ and R-SH bonds in the PEI-thiol silica particle sample (Badertscher *et al.*, 2009).

The signals at approximately 1405, 1260 and 805 cm⁻¹ (Figure 5.1) are the result of bond vibration of the propyl chain connecting the thiol group to the central Si in the hydrolysed/polymerised 3mPTMOS species. The band observed at 2565 cm⁻¹ corresponds to the expected weak absorbance band from S-H bond stretching (Badertscher *et al.*, 2009; Hernández-Pardròn *et al.*, 2004) which results from the thiol groups on the hydrolysed and polymerised 3mPTMOS molecules. Future work building upon this PEI-thiol silica particle characterisation study may investigate the number of thiol groups available on the surface of the PEI-thiol silica particles (Chapter 9).

5.5 Particle surface modification through disulfide bond formation

PEI-thiol silica particles synthesised with the 3mPTMOS alkoxysilane possess exposed surface thiol groups (Neville *et al.*, 2009). In the literature, surface thiol groups have been used to bind with various metal species (Neville *et al.*, 2009; Shah *et al.*, 2014). In this study, the surface thiol group was employed to covalently attach a modifying agent (modifier) to the silica surface through the formation of a disulfide bridge. Successful modification results in the modifying compound, which must possess a thiol group, reacting to form a disulfide bond with a thiol group on the PEI-thiol silica particle surface (Shah *et al.*, 2014). This results in a covalent bond between surface modification using this novel method.

Scheme 5.1. Schematic of PEI-thiol silica particle modification through disulfide bond formation where X is the potential modifying group. Reused with permission from 'Hyde, E.D.E.R., Seyfaee, A., Moreno-Atanasio, R., Aubin, J. Neville, F., Covalent surface modification of biomimetic silica particles', published in the Asia Pacific Confederation of Chemical Engineering Congress 2015: APCChE 2015, incorporating CHEMECA 2015. Copyright 2015 Engineers Australia.



In order to determine the success of the proposed surface modification technique, the modified silica particles were characterised using ATR-FTIR spectroscopy and zeta potential measurements.

5.5.1 Surface modification with 11-mercaptoundecanoic acid

Surface modification using the modifier 11-mercaptoundecanoic acid (MUA) introduces a long chained carboxylic acid group to the silica surface. The MUA modification therefore allows the particles to possess a carboxylic acid group for specific interactions. The modifier, MUA, possesses low aqueous solubility, but is highly soluble in ethanol, hence the modification reaction was conducted in both aqueous and ethanol media. In the ethanol medium, the MUA concentration was twice that of the concentration used for the water mediated reaction due to the higher solubility of MUA in ethanol compared with water. The ATR-FTIR spectrum of unmodified PEI-thiol silica particles (Figure 5.1) was compared with the spectra of the MUA modified PEI-thiol silica particles to determine the success of the modification technique (Figure 5.2).



Figure 5.2. ATR-FTIR spectra of the unmodified PEI-thiol silica particles and the MUA modified PEI-thiol silica particles (in water or ethanol). Reused with permission from 'Hyde, E.D.E.R., Seyfaee, A., Moreno-Atanasio, R., Aubin, J. Neville, F., Covalent surface modification of biomimetic silica particles', published in the Asia Pacific Confederation of Chemical Engineering Congress 2015: APCChE 2015, incorporating CHEMECA 2015. Copyright 2015 Engineers Australia.

In Figure 5.2, a number of weak peaks are present in the spectra of MUA modified particles that are not found in the spectrum of the unmodified PEI-thiol silica particles. The first of these additional absorbance bands was observed at 1560/1530 cm⁻¹ (water/ethanol reaction medium). This additional absorbance peak may result from bond vibrations in the carboxyl group (C=O) which was added through MUA modification. However, the absorbance band observed in the MUA modified sample has a lower wavenumber than predicted by literature (Badertscher *et al.*, 2009), thus, its identification as C=O vibration absorbance is inconclusive. In addition, the use of MUA in ethanol did not seem to significantly increase the surface modification or signal detected via ATR-FTIR spectroscopy.

The other ATR-FTIR absorbance band appearing in MUA modified PEI-thiol silica particles' spectra, but not in the unmodified particles' spectra, occurs at 500 cm⁻¹. This band corresponds to the wavenumber of disulfide bond absorbance (Badertscher *et al.*, 2009) and indicates formation of disulfide bridges between the particle surfaces and MUA modifiers was successful. However, as this absorbance band occurs within the

fingerprint region (<1000 cm⁻¹) of the infrared spectrum it is overlapped by the IR absorbance of other species and it is difficult to confirm the bands' significance.

Nevertheless, further analytical proof of MUA modification of the PEI-thiol silica particle surface was achieved using zeta potential measurements. The zeta potential curves of the unmodified and MUA modified PEI-thiol silica particles are given in Figure 5.3. This is also the first study to publish the characterisation of PEI-thiol silica particles using zeta potential measurements.



Figure 5.3. The zeta potential of the unmodified PEI-thiol silica particles and MUA modified (in water and ethanol) PEI-thiol silica particles are presented as a function of suspension pH. Particles were suspended in 10.0 mM NaNO₃ electrolyte solution with pH adjustments made with 1.00 M HCI/NaOH for zeta potential measurements. Reused with permission from 'Hyde, E.D.E.R., Seyfaee, A., Moreno-Atanasio, R., Aubin, J. Neville, F., Covalent surface modification of biomimetic silica particles', published in the Asia Pacific Confederation of Chemical Engineering Congress 2015: APCChE 2015, incorporating CHEMECA 2015. Copyright 2015 Engineers Australia.

In Figure 5.3, the zeta potential of the unmodified and modified particles is plotted as a function of pH. As anticipated, the zeta potential of the unmodified PEI-thiol silica particles was positive above pH 10 due to the presence of amine groups on the silica surface. These surface amine groups are the result of polyamine PEI molecules entrapped during particle synthesis. A point of zero charge (PZC) was observed from the

PEI-thiol silica particles at approximately pH 11.3. The observed PZC correlates well with the PZC of the PEI molecule given in the literature (pH 10.8) (Lindquist and Stratton, 1976; Vakurov *et al.*, 2012).

Comparing the zeta potential curves of the unmodified particles with the particles modified with MUA (Figure 5.3) establishes how MUA surface modification significantly changes the surface charge of the particles. As expected, surface modification with MUA led to a decrease in the zeta potential of the modified particles due to the addition of carboxylic acid groups. The overall zeta potential of the MUA modified particles, however, remained positive. These results indicate that the carboxylic acid groups attached to the surface are significantly fewer than the amine groups provided by the entrapped PEI molecule. In other words, while MUA surface modification was successful, it did not result in extensive coverage of the silica particle surface. The reduced coverage could be attributed either to an incomplete reaction between particle surfaces and the modifying agents, or to a low density of thiol groups on the PEI-thiol silica surface.

Unmodified and potentially modified PEI-silica particles were used in a control study, the zeta potential curves of these particles are presented in Figure 5.4. Overall, the zeta potential curve of the unmodified PEI-thiol silica particles possesses similar characteristics to the zeta potential curve of the PEI-silica particles (Chapter 4) as can be seen in Figure 5.4. This similarity was expected as both types of particles were synthesised with the entrapment of the PEI scaffolding molecule.



Figure 5.4. The zeta potentials of the unmodified PEI-thiol silica particles and the control particles: unmodified PEI-silica particles and MUA modified PEI-silica particles are presented as a function of suspension pH. Particles were suspended in 10.0 mM NaNO₃ electrolyte solution with pH adjustments made with 1.00 M HCl/NaOH for zeta potential measurements. Reused with permission from 'Hyde, E.D.E.R., Seyfaee, A., Moreno-Atanasio, R., Aubin, J. Neville, F., Covalent surface modification of biomimetic silica particles', published in the Asia Pacific Confederation of Chemical Engineering Congress 2015: APCChE 2015, incorporating CHEMECA 2015. Copyright 2015 Engineers Australia.

At the reaction pH (8.0), MUA possesses a negatively charged carboxylic acid group and the amine surface groups of the PEI-thiol silica particles are positively charged. Thus, electrostatic adsorption of the MUA to the particle surface instead of covalent attachment of the modifier was a concern. PEI-silica particles, on the other hand, possess positively charged amine groups for electrostatic attraction but no thiol groups for the formation of a disulfide bonds, hence PEI-silica particles were used as a control.

Electrostatic adsorption would be indicated by a decrease in the zeta potential of MUA incubated PEI-silica particles, as the positively charged amine particle surface groups would be shielded by the adsorbed MUA molecules. However, in Figure 5.4, it can be observed that the zeta potential curve of the PEI-silica particles correlates within error with the zeta potential curve of the MUA modified PEI-silica particles. Hence, the zeta potential measurements of the control particles suggest that electrostatic adsorption of MUA was either non-existent or any MUA that was adsorbed was subsequently removed

during washing. Therefore, MUA modification of the PEI-thiol silica particles as established by the ATR-FTIR (Figure 5.2) and the zeta potential (Figure 5.3) results, was the result of covalent attachment of the modifier.

It is interesting to note that the MUA surface modification reaction undertaken in an aqueous medium led to a greater difference between the zeta potential curves of unmodified and modified particles than the MUA modification reaction performed in an ethanol medium (Figure 5.3). This difference suggests that the modification was less successful in an ethanol medium compared to a water medium, despite the higher concentration of MUA used in the ethanol mediated reaction. The greater success of the modification reaction performed in water, over the reaction performed in ethanol, may be due to one or both of the following factors: (1) the reaction was facilitated by an optimal reaction pH in the water medium and/or (2) the reaction was facilitated by an increased concentration of the oxidant, O₂, due to its higher solubility in the water medium (Battino *et al.*, 1983).

5.5.2 Surface modification with 4-aminothiophenol

The PEI-thiol silica particles were also functionalised with the modifier, 4aminothiophenol (4-ATP). The zeta potential curve of the 4-ATP modified PEI-thiol silica particles was compared with that of the unmodified PEI-thiol silica particles in Figure 5.5. The 4-ATP modification results in an additional amine functional groups at the expense of the thiol groups on the particle surface. Thus, the similar zeta potential curves observed for the 4-ATP modified particles and the unmodified PEI-thiol silica particles in Figure 5.5 were as expected. Above pH 7, the zeta potential of the 4-ATP modified particles was observed to be significantly lower than the unmodified particles. Therefore, these measurements suggest that upon modification the bulky phenyl groups of the 4-ATP modification act to shield the already present PEI amine surface groups and thus produce slightly lower zeta potential measurements then the unmodified particles (Dung *et al.*, 2008).



Figure 5.5. The zeta potentials of unmodified PEI-thiol silica particles and 4-ATP modified PEI-thiol silica particles are presented as a function of suspension pH. Zeta potential of as a function of pH. Particles were suspended in 10.0 mM NaNO₃ electrolyte solution with pH adjustments made with 1.00 M HCI/NaOH. Reused with permission from 'Hyde, E.D.E.R., Seyfaee, A., Moreno-Atanasio, R., Aubin, J. Neville, F., Covalent surface modification of biomimetic silica particles', published in the Asia Pacific Confederation of Chemical Engineering Congress 2015: APCChE 2015, incorporating CHEMECA 2015. Copyright 2015 Engineers Australia.

Zeta potential measurements alone were not sufficient to determine the success of the 4-ATP modification reaction as the 4-ATP functionalised the particle surface with additional amine groups. ATR-FTIR spectroscopy was used to characterise the modified particles and determine whether the modification reaction was successful. The ATR-FTIR spectrum of 4-ATP modified PEI-thiol silica particles was presented alongside the unmodified PEI-thiol silica particles spectrum in Figure 5.6.



Figure 5.6. ATR-FTIR spectra of the unmodified PEI-thiol silica particles and 4-ATP modified PEI-thiol silica particles. Reused with permission from 'Hyde, E.D.E.R., Seyfaee, A., Moreno-Atanasio, R., Aubin, J. Neville, F., Covalent surface modification of biomimetic silica particles', published in the Asia Pacific Confederation of Chemical Engineering Congress 2015: APCChE 2015, incorporating CHEMECA 2015. Copyright 2015 Engineers Australia.

A number of differences can be clearly observed in Figure 5.6 between the ATR-FTIR spectra of the unmodified and 4-ATP modified particles. One difference is the weak absorbance bands at 3470 and 3360 cm⁻¹ observed in the 4-ATP modified particle spectrum and not in the unmodified particle spectrum. The absorbances at 3470 and 3360 cm⁻¹ correspond with the infrared absorbance for aromatic nitrogen-hydrogen bond vibrations, suggesting 4-ATP modifier attachment (Badertscher *et al.*, 2009).

The peaks at 1625, 1600 and 1495 cm⁻¹, were also observed only in the ATR-FTIR spectrum taken after 4-ATP modification. These three peaks correspond to the multiple absorbance bands expected in the range of 1625-1575 cm⁻¹ due to carbon-carbon bond vibrations of the aromatic ring (Badertscher *et al.*, 2009) thus further supporting successful attachment of the 4-ATP modifier.

The last additional peak observed in the modified particle spectra is at 505 cm⁻¹. This absorbance peak may result from disulfide bond vibration (Badertscher *et al.*, 2009).

On the other hand, it is important to note that the multiple absorbance bands relating to aromatic C-H bond vibrations in the 4-ATP structure, expected at 3080-3030 cm⁻¹

(Badertscher *et al.*, 2009), were not observed in the modified particle spectrum. However, it is possible that the aromatic C-H absorption bands are present but are hidden by the broad peak at approximately 2930 cm⁻¹, which results from the combined signal of C-H/N-H₃⁺ and R-SH bond vibrations in the bulk PEI-thiol silica material (Figure 5.1) (Badertscher *et al.*, 2009).

As electrostatic adsorption is not an issue for this particular modifier and non-specific binding of the modifier is unlikely after washing, the changes in the ATR-FTIR spectrum after 4-ATP modification strongly indicate covalent surface modification was successful with the 4-ATP modifier.

5.6 Conclusions

The work in this chapter aimed to develop a novel surface modification technique without the necessity of using a silane coupling agent as an intermediate step, which is commonly carried out. The surface modification technique utilised the thiol surface groups of the fabricated PEI-thiol silica particles for the covalent attachment of the desired functional group through the formation of disulfide bridges between the silica surface and the potential surface modifier.

The first step was the production of the PEI-thiol silica particles which were synthesised with intrinsic thiol surface groups. The thiol surface groups were supplied in the silica source (3mPTMOS) used for particle synthesis. The PEI-thiol silica particles were characterised using ATR-FTIR spectroscopy and zeta potential measurements, techniques that demonstrated the presence of the thiol groups.

The second step was the covalent attachment of the modifiers, 11-mercaptoundecanoic acid and 4-aminothiophenol, which functionalised the particle surfaces with carboxylic acids and bulky phenyl/amine groups, respectively. The surface modified particles were also characterised using ATR-FTIR spectroscopy and zeta potential measurements in solutions of varying pH. The results of these characterisation techniques indicate that the novel surface modification methodology reported in this chapter is able to successfully modify the PEI-thiol silica particle surfaces through the covalent attachment of the desired functional groups. Therefore, we have simplified the traditional surface modification method by avoiding the necessity of the intermediate step of using a silane coupling agent.
CHAPTER SIX

Fabrication and scale up of biomimetic silica shell – magnetic core particles

Publications:

Hyde, E.D.E.R., Moreno-Atanasio, R., Neville, F. (2017). Fabrication of magnetic core PEI-silica shell particles. *Materials Research Bulletin*, *96* (3), 222-232.

Statement of Contribution

Chapter 6

Hyde, E.D.E.R., Moreno-Atanasio, R., Neville, F. (2017). Fabrication of Magnetic Core PEI-Silica Shell Particles. *Materials Research Bulletin*, *96*, 222-232.

By signing below, I confirm that Research Higher Degree candidate Emily Hyde contributed by collaborating in the experimental design of and taking primarily responsibility for all experimental and analysis work. In addition, Emily Hyde contributed by taking primarily responsibility for preparing, drafting and editing of the journal publication listed above. Dr Roberto Moreno-Atanasio and Dr Frances Neville contributed by collaborating in the experimental design of the project, and by supervision and critical review.

I thereby certificate that this statement of contribution is accurate:

Emily Hyde

·····

Frances Neville

Roberto Moreno-Atanasio

6.1 Introduction

Core-shell particles seamlessly combine the advantageous properties of the core and the shell materials into a single entity. As discussed in Section 2.4, magnetic core-silica shell particles in particular have garnered much recent research attention (Gawande et al., 2015; Javidi and Esmaeilpour, 2016; Kalantari et al., 2013; Liu and Choi, 2015c; Melnyk et al., 2016; Roto et al., 2016; Zhang et al., 2013). Magnetic core-silica shell particles combine the magnetism afforded by their magnetic core with the beneficial properties of the silica shell, including ease of functionalisation, physical/chemical stability and biocompatibility (Jal et al., 2004; Roto et al., 2016; Zhang et al., 2013; Chapters 4 and 5). The combined properties allow magnetic core-silica shell particles to be utilised in catalysis, environmental clean-up, magnetorheology, adsorption and biomedical applications (Dutz et al., 2009; Esmaeili-Shahri and Es'haghi, 2015; Gawande et al., 2015; Gutiérrez et al., 2015; Li et al., 2009b; Liu and Choi, 2015c; Roto et al., 2016; Shi and Asefa, 2007). Key separation applications of the magnetic coresilica shell particles include heavy metal ion removal (Hua et al., 2012; Ngomsik et al., 2005; Zou et al., 2016), recovery of specific mineral fine particles (Gray et al., 1994) and CO₂ capture (Li et al., 2017). These applications were discussed in detail in Section 2.5.

To develop core-shell particles for the abovementioned applications, a number of studies (Roto *et al.*, 2016; Sacanna *et al.*, 2012; Vogt *et al.*, 2010; Wang *et al.*, 2015a) have been dedicated to silica shell fabrication techniques (discussed in Section 2.4.1). These techniques have been particularly focused on shell synthesis methods that allowed the introduction of enhanced or tunable surface properties, such as, thiol or amine functionalisation, control over shell thickness or control over morphological features (Bao *et al.*, 2011; Biradar *et al.*, 2011; Chen *et al.*, 2005; Du *et al.*, 2009a; Kalantari *et al.*, 2013; Kobayashi *et al.*, 2005; Roto *et al.*, 2016; Stöber *et al.*, 1968; Vogt *et al.*, 2010; Wang *et al.*, 2015a). However, these methods of silica shell fabrication often require an unideal combination of complex procedures, long reactions times, high temperatures and harsh conditions (Roto *et al.*, 2016; Vogt *et al.*, 2010; Wang *et al.*, 2015a).

This chapter aims to develop coating techniques adapted from the PEI-silica, PEI-thiol silica and NaOH-silica particle fabrication processes (Neville *et al.*, 2009; Chapter 4). As discussed in Chapters 2, 4 and 5, PEI-silica, PEI-thiol silica and NaOH-silica particle synthesis techniques have the advantages of the in-built surface functionalisation, low reaction temperatures, facile methods and short synthesis times (Neville *et al.*, 2009; Chapters 4 and 5). These advantages also make the same methods attractive for shell synthesis, especially in comparison to the long reaction times, complex methodologies

and high temperature requirements of previous shell synthesis techniques in the literature (Roto *et al.*, 2016; Vogt *et al.*, 2010; Wang *et al.*, 2015a).

This chapter begins with the characterisation of the carbonyl iron core material (Section 6.2) and an investigation of the magnetic separation technique used to remove noncoating silica (Section 6.3). In Section 6.4, the PEI-silica shell fabrication techniques are developed and characterised. The shell particle fabrication process was also scaled up by volume factors of 10 and 50. To expand the variety of surface properties and thus applications of the core–shell particles, the development of PEI-thiol silica coatings was also considered in this chapter. The PEI-thiol silica shells offer the dual functionality of thiol and amine surface groups. PEI-thiol silica shell fabrication process is discussed in Section 6.5, alongside the scaled-up PEI-thiol silica shell fabrication reaction. A coating utilising the NaOH-silica synthesis technique, developed in Chapter 4, was also investigated with the results presented in Appendix A (Section A.1).

6.2 Carbonyl iron core characterisation

Carbonyl iron (\geq 95% Fe basis, product C3518) was purchased from Sigma-Aldrich (Section 3.2.1) and used as the magnetic core material. Carbonyl iron is manufactured through the purification of liquid iron. First, the iron is converted into iron pentacarbonyl. The iron pentacarbonyl is purified through distillation. Carbonyl iron is then produced from the thermal decomposition reaction of the purified iron pentacarbonyl. The relative purity and sphericity of the carbonyl iron particles has made them an attractive material for research studies as well as other powder metallurgy applications in the food industry and in electronics (Bloemacher, 1990).

As specifications were not provided by the manufacturer, the carbonyl iron power was characterised using scanning electron microscopy (SEM) imagining (Section 3.7.1). The preparation of SEM samples is outlined in Section 3.7.1.1, in this case the samples were not carbon coated. SEM images were analysed with Zen 2 blue edition software (Zeiss).

Analysis of the SEM images has shown the carbonyl iron particles were highly polydispersed with an average diameter of 2100 ± 1000 nm and with an approximate diameter range of 500 nm and 5000 nm (Figure 6.1). Most particles appeared spherical in shape. However, some particles were observed to be elongated or conjoined. It is unclear whether the observed conjoined particles were artefacts of the drying process in SEM sample preparation or resulted from the production process.



Figure 6.1. Characterisation of the carbonyl iron core material. (A) SEM image taken using the secondary electron detector of uncoated carbonyl iron particles. (B) Particle size distribution graph of the carbonyl iron particles. Particle size analysis of the SEM image was conducted using the software ZEN 2.3 Blue edition (Zeiss) after analysis of 180 individual particles. Reprinted from Materials Research Bulletin, *96* (3), 222-232, E.D.E.R. Hyde, R. Moreno-Atanasio, F. Neville, Fabrication of magnetic core PEI-silica shell particles, Copyright 2017, with permission from Elsevier.

6.3 Magnetic separation

In contrast to previous work on PEI-silica shell fabrication (Neville *et al.*, 2012), this study relied on magnetic separation to remove any non-magnetic (core-free silica) from the product before core–shell particle characterisation. Therefore, before the fabrication of the core–shell particles begun, the magnetic separation process was assessed to determine whether non-coating silica (a by-product of the coating reactions) could be removed using a facile magnetic separation process.

6.3.1 Methodology

The magnetic separation process is detailed in Section 3.5.1, with a summary of the method given here. First, PEI-silica particles were synthesised in accordance with the previously specified method (Neville *et al.*, 2009) (Section 3.3.1). PEI-silica particles (~9 mg mL⁻¹) were suspended with carbonyl iron (~5 mg mL⁻¹) (characterised in Section 6.2) in a 9:1 water:methanol medium. After thorough mixing, a permanent neodymium magnet was used to trial the separation of the magnetic carbonyl iron from the non-magnetic PEI-silica particles. The magnet was placed on the outside of a polypropylene microcentrifuge tube containing the suspension and the supernatant removed with a glass pipette. The non-magnetic PEI-silica particles that were not attracted to the magnetic remained suspended in solution and were removed with the supernatant. The magnetic

particles remaining in the microcentrifuge tube were subsequently washed thrice through resuspension in 1.000 mL water and magnetic separation as described above.

SEM (Section 3.7.1) and energy dispersive x-ray spectroscopy (EDX) (Section 3.7.2) analysis with a Zeiss Sigma FEGSEM was conducted to assess if magnetic separation had been attained. Samples were prepared as per Section 3.7.1.2 and carbon coated before imaging.

6.3.2 Results

In Figure 6.2, SEM imaging shows a mixture of PEI-silica particles (Section 3.3.1) and carbonyl iron particles (Section 6.2) prior to and after the magnetic separation and washing process.



Figure 6.2. SEM images (secondary electron detector) of a mixture of carbonyl iron and PEI-silica particles (A) before magnetic separation and (B) after magnetic separation. Reprinted from Materials Research Bulletin, *96* (3), 222-232, E.D.E.R.
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The small uniform silica particles in the image (Figure 6.2A) are PEI-silica particles, whereas the large particles with a rougher surface are the carbonyl iron particles, as can also be observed in Figure 6.1A. The small PEI-silica particles, seen in Figure 6.2A (before the magnetic separation), are not observed in Figure 6.2B where only carbonyl iron was seen. This comparison suggests that the nonmagnetic PEI-silica particles were successfully removed using the magnetic separation technique (Section 6.3.1) leaving behind the magnetic carbonyl iron core material (Figure 6.2B). It should be noted that

the carbonyl iron cores are polydispersed in size and any small particles visible are also carbonyl iron (similar small particles can also be seen in the image of pure carbonyl iron, Figure 6.1A). This point will be further demonstrated by using EDX.

The success of the magnetic separation process was also assessed by performing an EDX compositional analysis, presented in Figure 6.3. As discussed in Section 3.7.2, characteristic X-ray emission energies detected in EDX analysis can be used to identify the elemental composition of a specific area/spot. EDX analysis was conducted over a large area of the magnetically separated sample (originally PEI-silica particles and carbonyl iron particles) to determine, through the identification of a Si peak, whether any silica remained. A large area was used for the EDX analysis for the magnetic separation assessment as it more definitively demonstrated whether all PEI-silica was removed through magnetic separation or not.



Figure 6.3. EDX spectra of a mixture of PEI-silica and carbonyl iron after magnetic separation. Reprinted from Materials Research Bulletin, *96* (3), 222-232, E.D.E.R.
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Figure 6.3 shows the EDX spectrum of a large selected area of particles after magnetic separation. The absence of a silicon (Si) peak at 1.7 keV (Neville *et al.*, 2013a) indicates that the PEI-silica particles were successfully removed through magnetic separation. Hence, this study demonstrates that the core-free silica by-product of the coating synthesis can be successfully removed by a facile process. Thus, in Sections 6.4 and

6.5, the core–shell particles fabricated were magnetically separated and washed using this process.

6.4 PEI-silica shell – carbonyl iron core particles

6.4.1 Background

PEI-silica particle synthesis employs the biomimetic polyamine, polyethyleneimine (PEI), to induce silication in mild conditions and an aqueous reaction medium within a relatively short reaction period (Neville *et al.*, 2016). Previous studies have shown the advantage of morphological control over particle size and size distribution that can be exercised through variations in the reactant concentrations and mixing conditions of the PEI-silica method (Neville and Moreno-Atanasio, 2012; Seyfaee *et al.*, 2014). Furthermore, PEI-silica includes an inbuilt amine functionalisation resulting from the entrapped PEI (polyamine) template molecule (Neville *et al.*, 2013a) (Section 2.3.1.3). Amine functionalised magnetic core-silica shell particles display an excellent adsorptive capacity for heavy metal ions and carbon dioxide (Wang *et al.*, 2010a; Zelenák *et al.*, 2008). PEI-silica has also been shown to possess hydrophobic surface properties (Neville *et al.*, 2016).

In this chapter, seven different PEI-silica coating processes for carbonyl iron cores were investigated with the aim of tuning the properties of the silica shell fabricated. The morphologies obtained by the different methods and four concentrations of the silica precursor, trimethoxymethylsilane (TMOMS), were compared. In addition, the effects of double silica coats versus a single coat were contrasted. The PEI-silica shell was extensively characterised via SEM, EDX and attenuated total reflectance - Fourier transfer infrared (ATR-FTIR) spectroscopy. Through these characterisation techniques the PEI-silica methodology and reactant concentration utilised could be related to shell coverage, morphology and thickness. Following the successful coating with the PEI-silica shell, a select few methodologies were scaled up by factors of 10 and 50.

6.4.2 Methodology

In this study, seven coating synthesis methods were trialled in 1.000 mL reactions; these methods are described in detail in Section 3.5.2. A summary of the different coating methods used in this study are presented in Table 6.1.

Table 6.1. The coating methods investigated in this study with a brief description of the procedures used for each. After the procedure summarised below the coating reaction was then allowed to proceed for 30 min. Reprinted from Materials Research Bulletin, 96 (3), 222-232, E.D.E.R. Hyde, R. Moreno-Atanasio, F. Neville, Fabrication of magnetic core PEI-silica shell particles, Copyright 2017, with permission from Elsevier.

Method A		Hydrolysed TMOMS incubated with carbonyl iron cores	
	Two tube	(15 min) before all other reactants added	
Method B	methods	Carbonyl iron cores and PEI were incubated for 15 min,	
		then all other reactants added	
Method C		Sonication between each reactant addition with TMOMS	
	Sonication	(neat) added as the first reactant	
Method D	methods	Sonication between each reactant addition with PEI	
		added as the first reactant	
Method E	All in one	All reactants added simultaneously	
Method F		Following the addition of all other reactants, hydrolysed	
		TMOMS was added in even amounts at 1 min intervals	
	Slow addition	over 10 min	
Method G	methods	All reactants excluding PEI were combined with Fe, then	
		PEI was added in even amounts at 1 min intervals over	
		10 min	

For the coating methods in Table 6.1, the concentrations of reactants were 5.0 ± 0.3 mg mL⁻¹ carbonyl iron particles, 1:9 methanol:H₂O, 50.0 mM phosphate buffer (PB), 2.50 mg mL⁻¹ PEI and a TMOMS concentration of 50, 100, 200 or 300 mM. The total reaction volume for these experiments was 1.000 mL. In the methods requiring pre-hydrolysed TMOMS, the hydrolysis reaction was conducted by incubating 1.00 M TMOMS in 1.00 mM HCl for 15 min prior to being added to the synthesis reaction. Also, for all methods, after reactants were added, synthesis was conducted at room temperature (293-298 K) for 30 min. During the synthesis reaction time, tubes were upended at 5 min intervals to prevent settling of the carbonyl iron particles.

After the coating reactions were complete, magnetic separation (Section 6.2) was used to separate the coated magnetic particles from the nonmagnetic by-product and unused reactants. The coated magnetic particles were subsequently washed thrice through resuspension in ~1 mL water.

Following the success of the 1.000 mL coating reactions, Method D with 100 mM TMOMS and Method G with 200 mM TMOMS were later scaled up by factors of 10 and 50. The methodology of the scale up process can be found in Section 3.5.2.5. In short, while all the reactant concentrations and the reaction procedures remained the same as

described previously in this section, the volume of the shell fabrication reactions were scaled up by 10 and 50 times, so that the final volume of the reactions were 10.000 and 50.000 mL.

Core-shell particles were characterised using ATR-FTIR spectroscopy as described in Section 3.7.3, with the sample preparation described in Section 3.7.3.2. Core shell particles were also characterised using SEM imaging (Section 3.7.1) and EDX analysis (Section 3.7.2). Samples prepared as per Section 3.7.1.2 and were carbon coated prior to imaging. EDX spot composition analysis was performed on the centre of at least 3 randomly selected particles in the sample. For core-shell particles, the EDX analysis was conducted on a single spot to better reflect the relative silica thickness of each sample. The peak heights of Si and Fe element peaks from the EDX spectra were measured and the Si:Fe peak height ratio calculated. For each sample, the average Si:Fe peak heights for the three particles in that sample were recorded as an indicator of silica shell thickness through qualitative comparison.

6.4.3 Results

The core-shell particles were thoroughly characterised after the PEI-silica shell fabrication, to assess the features of the PEI-silica coating produced. The characterisation was performed using ATR-FTIR spectroscopy, SEM and EDX measurements. Through the characterisation of the PEI-silica shell, conclusions could be drawn regarding the effects of the coating methodology, reactant concentration and double versus single layer coating on the resulting PEI-silica coat morphology, thickness and coverage.

6.4.3.1 ATR-FTIR spectroscopic characterisation

ATR-FTIR spectroscopy was used to detect PEI-silica in the core–shell particles through the identification of key PEI-silica vibrational peaks in the sample's spectrum. Figure 6.4 shows the spectra of core–shell particles made using Method A at 50 and 200 mM TMOMS. In addition, and for comparison, the spectra of pure carbonyl iron and pure PEIsilica particles are also presented. The full set of spectra are provided in Appendix A (Section A.2).



Figure 6.4. ATR-FTIR spectra of pure carbonyl iron, PEI-silica and PEI-silica shell – carbonyl iron core (with PEI-silica shells fabricated through Method A with 50 mM and 200 mM TMOMS) particles. Reprinted from Materials Research Bulletin, *96* (3), 222-232, E.D.E.R. Hyde, R. Moreno-Atanasio, F. Neville, Fabrication of magnetic core PEI-silica shell particles, Copyright 2017, with permission from Elsevier.

In Figure 6.4, the carbonyl iron spectrum has only one distinguishable feature, a very wide peak at approximately 500 cm⁻¹. The PEI-silica spectrum, however, contains a number of key signals which can be identified as vibrational absorption of the C-H bond at 2970 cm⁻¹, Si-methyl bond at 1270 cm⁻¹, Si-O-Si bonds at 1000 cm⁻¹ and the Si-O bond at 765 cm⁻¹ (Neville and Seyfaee, 2013b; Seyfaee *et al.*, 2014). The C-H and methyl groups arise in PEI-silica due to entrapped PEI molecules and the methyl side chain of the TMOMS silica source.

In the example core–shell particle spectra (Figure 6.4), the PEI-silica shell was fabricated using Method A with TMOMS concentrations of 50 and 200 mM, respectively. In the spectrum of the core–shell particles coated with a higher TMOMS concentration (200 mM) the peaks identified as PEI-silica peaks correlate with those of the pure PEI-silica spectrum. These peaks are also strong and clearly visible, indicating a significant amount of PEI-silica present in the sample. In contrast, core–shell particles coated with a lower concentration of TMOMS (50 mM) have a comparatively weak PEI-silica signal, with only the prominent SiO₂ peaks present, indicating that relatively little silica was present. As magnetic separation was shown to be successful at removing excess core-free PEI-silica

(Section 6.3) identification of PEI-silica in the sample was taken as a strong indicator of PEI-silica shell formation.

To avoid repetition, the ATR-FTIR spectra of the remaining coating methods and concentrations can be found in Appendix A (Section A.2). The results from these spectra were summarised according to the existence and strength of the PEI-silica peaks. The summary is presented in Table 6.2. The "Weak" and "Strong" labels were qualitatively evaluated using the Spectrum 10 software.

Table 6.2. Summary of ATR-FTIR spectroscopy results for all coating methods and TMOMS concentrations. The full set of spectra can be found in Appendix A (Section A.2). The core–shell particle spectra were rated as no, weak, or strong, based on the existence and strength of the characteristic PEI-silica signals in their ATR-FTIR spectrum, as follows: "No" – no detectable PEI-silica signal, "Weak" – not all PEI-silica peaks detected and the peaks that were present had a weak signal, "Strong" – all characteristic PEI-silica peaks clearly observed.

TMOMS	Coating Method						
Conc. (mM)	Α	В	С	D	E	F	G
50	Weak	No	Strong	Strong	Weak	No	No
100 – 300	Strong	Strong	Strong	Strong	Strong	Strong	Strong
100 x2*	Strong	Strong	Strong	Strong	Strong	Strong	Strong

* Double coat with a 100 mM TMOMS coating.

At concentrations greater than or equal to 100 mM TMOMS, core–shell particles were observed to absorb at the characteristic PEI-silica wavenumbers, indicating silica shells were formed for all methods at these higher TMOMS concentrations. However, for the lowest concentration tested (50 mM TMOMS) only Methods C and D (both sonication coating methods) displayed all the PEI-silica peaks. Moreover, Methods A (two tube method with TMOMS added first) and E (all in one method) produced a weak PEI-silica signal indicating a low amount of silica being present. Possible theories as to why these methods (A, C-E) were able to produce a lower amount of silica are discussed in Section 6.4.4.1.

6.4.3.2 EDX characterisation

The average EDX Si to Fe ratio peak heights of three randomly chosen particles within each sample were used to produce Figure 6.5. These results are an indicator of comparative silica shell thickness. However, it is important to note, that the Si:Fe ratio is qualitative not quantitative, and thus this information can only be analysed through comparison with the other results. Future work, as described in Chapter 9, will investigate determining shell thickness quantitatively.



Method A Method B Method C Method D Method E Method F Method G

Figure 6.5. The average ratio of the Si:Fe EDX compositional peaks indicating silica shell thickness for each coating method and TMOMS concentration. Reprinted from Materials Research Bulletin, *96* (3), 222-232, E.D.E.R. Hyde, R. Moreno-Atanasio, F. Neville, Fabrication of magnetic core PEI-silica shell particles, Copyright 2017, with permission from Elsevier.

In Figure 6.5, a clear trend is observed showing a general increase in the Si:Fe peak ratio with increasing TMOMS concentration. The EDX measurements were taken from spot samples in the middle of each core–shell particle, hence this increase in the Si:Fe peak ratio suggests a thicker silica shell arises from a higher concentration of the silica precursor reactant, TMOMS. The notable exception to this trend is the 300 mM TMOMS Method E (all in one) coating, however, this measurement could be an outlier.

The 200 mM TMOMS single coatings were also compared with the 100 mM TMOMS double coating methodology in Figure 6.5 (*i.e.* black and white bars respectively). While

the EDX ratios indicate that methods B, C, D and G produced thicker shells when employing a double coat, the EDX ratios of the other methods trailed seem to indicate thinner shells were produced through double coating.

6.4.3.3 SEM characterisation

Scanning electron microscopy (SEM) images were taken using two types of detectors, secondary electron, presented in Table 6.3, and backscattered electron, shown in Table 6.4. These two scanning methods allow for an in-depth characterisation of the morphology and presence of the coating, respectively.

Comparing the images at 50 mM TMOMS in Tables 6.3 and 6.4, especially the backscattered images (Table 6.4), it appears that Methods A, C and D produced an observable silica shell. For these methods at 50 mM TMOMS the silica is observed as a thin grey shadow in the backscattered detected images and is particularly evident in the Method C image. The surfaces of all other methods (B, E, F, G) at the 50 mM TMOMS concentration appear similar between the secondary electron (Table 6.3) and backscattered electron (Table 6.4) detected images indicating the surface was (coating-free) carbonyl iron. This result is in agreement with the ATR-FTIR spectroscopy results (Table 6.2), in that, no silica was detected in the ATR-FTIR spectra for methods B, F and G, but characteristic silica peaks were observed for Methods C and D. Very small ATR-FTIR silica peaks were also observed for core–shell particles produced using Methods A and E. However, for Method E this coating is not observable in the SEM images, a possible reason for this inconsistency in results is discussed in Section 6.4.4.1.

TMOMS Concentration (mM)										
50	100	200	300	100 (x2 coats)						
Pethod A										
Method B				2 для						
Method C			3.3	2 <u>u</u> m						
Method D			0357 0357	A Z im						
Method E				2 µm						
Method F				200						
Method G				<u>2 µт</u>						

Table 6.3. SEM images, taken using the secondary electron detector, of PEI-silica coated carbonyl iron particles fabricated using different methods and TMOMS concentrations. Reprinted from Materials Research Bulletin, *96* (3), 222-232, E.D.E.R. Hyde, R. Moreno-Atanasio, F. Neville, Fabrication of magnetic core PEI-silica shell particles, Copyright 2017, with permission from Elsevier.



Table 6.4. SEM images, taken using the backscattered electron detector, of PEI-silica coated carbonyl iron particles fabricated using different methods and TMOMS concentrations. Reprinted from Materials Research Bulletin, *96* (3), 222-232, E.D.E.R. Hyde, R. Moreno-Atanasio, F. Neville, Fabrication of magnetic core PEI-silica shell particles, Copyright 2017, with permission from Elsevier.

At TMOMS concentration 100 mM and greater, some particles in each sample appear to have a grey coating in the backscattered image (Table 6.4) when compared with the secondary electron image (Table 6.3), indicating the presence of a silica coating. The thickness of the silica coating, however, in most images is highly variable, appearing to coat some particles thickly while other particles in the sample appear uncoated or only thinly coated. The most consistent coating thicknesses appear for the core–shell particles fabricated by Methods C and D.

The comparison of the morphology of the different methods at 100 mM TMOMS and higher, (Table 6.3) shows that Methods A, B, E-G produced shells of varying roughness, which in most cases appear to be formed from interlinked small silica spheres with different amounts of core particle surface coverage (Table 6.4). These shells appear smoother when a double coat (100 mM TMOMS x2) synthesis was employed, compared with the 200 mM TMOMS single coat.

In contrast, the sonication methods (C, D) produced a smooth gel-like shell morphology (Table 6.3). Interestingly, the morphology of the 50 mM Method A coating is similar to the coatings produced by the sonication methods with a smooth gel-like coating instead of the rough shell formed by Method A of all other TMOMS concentrations (Table 6.3).

All core–shell methods resulted in the fabrication of at least some multicore particles. As discussed in Section 6.2, the core material carbonyl iron (Figure 6.1) appears to have a tendency towards conjoined particles which is likely the route of these multicore particles. However, in the case of the core–shell particles formed using the sonication methods (C, D) this tendency towards multicore coatings appears particularly pronounced (Tables 6.3 and 6.4). This led to larger numbers of cores per core–shell entity than observed for other methods and a clear gel-like silica coating binding the core particles together (Table 6.4). In addition, this multicore tendency appears more pronounced at higher TMOMS concentrations. A similar tendency to multicore coatings appears for Method F (TMOMS added slowly).

In Figure 6.8, examples of the SEM images for both the rough shell morphology (Method G 100 mM TMOMS) and gel-like shell morphology (Method D 200 mM) are shown at a higher magnification than seen in Table 6.3. One of the three EDX spectra taken are also shown for each of the samples, where characteristic Si and Fe peaks can be clearly observed indicating silica coating of the carbonyl iron core. These EDX spectra were used, alongside addition spectra taken of other particles in the same sample, to determine the average Si:Fe ratio as presented in Figure 6.5.



Figure 6.8. SEM images using the secondary electron detector of PEI-silica coated carbonyl iron particles with 25,000X magnification. (A) Rough "raspberry-like" coating morphology was produced using Method G, 100 mM TMOMS. (B) Gel-like coating morphology was produced by Method D, 200 mM TMOMS. Adapted from Materials Research Bulletin, *96* (3), 222-232, E.D.E.R. Hyde, R. Moreno-Atanasio, F. Neville, Fabrication of magnetic core PEI-silica shell particles, Copyright 2017, with permission from Elsevier.

6.4.4 Discussion

To investigate the PEI-silica coating methodologies trialled in this study, each coating methodology was compared on their ability to form a shell and the shell coverage throughout the sample (Section 6.4.4.1), the morphology of the shell (Section 6.4.4.2) and the relative shell thickness (Section 6.4.4.3).

6.4.4.1 Shell surface coverage

As magnetic separation is able to separate the silica shell – carbonyl iron core from free silica (Section 6.3), the ATR-FTIR spectroscopy (Table 6.2) and EDX (Figure 6.5) results are expected to provide answers as to which methods and concentrations are able to produce silica shells. In addition, SEM results (Tables 6.3 and 6.4) provide a visual indicator of the presence or absence of silica shells on the carbonyl iron cores. By investigating the shells created from different TMOMS concentrations (50, 100, 200 and 300 mM), it can be observed that at the lowest TMOMS concentration studied (50 mM), formation of a silica shell was strictly dependent on the method employed (Tables 6.2-6.4, Figure 6.5). However, at TMOMS concentrations of 100 mM and higher all coating methods resulted in at least some silica shell coverage of the core particles (Tables 6.2-6.4, Figure 6.5).

First, the shells produced with 50 mM TMOMS will be discussed. At 50 mM TMOMS, only the sonication methods (C and D) and the TMOMS incubated two tube method (A) were observed by all characterisation techniques to have produced a silica shell (Table 6.2, Figures 6.5–6.7). In contrast, the existence of a silica shell was only observed for 50 mM TMOMS Method E in the ATR-FTIR and EDX spectra (Table 6.2, Figure 6.5) but not obvious via SEM imaging (Figures 6.6 and 6.7). This indicated that, in comparison with 50 mM TMOMS Methods A, C and D, 50 mM TMOMS Method E produced either a very thin coating or that only a limited number of particles in the sample were coated.

Previous studies on PEI-silica particle synthesis and similar particle synthesis techniques have determined reactions with lower TMOMS concentrations require a longer reaction time to reach their maximum size (Neville *et al.*, 2016). Hence, it can be theorised that given a longer reaction period, methods other than A, C and D may have produced a substantial silica shell. However, this theory will need to be addressed in future work. In the case of Methods C and D, the agitation afforded in the sonication may increase the reactant collision rate (Chen and Kalback, 1967) accelerating the silication reaction. This accelerated silication reaction in the sonication methods may have allowed a substantial silica shell to form within the 30 min reaction time frame, even at a low TMOMS concentration (50 mM).

The limited or complete lack of coverage for PEI-silica shell fabrication at 50 mM TMOMS, in comparison with the higher TMOMS concentrations studied, agree well with the results presented in Seyfaee *et al.* (2014; 2015a). Seyfaee *et al.* (2014; 2015a) investigated the effect of TMOMS concentration on PEI-silica particles formation. They demonstrated that for synthesis reactions employing TMOMS concentrations below a

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certain threshold value, 25 mM TMOMS (Seyfaee *et al.*, 2014; 2015a), the no PEI-silica particles were formed regardless of the length of the reaction period. For the coating reactions studied in this chapter the threshold concentration appears slightly higher at approximately 50 mM TMOMS concentration. However, future studies examining a range of low TMOMS concentrations, as performed by Seyfaee *et al.* (2014; 2015a), will be required to accurately pinpoint the concentration threshold for PEI-silica shell fabrication.

For PEI-silica shells synthesised with TMOMS concentrations greater than 50 mM (*i.e.* 100-300 mM TMOMS), there are clear differences in the surface coverage depending on the coating fabrication method. In order to compare the different methods, two aspects of silica surface coverage were considered. The first aspect was the distribution of the coating over the entire sample, that is, whether or not every particle within the sample appeared coated. The second aspect considered the shell coverage of individual particles, that is, whether the entire core was covered by the shell or if some areas of the core material remained exposed after coating.

The sonication methods (C, D) appear to very effective in coating all of the particles within the sample (Table 6.3). In addition, individual particles within the sample seem fully coated, that is, particles do not seem to possess regions where their core material is exposed. The effectiveness of Methods C and D is possibly due to the sonication mixing increasing the likelihood of all carbonyl iron cores coming into contact with the silica reactants. This high coverage coating would likely make Methods C and D ideal for protecting the core material from chemical instability in harsh conditions (Roto *et al.*, 2016).

PEI-silica coating fabrication using all in one and two tube methods (Methods A, B, E) seem to have produced PEI-silica shells with a highly varied coating distribution, where some particles appear coated, while others possess no visible silica shell (Figures 6.6 and 6.7). The coating of individual particles also appears uneven, with some sections of individual particles appear coated whereas in other sections of the same particle the core material remains uncoated (Figures 6.6 and 6.7).

Despite the lack of shell coverage consistency, where the presence of a shell was observed, this shell possessed a rough coating morphology, known as a "raspberry-like" coating which will be discussed further in Section 6.4.4.2.1 (Bao *et al.*, 2011; Chen *et al.*, 2005; Liu and He, 2007; Xu *et al.*, 2007). Similar shell characteristics were recorded for the raspberry-like polystyrene core-carbon black shell particles fabricated by Bao *et al.* (2011) and the polystyrene-silica core-shell particles in Du and coworkers' study

(2009a). The correlation with literature studies (Boa *et al.*, 2011; Du *et al.*, 2009a) indicates the incomplete shell coverage and raspberry-like morphology often occur together.

For the slow addition methods (Methods F, G), both aspects of shell surface coverage are somewhat improved with respect to Methods A, B and E, despite their similar raspberry-like shell morphology. The improvement in shell surface coverage may be attributed to the slow addition (Methods F, G) involving inverting mixing every minute throughout the first 10 min of the reaction, which, similarly to the sonication methods (Methods C, D), results in more opportunities for collision between silica reactants and the carbonyl iron core. In contrast, in the two tube (Methods A, B) and all in one (Method E) methods the reaction tubes were only mixed during the 30 min reaction period where all coating methods were given intermittent mixing (Section 6.4.2). Hence, it is expected further improvement in coating coverage could be achieved through continuous agitation throughout the coating process.

Comparing the double coating (100 mM TMOMS x2) and single coating processes (200 mM TMOMS) (Tables 6.3 and 6.4), it appears that the both aspects of the shell surface coverage either slightly improve (Methods A, B) or remain about the same (Methods C, D, E, F, G).

Overall, the two sonication methods of coating (Methods C, D), were observed to produce high coverage, uniform silica shells. These high coverage coatings will likely prove useful as a protective shield for the core material (Roto *et al.*, 2016). The other methods (Methods A, B, E, F, G), did not produce the same degree of surface coverage in the coating process, leaving some particles or some parts of the core material entirely uncoated.

6.4.4.2 Shell morphology

Shell morphology may be as important as shell coverage or thickness as it is directly related to apparent surface area (Polshettiwar *et al.*, 2010; Tian *et al.*, 2015; Zhang *et al.*, 2014a) and hydrophobicity (Bao *et al.*, 2011; Du *et al.*, 2009a). The morphological features of the PEI-silica shell with varying coating methodology and TMOMS concentration can be compared via the SEM images presented in Table 6.3 and the morphology observed at a higher magnification in Figure 6.8. Except the sonication methods (Methods C, D) and Method A at 50 mM TMOMS, all other methodologies and concentrations tested produced rough raspberry-like silica shells (Figure 6.8A). The

sonication methodologies (Methods C, D) on the other hand produced a smooth gel-like coating (Figure 6.8B). The raspberry-like morphology of Method A (two tube method) and the smooth gel-like shell of Method C correlate with previously reported results, which used PEI-silica coating with TMOMS incubation (similar to Method A) and sonication (similar to Method C), respectively, with 100 mM TMOMS (Neville and Moreno-Atanasio, 2012).

6.4.4.2.1 Raspberry-like morphology

In Table 6.3, it can be observed that raspberry-like shell morphologies were produced in Methods A, B, E, F and G (100–300 mM TMOMS) (Table 6.3). In addition, Figure 6.8A shows a more detailed image at higher magnification of the Method G 200 mM TMOMS concentration coating. Similar raspberry-like coatings have been shown to impart an enhanced degree of hydrophobicity or superhydrophobicity on the core–shell particle surface (Bao *et al.*, 2011; Du *et al.*, 2009a). The hydrophobic behaviour of these surfaces may be useful in the construction of hydrophobic films or for selective interactions with hydrophobic materials (Du *et al.*, 2009a; Rubio and Hoberg, 1993). Future work will investigate whether hydrophobicity/superhydrophobicity properties are present in the raspberry-like core–shell particles produced in this study.

Many previous studies produced raspberry-like coatings in a two-step process. First, small particles were synthesised and then, in a second reaction, small particles were attached to the core (Bao *et al.*, 2011; Chen *et al.*, 2005). Instead of this two-step process, the raspberry-like shape of the shells produced in Methods A (100–300 mM TMOMS), B, E-G, simplify the production of raspberry-like PEI-silica coating to a single reaction. Du *et al.* (2009a) also developed a single-reaction sol-gel process for a raspberry-like silica coating on a polystyrene core material. However, Du and coworkers (2009a) worked with a modified Stöber process to the silica shell which does not possess the advantageous mild reaction conditions, amine functionalisation and fast reaction times of the PEI-silica methods discussed herein.

The morphological features of the raspberry-like coatings produced seem to fall on a spectrum. In some cases, fully individualised particles appear stuck on the surface of the core (Figure 6.8A), while, in other cases, the coatings appear as rough surface without discernible individual particles. The degree to which the silica particles comprising the raspberry-like coatings are individualised appears to be dependent on the method of coating and TMOMS concentration (Table 6.3). For example, the samples of Method A (TMOMS incubated with Fe prior coating reaction) with Method B (PEI incubated with Fe

prior to coating reaction). In Method A, the PEI-silica raspberry-like coating is clearly mostly made of individual particles aggregated on the Fe surface. This is especially apparent at higher concentrations (300 mM TMOMS) where the silica particles forming the raspberry-like coating are of a comparatively large size. In contrast, in Method B, especially at 100 mM TMOMS concentration, the silica coating appears rough, but the individual particles are difficult to distinguish. Hence, it may be said that while Method A (TMOMS incubated with Fe prior coating reaction) favours the nucleation and growth of individual PEI-silica particles that later attach to the Fe surface, Method B shows a tendency towards precipitation of silica directly onto the carbonyl iron core, alongside individual PEI-silica particle formation as in Method A. These differences between Method A and B, may result from the PEI accumulating on the Fe surface before the reaction in Method B, leading to less free PEI to form PEI-silica nuclei for individual PEI-silica particle formation (Seyfaee *et al.*, 2014).

The sizes of the PEI-silica particles comprising the raspberry-like shells also appear to be dependent on the methodology and TMOMS concentration (Table 6.3). For example, the largest PEI-silica particles found forming the raspberry-like silica shell appeared for the slow addition methods (Methods F, G) where the PEI-silica particles forming the raspberry-like coating were as large as ~1 μ m (300 mM TMOMS Method F, Table 6.3). In this work, the size of the silica particles making up the raspberry-like coating increases with increasing TMOMS concentration. These results agree well with Du and coworkers' work (2009a) where a modified Stöber method was used to form a raspberry-like silica coating.

The morphological features of the double coating (100 mM TMOMS x2 coats, Method A, B, E-G) when compared with the raspberry-like single coating (200 mM TMOMS, Method A, B, E-G) still appear rough but less raspberry-shaped, *i.e.* more smoothed over (Table 6.3). These results could be due to the second coat of the PEI-silica being more likely to treat the already formed PEI-silica coat as a type of secondary nuclei. Therefore, silica would polymerise directly onto the core–shell particles smoothing over the raspberry-like morphology, instead of producing more individual PEI-silica particles that later aggregate on the surface.

6.4.4.2.2 Gel-like morphology

Methods C and D (the sonication methods, single and double coats) produced particle morphologies with a smooth gel-like coating (Figures 6.6 and 6.8B). It is likely that this coating morphology is the result of sonication disrupting the formation of free silica nuclei/particles that would later aggregate to the carbonyl iron core (such as in the formation of raspberry-like coatings). The sonication methods (C, D) also have a tendency towards the encapsulation of multicore particles (Table 6.3). These results correlate with Yang *et al.* (2005) where it was reported that increasing the period of sonication during the Stöber method coating reaction resulted in a higher number of entrapped Fe₃O₄ cores. As discussed in Section 6.4.4.1, coatings encapsulating multiple magnetic cores have been demonstrated to display high temperature stability (Li *et al.*, 2009b), as well as, enhanced stability against unwanted aggregation and sedimentation (Gutiérrez *et al.*, 2015). However, this study has shown the tendency to form multicore particles is reduced at the lowest TMOMS concentration, especially in Method D (Table 6.3), where the core shell particles appear individualised.

6.4.4.3 Relative shell thickness

The relative shell thickness of each sample was inferred from the SEM backscattered images (Table 6.4) and the average of 3 particle's compositional peak height ratios of Si:Fe, for each sample, as recorded by EDX (Figure 6.5). In both cases (Figure 6.5 and Table 6.4) the results indicate an increase in the amount of silica, suggesting that shell thickness appeared to increase as a function of TMOMS concentration (Du *et al.*, 2009a; Kobayashi *et al.*, 2005).

The only exception to this trend was Method E at 300 mM TMOMS, where the Si:Fe average ratio decreased with respect to higher concentrations (Figure 6.5). Similarly, in Table 6.4, the backscattered SEM image of the coating also appears reduced in comparison to the same method at 100 and 200 mM TMOMS. The observed discrepancy could be an indication of the disperse range of coating thicknesses throughout the sample due to the "all in one" reaction methodology without continuous mixing (Method E). However, this hypothesis is yet to be confirmed. Due to the nature of the analysis method, only a small sample from each methodology could be examined by the SEM/EDX techniques at a time, so in the case of widely variant products the small sample analysed may not be indicative of the whole sample.

The results presented in Figure 6.5 indicate the thickest shells were produced by Method A at 200 and 300 mM TMOMS concentrations. In Tables 6.3 and 6.4, it can be observed that these thick shells are the result of large defined PEI-silica particles forming the coating on the surface. The particles with this raspberry-type coating are most defined in Method A. The EDX Si:Fe average ratios (Figure 6.5) also indicate Method A produced the largest range of shell thicknesses with TMOMS concentration, indicating the shell

thickness was tunable. The increase in thickness with TMOMS concentration was also observed for Method B but to a lesser extent. This ability to tune the shell thickness with reactant concentration may increase the suitability of the core–shell product for some applications, including biomedical and magnetorheological applications (Dutz *et al.*, 2009; Gutiérrez *et al.*, 2015; Jal *et al.*, 2004).

Interestingly, Methods C and D (sonication methods) seemed to possess a shell thickness that varied little with TMOMS concentration increase from 50 to 200 mM (Figure 6.5), which reduces the ability to tune the shell thickness. The reason for this is unclear and investigating this further could form part of a future study.

For methods were the addition of PEI was made prior to TMOMS (Methods B, C, F) a lower EDX Si:Fe ratio was measured suggesting a thinner shell, in comparison to the counterpart methods (Methods A, C, G) where TMOMS was added first. Further study of the mechanism of both process will be required to determine the cause of these trends. The effect of using a double coat instead of a single coat on coating thickness was also dependent on the methodology used, with Methods B, C, D and G appearing to possess a thicker shell with the double coat over the single coat, whereas the other methods showed the opposite trend.

6.4.5 Scale up

The ability to scale up the production of the core-shell particles is vital to the feasibility of using the particles in industrial scale processes. In this section, following the successful production of the PEI-silica shell in 1 mL reactions, the PEI-silica shell fabrication process was later scaled up by factors of 10 and 50 to investigate the effect of scale up on the core-shell particles produced.

As Methods D and G (Figure 6.8) were found to produce the best examples of the gellike and raspberry-like morphologies, respectively, they were chosen for the scaling up procedure. TMOMS concentrations of 100 mM for Method D and 200 mM for Method G were chosen for the scale up, as these conditions were observed to produce well defined gel-like and raspberry-like morphologies (Figure 6.8).

For scale up, the PEI-silica shell fabrication process was conducted in 10 and 50 mL reaction vessels, in contrast to the 1 mL reaction volume used for shell fabrication in Section 6.4.3 and 6.4.4. The scaled up shell fabrication method is described in Sections 3.5.2.5 and 6.4.2.

6.4.5.1 Gel-like coating morphology

In a 1 mL reaction, the sonication method (Method D) produced a smooth gel-like PEIsilica shell with excellent carbonyl iron core coverage and a tendency toward multicore particles as discussed previously in Section 6.4 (Figures 6.9A, B; Section 6.4.3). In this subsection, the sonication method (Method D) was scaled up by 10 and 50 times to investigate the effect of increased reaction size on the core-shell particles produced. In Figure 6.9, the core-shell particles produced using Method D in 1, 10 and 50 mL reactions were compared.



Figure 6.9. SEM images of the gel-like PEI-silica shell – carbonyl iron core particles fabricated using Method D and 100 mM TMOMS with (A, B) the original 1 mL fabrication reaction being compared with the fabrication process scaled up by a factor of (C, D) 10 and (E, F) 50. Images were taken with the secondary electron detector (A, C, E) and the backscattered electron detector (B, D, F).

Secondary electron detected SEM images (Figures 6.9A, C, E), show that the increase in reaction volume (from 1 mL to 10 and 50 mL) did not change the smooth gel-like morphology of the PEI-silica shell produced. From the backscattered electron detected SEM images (Figures 6.9B, D, F), it appeared that the PEI-silica shell coated all carbonyl iron cores in the sample, indicating the Method D fabrication method retained excellent surface coverage for all reaction volumes. However, when examining the core–shell particles fabricated in the 1 mL Method D reaction (Figure 6.9B), the dark grey of the PEI-silica shell appears heavier on some carbonyl iron core particles and lighter on others. This uneven coating thickness was not observed in the 10 and 50 x scaled up

coatings (Figures 6.9D, F). In addition, the PEI-silica shell produced in the scaled up reactions was thinner overall than the 1 mL PEI-silica shell, as can be observed in the backscattered electron detected images (Figures 6.9B, D, F). As inconsistent shell coverage was identified as a major issue for the fabrication process (Section 6.4.4.1), the more even shell thickness of the scaled-up process, as observed in Figures 6.9D and 6.9F, can be seen as an improvement over the original 1 mL reaction.

Overall, it was observed that the fabrication process of Method D could be successfully scaled up by 10 and 50 times without sacrificing the smooth gel-like morphology of the PEI-silica shell. However, the scale up did result in a thinner layer of silica coverage. Comparing the 10 x and 50 x scale up fabricated coatings, the quality and morphology of the coats produced were very similar and thus were a promising indicator for further scale up.

6.4.5.2 Raspberry-like coating morphology

The slow addition method (Method G) in 1 mL reactions was used to produce PEI-silica shell – carbonyl iron core particles with a raspberry-like morphology (Sections 6.4.3 and 6.4.4). In this section, the Method G shell fabrication reaction was scaled up to 10 and 50 mL. The core–shell particles produced in the scaled up 10 and 50 mL processes were compared with core–shell particles fabricated using the original 1 mL-reaction using SEM imaging in Figure 6.10.



Figure 6.10. SEM images of the raspberry-like PEI-silica shell – carbonyl iron core particles fabricated using Method G and 200 mM TMOMS with (A, B) the original 1 mL fabrication reaction being compared with the fabrication process scaled up by a factor of (C, D) 10 and (E, F) 50. Images were taken with the secondary electron detector (A, C, E) and the backscattered electron detector (B, D, F).

The images taken by the backscattered electron detector (Figures 6.10B, D, F) show that PEI-silica shells were produced for all reaction volumes, as can be observed by the coating of the light grey carbonyl iron core particles with the dark grey PEI-silica shell material. The coating thickness and surface coverage of carbonyl iron cores appeared to vary little with increasing reaction vessel size from 1 to 10 mL as suggested by the similarity in the level of grey PEI-silica coating observed in the backscattered electron detected images. However, overall, slightly poorer coverage was observed for the 50 mL reaction when compared with the smaller reaction sizes of 1 and 10 mL. All Method G reactions were mixed after incremental additions of PEI and every 5 min throughout the 30 min reaction by upending the reaction tube (Section 3.5.2). A possible cause of the slightly poorer shell coverage from the 50 mL reaction components when the reaction tube was not sufficient to completely homogenise the reaction components when the reaction volume was increased. Hence, more thorough mixing methods, such as vortex mixing, may improve the shell coverage of 50 mL Method G PEI-silica shell fabrication process and will be considered in future work.

The influence of scaling up the slow addition method (Method G) on the PEI-silica shell morphology was investigated by comparing the images taken by the secondary electron detector (Figures 6.10A, C, E). In Section 6.4.4, PEI-silica shell fabricated using 1 mL

Method G shell fabrication was observed to possess a raspberry-like morphology. In the literature, similar raspberry-like coatings have been associated with hydrophobicity or superhydrophobicity expanding the interactions available to the core-shell particles produced with the raspberry-like shell morphology (Bao *et al.*, 2011; Du *et al.*, 2009a). The raspberry-like morphology of PEI-silica shells fabricated in a 1 mL reaction (Figure 6.10A) is maintained for the 10 x scale up (Figure 6.10D). However, when increasing the reaction volume by a factor of 50, the PEI-silica shells produced appear smoother, which may reduce the potential hydrophobicity/superhydrophobicity (Bao *et al.*, 2011; Du *et al.*, 2009a) of the core-shell particles produced.

Overall, the raspberry-like coating was successfully scaled up by a factor of 10 using Method G with 200 mM TMOMS concentration. The 10 mL reaction resulted in a coating of similar morphology and coverage to the original 1 mL reaction examined in Section 6.4.3 and 6.4.4. However, by scaling up by a factor of 50, the shell coverage of the carbonyl iron core particles and the roughness of the raspberry-like coating surface were both reduced. In future work, improvement to the PEI-silica shell coverage fabricated in 50 mL reaction may be possible through utilisation of more vigorous mixing techniques during fabrication.

6.5 PEI-thiol silica shell – carbonyl iron core particles

6.5.1 Background

In Neville *et al.* (2009), the biomimetic PEI-catalysed silica synthesis technique was adapted to produce thiol functionalised PEI-thiol silica particles by using 3-mercaptopropyltrimethoxysilane (3mPTMOS) as the reactant silane. The activity of the thiol surface groups was demonstrated by the single layer attachment of PEI-thiol silica particles onto a gold electrode surface (Neville *et al.*, 2009). In addition, Chapter 5 presents a method of facile covalent surface modification utilising the thiol surface groups of the PEI-thiol silica particles. Moreover, the thiol functionalisation of the PEI-thiol silica surface, itself, considerably expands the number of specific surface interactions possible with the silica surface (Bao *et al.*, 2017; Fang *et al.*, 2014; Neville *et al.*, 2009; Yantasee *et al.*, 2007).

As demonstrated by the attachment of PEI-thiol silica particles onto a gold electrode surface (Neville *et al.*, 2009), thiol groups have a well-known affinity to Au surfaces. Fang *et al.* (2014) achieved successful adsorption of gold nanoparticles (5 nm) onto thiol-functionalised mesoporous silica shell – magnetite core particles (130 nm). In Fang *et*

al. (2014), the thiol-functionalisation was introduced in post-synthesis reaction through the precipitation of 3mPTMOS.

Yantasee et al. (2007) demonstrated the use of thiol functionalised magnetic iron oxide nanoparticles for the removal of the toxic soft metals, such as Hg, Ag, Pb, Cu and As. In Yantasee et al. (2007), the preparation of the iron oxide core and functionalisation of the surface with dimercaptosuccinic acid was a complex, multi-step process which required the use of high temperatures (300 °C). Boa et al. (2017) utilised amine and thiol functionalised silica coated magnetic nanoparticles for the high capacity and reusable recovery of Hg(II) and Pb(II) ions from wastewater. Both the amine and thiol groups were believed to actively adsorb the heavy metal ions, the amine sites through chelation and the thiol sites through cation exchange. Overall, the dual functionalisation was held responsible for the high adsorption capacity of the core-shell particles developed by Boa et al. (2017). The functionalisation process itself was, once again, conducted postsynthesis. The amine surface groups were added through the polymerisation of 3aminopropyltrimethysilane and the thiol functionalisation via the polymerisation of (chloromethyl)thiirane. However, these published methods of thiol functionalised silica shell fabrication require multiple steps, complex procedures, long reactions times and/or high temperatures (Boa et al., 2017; Yantasee et al., 2007).

In this section, the shell fabrication methods developed for PEI-silica shell synthesis were expanded to impart the core-shell particles with dual amine/thiol functionality to produce thiol-functionalised silica coats (Boa *et al.*, 2017; Yantasee *et al.*, 2007). Drawing inspiration from Neville *et al.* (2009), this study utilised the reactant silane 3mPTMOS with the PEI/PB silication system to produce a PEI-thiol silica shell. In Section 6.4, two main PEI-silica shell morphologies, gel-like and raspberry-like, were obtained through the use of sonication and slow reactant addition, respectively, during the shell fabrication process. Similarly, in this section, the methods for obtaining the two main PEI-silica shell morphologies were used here with the aim to achieve both gel-like and raspberry-like PEI-thiol silica shells. Scale up of the PEI-thiol silica shell fabrication reaction by a factor of 10, was also considered in this section to investigate the effect of increased reaction volume on the PEI-thiol silica shell fabrication process.

6.5.2 Methodology

As discussed in Section 6.4.5, the most well defined examples of the gel-like and raspberry-like morphologies were achieved using the sonication method (Method D) and slow addition method (Method G), respectively (Figure 6.8). Hence, the PEI-thiol silica shell fabrication was attempted using Methods D and G, with the TMOMS silica precursor replaced with 3-mercaptopropyltrimethoxysilane (3mPTMOS). The methods for PEI-thiol silica coating can be found in Section 3.5.3. 3mPTMOS concentrations of 100 mM for Method D and 200 mM for Method G were selected. In addition, to the 1.000 mL reaction, a scaled-up 10.000 mL reaction was also considered with all reaction volumes amplified by a factor of 10.

The PEI-thiol silica shell – carbonyl iron core particles were characterised via SEM (Section 3.7.1) and EDX analysis (Section 3.7.2). Samples were prepared and carbon coated, as per the instructions in Section 3.7.1.2.

6.5.3 Results and discussion

To expand the variety of surface properties and thus applications of the core–shell particles, PEI-thiol silica shell fabrication was developed by adapting methods from Section 6.4. The sonication method (Method D) and the slow addition method (Method G) were adapted for PEI-thiol silica fabrication and are presented Section 6.5.3.1 and Section 6.5.3.2, respectively.

6.5.3.1 Sonication method

In Section 6.4, the sonication method (Method D) produced a smooth gel-like PEI-silica shell. The gel-like PEI-silica shell provided excellent coating coverage making it appropriate as a protective coating for the carbonyl iron core material (Roto *et al.*, 2016). In addition, the gel-like PEI-silica shell – carbonyl iron core particles had a tendency towards the production of multiple cores which in the literature have been shown increase thermal and aggregation stability of the core–shell particles (Dutz *et al.*, 2009; Gutiérrez *et al.*, 2015; Li *et al.*, 2009b). Due to these advantages, a gel-like morphology was sort after for the PEI-thiol silica coating as well.

In Figure 6.11, the SEM images of the PEI-thiol silica shell – carbonyl iron core particles produced using the sonication method (Method D) are presented. Alongside the core–shell particles produced using the original 1 mL PEI-thiol silica shell fabrication process,

the core–shell particles produced using 10 mL scaled-up reactions are also presented in Figures 6.11C-D.



Figure 6.11. SEM images taken via the secondary electron detector (A,C) and backscattered electron detector (B,D) of the PEI-thiol silica – carbonyl iron particles fabricated using Method D and a concentration 100 mM 3mPTMOS. Reactions were conducted in (A-B) a 1 mL reaction vessel and (C-D) a 10 mL reaction vessel.

The fabrication of the PEI-thiol silica shell using Method D resulted in excellent shell coverage of the carbonyl iron core particles and had a tendency toward producing multicore particles (Figure 6.11). These features have been found to be advantageous to core protection and suspension stability (Dutz *et al.*, 2009; Gutiérrez *et al.*, 2015; Li *et al.*, 2009b; Roto *et al.*, 2016) and are similar to those of PEI-silica shells produced using Method D in Section 6.4.

After the Method D shell fabrication process was scaled up by a factor of 10 (Figures 6.11C, D), the PEI-thiol silica shell remained high coverage. However, the gel-like PEI-thiol silica shell appeared to possess raised 'bumps', unlike the completely smooth character of the gel-like PEI-silica shell synthesised using the same methodology. The roughness of the PEI-thiol silica shell is more pronounced in the 10 mL reaction (Figures

6.11C, D), however, it can also be observed, albeit to a lesser extent, in the 1 mL reaction (Figures 6.11A, B).

In laboratory experiments, PEI-thiol silica particles synthesised from 3mPTMOS were observed to form significantly more rapidly than PEI-silica particles synthesised from TMOMS. These observations indicate that 3mPTMOS silane, used for PEI-thiol silica shell fabrication, has significantly higher silication activity than the TMOMS silane, used for PEI-silica shell formation. Thus, the slightly rough character of the PEI-thiol silica shell could be the result of the 3mPTMOS rapidly forming free silica particles in solution which later become attached to the core surface, similar to the raspberry-like methods in Section 6.4.4.1. For PEI-silica shell fabrication (Section 6.4), the sonication process appeared to eliminate the formation and later attachment of self-nucleated silica particles producing only a smooth gel-like shell. However, for the PEI-thiol silica shell the sonication method seemed only to reduce the amount and size of self-nucleated individual silica particles, resulting in the presence of small bumps in the silica shell.

The EDX spectra of PEI-thiol silica shell – carbonyl iron core particles produced in 1 mL and 10 mL reactions are presented in Figure 6.12. The EDX compositional analyses were conducted on a single spot in the middle of the core–shell particle analysed, as in Section 6.4, to provide qualitative compositional information. Multiple particles were analysed per sample. However, for brevity and clarity, only one representative spectrum for each sample type is presented here for qualitative elemental analysis.





The EDX spectra of the PEI-thiol silica shell – carbonyl iron core particles, synthesised in both 1 mL and 10 mL reactions (Figure 6.12), show the presence of both Si and Fe characteristic peaks as observed in Section 6.4.3. These peaks are accompanied by a characteristic S peak at 2.31 keV (Crawford *et al.*, 2011), due to the thiol functionalised 3mPTMOS silane used for PEI-thiol silica shell synthesis. The S peak is not present in the PEI-silica shell – carbonyl iron core particles in Section 6.4.3, as the thiol functional group is not present in the TMOMS silane molecule used for PEI-silica shell fabrication.

Overall, Method D successfully produced PEI-thiol silica – carbonyl iron particles. The PEI-thiol silica shell was similar in coverage to the PEI-silica shell produced using Method D in Section 6.4. However, the morphology of the PEI-thiol silica shell was slightly rougher than the corresponding PEI-silica shell (Section 6.4), especially for the 10 mL PEI-thiol silica shell fabrication. The presence of the thiol functionalisation was confirmed via EDX spectroscopy. As discussed in Section 6.5.1, the thiol functionalisation of the PEI-thiol silica shell expands the number of interactions available to the core–shell particles, including facilitating strong interactions with soft heavy metal ions and gold surfaces (Boa *et al.*, 2017; Fang *et al.*, 2014; Yantasee *et al.*, 2007).

6.5.3.2 Slow addition method

PEI-thiol silica shells were fabricated using Method G which was found to produce a raspberry-like PEI-silica shell morphology in Section 6.4. As in Section 6.5.3.1, the PEI-thiol silica shell fabrication reaction using Method G was performed in 1 and 10 mL reaction vessels to assess the effect of reaction scale up on the core–shell particles produced. SEM images of the 1 and 10 mL PEI-thiol silica shell – carbonyl iron core particles produced using Method G are presented in Figure 6.13.



Figure 6.13. SEM images taken via the secondary electron detector (A,C) and backscattered electron detector (B,D) of the PEI-thiol silica – carbonyl iron particles fabricated using Method G and a concentration 200 mM 3mPTMOS. Reactions were conducted in (A-B) a 1 mL reaction vessel and (C-D) a 10 mL reaction vessel.

Method G was observed to result in a PEI-thiol silica shell of extremely uneven coverage (Figure 6.13). The lack of shell surface coverage was particularly evident in 10 mL reaction where some carbonyl iron core particles appear entirely uncoated. Surface coverage was also identified as an issue in Section 6.4.4.1 for raspberry-like PEI-silica shells (including Method G shells), however, to a lesser extent than observed in Figure 6.13.

The morphology of the PEI-thiol silica shell synthesised using Method G was also not consistent, while some carbonyl iron core particles were coated with a layer of raspberry-like PEI-thiol silica shell, other core particles were very sparsely coated, and where they were coated, the coating was made of extremely large spherical silica particles. Although, the rough surface of the raspberry-like coating has been found useful in enhancing the surface hydrophobicity of core–shell particles (Bao *et al.*, 2011; Du *et al.*, 2009a), the very uneven surface coverage will likely diminish the applications of the PEI-thiol silica shell – carbonyl iron core particles synthesised using Method G.

The PEI-thiol silica particles were also characterised using EDX analysis with the results presented in Figure 6.14. As in Section 6.5.3.2, a spot in the centre of a randomly chosen core–shell particle was selected for analysis.



Figure 6.14. EDX spectra of the PEI-thiol silica – carbonyl iron particles fabricated using Method G and a concentration 200 mM 3mPTMOS. Reactions were conducted in (A) a 1 mL reaction vessel and (B) a 10 mL reaction vessel. SEM images in the top, right corner of the spectra show white "+" signs for the placement of the EDX spot analysis.

The EDX spectra of the raspberry-like PEI-thiol silica shell – carbonyl iron core particles (Figure 6.14) appeared similar to the gel-like PEI-thiol silica shell – carbonyl iron core particle spectrum (Section 6.4), as expected. When comparing the core–shell particle produced using the two different reaction vessel sizes, the EDX analysis of the particles produced similar EDX spectra. As for Section 6.5.3.2, the Method G PEI-thiol silica shell – carbonyl iron core particles produced emission peaks at X-ray energies characteristic of Fe, S and Si (Figure 6.14), indicating the particles analysed were carbonyl iron cores coated with PEI-thiol silica.

Alongside the results presented in Figure 6.14, other particles were analysed with EDX within each sample. Some of the particles produced using the Method G PEI-thiol silica coating method showed no X-ray peaks characteristic Si or S in their EDX spectra (data not shown), indicating no PEI-thiol silica coating was present on those particles. These results support the conclusion drawn earlier from the SEM images that the Method G coating for PEI-thiol silica shells was uneven and inconsistent.
Overall, Fe particles were able to be nominally coated with PEI-thiol silica shells using the slow addition method (Method G). However, the coating produced consisted largely of massive silica spherical particles attached to the carbonyl iron core and the coating was extremely uneven leaving some particles completely uncoated.

6.6 Conclusions

The synthesis of PEI-silica and PEI-thiol silica shells for magnetic particles could provide a more environmentally friendly alternative to traditional silica shell synthesis techniques. In addition, PEI-silica fabrication produces a silica shell pre-functionalised with amine groups. Amine functionalisation has been shown to greatly enhance the adsorption capacity of silica surfaces for heavy metal ions and carbon dioxide (Wang *et al.*, 2010a; Wang *et al.*, 2015a; Zelenák *et al.*, 2008). Furthermore, PEI-thiol silica shell – carbonyl iron core particles possess a dual thiol/amine functionalisation. The thiol/amine functionalisation has known adsorption affinity for soft heavy metal ions and gold surfaces (Boa *et al.*, 2017; Fang *et al.*, 2014; Yantasee *et al.*, 2007).

Seven PEI-silica shell synthesis methods were investigated, all with a total fabrication time of less than 1 h, and characterised using ATR-FTIR spectroscopy, SEM and EDX techniques. From these results, the methodologies of the PEI-silica shell fabrication were contrasted based on their morphology and shell thickness as well as their ability to form a high surface coverage shell. Varying the shell fabrication method and reactant concentration was observed to successfully tune the shell characteristics. The results also confirmed the successful removal of non-magnetic by-products (namely core-free silica) through the use of magnetic separation after the core-shell silication reaction.

A raspberry-like coating morphology was produced through one- (E) and two-pot (A, B) methods, as well as, through slow addition methods (F, G). Similar raspberry-like shells in the literature have been shown to possess hydrophobic/superhydrophobic properties (Bao *et al.*, 2011; Du *et al.*, 2009a) and this current work demonstrates the production of the raspberry-like coating through a single reaction process. Large variations in coating thickness and coverage were also evident when using these synthesis methods (A, B, E-G). When a double coat methodology was applied using Methods A and B it was observed to smooth over the morphology and improve the coverage of the PEI-silica shell when compared with a single coat of the same final reactant concentration.

The coating methods involving sonication (C, D) produced the highest coverage coating, appearing to produce an effective silica shell even at the lowest TMOMS concentration.

The morphology of the shells produced using the sonication methods were observed to be smooth and gel-like with excellent coverage over the particle surface. This type of shell may provide a useful protective coating for the core material (Roto *et al.*, 2016). The sonication methods also tended towards the production of multicore particles. However, single core particles could be produced using the lowest TMOMS concentration in Method D.

The gel-like (Method D) and raspberry-like (Method G) PEI-silica shell fabrication process were successfully scaled up by a factor of 10, producing the same level of surface coverage and a similar morphology to the original 1 mL shell fabrication reaction. Scale up by a factor of 50 was successful for the Method D gel-like PEI-silica shell synthesis but resulted in a reduced coverage and smoother shell for the Method G raspberry-like PEI-silica shell.

The sonication (D) and slow addition (G) coating fabrication processes were also trialled for PEI-thiol silica shell synthesis. The PEI-thiol silica shell coating produced using the slow addition method (G) resulted in poor surface coverage, particularly when the reaction was scaled up by a factor of 10. In contrast, PEI-thiol silica shell produced using the sonication method (D), while not as smooth as the equivalent PEI-silica shell (Method D), resulted in an even surface coating with high surface coverage. The Method D PEI-thiol silica shell was also found to evenly coat particles when scaled up by a factor of 10, although the scale up was also found to increase the roughness of the coating. The increased roughness of PEI-thiol silica shell, however, could be advantageous in producing a shell with both protective (Roto *et al.*, 2016) and hydrophobic properties (Bao *et al.*, 2011; Du *et al.*, 2009a).

In conclusion, this chapter has demonstrated that the PEI-silica and PEI-thiol silica synthesis methods can be adapted to produce magnetic core-shell particles. Successful scale up of the shell fabrication process was also demonstrated in this chapter. It has been shown that variations in the fabrication methodologies and concentrations can produce a wide range of tunable features, including raspberry-like shell surfaces for enhanced hydrophobicity (Bao *et al.*, 2011; Du *et al.*, 2009a), high coverage shells for core material protection (Roto *et al.*, 2016), and multicore particles for heightened thermal and aggregation stability (Dutz *et al.*, 2009; Gutiérrez *et al.*, 2015; Li *et al.*, 2009b) all through facile single reaction processes. This study paves the way for future work to more easily select the coating methodology and type best suited for providing the particular core-shell particle features and functionalisations desired.

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CHAPTER SEVEN

Recovery of Cu(II) from solution using biomimetic silica shell – magnetic core particles

7.1 Introduction

The removal of heavy metal ions from aqueous environments is of ongoing significance not only in Australia but internationally (Mahmood and Malik, 2014; Taylor *et al.*, 2010; Wongsasuluk *et al.*, 2014; Yi *et al.*, 2011). Many heavy metals are known to be toxic and/or carcinogenic. The accumulation of these heavy metals within the human body, due to contaminated drinking water or through the food chain, can result in serious health issues (Boa *et al.*, 2017; Dieter *et al.*, 1999; O'Donohue *et al.*, 1999; Zhou *et al.*, 2004). Heavy metal ion contamination is also a serious environmental concern due to their toxicity to the exposed fauna and flora, as well as, the aforementioned pollution of the food chain (Boa *et al.*, 2017; Baldwin *et al.*, 2003; Fernandes and Henriques, 1991; Zhou *et al.*, 2004). Moreover, recycling of metals from wastewaters is likely to develop into an increasingly relevant field of study as mineable metal ore deposits become scarce (Bao *et al.*, 2016b). Developing a facile, efficient and economically feasible means of removing/recovering heavy metals ions from waste streams, drinking water, wastewater and natural waterways is, thus, of ongoing engineering interest (Anbia *et al.*, 2015; Boa *et al.*, 2017; Li *et al.*, 2013a; Zhang *et al.*, 2012a).

In Section 2.5.2, the development and use of core-shell magnetic carrier particles was identified as an attractive solution for heavy metal removal (Hua et al., 2012; Ngomsik et al., 2005; Zou et al., 2016), featuring low energy consumption, low operating costs, high vield and limited risk of secondary contamination (Raitani et al., 2012). Previous studies have employed functionalised core-shell magnetic carrier particles to selectively interact with the heavy metal ions, allowing the attached ions to be removed through magnetic separation (Section 2.4) (Anbia et al., 2015; Boa et al., 2017; Li et al., 2013a; Moffart et al., 1994; Zhang et al., 2012a). However, the synthesis and functionalisation of the silica shell in these studies (Anbia et al., 2015; Boa et al., 2016; 2017; Li et al., 2013a; Tang et al., 2013; Wang et al., 2015a; Zhang et al., 2012a) required a detrimental combination of multiple steps, complex procedures, harsh conditions, long synthesis times and/or high temperatures, all of which are disadvantages when considering potential scale up of the core-shell synthesis process (Section 2.4.1). In contrast, the PEI-silica shell synthesis techniques developed in Chapter 6, offer one-pot, facile processes to produce an amine (or amine/thiol) functionalisation and silica coating under mild, roomtemperature reaction conditions with a proven potential for reaction scale up (Chapter 6). These advantages improve the feasibility of large scale heavy metal ion recovery with the PEI-silica shell - carbonyl iron particles developed in this project.

In this chapter, the PEI-silica coated carbonyl iron particles developed in Chapter 6 were used as magnetic carrier particles for removal of the heavy metal ion, Cu(II). The

biomimetic fabrication of the PEI-silica shell for the core-shell particles in this study imparts the surface with an amine functionalisation without the disadvantages of complex/multi-step procedures, harsh conditions and/or high temperatures required for previous core-shell synthesis methods (Section 2.4.1) (Anbia *et al.*, 2015; Boa *et al.*, 2017; Li *et al.*, 2013a; Moffart *et al.*, 1994; Zhang *et al.*, 2012a).

7.2 Background

The utilisation of magnetic carrier particles for metal ion removal was discussed at length in Section 2.5.2. In magnetic carrier particles studies, the development of the metal ion adsorbent surface coating/functionalisation was of the upmost importance to ensure effective, selective and, in some cases, reusable removal of the heavy metal ions via magnetic separation (Anbia *et al.*, 2015; Boa *et al.*, 2017; Li *et al.*, 2013a; Zhang *et al.*, 2012a).

Amine and thiol functionalisations of magnetic core particles, in particular, have proven effective in the removal of heavy metal ions from aqueous environments (as discussed in Section 2.5.2) (Anbia et al., 2015; Boa et al., 2017; Li et al., 2013a; Zhang et al., 2012a). Chelation was identified as one of the most common mechanisms for selective adsorption of heavy metal ions onto solid adsorbents (Boa et al., 2016; 2017; Li et al., 2013a; Zhang et al., 2012a). Chelation or complex ion formation involves the formation of a coordinate covalent bond between a ligand species (which possesses at least one lone electron pair) and a positively charged metal ion (Lawrance, 2010). During the chelation process, the ligand species (acting as a Lewis base) donates its lone pair of electrons to the metal ion species (acting as a Lewis acid), forming a ligand-metal ion complex ion (Lawrance, 2010). When employing chelation for heavy metal ion removal, Schiff base ligands are often the most useful as they are able to form reversible coordinate bonds with heavy metal ions and so allow the adsorbent material to be regenerated (Moftakhar et al., 2016). Schiff base ligands are those ligands that possess their lone electron pair/s on N or O atoms. These ligand species have been utilised in the literature to functionalise the magnetic carrier particles allowing for the adsorption of heavy metal ions (Anbia et al., 2015; Bao et al., 2017; Li et al., 2013a; Zhang et al., 2012a).

In this work, in built amine functionalisation is introduced through the PEI-silica synthesis technique. The PEI-silica synthesis technique utilises the biomimetic polyamine polyethyleneimine (PEI) to direct and scaffold silica particle synthesis in mild reaction conditions (Neville *et al.*, 2009) (Section 2.2.2.4). The PEI molecule is therefore

entrapped within the silica surface functionalising the PEI-silica surface. Additionally, Chapter 4 demonstrated that post-synthesis PEI surface modification of silica particles (NaOH-silica) could be achieved through a rapid, facile process creating a reversible method of PEI functionalisation.

Regeneration of the magnetic carrier particle surface, permitting multiple reuses, is possible through exploiting the stability of the ion-ligand complex formed during adsorption (Anbia *et al.*, 2015; Gutha *et al.*, 2017; Li *et al.*, 2013a; Liu *et al.*, 2013; Ojemaye *et al.*, 2017; Zhang *et al.*, 2012a). The minimum requirement to ensure efficient Cu(II) adsorption/removal and desorption/regeneration of the adsorbent surface is to be able to measure the stability of Cu(II)-PEI complex quantitatively. Wen *et al.* (2017) used spectroscopic measurements to observe the Cu(II)-PEI complex. The Cu(II)-PEI complex ion, which has a distinctive blue colour, has been shown to produce a strong absorbance peak at 275 nm. Alone neither PEI or Cu(II) absorb at 275 nm, thus, this wavelength has often been utilised in quantitative spectroscopic analysis of the Cu(II)-PEI complex in order to determine PEI or Cu(II) concentrations (Chapter 4) (Wen *et al.*, 2017; Ungaro *et al.*, 2003).

Absorbance at 275 nm was used by Wen et al. (2017) to investigate the stability of the Cu(II)-PEI complex ion. It was observed that the Cu(II)-PEI interaction had a strong dependence on solution pH. At pH 6, the Cu(II)-PEI complex absorbance at 275 nm reached a maximum (Wen et al., 2017), indicating the strength of the Cu(II)-PEI interaction was at its highest. As the pH was decreased from pH 6 to 2, however, the absorbance of the Cu(II)-PEI complex dropped rapidly, until finally producing no measurable absorbance at pH 2 (Wen et al., 2017). The lack of Cu(II)-PEI absorbance at pH 2, indicates the two species were no longer interacting. Therefore, in the work presented in Chapter 7, pH 6 was used for adsorption and regeneration was carried out at low pH (~3). Previous work has also utilised low pH to regenerate carrier particles for reuse. Typically, acids HCl or HNO₃ were used for desorption, with acid concentrations ranging from 10 to 500 mM (Abou El-Reash, 2016; Anbia et al., 2015; Gutha et al., 2017; Li et al., 2013a; Liu et al., 2008a; 2013; Ojemaye et al., 2017; Wu et al., 2016; Zhang et al., 2012a). However, for carrier systems tested over multiple adsorption – desorption cycles a reduction in adsorption capacity was reported (Anbia et al., 2015; Gutha et al., 2017; Li et al., 2013a; Liu et al., 2013; Ojemaye et al., 2017; Wu et al., 2016; Zhang et al., 2012a).

The study presented in this chapter aimed to investigate the use of the PEI-silica coated carbonyl iron particles for the removal of Cu(II) from an aqueous environment. In order

to reduce the waste from and increase the economic feasibility of the process, recycling of the core-shell particles was also investigated via the exploitation of the Cu(II)-PEI complex ion's stability and its dependence on pH.

7.3 Methodology

The methodology for this chapter is given in full in Section 3.6.1. In short, PEI-silica coated carbonyl iron particles (core-shell particles) were synthesised using Method D (100 mM TMOMS) and Method G (200 mM TMOMS) in 10.000 mL reactions (Section 3.5.2.5). Methods D and G were chosen as representative of the two coating morphologies, gel-like and raspberry-like, respectively, as observed in Chapter 6.

Generally, Cu(II) adsorption (Section 3.6.1) was achieved by resuspending 5.0 ± 0.3 mg of dried core-shell particles in 32.0 mM PB (pH 6.0) (Wen *et al.*, 2017) and 5.00 mM CuSO₄ with a total volume of 1.000 mL. Various amounts of core-shell particles (1.5 to 12.0 ± 0.3 mg) and CuSO₄ concentrations (2.50 to 20.0 mM) were also investigated. The mixture was incubated for 10 min with constant vortex mixing at 1000 rpm. After incubation, the core-shell particles were separated from the supernatant via magnetic separation (Section 3.6.1).

Cu(II) desorption from the core-shell particles was performed through incubation in 1.00 mM HCl (pH \sim 3) for 10 min with 1000 rpm vortex mixing (Section 3.6.1). Particles were then washed twice with water before characterisation or re-adsorption. Re-adsorption followed the procedure for adsorption as outlined above.

The supernatant from Cu(II) adsorption experiments was recovered and immediately tested using UV-vis spectroscopy (Section 3.7.6). A detailed methodology is given in Section 3.7.6.3. The strong absorbance of the Cu(II)-PEI complex at 275.0 nm, alongside use of the Beer-Lambert law, was used to determine spectroscopically the concentration of Cu(II) remaining unadsorbed in solution (Wen *et al.*, 2017; Ungaro *et al.*, 2003). The adsorption capacity and removal efficiency were determined as per Lo *et al.* (2012).

Characterisation of the core-shell particles after adsorption and desorption was performed with SEM (Section 3.7.1) and EDX techniques (Section 3.7.2). Samples were prepared using the methods outlined in Sections 3.7.1.2 and 3.7.2.2, with samples prepared on silicon wafers then coated with carbon prior to SEM/EDX analysis.

7.4 Results and discussion

The PEI-silica – carbonyl iron (core-shell) particles fabricated in Chapter 6 were investigated for their heavy metal ion recovery potential. The heavy metal ion Cu(II) was chosen for removal due to its known interaction with amine surface groups (Anbia *et al.*, 2015; Li *et al.*, 2013a; Wen *et al.*, 2017; Ungaro *et al.*, 2003; Zhang *et al.*, 2012a).

7.4.1 Preliminary study: incubation time

Through preliminary studies it was found that incubation times of 10, 30 and 60 min produced no significant difference in the amount of Cu(II) found in the supernatant. This result suggests that the system reaches equilibrium within 10 min. Hence as described in Section 7.2, a 10 min incubation time was used throughout this study.

7.4.2 Preliminary study: buffer selection

The interaction between PEI and Cu(II) is strongest at pH 6.0 (Gutha *et al.*, 2017; Liu *et al.*, 2013; Wen *et al.*, 2017; Zhang *et al.*, 2012a) (Section 7.2). During the preliminary studies for this chapter, the interaction between Cu(II) ions and PEI-silica coated particles was tested with MES buffer (pH 6.0 at 16.0, 32.0, 48.0 mM) and phosphate buffer (PB) (pH 6.0 at 32.0 mM) (Appendix B, Section B.1). These studies were undertaken to determine the effect of buffer selection on the adsorption capacity of the raspberry-like PEI-silica coated magnetic particles. Utilising MES buffer at pH 6.0, resulted in a measurable amount of Cu(II) being adsorbed by the particles correlating with the literature on the importance of pH control (Moftakhar *et al.*, 2016; Wen *et al.*, 2017; Zhang *et al.*, 2012a). Increasing the concentration of MES buffer in the solution resulted in slightly better adsorption of the Cu(II) ion onto the core-shell particles. However, overall the MES buffered solutions obtained a relatively low adsorption capacity and recovery of Cu(II) (< 35 mg Cu(II) per g particles even at 48.0 mM MES buffer) compared with Cu(II) recovery with PB with the same adsorbent core-shell particle dose (~71 mg g⁻¹).

Literature studies (Moradi *et al.*, 2012; Ungaro *et al.*, 2003; Wen *et al.*, 2017), even those using Cu(II)-PEI complexation for Cu(II) concentration spectroscopic quantification, have often used PB, or other phosphate ion containing buffers, to control the pH of the complexation reaction. The use of these phosphate containing buffers is in spite of the known insolubility of the copper phosphate salt. Following these studies, PB was used to adjust the pH during the core-shell particle incubation with the Cu(II) ion solution in

this chapter. A PB concentration of 32.0 mM was selected for the experiments reported in this chapter. The selected PB concentration was based on Wen and coworkers' (2017) study on spectroscopic quantification of Cu(II) concentration. The use of PB resulted in a significant improvement in adsorption capacity of the core-shell particles with respect to the same system using MES buffer (Appendix B, Section B.1). It is possible that the PB enhances the adsorption capacity of the core-shell particles in two ways. In the first way, by acting as a buffer and maintaining incubation solution at pH 6.0 to ensure the optimum interaction strength between the Cu(II) ions and the PEI surface. In the second way, by reacting with the free Cu(II) ions to form insoluble copper phosphate which can also be collected by the core-shell particles during magnetic separation. This assumption is supported by the fact that no solids were detected in the supernatant prior to UV-vis measurement of the supernatant.

7.4.3 Cu(II) adsorption – desorption onto the core-shell particles

Reusability is a key concern in the development of the PEI-silica shell – magnetic core ion separation system for this project. Hence the ability to successfully adsorb, desorb and re-adsorb the Cu(II) ions was of the upmost importance. EDX was used to qualitatively determine the elemental composition of the core-shell particles before adsorption, after Cu(II) adsorption and after the acidic desorption of the Cu(II) ions, these results are presented in Figure 7.1.



Figure 7.1. EDX spectra of the (A,C,E) gel-like and (B,D,F) raspberry-like PEI-silica shell – magnetic core particles (A,B) before Cu(II) incubation, (C,D) after Cu(II) adsorption and (E,F) after the acidic desorption of Cu(II).

In Figures 7.1A-B, the EDX spectra of the core-shell particles before adsorption possesses peaks characteristic of Si, O, Fe and C. The presence of these elements is

due to the PEI-silica shell and carbonyl iron core particles, the silicon wafer base and carbon coating of the sample (Sections 3.7.1 and 3.7.2) (Crawford *et al.*, 2011).

In Figures 7.1C-D, measured following Cu(II) adsorption, an additional peak at 0.930 keV, characteristic of Cu, was observed indicating the successful adsorption of Cu(II) ions onto the core-shell surface. This Cu peak was clearly observed for both the gel-like and raspberry-like coated particles, indicating both particle coatings were able to successfully adsorb Cu(II) ions from solution. In Figure 7.1D, the peak characteristic of phosphorous (P), 2.01 keV, was also present and labelled for the gel-like core-shell particles following Cu(II) adsorption. The P peak can be similarly observed in the spectra of the raspberry-like core-shell particle after Cu(II) adsorption (Figure 7.1C), although in this case the signal is not strong enough to be distinguished from the noise by the labelling program. The presence of P in both the Cu(II) adsorbed samples is a further indication that the phosphate ions, introduced with the phosphate buffer, play a role in Cu(II) adsorption, as was discussed in Section 7.4.2.

In the spectra featured in Figures 7.1E-F, which measured core-shell particles after acid desorption in 1 mM HCI, the Cu peak was no longer present. The lack of Cu peak suggests that desorption was successful at removing the adsorbed Cu(II) ions from both types of core-shell particles. The acid concentration required for successful Cu(II) desorption in this study is comparable to literature desorption studies where acid concentrations between 10 and 500 mM were reported (Abou El-Reash, 2016; Anbia *et al.*, 2015; Gutha *et al.*, 2017; Li *et al.*, 2013a; Liu *et al.*, 2013; Ojemaye *et al.*, 2017; Wu *et al.*, 2016) (Section 7.4.4).

After desorption, the EDX spectra of both coating morphologies continue to show the Si, O and Fe peaks similar to the 'before adsorption' spectra. In addition, the morphological features in the SEM images, in the top right corner of the spectra, of the core-shell particles remain similar to 'before adsorption' (Figure 7.1). The similarities between the 'before adsorption' and 'after desorption' indicate that the core-shell particle structure remained intact throughout the acidic desorption process. These results suggest the acidic desorption process at pH ~3 is capable of regenerating the PEI-silica adsorbent surface, while still being mild enough to ensure the core-shell particles can be reused after Cu(II) desorption. The desorption the Cu(II) ions from the core-shell particle surface likely results from the weakening the Cu(II)-PEI interaction in acidic conditions, as discussed in Section 7.2 (Wen *et al.*, 2017).

The adsorption at pH 6.0 and desorption in 1 mM HCI (pH ~3) strongly indicate mechanism for Cu(II) adsorption onto the PEI-silica shell surface is through the formation

of Cu(II)-PEI complex ions, as discussed in Section 7.2. The Cu(II)-PEI complex in solution is known to be a distinctive blue colour (Wen et al., 2017). This distinctive blue colouring of the Cu(II)-PEI complex ion was used to visually confirm complex ion formation on the PEI-silica surface. PEI-silica particles and a control group of PEI-free NaOH-silica particles were incubated with Cu(II) ions for the same amount of time (10 min). Both the PEI-silica and NaOH-silica particles were white in colour prior to incubation with Cu(II). Following centrifugation and multiple washing steps, the colours of the two types of particles were visually compared (Appendix B, Section B.2). It was observed that throughout the sample the PEI-silica particles took on a blue hue following incubation with the Cu(II) ions, whereas, the PEI-free NaOH-silica particles remained white in colour. These results suggest that Cu(II)-PEI complex formation is the most likely candidate for Cu(II) adsorption onto the PEI-silica coated core-shell particles. A very thin layer of blue-green solid was observed on top of the NaOH-silica particles (Figure B.2B). This layer is likely due to the formation of insoluble copper phosphate as discussed in Section 7.4.2. However, for the NaOH-silica particles, the copper phosphate does not attach to the particle surface, unlike in the case of PEI-silica, and so, when centrifugated, the blue green solid remains on top of the NaOH-silica particles, instead of being dispersed throughout the solid sample.

A preliminary investigation into the adsorption and desorption Cu(II) using PEI-thiol silica – carbonyl iron particles (fabricated in Chapter 6) was also conducted. The EDX analysis of the PEI-thiol silica - carbonyl iron particles following Cu(II) adsorption and acidic desorption are included in Appendix B (Section B.3).

7.4.4 Adsorption – desorption cycles

Adsorption of Cu(II) was investigated over multiple adsorption – desorption cycles to observe the viability of recycling PEI-silica shell – carbonyl iron core carrier particles. Cu(II) ion recovery using the core-shell particles was tested over five cycles (Figure 7.2). To determine the amount of Cu(II) adsorbed in each adsorption cycle, the Cu(II) remaining in the supernatant was tested spectroscopically and the Cu(II) adsorbed calculated (Section 3.7.6.3). In Figure 7.2, the adsorption capacity and removal efficiency of Cu(II) over five reuse cycles for the raspberry-like and gel-like PEI-silica shell – magnetic core particles are presented.



Figure 7.2. The (A) adsorption capacity and (B) removal efficiency of the PEI-silica shell – carbonyl iron core particles for Cu(II) removal, with a fixed initial concentration of 5.00 mM Cu(II) and fixed core-shell particle dose of 5.0 mg, taken over five adsorption – desorption reuse cycles. Desorption conducted in 1.00 mM HCI. The Cu(II) adsorption data for the gel-like PEI-silica shell morphology is presented by the red spotted columns and the raspberry-like PEI-silica shell morphology by the black stripped columns.

In Figure 7.2, the adsorption capacity and removal efficiency of the gel-like PEI-silica shell – magnetic core particles were compared with that of the raspberry-like PEI-silica shell – magnetic core particles over five reuse cycles of adsorption and desorption. In the first cycle, the core-shell particles with both coating morphologies performed

similarly. The raspberry-like coating had a slightly higher adsorption capacity, 46 ± 3 mg Cu(II) adsorbed per g core-shell particle, and a removal efficiency of 72 ± 5 %, while the gel-like core-shell particles possessed an adsorption capacity and removal efficiency of 40 ± 2 mg g⁻¹ and 64 ± 3 %, respectively. The superior performance of the raspberry-like core-shell particles could be due to the roughness of the raspberry-like shell which may introduce a greater adsorption surface area than the smooth gel-like morphology (Chapter 6).

A decrease in adsorption capacity of the core-shell particles with reuse is observed, particularly for the gel-like coated particles (Figure 7.2). It is also observed, to a lesser extent, for the raspberry-like coated particles. After the first cycle, the gel-like core-shell particles decreased in adsorption capacity at an approximate rate of 3.9 mg g⁻¹ per adsorption – desorption cycle. In contrast, the raspberry-like core-shell particles decreased in adsorption capacity at a more gradual rate of 2.9 mg g⁻¹ per adsorption – desorption capacity at a more gradual rate of 2.9 mg g⁻¹ per adsorption – desorption capacity at a more gradual rate of 2.9 mg g⁻¹ per adsorption – desorption state at a more gradual rate of 2.9 mg g⁻¹ per adsorption – desorption cycle for the first two adsorb/desorb cycles before plateauing for the remaining three measurements at an average adsorption capacity of 37.5 ± 0.5 mg g⁻¹.

As mentioned above, the decrease in adsorption capacity with reuse was particularly pronounced for the gel-like particles. It is possible that the decrease in adsorption capacity for the gel-like core-shell particles, may result from the incomplete polymerisation of the silica shell. The raspberry-like coating is formed from the individual PEI-silica particles attaching to the carbonyl iron core surface (Chapter 6), which suggests the silica in the shell undergoes complete polymerisation. In contrast, the smooth gel morphology of the gel-like silica shell may result from incomplete silica polymerisation, so parts of the silica shell are composed of some smaller monomers, dimers and oligomers. These smaller silica molecules are less stable and more reactive and, therefore, over multiple cycles are more likely break away during vigorous mixing or react with other components in the system leaving the carbonyl iron core. These factors could lead to a more distinct and ongoing degradation of the gel-like PEI-silica shell when compared with the raspberry-like shell.

7.4.5 Effect of core-shell particle adsorbent dose

In an effort to optimise the Cu(II) adsorption and magnetic removal by the core-shell carrier particles, the effect of adsorbent dose (*i.e.* mass of core-shell particles) was investigated. In Figure 7.3, the adsorption capacity and removal efficiency of core-shell particles with masses between 1 and 12 mg were investigated for a fixed initial Cu(II) concentration of 5 mM (Figure 7.3).



Figure 7.3. (A) Adsorption capacity and (B) removal efficiency of the PEI-silica shell – carbonyl iron core particle and Cu(II) system, with a fixed Cu(II) initial concentration of 5.00 mM, presented as a function of the core-shell particle dose (mg). The Cu(II) adsorption data for the gel-like PEI-silica shell morphology is presented by the red squares and the raspberry-like PEI-silica shell morphology by the black circles.

The overall performance of the gel-like particles was found to be slightly worse than the raspberry-like morphology, especially at low core-shell particle adsorbent doses (Figure 7.3). As suggested in Section 7.4.3, this may be the result of the raspberry-like morphology facilitating a larger specific adsorbent surface area. For the raspberry-like PEI-silica coated particles, a maximum adsorption capacity of $160 \pm 10 \text{ mg g}^{-1}$ was

obtained for an adsorbent dose of 1.0 mg core-shell particles. This observed Cu(II) maximum adsorption capacity was found to be comparable to, if not better than, the recent literature values for different systems (Abou El-Reash, 2016; Anbia *et al.*, 2015; Gutha *et al.*, 2017; Li *et al.*, 2013a; Liu *et al.*, 2008a; 2013; Ojemaye *et al.*, 2017; Wu *et al.*, 2016; Zhang *et al.*, 2012a) as summarised in Table 7.1.

 Table 7.1. A summary of recently developed magnetic carrier particle - Cu(II) ion

 adsorption-desorption systems in the literature.

Magnetic carrier particles	Cu(II) adsorption capacity	Cu(II)	
	(mg g ⁻)	desorption	
Raspberry-like PEI-silica shell	160 ± 10	Yes	
coated carbonyl iron microparticles	(pH 6.0, 10 min,	(1.00 mM HCI)	
(current study)	1.0 mg mL ⁻¹ adsorbent)		
Cysteine-glutaraldehyde modified,	~140	Yes	
cross-linked chitosan – magnetite	(pH 5.0, 4 h,	(10 mM	
microparticles	0.4 mg mL ⁻¹ adsorbent)	Na ₂ EDTA)	
(Abou El-Reash, 2016)			
Melamine functionalised,	126*	Yes	
mesoporous silica coated	(pH 4.0, 90 min,	(300 mM HCl)	
magnetite particles	1 mg mL ⁻¹ adsorbent)		
(Anbia <i>et al.</i> , 2015)			
Epichlorohydrin modified,	123*	Yes	
crosslinked chitosan - magnetite	(pH 6.0, 60 min,	(40 mM HCI)	
microparticles	10 mg mL ⁻¹ adsorbent)		
(Gutha <i>et al.</i> , 2017)			
Amine functionalised, silica coated	24	Yes	
magnetite nanoparticles	(pH 6.0, 240 min,	(pH 1.0, HNO ₃)	
(Li <i>et al.</i> , 2013a)	0.1 mg mL ⁻¹ adsorbent)		
Humic acid coated magnetite	46*	Not tested	
nanoparticles	(pH 6.0, 15 min,		
(Liu <i>et al.</i> , 2008a)	10 mg mL ⁻¹ adsorbent)		
EDTA-functionalised magnetite	44	Yes	
nanoparticles	(pH 6.0, 5 min,	(10 mM HCI)	
(Liu <i>et al.</i> , 2013)	0.1 mg mL ⁻¹)		
4-(((E)-	~50	Yes	
Phenylmethylidene)amino)benzoic	(pH 5.0, 45 min,	(mixture of	
acid / amine functionalised nickel	2 mg mL ⁻¹ adsorbent)	100 mM HNO₃	
ferrite nanoparticles		and HCI)	
(Ojemaye <i>et al.</i> , 2017)			
L-arginine modified cross-linked	135	Yes	
chitosan – magnetite nanoparticles	(pH 5.5, 13 min,	(500 mM HCl	
(Wu <i>et al.</i> , 2016)	0.50 mg mL ⁻¹ adsorbent)	and 500 mM	
		NaOH)	
Amine functionalised silica shell -	65 ± 3	Not tested	
multicore magnetite microparticles	(pH 6.0, 2 h,		
(Zhang <i>et al</i> ., 2012a)	0.50 mg mL ⁻¹ adsorbent)		

* theoretical maximum adsorption capacity given (as calculated by the Langmuir isotherm) as experimental adsorption capacities not provided.

Both gel-like and raspberry-like morphologies exhibited similar Cu(II) adsorption trends as a function of core-shell particle mass (Figure 7.3) and so both carrier particle types will be discussed simultaneously. In Figure 7.3B, it was observed that the increase in adsorbent mass, up until ~10 mg core-shell particles, correlated with an increase in removal efficiency. The improvement to removal efficiency is associated with the increase in adsorbent surface area with larger adsorbent doses, and the resulting increase in the number of active sites for Cu(II) adsorption (Anbia et al., 2015; Das and Mondal, 2011; Padmavathy et al., 2016). The increase in removal efficiency with adsorbent mass was observed to plateau at around 10 mg, after this point further additions of core-shell particles was not observed to significantly affect adsorption. This plateau in removal efficiency is likely the result of the establishment of an equilibrium between the ion attached at the adsorbent site and the ion free in solution (Balarak et al., 2015; Das and Mondal, 2011). At this equilibrium point, the raspberry-like PEI-silica coated particles achieved a removal efficiency of approximately 85 %, while a slightly lower removal efficiency of ~80 % was observed for gel-like PEI-silica coated particles (Figure 7.3B).

In contrast, increasing the mass of core-shell particles resulted in a decrease in the adsorption capacity of both types of core-shell particles (Figure 7.3A). Similar trends were observed by Nsami and Mbadcam (2013) for methyl blue adsorption onto activated carbon and by Das and Mondal (2011) in their study using calcareous soil to adsorb Pb(II) ions. One explanation for this trend is that as the adsorbent dose increases, despite more Cu(II) ions being adsorbed (Figure 7.3B), the rate of increase in available adsorption sites is greater than the increase in the number of Cu(II) ions occupying adsorption sites at equilibrium (Ren et al., 2013). Thus, an increase in adsorbent dose leads to more and more unoccupied adsorption sites, even as more Cu(II) ions are adsorbed, and a decrease in the adsorption capacity. An additional cause for the decrease in adsorption capacity may be attributed to a reduction in the specific surface area available for adsorption due to overlapping or aggregation of adsorption sites as observed in other studies (Das and Mondal, 2011; Nsami and Mbadcam, 2013). However, future studies will be needed to determine whether aggregation is an influencing factor for the PEI-silica - carbonyl iron carrier particle system. Overall, while the total adsorption sites available increases, as indicated by the trend in Figure 7.3B, the specific adsorption sites or adsorption site per gram of core-shell particles is reduced (Figure 7.3A).

7.4.6 Concentration adsorption isotherm

An adsorption isotherm portrays the equilibrium relationship, at a particular temperature, between the two adsorbate phases, that is, the adsorbate free in solution and the adsorbate adsorbed onto the core-shell particle surface (Nsami and Mbadcam, 2013). As discussed in Section 7.4.1, equilibrium was achieved after 10 min incubation for room temperature reactions. The adsorption isotherm for this study was obtained by measuring the adsorption/magnetic removal of Cu(II) with a fixed dose of core-shell adsorbent (5.0 mg) and a varied initial concentration of Cu(II) (2.5 - 20 mM). Experiments were performed at room temperature (298 K). The concentration isotherms are presented in Figure 7.4A and the removal efficiency as a function of Cu(II) initial concentration is presented in Figure 7.4B.



Figure 7.4. The (A) adsorption capacity and (B) removal efficiency of the PEI-silica shell – carbonyl iron core particles, with a fixed core-shell particle dose of 5.0 mg, presented as a function of the initial concentration of Cu(II) (mM). The Cu(II) adsorption data for the gel-like PEI-silica shell morphology is presented by the red squares and the raspberry-like PEI-silica shell morphology by the black circles.

From Figure 7.4A, the adsorption capacity of the core-shell particles increases with increasing initial Cu(II) concentration until a maximum or adsorption saturation plateau (ASP) is reached at approximately 15 mM for both morphologies. This trend can be explained by a higher percentage of active sites on the adsorbent core-shell particles becoming occupied as a result of the increasing concentration of Cu(II). In contrast, the

removal efficiency plateaus before decreasing with higher concentrations of Cu(II) (Figure 7.4B). In the plateau region and low Cu(II) concentrations, additions of Cu(II) ions are adsorbed by the core-shell particles, which results in the increase adsorption capacity (Figure 7.4A) but does not affect the overall percentage of the adsorbed Cu(II) (Figure 7.4B). However, with further increases to the initial Cu(II) concentration the available active sites diminish leading to more Cu(II) ions remaining unadsorbed in solution.

The adsorption capacity and removal efficiency of the core-shell particle types were very similar. The exception being at low Cu(II) initial concentrations (5 mM) where, as was observed in Sections 7.3.4 and 7.3.5, the performance of the particle with a raspberry-like shell morphology was superior to those with a gel-like shell (Figure 7.4). At 20 mM Cu(II), the raspberry-like and gel-like core-shell particles have very similar adsorption capacities of 84 ± 2 mg g⁻¹ and 83 ± 6 mg g⁻¹ respectively.

In order to sufficiently describe the equilibrium state between the two adsorbent phases of the adsorption system, adsorption isotherm models are utilised (Nsami and Mbadcam, 2013). The two most common adsorption isotherm models are the Langmuir isotherm and the Freundlich isotherm. At equilibrium, the Langmuir and Freundlich isotherms may be linearised and written as Equation 3.4 and 3.6 (Section 3.7.6.3.1) (Huang and Shih, 2016; Nsami and Mbadcam, 2013). In Figure 7.5, the concentration isotherm data collected experimentally was fitted to the Langmuir and Freundlich isotherm models (as per Section 3.7.6.3.1) to determine which model best described the behaviour of the Cu(II) – core-shell particle adsorption system.



Figure 7.5. Concentration isotherm data for Cu(II) ion adsorption onto the PEI-silica shell – carbonyl iron core particle surface as fitted to (A, B) the Langmuir adsorption model; and (C, D) the Freundlich adsorption model.

The line of best fit in Figure 7.5 allowed the Langmuir and Freundlich model parameters to be calculated. The calculated parameters are presented in Table 7.2.

	R ²	Qm	KL	1/n	K _f
		(mg g⁻¹)	(L mg⁻¹)		
Langmuir isotherm					
Gel-like shell	0.987	98.0	0.00751	-	-
Raspberry-like shell	0.999	92.6	0.0114	-	-
Freundlich isotherm					
Gel-like shell	0.955	-	-	0.380	7.28
Raspberry-like shell	0.943	-	-	0.271	14.4

 Table 7.2. Calculated Langmuir and Freundlich adsorption model parameters for the

 Cu(II) ion – PEI-silica shell – carbonyl iron core particle adsorption system.

The concentration isotherm data for Cu(II) adsorption onto the core-shell particle surface was observed to fit both isotherm models (R^2 -value > 0.9) (Figure 7.5 and Table 7.2). For both the raspberry-like and gel-like shell morphologies, however, the fit was observed to be better for the Langmuir model isotherm than the Freundlich, as indicated by the higher R^2 -value (Figure 7.5A,B and Table 7.2). The Langmuir adsorption model applies where adsorption is monolayered with finite active adsorption sites, while the Freundlich isotherm is an empirical expression that can fit both monolayer and competitive multilayer adsorption systems (Saadi *et al.*, 2015). Thus, the excellent fit of the Langmuir isotherm model, and the good fit of the Freundlich isotherm model, indicate that the Cu(II) – core-shell particle adsorption system studied here is dominated by monolayer adsorption with a finite number of adsorption sites (Anbia *et al.*, 2015; Huang and Shih, 2016; Nsami and Mbadcam, 2013).

As discussed in Section 7.4.3, the mechanism proposed for Cu(II) – core-shell particle adsorption is chelation between the Cu(II) ions and the amine surface groups of the PEI-silica coated surface. For the proposed adsorption mechanism, adsorption onto the coreshell surface is the result of the N atoms (of exposed amine groups on the core-shell particle surface) donating their lone electron pairs to the Cu(II), resulting in a coordinate covalent bond. Each N atom only has one set of lone electrons to donate to the Cu(II). Thus, the good fit of the Langmuir (and Freundlich) adsorption models, which indicate active adsorption sites are finite and monolayered, correspond with the proposed adsorption mechanism.

The chelation mechanism is further supported by the 1/n parameter calculated from the Freundlich isotherm, Table 7.2. The 1/n parameter is a measure of homogeneity (Liu, 2015a; Shahbeig *et al.*, 2013). 1/n values below unity, such as, obtained for the system studied here, indicate adsorption is the result of chemisorption (Shahbeig *et al.*, 2013). The calculated n values for this adsorption system (2.63 (gel-like) and 3.69 (raspberry-like)) are also within the range of 1-10, indicating favourable adsorption (Li *et al.*, 2013a).

The calculated maximum adsorption capacity, Q_m (mg g⁻¹), was 98.0 mg g⁻¹ for the gellike adsorption surface and 92.6 mg g⁻¹ for the raspberry-like adsorption surface (Table 7.2). These calculated values are in close agreement with the experimental data (Figure 7.4). Interestingly, the gel-like coated particles were determined to have a higher calculated maximum adsorption capacity than the raspberry-like core-shell particles, despite the opposite being observed experimentally (Sections 7.3.4 and 7.3.5). However, the Langmuir isotherm fit was slightly worse for the gel-like core-shell particles compared with the raspberry-like core-shell particles (Figure 7.5 and Table 7.2), so this discrepancy may fall within error.

7.5 Conclusions

This study utilised the PEI-silica shell – carbonyl iron core particles developed in Chapter 6 as magnetic carrier particles for the magnetic removal of Cu(II) ions from aqueous solution. Cu(II) adsorption at pH 6.0 onto the core-shell particles and their successful magnetic removal was confirmed by EDX analysis, as was desorption of Cu(II) in 1 mM HCI (at pH ~3). The conditions used for adsorbent regeneration in this study were less acidic than other core-shell systems reported in the literature. The dependence of the Cu(II) adsorption on pH, indicated that the mechanism for ion adsorption was chelation, which correlates with previous literature studies utilising amine functionalised magnetic carrier particles.

In the interest of potential industrial scale up of this ion recovery-magnetic carrier system, reusability of the core-shell material was a key factor. Adsorption – desorption experiments were conducted over five cycles. The gel-like PEI-silica coated carrier particles were observed to continuously lose adsorption capacity over the five cycles. In comparison, the raspberry-like core-shell particles were observed to initially decrease in adsorption capacity over the first couple of cycles before plateauing. These results are a positive indicator of the regeneration capacity of the raspberry-like core-shell particles. Reuse of the core-shell particles is highly advantageous reducing waste and keeping core-shell production cost to minimum. The ability to regenerate and reuse the

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core-shell carrier material is a particular benefit of the magnetic carrier particle technology in comparison with other heavy metal removal technologies, such as, chemical precipitation and solvent extraction (Bao *et al.*, 2017).

The highest adsorption capacity of the PEI-silica shell – carbonyl iron particles, 160 ± 10 mg g⁻¹, was achieved for a core-shell particle dose of 1.0 mg. This Cu(II) adsorption capacity was found to be a comparatively high compared with the literature and without the synthesis disadvantages of other studies, which included multiple step/complex procedures, harsh conditions, long fabrication times and/or high temperatures.

The Langmuir and Freundlich isotherm models were determined to closely fit the experimental data, with the former model performing slightly better. The fit of the Langmuir model in particular indicates that the Cu(II) adsorption was a monolayer with a fixed number of active adsorption sites. The monolayer adsorption model fits well with the prevailing theory that chelation was the mechanism for Cu(II) adsorption. In addition, the maximum adsorption capacity as calculated through the Langmuir isotherm model was comparable to the experimental values.

In conclusion, this chapter demonstrates the successful application of the PEI-silica shell - carbonyl iron particles as magnetic carrier particles for the recovery of Cu(II) ions. The adsorption capacity of these core-shell particles was observed to be comparable to, or better than, current literature utilising magnetic carrier systems for the removal of Cu(II) ions. Moreover, the PEI-silica – carbonyl iron carrier particle system possessed several important advantages over other previous studies, including a facile, rapid PEI-silica shell synthesis in mild conditions with proven scalability, morphological control of the shell and inbuilt amine functionality. In addition, reusability of the PEI-silica shell – carbonyl iron carrier particle system was established, further demonstrating the advantages magnetic core-shell carrier particle method of heavy metal ion removal.

CHAPTER EIGHT

Interaction of core-shell particles with fine particles for recovery applications

8.1 Introduction

Facile separation of suspended fines or colloidal particles, especially their selective separation, are of interest in a number of industries, including mineral beneficiation (Gray *et al.*, 1994; Raitani *et al.*, 2012; Singh *et al.*, 2014; Yuan *et al.*, 2017) and waste management (Mwilu *et al.*, 2014; Tang *et al.*, 2017). Magnetic separation is an easily operated, low energy, high yield approach to fine particle separation (Raitani *et al.*, 2012). For the separation of non-magnetic materials, magnetic carrier particles can be used. Magnetic carriers are designed to, specifically or non-specifically, attach to, and impart magnetism on, non-magnetic fine particles. The imparted magnetism allows target fine particles to be magnetically separated via the application of an external magnetic field.

In Chapter 6, synthesis techniques to produce core-shell microparticles were developed, including methods to produce PEI-silica and PEI-thiol silica coated carbonyl iron particles. Chapter 7 investigated the use of PEI-silica shell – carbonyl iron core particles as magnetic carrier particles for Cu(II) ion recovery through magnetic separation. In this chapter, the application of the core-shell particles as carrier particles was extended to the recovery of fine particle powders. Overall, Chapter 8 contains a preliminary study conducted to investigate the interaction of core-shell particles (synthesised in Chapter 6) with clay, metalloid/metal oxide and Au nanoparticles.

8.2 Background on magnetic carrier particles and interaction mechanisms

A comprehensive review of the recent research into the recovery of fine particles using magnetic carrier particles is given in Section 2.5.1. In short, suspended fine particles, particularly those arising from mineral beneficiation, are notoriously difficult to dispose of, or purify (Tang *et al.*, 2017). Applying the magnetic carrier/magnetic separation technique to suspensions of waste fines has been shown to rapidly increase the rate of settlement and significantly reduce the final volume of waste to be disposed of, usually in tailing dams (Tang *et al.*, 2017). In contrast, magnetic carriers designed for selective adsorption can aid the separation/purification of fine particles for the recovery of a specific targeted material.

As discussed in Section 2.5.1, most research demonstrating selective separation with magnetic carrier particles employed magnetite carriers (Anastassakis, 1999; 2002; Prakash *et al.*, 1999; Raitani *et al.*, 2012; Singh *et al.*, 2014; Yuan *et al.*, 2017). Generally,

specific adsorption, resulting in selective separation, in these magnetite carrier systems, was provided by surfactant additives and/or pH control (Anastassakis, 1999; 2002; Prakash *et al.*, 1999; Raitani *et al.*, 2012; Singh *et al.*, 2014; Yuan *et al.*, 2017). In these studies, the surfactant additive was used to specifically attach to the magnetic carrier particle and/or target material functionalising the materials for better or more selective interaction between target and carrier particles. For example, in Anastassakis (1999) the surfactant additive (dodecylamine) was used to selectively remove serpentine particles from a serpentine/magnesite mixture. In the study, dodecylamine selectively coated magnetite and serpentine particles, within the pH range 6 and 9, increasing the hydrophobicity of their surfaces. The hydrophobic dodecylamine-coated magnetite and serpentine particles were then able to selectively flocculate together and be recovered via magnetic separation. While the uncoated magnetic particles remained in suspension unaffected by the application of an external magnetic field.

The use of surfactant additives, as in Anastassakis (1999), however, may result in secondary contamination, increased reagent costs and reduced recyclability. The use of surfactant additives to provide specificity are particularly unfavourable when compared to the specificity provided by functionalised core-shell carrier particle approach, which do not possess the surfactant additive disadvantages (Gray *et al.*, 1994). Moreover, unlike the literature investigating heavy metal separation using carrier particles (Section 2.5.2), no studies considered the recyclability of functionalised magnetic carrier particles for fine particle separation. Recycling of the carrier particles could reduce secondary contamination of the separated concentrate and the economic/environmental costs of carrier synthesis.

From previous studies (discussed in Section 2.5.1), the key mechanisms governing attachment between magnetic carrier particles and target particles are the electrostatic force (Anastassakis, 1999; 2002; Prakash *et al.*, 1999; Yuan *et al.*, 2017), the hydrophobic effect (Anastassakis, 1999; 2002; Gray *et al.*, 1994; Raitani *et al.*, 2012; Yuan *et al.*, 2017) and van der Waals (VDW) forces (Anastassakis, 2002; Yuan *et al.*, 2017). In addition, nanoparticles (*i.e.* particles with diameters of 100 nm or less) experience a strong adhesion force which significantly effects their behaviour following a collision with other particles/surfaces, making adhesion another important consideration (Guo *et al.*, 2014). The electrostatic, hydrophobic, VDW and adhesion forces are discussed in Sections 8.2.1, 8.2.2, 8.2.3 and 8.2.4, respectively.

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8.2.1 Electrostatic force

Particles suspended in water, or any other medium possessing a high dielectric constant, will often possess a surface charge. The particle surface charge typically arises due to the ionisation/dissociation of surface groups or the adsorption/binding of ions onto the particle surface (Guo *et al.*, 2014). Oppositely charged ions within the liquid medium act to neutralise the charged surface by enveloping the particle's exterior. The surrounding layer of ions is known as the electrical double layer (EDL).

The EDL consists of two layers. The layer closest to the surface, known as the Stern layer, comprises of tightly held ions adsorbed onto the particle surface. The ions in the Stern layer are not able to be dislodge via thermal diffusion. The secondary layer is known as the diffuse double layer, where ions are held less securely and, thus, remain mobile as a result of thermal diffusion. On the boundary between the Stern and diffuse double layer is the shear plane; it is the potential at the shear plane that is measured as the zeta potential of the particle (Guo *et al.*, 2014; Israelachvili, 2011).

Moving toward the particle surface, through the diffuse and Stern layers, the electrokinetic potential increases, at first exponentially then linearly with distance (Guo *et al.*, 2014; Israelachvili, 2011). Thus, two approaching particles with the same charge will experience an increasingly strong repulsive force as the distance between them decreases due to overlap of their respective EDL fields. Depending on the system, the repulsive force as the EDLs of two particles overlap may overwhelm the other attractive forces (*e.g.* VDW forces, Section 8.2.3) and prevent particle aggregation (Israelachvili, 2011). In contrast, two oppositely charged particles will experience an increasing attractive force upon approach, promoting particle aggregation.

Repulsion and attraction due to electrostatic forces was observed as a major consideration in previous magnetic carrier research (Anastassakis, 1999; 2002; Prakash *et al.*, 1999; Yuan *et al.*, 2017). Interaction between the PEI-silica coated carbonyl iron carrier particles and the target fine particles is, thus, also expected to be influenced by electrostatic forces. Hence, the zeta potential of the core-shell particles was significant in this study. Unfortunately, the large particle sizes and heavy density of the carbonyl iron core rendered the zeta potential measurement of core-shell particles and carbonyl iron core particles impossible using a mobility based light scattering technology, such as, the Malvern Zetasizer (Section 3.7.5). Thus, the zeta potential curve of PEI-silica particles measured by Neville *et al.* (2013a) (Figure 8.1) was used as a guide to the zeta potential of the core-shell particles.



Figure 8.1. Zeta potential as a function of pH for PEI-silica particles. Reprinted from Colloids and Surfaces A: Physicochemical and Engineering Aspects, 431, Neville, F., Murphy, T., Wanless, E.J., The formation of polyethyleneimine–trimethoxymethylsilane organic–inorganic hybrid particles, 42-50, Copyright (2013), with permission from Elsevier.

PEI entrapment during PEI-silica synthesis imparts an amine surface functionalisation and a strong positive charge in acidic and neutral solutions. An increasingly strong positive charge was observed as pH decreased from 10 (Neville *et al.*, 2013a; Figure 8.1). The point of zero charge (PZC) of the PEI-silica particles (Neville *et al.*, 2013a; Figure 8.1) was observed at approximately pH 11.5. In Chapter 5, the PZC of PEI-silica particles was observed at 11 (Chapter 5) while in the literature, the PZC for PEI is generally agreed to occur at pH 10.8 (Lindquist and Stratton, 1976; Vakurov *et al.* 2012). Thus, the zeta potential curve is in good agreement with previous experimental work in this thesis and the literature.

By comparing the zeta potential curve of the PEI-silica shell with that of the material targeted for adsorption, the adsorption pH can be tuned to achieve maximum electrostatic attraction between the target and carrier particles. In addition, at the PZC the PEI-silica shell is neutrally charged (pH 10-11) eliminating electrostatic attraction between the core-shell carrier particles and the target materials. The lack of electrostatic attraction could allow for desorption of the fine particles and the regeneration of the coreshell carrier particles for reuse.

8.2.2 Hydrophobic interaction

The hydrophobic effect results from water-inert surfaces being submerged in water and causing an increased solvent structure at the water-solid interface (Israelachvili, 2011). This solvent structure decreases the entropy of the system as water molecules have reduced rotational freedom in their organised state. When a solid surface joins with another solid surface, the solvent molecules are diffused from the solid-liquid interface. In the case of hydrophobic solids, this diffusion of the solvent molecules is energetically favourable as the diffused solvent molecules resume their full freedom of movement. In other words, it is more energetically favourable for two hydrophobic surfaces to be in contact than for the surfaces to be surrounded by water molecules (Israelachvili, 2011).

Previous experimental work has shown PEI-silica particles to be hydrophobic in nature (Neville *et al.*, 2016), likely due to the presence of surface methyl groups which result from the TMOMS silane used for synthesis. Thus, the PEI-silica coated carrier particles are expected to be similarly hydrophobic and will experience the hydrophobic effect with other hydrophobic particles introduced into the aqueous environment.

8.2.3 van der Waals forces

The van der Waals (VDW) forces are weak, typically attractive, interaction forces that act between all particles and molecules in a system (Israelachvili, 2011). London or dispersion forces, in most cases, account for the majority of the VDW interaction energy (Goodwin, 2004). Dispersion forces between molecules are the result of instantaneous fluctuations in the electron density around the individual molecules. These fluctuations induce an aligned electron density in the nearby molecules and result in an overall decrease in the system's energy (Atkins and de Paula, 2009). The strength of this force is directly proportional to the polarizability of the molecules. However, overall VDW forces are relatively weak, the VDW interaction energy being generally one to two orders of magnitudes smaller than a typical chemical bond (Guo *et al.*, 2014). VDW forces are also long-range, acting over distances of up to 10 nm and down to 0.2 nm.

The van der Waals interaction energy, E_{vdW} (J), for the non-retarded case, between two spherical particles can be approximated as a function of shortest separation distance between particle surfaces, h (m), using the expression in Equation 8.1 (Hamaker, 1937),

$$E_{\nu dW} = -\frac{A_H}{6} \left(\frac{2a_1 a_2}{h^2 - (a_1 + a_2)^2} + \frac{2a_1 a_2}{h^2 - (a_1 - a_2)^2} + \ln\left[\frac{h^2 - (a_1 + a_2)^2}{h^2 - (a_1 - a_2)^2}\right] \right)$$
8.1

where A_H (J) is the Hamaker constant, a function of the particle material and environment; and a_1 (m) and a_2 (m) are the radius of the two interacting particles.

The range for which the above expression accurately calculates the VDW interaction energy is down to a separation distance (h) of 0.4 nm. At close approach (h < 0.4 nm) particles often negate the assumption intrinsic to Equation 8.1 of atomic smoothness. Also, forces resulting from the electron orbital overlap contribute higher repulsion energy between particles than predicted by Equation 8.1 (Goodwin, 2004). Once the particles are at the point of contact, VDW equation becomes void as particle deformation and surface adhesion (Section 8.2.4) become vital to the calculation of particle interaction energy and are not included in Equation 8.1 (Goodwin, 2004). At this stage, models of adhesion force, which will be discussed in Section 8.2.4, are needed to calculate the interaction energy between particles in an accurate way.

8.2.4 Adhesion force

The adhesion force is the force needed to be overcome to allow two 'unlike' entities in contact to be separated. In general, the adhesion force is governed by a combination of a large number of short and long-range forces, including, but not limited to, electrostatic, van der Waals, capillary, solvation and structural forces (Guo *et al.*, 2014). A related property, the cohesion force, is influenced by the same range of forces, but is defined as the force needed to be overcome to separate 'like' objects in contact (Israelachvili, 2011). For this chapter, which investigates the interaction between PEI-silica coated magnetic carrier particles and various fine particle species targeted for separation, the adhesion force is the most relevant.

The field of adhesion mechanics is built on the Hertz, Johnson-Kendall-Roberts (JKR) (Johnson *et al.*, 1971) and Derjaguin-Muller-Toporov (DMT) (Derjaguin *et al.*, 1975) theories which model the behaviour of two contacting surfaces. The most relevant theory for a particular system is dependent on the size, elasticity, hardness and surface energy of the particles in question. The Hertz theory is the most facile, describing the behaviour of two completely rigid spherical particles and neglecting the effect of surface forces. However, as the size of the interacting particles decreases, the surface forces play an increasingly significant role, reducing the applicability of the Hertz theory for small

particle interactions, especially interactions between nano-sized entities (<100 nm) (Guo et al., 2014).

The JKR theory best describes systems of easily deformed, large particles with high surface energies, whereas the DMT theory can be used to describe the contact behaviour of small, hard objects with low surface energies (Derjaguin *et al.*, 1975; Guo *et al.*, 2014; Johnson *et al.*, 1971). Further models have been developed to describe the behaviour of objects with properties falling in between those described by the JKR and DMT theories (Maugis, 1992). The theories themselves are beyond the scope this thesis, but further details can be found in Israelachvili (2011) and Guo *et al.* (2014). In any case, the suitability of the Hertz, JKR and DMT theories to accurately describe the behaviour of nanoparticles is still under discussion.

More relevant to this study is that the adhesion force determines the external pulling force required to detach two particles in contact. Moreover, the adhesion energy provides information on the equilibrium thermodynamic state of the system, including the probability of finding particles attached or not attached, as well as, the mean-lifetime of particle-particle contact. For nanoparticles (diameter < 100 nm), the adhesion energy is often comparable or greater than thermal energy (kT), and thus the mean-lifetime of particle-particle contact becomes significant (Israelachvili, 2011). In these systems, the adhesion force begins to play a major role in the interaction behaviour of the nanosized objects with other particles and surfaces.

Overall, this chapter investigates the use of PEI-silica shell – carbonyl iron core particles, synthesised in Chapter 6, as selective magnetic carriers for the separation for a number of common clays (Section 8.4) and metalloid oxides (Section 8.5). The clays chosen were talc, montmorillonite and kaolin, while the metal/metalloid oxides investigated were quartz and TiO₂. The core-shell particles coated with PEI-thiol silica and PEI-silica were also investigated for their interaction with Au nanoparticles (Section 8.6).

8.3 Methodology

In this chapter, the fine particle recovery potential of the core-shell particles, whose synthesis was reported in Chapter 6, was explored. The PEI-silica coated iron particles were tested to assess their interaction with various fine particles, *i.e.* talc, montmorillonite, kaolin, quartz and titanium oxide (TiO₂). PEI-silica and PEI-thiol silica coated iron particles were also tested for their interaction with colloidal gold nanoparticles

(Au). The methods used are outlined in Section 3.5.2, however, a brief summary follows in the following sections.

8.3.1 Interaction of PEI-silica shell – carbonyl iron core particles with clays and metal oxides

The interaction experiments with the clay and metal oxide particles was followed the procedure detailed in Section 3.6.2.

In short, the PEI-silica shell – carbonyl iron core carrier particles were synthesised using the methods reported in Chapter 6 in 10.000 mL reaction tubes (Section 3.4.2). As in Chapter 7, both the gel-like (Method D) and raspberry-like (Method F) coatings were prepared, using 100 and 200 mM TMOMS, respectively.

The purchased (Sigma-Aldrich) fine particle powders (talc, montmorillonite, kaolin and quartz) and TiO₂ nanoparticles were characterised using SEM (Section 3.7.1) and zeta potential measurements (Section 3.7.5). SEM samples were prepared as per Section 3.7.1.2 and carbon coated prior to placement in the instrument. Zeta potential measurements were made as per Section 3.7.5.2. For zeta potential measurements particle samples were suspended in 10.0 mM NaNO₃ base electrolyte solution pH-adjusted with 1.00 M NaOH/HCI.

Core-shell particles $(3.0 \pm 0.3 \text{ mg mL}^{-1})$ were incubated at a one to one weight ratio with the fine particles $(3.0 \pm 0.3 \text{ mg mL}^{-1})$. The suspension was buffered at pH 4.0, 7.0 or 10.0 through the addition of 100 mM succinic acid buffer, phosphate buffer (PB) or gly-gly, respectively. The suspension was vortex mixed (2000 rpm for 5 s) every 150 s during the 10 min incubation period to prevent settling. After incubation for 10 min, magnetic separation (Section 3.6.1) was used to remove any unattached fine particles with the supernatant and the core-shell particles washed twice with water.

Fine particles were desorbed from the core-shell particles by suspending the fine particle – core-shell particle sample in 3.00 mM NaOH (pH ~11.5) and vortex mixing at 2000 rpm for 10 min. Core-shell particles were than magnetically separated (Section 3.5.1) and washed twice with water.

The interaction of the core-shell particles with the fine particles materials were assessed using SEM imaging. Samples were prepared on SEM stubs using the method outlined in Section 3.7.1 and were coated with carbon. EDX analysis, as discussed in Section 3.7.2, was also used for fine particles containing elements that could be distinguished from the core-shell particles and the carbon coated stub background. The background
EDX spectrum and is presented in Figure 8.2. As can be seen in Figure 8.2, x-ray energy peaks detected correspond to the emission/s characteristic of the elements AI, Cu and O. An additional peak at 0.28 keV corresponds to the x-ray emission of C due to the carbon coating and is not labelled by the program.



Figure 8.2. EDX spectrum of the carbon coated stub (background).

8.3.2 Interaction of PEI-silica and PEI-thiol silica shell – carbonyl iron core particles with colloidal Au

The interaction between the core-shell particles and Au nanoparticles was conducted as per Section 3.6.2.1. The PEI-silica shell – carbonyl iron core and PEI-thiol silica – carbonyl iron core carrier particles were synthesised using the gel-like coating method (Method D) from Chapter 6 in 10.000 mL reaction tubes (Sections 3.5.2 and 3.5.3).

The Au nanoparticles $(10 \pm 2 \text{ nm diameter})$ were purchased (Sigma-Aldrich) as a stabilised suspension (~6.0 × 10¹² particles mL⁻¹) in 0.1 mM phosphate buffer saline and were used as received. Interaction experiments were performed by incubating the coreshell particles (3 ± 0.3 mg mL⁻¹) with the Au nanoparticles (~1.8 × 10¹² Au particles mL⁻¹) within a 100 mM PB buffered solution at pH 8.0 (Ruan *et al.*, 2015).

As with the fine particle interactions (Section 8.3.1) the suspension was vortex mixed (5 s at 2000 rpm) every 150 s throughout the 10 min incubation period. Magnetic separation (Section 3.5.1) and two water-washes followed incubation to remove unattached nanoparticles. After washing the core-shell particles were characterised through SEM imaging (Section 3.7.1) and EDX spectroscopy (Section 3.7.2). Samples were prepared

as per the method in Section 3.7.1.2 and were carbon coated prior to SEM imaging and EDX analysis.

8.4 Interaction with clays: talc, montmorillonite and kaolin

Clay minerals are naturally-occurring soil particulates, generally defined as having diameters less than 2 µm (Lavelle and Spain, 2003; Saka and Güler, 2006). Ubiquitous in soils, clays often dominate the physicochemical properties of the natural sediments they are found in. Hence the behaviour of clays in aqueous suspensions is vital to the understanding of environmental processes (Lavelle and Spain, 2003; Saka and Güler, 2006). Industrially, clays have been used extensively as industrial products and as part of industrial processes due to their large surface areas, capacity for cation exchange and affinity for organic and inorganic compound adsorption (Arseguel and Babouléne, 1994; Lee *et al.*, 2012; Lv *et al.*, 2014; Saka and Güler, 2006; Sprynskyy *et al.*, 2011). The clays investigated for their interaction with the core-shell particles in this chapter were talc, montmorillonite and kaolin.

As a pervasive presence in soils worldwide, clays form one of the major contaminates of valuable mineral ore deposits, including the mineral deposits of nickel, copper, platinum and diamond-bearing ores (Aplan, 1997; Feng et al., 2012; Wiese et al., 2015; Zhao et al., 2015). In fact, a montmorillonite mineral clay content as high as 80 % has been found in some mined ore deposits (Chen et al., 2017). The presence of clays in the mineral ore deposits has been found to have a detrimental effect on ore processing by fine particle flotation (Wang et al., 2015d). For flotation units separating on the basis of hydrophobicity (e.g. coal flotation) electrostatic attachment of fine clays (a.k.a. 'slime coating') significantly hinders mineral separation (Chen et al., 2017; Oats et al., 2010; Xing et al., 2017). Moreover, flotation separation of positive charged minerals will be significantly supressed by the presence of any positively charged clay particles (Chen et al., 2017). Entrainment of the clay fines, also poses a significant problem in froth flotation by reducing the final grade of the flotation concentrate (Chen et al., 2017). Overall, the presence of clays in fine particle flotation has been observed to increase reagent consumption, reduce selectivity, result in poorer flotation kinetics, lower flotation recovery and require increased downstream processing (Chen et al., 2017; Feng et al., 2012; 2017; Oats et al., 2010; Wang et al., 2015d; Wiese et al., 2015; Xing et al., 2017; Zhao and Peng, 2012; Zhao et al., 2015). In addition, as a waste material of mineral beneficiation, clays are disposed of as tailing slurries. Unfortunately, slurries consisting

of even small percentages of clay minerals are more difficult to dewater and require larger areas for their disposal in tailing dams (Chen *et al.*, 2017; Zhijun *et al.*, 2013).

Despite the negative issues mentioned above, clays have also attracted interest as valuable products in their own right. Talc has applications as an adsorbent for the removal of environmental pollutants, such as, uranium, aromatics and dyes (Arseguel and Babouléne, 1994; Lee *et al.*, 2012; Sprynskyy *et al.*, 2011), and as an inert additive to drug tablets (Lv *et al.*, 2014). Montmorillonite has been utilised as a host for the polymerisation of polymer chains (Vilela *et al.*, 2007) and to remove a variety of dyes and colorants from waste water streams (Almeida *et al.*, 2009; Tahir *et al.*, 2010). While kaolin has received recent research attention as a performance-enhancing filler for cements (Du *et al.*, 2014; Harbi *et al.*, 2017), an inexpensive anti-haemorrhagic additive for wound dressings (Lundin *et al.*, 2017) and a catalytic support (Guo *et al.*, 2014; Shirzad-Siboni *et al.*, 2014). Therefore, the removal and recovery of clays is of significant interest for mineral processing and environmental preservation. Recovered clay products may also have potential uses in multiple commercial fields.

8.4.1 Characterisation of clays: talc, montmorillonite and kaolin

Chemically, clays are anisotropic, hydrated phyllosilicates consisting of parallel layers of tetrahedral silicates (Si-O/OH) and octahedral metal oxides (such as Mg-O/OH or Al-O/OH) held together through the common oxygen atoms. Talc (Mg₃Si₄O₁₀(OH)₂), for example, consists of a single layer of octahedral Mg-O/OH sandwiched between two tetrahedral Si-O/OH layers (a TOT structure) (Piniazkiewicz *et al.*, 1994; Wang and Somasundaran, 2005; 2006). Similarly, montmorillonite (H₂Al₂(SiO₃)₄.*n*H₂O) is TOT-structured with a middle Al-O/OH layer sandwiched by a layer of silicate on either side (Vilela *et al.*, 2007; Xing *et al.*, 2017; Zhao and Peng, 2012). Kaolinite (Al₂Si₂O₅(OH)₄), on the other hand, has a 1:1 ratio of Al-O/OH to Si-O/OH sheets with a TO structure (Xing *et al.*, 2017; Zhao and Peng, 2012). Investigated in this study is kaolin which is an impure form of kaolinite.

The 2:1 (TOT) triple layer structured clays, talc and montmorillonite, have a sheet thickness of approximately 1 nm, while double layered 1:1 (TO) clays, such as kaolinite, have a thickness of around 0.7 nm. Multiple sheets are weakly joined together through van der Waal forces forming a layered plate-like structure (Piniazkiewicz *et al.*, 1994; Wang and Somasundaran, 2005; 2006). These layered plate-like particulates can be observed in the SEM images taken of the clays via the secondary electron detector in Figure 8.3.

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Figure 8.3. Secondary electron detector SEM images of ground fine particle clays: (A) talc; (B) montmorillonite; and (C) kaolin.

In agreeance with the literature (Galet and Dodds, 2009; Sprynskyy *et al.*, 2011; Tahir *et al.*, 2010), the SEM images taken for this work (Figure 8.3), show the talc, montmorillonite and kaolin powders consist of irregular crystalline particles with layered plate-like structures. The flat face side of the talc platelets was observed to be significantly larger on average than the other two clays studied. Talc particles had a highly disperse range of sizes, with an absolute top face-plane size of 10 μ m, as indicated by the manufacturers. However, the montmorillonite and kaolin particles appeared similar in size, appearing to have an average face-plane size of approximately 2 μ m.

Due to the sheet like nature of clay, clay particles possess several types of surfaces from which its unique anisotropic properties are derived (Zhao and Peng, 2012). On the edge of the clay sheets are broken Si-O, Mg-O or Al-O bonds which behave as exposed hydroxyl groups. These hydroxyl groups contribute some hydrophilicity to the structure, as well as, a positive or negative charge depending on the solution pH (Wang and Somasundaran, 2005; 2006). On the other hand, the flat faces (or basal faces) of the clay particles are largely absent of hydroxyl or active ions forming a continuous silicate or metal oxide layer. In the case of talc, this continuous silicate layer results in the basal face of the plate-like particles possessing hydrophobicity (Wang and Somasundaran, 2005; 2006). For montmorillonite, the basal surface of the clays possesses a constant negative charge which is independent of the pH, due to isomorphous substitutions of Si(IV) with Al(III) within the lattice (Zhao and Peng, 2012). Conversely, kaolinite (and kaolin) as a double layered 1:1 (TO) clay possess two types of basal planes, one being uncharged (similar to talc) and the other with a constant negative charge due to isomorphous substitutions (similar to montmorillonite) (Williams and Williams, 1978). It is theorised that in solution, the uncharged planes flocculate to form doublets, resulting in only the pH-independent negatively charged basal face being exposed (Williams and

Williams, 1978). The variation in surface properties for a particular clay particle allows it to interact with a range of different materials (Zhao and Peng, 2012).

The zeta potential of the clays as a function of pH are presented in Figure 8.4.



Figure 8.4. Zeta potential as a function of pH of ground fine particle clays: (A) talc; (B) montmorillonite; and (D) kaolin. Clay particles were suspended in a base electrolyte of 10.0 mM NaNO₃ pH-adjusted with 1.00 M NaOH/HCl for measurement.

The zeta potential of talc was observed to be largely dependent on the solution pH (Figure 8.4A). This zeta potential is defined solely by the exposed Si-OH and Mg-OH groups on the edges of the talc crystalline sheet structure as the flat basal face of particles is uncharged and hydrophobic (Tarasevich, 2007). In highly acidic pH the zeta potential of talc is positive, reaching a PZC around pH 3. From pH 3-12, the zeta potential of talc becomes increasingly negative as a result of the dissociation of the exposed hydroxyl groups around the edges of the crystalline platelets (Wang and Somasundaran, 2005; 2006). The zeta potential curve obtained for this study correlates well with the literature (Wang and Somasundaran, 2005; 2006). In terms of hydrophobicity, the anisotropic nature of the talc structure gives the edges a hydrophilic/charged nature while the basal faces of the crystalline sheets are hydrophobic (Tarasevich, 2007).

For montmorillonite (Figure 8.4B), the zeta potential remains negative for the entire pH range investigated. The zeta potential of the surface displayed very little dependence on pH, decreasing only slightly with pH adjustment from 2-12. This result is in agreement with the literature (Saka and Güler, 2006). As discussed above the basal plane aspect of the montmorillonite particles possesses a constant, pH-independent, negative charge due to the substitution of Al(III) for Si(IV) in the structure (Zhao and Peng, 2012). This accounts for the consistently negative charge of the montmorillonite sample (Figure 8.4B). However, the zeta potential becomes slightly more negative with increased pH

(Figure 8.4B). This is the result of edges of the montmorillonite's sheet structure consisting of hydroxyl groups, which have a pH-dependent charge. As for talc, dissociation of the hydroxyl groups increases with pH, producing an increasingly negative charge with higher pH. However, only ~1 % of the montmorillonite surface area can be assigned to the edges, so the charge of the overall montmorillonite sample is dominated by the pH-independent negative charge of the face surfaces (Figure 8.4B) (Saka and Güler, 2006).

The zeta potential curve for kaolin, (Figure 8.4C), had a similar trend to that of talc. Starting positive at low pH, reaching a PZC at around pH~3 and becoming increasing negative as the pH increased past 3. This trend is correlated by the literature (Moayedi *et al.*, 2011). For kaolin, like talc, the dissociation of the hydroxyl groups of the edges of the crystalline sheets played the dominate role in determining the zeta potential at a particular pH. The structure of kaolin is such that the exposed basal planes were pH-independent and negatively charged. However, unlike montmorillonite where the basal planes dominated the surface and thus the charge, in kaolin, the constant negative-charge of the exposed basal planes did not significantly influence the overall zeta potential trend.

8.4.2 Effect of pH on adsorption

As mentioned in Section 8.1, previous research has indicated that pH control plays a significant role in selective and effective attachment of the target material onto the carrier particles (Prakash *et al.*, 1999; Yuan *et al.*, 2017). This effect is believed to be due to the changes in electrostatic potential aiding or abetting attachment between the target particle and carrier particle surfaces with pH. Thus, pH control is likely to perform a similarly important role in the interaction between the PEI-silica core-shell carrier particles and the target clays in this study. In Section 8.4.1 the clay particles were characterised, and their structures discussed. The unique anisotropic nature of the clay platelets increases the complexity of the clay's potential interactions with other surfaces as certain parts of the clay, *i.e.* the edges versus face planes, have differing surface properties.

The interaction between the core-shell particles and the various clays at pH 4.0, 7.0 and 10.0 was examined using SEM imaging. Figures 8.5 and 8.6 present SEM images, taken by the secondary electron and backscattered electron detector, respectively. The interaction of clays with both the gel-like and raspberry-like PEI-silica coated carbonyl iron particles were investigated and gave very similar results indicating coating type

played a limited role in clay adsorption. However, in Chapter 7, the raspberry-like PEIsilica coating performed significantly better than the gel-like coating over multiple reuses, thus, the raspberry-like coating was chosen for further experiments in Section 8.4.3. For clarity, only the clay interaction with the raspberry-like PEI-silica – carbonyl iron core particles are presented in Figures 8.5 and 8.6. However, the clay interactions with the gel-like core-shell particles are presented in Appendix C (Figures C.1 and C.2).



Figure 8.5. SEM images taken of the raspberry-like PEI-silica – carbonyl iron particles incubated with (A-C) talc; (D-F) montmorillonite; and (G-I) kaolin. Core-shell particles and clays were incubated in 100 mM succinic acid buffer at pH 4.0, phosphate buffer (PB) at pH 7.0 and gly-gly buffer at pH 10.0. Images taken with the secondary electron detector.



Figure 8.6. SEM images taken of raspberry-like PEI-silica – carbonyl iron particles incubated with (A-C) talc; (D-F) montmorillonite; and (G-I) kaolin. Core-shell particles and clays were incubated in 100 mM succinic acid buffer at pH 4.0, phosphate buffer (PB) at pH 7.0 and gly-gly buffer at pH 10.0. Images taken with the backscattered electron detector.

After incubation with the clay, the core-shell particles were washed and magnetically separated multiple times, before being prepared for SEM imaging. Thus, the presence of significant amounts of remaining clay in the sample suggests adsorption of clay to the PEI-silica coated particles. The sample-representative SEM images presented in Figures 8.5 and 8.6 and Appendix C (Figures C.1 and C.2), show how the interaction between core-shell particles and clays is affected by incubation pH.

From Figure 8.5, the secondary electron detector images were used to identify the coreshell particles and clay particulates on the basis of their differing visual textures. The surface of the raspberry-like core-shell particles consists of smooth and rounded spheres forming the raspberry-like texture of the PEI-silica coating (as in Chapter 6). In contrast, the clays appear as layered, plate-like, irregularly shaped particles as observed in Figure 8.2. The backscattered electron detector images (Figure 8.6) provide contrast on the basis of average atomic number, such that heavier elements, e.g. the carbonyl iron cores, can be distinguished by appearing lighter in colour than the less heavy materials, including the silica coating and clays. Thus, the clays can be further distinguished from the core-shell particles especially where there are irregularly-shaped carbonyl iron cores that could be mistaken for clays when considering visual texture alone.

In Figures 8.5A-C and 8.6A-C, the interaction between talc particulates and core-shell particles can be observed for all pH conditions studied, with more talc attached at pH 4.0 and 7.0, although it is still possible to distinguish some talc at pH 10.0. However, for montmorillonite (Figures 8.5D-F and 8.6D-F) and kaolin clays (Figures 8.5G-I and 8.6G-I) only incubating at pH 4.0 and 7.0 resulted in significant quantities of clay becoming attached to the core-shell particles. As discussed in Section 8.2, adsorption between core-shell particles and clays are expected to result from a combination of forces which will be discussed as follows.

For talc, electrostatic attraction between the PEI-silica (Figure 8.1) and talc (Figure 8.3A) surfaces due to their respective positive/negative charges is expected to occur at pH>3 through to pH<11. In comparison with the samples incubated at pH 4.0 and 7.0, the talc/core-shell particle sample incubated at pH 10.0 (Figures 8.5C and 8.6C) was observed to have significantly less adsorbed talc particulates. The reduced interaction between the PEI-silica coated carbonyl iron and the talc reflects the reduced positive charge of the PEI-silica coating as the surface approached its PZC (Figure 8.1). Incubation in an acidic environment (pH 4.0) (Figures 8.5A and 8.6A) was observed to have a slight advantage in promoting talc – core-shell particle interaction compared with incubation at pH 7.0 (Figures 8.5B and 8.6B). This may be due to the increasing positive charge of the PEI-silica coating with increasing acidity (Figure 8.1).

In addition to the electrostatic force, the hydrophobic effect (Section 8.2.2) is also expected to play a role in the interaction between the core-shell particles and the clays (Section 8.2.1.2). As discussed in Section 8.2.4.1, the flat faces of the talc particulates are hydrophobic in nature (Wang and Somasundaran, 2005; 2006). In the literature, the hydrophobic effect was identified as the mechanism for carboxymethyl cellulose adsorption onto the basal faces of talc particles (Morris *et al.*, 2002). In the interaction experiments performed herein, the hydrophobic effect is expected to lead to energetically favourable adsorption of talc basal planes onto the PEI-silica coating of the carrier particles (Neville *et al.*, 2016). This hydrophobic effect is reflected in the SEM images presented in Figure 8.5A-C and 8.6A-C. For all pH conditions, the talc platelets appear to attach with their flat side against the PEI-silica coated particles. In addition, adsorption was observed at pH 10.0 despite the limited electrostatic attraction force as the PEI-silica

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surface approached the PZC. On the other hand, montmorillonite and kaolin, which were not influenced by the hydrophobic effect, did not experience any adsorption at pH 10.0, as will be discussed below.

As discussed in Section 8.4.1, the basal faces of the montmorillonite particles are pHindependent and negatively charged. In contrast, the edges of the montmorillonite platelets are pH-dependent, but account for a very small fraction (~1 %) of the total montmorillonite particle area (Saka and Güler, 2006), so do not significantly impact the overall charge of the clay platelets. Thus, montmorillonite exhibits a zeta potential which is negative and mostly independent of pH for pH 2-12. In addition, unlike talc, neither facets (basal faces or edges) of the montmorillonite structure are hydrophobic in nature (Tarasevich et al., 2007). Hence, the dominate force governing interaction between the montmorillonite and PEI-silica shell is electrostatic. The difference in the electrostatic potential is greatest at acidic pH and drops to zero once the PEI-silica shell reaches its PZC around pH 11 (Figure 8.1). These conditions are reflected in Figure 8.5D-F and 8.6D-F. At pH 4.0 and 7.0 (Figures 8.5D-E and 8.6D-E), the PEI-silica shell is definitively positive (Figure 8.1) while the montmorillonite is negative (Figure 8.3), hence the difference in electrostatic charge results in the attachment of the clay to the core-shell particles. However, at pH 10.0 (Figures 8.5F and 8.6F) very little/no clay attachment was observed, this was expected as the PEI-silica approached a neutral surface charge, and, unlike talc, montmorillonite did not experience the hydrophobic effect.

Similarly, kaolin does not have exposed hydrophobic surfaces, so does not interact with the PEI-silica shell through the hydrophobic effect. Hence the main source of interaction between the core-shell particles and kaolin clay particulates is through electrostatic attraction. As with montmorillonite, kaolin clays attached to the core-shell particles at pH 4.0 and 7.0 (Figures 8.5G-H and 8.6G-H) but not at pH 10.0 (Figures 8.5I and 8.6I). Incubation at pH 7.0 resulted in the highest amount of clay being adsorbed (Figures 8.5H and 8.6H). This is expected as at pH 7.0 the difference between the negative and positive charges of the kaolin and PEI-silica surfaces, respectively, was at its highest. A charge difference was also clear at pH 4.0, which resulted in kaolin attachment (Figures 8.5G and 8.6G). However, at pH 10.0 the PEI-silica surface approached the PZC, resulting in very little adsorption of the kaolin clay (Figures 8.5I and 8.6I).

Overall, pH adjustment exercised control over the degree to which clays adsorbed onto the core-shell surface. This was especially true for montmorillonite and kaolin clays where the interaction was based on electrostatic forces and not influenced by the hydrophobic effect, as was the case with talc adsorption.

8.4.3 Adsorption-desorption cycle

Reuse is a vital component of the core-shell recovery technology being developed for this thesis, thus the adsorption – desorption - re-adsorption cycle of the clay powders was of significant interest in this study. For this purpose, the neutral condition of pH 7.0 was chosen for the adsorption component as all clays experienced significant adsorption at pH 7.0 (Section 8.4.2). Desorption was achieved through vigorous mixing (vortex mixing at 2000 rpm) and incubation at high pH (11.5) where the PEI-silica coating is expected to have reached or surpassed (becoming negatively charged) its PZC (Figure 8.1, Chapter 5). Thus, at pH 11.5 electrostatic attraction between the clays and PEI-silica shell is expected to be removed, in addition shear forces from the vortex mixing are predicted to help with detachment.

In Chapter 7, the raspberry-like PEI-silica coating performed significantly better than the gel-like coating over multiple reuses, hence the raspberry-like coating was used for the adsorption – desorption studies (as in Section 8.4.2). The SEM images of the core-shell particles system following adsorption, desorption and re-adsorption of the clays are given in Figures 8.7 and 8.8.









As in Section 8.4.2, secondary and backscattered electron detector SEM images, (Figures 8.7 and 8.8), are included to better elucidate the clay attachment. Significant coverage of the core-shell particles with clay was observed upon adsorption at pH 7.0 for all clays studied (Figures 8.7A,D,G and 8.8A,D,G) as expected from Section 8.2.4.2.

Desorption was achieved through incubation at pH 11.5 with vigorous vortex mixing at 2000 rpm for 10 min (Section 8.3.1). The core-shell particles were then magnetically separated from the desorbed clays. By first examining the core-shell particles, it appears that the high pH and vigorous vortex mixing did not visually impact the integrity of the core-shell structure.

After desorption, limited or no clay remained on the core-shell particles for any of the clay samples (Figures 8.7B,E,H and 8.8B,E,H). This was expected for montmorillonite and kaolin samples where the electrostatic attraction between clay and PEI-silica surface

was the primary attachment mechanism and the hydrophobic effect was not significant. Therefore, for montmorillonite and kaolin, adjusting the pH to 11.5 removed the electrostatic interaction force by neutralising the PEI-silica surface charge and thus allowed the clays to desorb.

In the case of talc, the basal faces of the talc structure were hydrophobic in nature, resulting in talc attachment even at pH 10.0 (Figures 8.5C and 8.6C) when the electrostatic forces were significantly reduced. However, in spite of this, desorption of the talc was observed in Figures 8.7B and 8.8B. As the hydrophobic effect is independent of pH, desorption of talc particles likely results from the shear force from the vigorous vortex mixing during the desorption and subsequent washing procedures. For confirmation of the talc desorption at pH 11.5 with vigorous stirring, the EDX spectra of the adsorbed and desorbed talc was obtained and are presented in Figure 8.9.



Figure 8.9. EDX spectra of the PEI-silica shell (raspberry-like) – carbonyl iron core particles after (A) adsorption of talc at pH 7.0 and (B) desorption of talc at pH 11.5 with vortex mixing at 2000 rpm. Core-shell particles and clays were incubated in 100 mM phosphate buffer at pH 7.0 for adsorption and in 3.00 mM NaOH at pH 11.5 for desorption. The corresponding SEM image of the area analysed by EDX is given in the top right corner of each spectrum.

In Figure 8.9A, the EDX spectrum after adsorption of talc has a distinctive magnesium peak at 1.25 keV (Crawford *et al.*, 2011). This magnesium peak is not observed in the background spectrum (Figure 8.2). Thus, the Mg peak in Figure 8.9A relates to the presence of talc (Mg₃Si₄O₁₀(OH)₂) in the sample (Piniazkiewicz *et al.*, 1994). After desorption (Figure 8.7B) no Mg peak can be observed over the background noise,

signifying there is no significant concentration of Mg still present in the sample and that the majority of the talc has been successfully desorbed.

Re-adsorption of the clay particles was also attempted through incubation of the clays and desorbed core-shell particles at pH 7.0 (Figures 8.7C,F,I and 8.8C,F,I). In addition, re-adsorption was successful for all clays trialled, although to a lesser degree than the initial adsorption process. Talc particles showed the highest degree of re-adsorption, while montmorillonite and kaolin were adsorbed in smaller amounts. As discussed in Section 8.4.2, talc possesses the dual adsorption forces of electrostatic attraction and the hydrophobic effect, whereas montmorillonite and kaolin adsorb on the basis of mainly electrostatic attraction. This suggests that the electrostatic force of attachment is weakened for the re-adsorption process resulting in a reduced amount of clay being adsorbed.

Future research will investigate this decrease in re-adsorption following desorption. Mechanical or chemical degradation of the PEI-silica shell during the desorption process may play a role in the reduced clay attachment upon re-adsorption, although no degradation was visually observed in Figures 8.7 and 8.8 of this study. Future work will investigate increasing the number of pre-incubation washes of the core-shell particles following desorption and incubation of the core-shell particles in pH 7.0 prior to addition of the clay which may improve re-adsorption.

Overall, it was found that clays were able to be separated from solution at pH 7.0 using the core-shell particles as carrier particles, with the magnetic separation, due to the magnetic core of the core-shell carrier particles. By increasing the pH to 11.5 and introducing shear forces through vigorous vortex mixing, the clay particulates could be removed from the core-shell particles. This desorption process may enable the magnetic removal of the core-shell carrier particles leaving behind an uncontaminated clay product. The core-shell particles were also able to be recycled; the desorption process allowing the core-shell particles to be regenerated for subsequent clay adsorption and magnetic recovery, as demonstrated through clay re-adsorption. However, the re-adsorption process was found to adsorb clays to a lesser extent than the fresh core-shell particles, especially for montmorillonite and kaolin samples. This reduction in clay adsorption is possibly the result of the degradation of the PEI-silica shell. Hence future studies will be necessary to optimise the regenerative process.

8.5 Interaction with metal/metalloid oxides: quartz and TiO₂

Metal and metalloid oxides, quartz (SiO₂) and titanium oxide (TiO₂), are important materials in a number of industrial and research fields as will be discussed in this section. The purification or extraction of these materials are therefore of economic importance.

Due to its hardness and availability, quartz in the form of sandstone or as a filler for concrete is used extensively in construction (Rafferty, 2012). The high melting temperature, low coefficient of thermal expansion and chemical inertness make relatively pure quartz ideal as a refractory material for lining furnaces and kilns. Pure quartz as a colourless, transparent material with a high lustre is mined for glass and porcelain manufacture (Rafferty, 2012). Quartz is also mined as a raw material for other processes including the manufacture of synthetic silicas (Iler, 1979; Petruk, 2000; Wason, 1987). In addition, quartz is used extensively in optics, analytical chemistry and in the development of sensitive weighing machines and chemical sensors (Brunink *et al.*, 1996; Deakin and Buttry, 1989; Makaraviciute *et al.*, 2014; Rafferty, 2012; Ramón *et al.*, 2014; Tsai, 1990).

Quartz is associated with the majority of naturally occurring ores. Froth flotation can remove quartz as part of a mixed waste stream while a hydrophobic mineral ore concentrate is recovered via the froth (Filippov *et al.*, 2013). Alternatively, quartz flotation (or reverse flotation) techniques rely on the adsorption of anionic or cationic collectors onto the quartz surface allowing the quartz to be removed in the froth concentrate (Cao *et al.*, 2013; Filippov *et al.*, 2013; Sahoo *et al.*, 2015).

As discussed in Section 2.5.1, a few studies have used magnetic carrier separation for quartz recovery. Tang *et al.*, (2017) reused magnetic waste material, referred to as EAF (electric arc furnace) dust, as carrier particles to aggregate and collect micron-sized quartz and gypsum waste particles. The magnetic carrier particle process using EAF dust was found to be highly successful at reducing the volume and settling time of the suspended waste material. However, no selectivity was achieved using this method, nor was desorption or reusability discussed for this system. Selective recovery of quartz using magnetite carrier nanoparticles was achieved with the use of dodecylamine and kerosene additives (Anastassakis, 2002). Unfortunately, additives may result in secondary contamination and reduce the recyclability of the system in comparison to more permanent means of functionalisation.

Titanium oxide (TiO₂) is a highly versatile material finding use in a number of important industrial processes including the manufacture of paint, paper and sunscreen, where TiO₂ acts to increase the opacity or add UV-resistance (Jacobs *et al.*, 2010). In nanoparticle form, TiO₂ is a non-soluble, non-toxic material with a large catalytic surface

area and high photocatalytic activity making it ideal for the degradation of organic pollutants and bacterial sterilisation (Chin *et al.*, 2010; Lee *et al.*, 2012). Thus, the selective separation of TiO_2 may be of commercial interest for the purification of TiO_2 following synthesis or the beneficiation of mined TiO_2 .

Magnetic particles functionalised with TiO₂ nanoparticles have also received academic interest for photocatalytic applications (Chin *et al.*, 2010; Yao *et al.*, 2015). TiO₂ functionalised magnetic particles combine the advantages of magnetic recovery with the high photocatalytic features of the TiO₂ nanoparticles. However, direct contact between the magnetic material and nanoparticles may decrease the photocatalytic activity of the TiO₂ (Yao *et al.*, 2015). Thus, this current work investigating the adsorption of TiO₂ nanoparticles onto the PEI-silica coated carbonyl iron particles may have an additional application in providing a novel pathway for photocatalytic pollution management.

8.5.1 Characterisation of metal/metalloid oxides: quartz and TiO₂

Before probing the interaction of quartz and TiO_2 with the core-shell particles, the oxides were characterised using SEM imaging and zeta potential measurements.

Crystalline quartz consists of a three-dimensional lattice framework of SiO₄ tetrahedrons (Clausen *et al.*, 2001). SEM imaging of the quartz sample, presented in Figure 8.10A, showed irregular crystalline fragments with a large range of sizes (~50 nm to ~5 μ m). The crystalline structure of quartz can be observed in the sharp edges and flat planes of the quartz particles. The particle fragments observed in Figure 8.10A, are similar in shape and morphology to the quartz observed by Clausen *et al.* (2001), but smaller in size than the 1.5 to 15 μ m size range they observed. The smaller size the fragments observed in Figure 8.10A may be due to the grinding performed before measurement (Section 8.2.2).



Figure 8.10. Secondary electron detector SEM images of ground fine particle metal/metalloid oxides: (A) quartz; and (B) TiO₂.

According to the manufacturer, the TiO_2 sample was comprised of ~21 nm diameter spherical nanoparticles (via TEM). However, the SEM imaging used in this work (achieving a maximum magnification of 50,000 x) could not achieve the level of resolution required to observe the individual particles. As can be observed in Figure 8.10B, the TiO_2 nanoparticles formed aggregates, some with dimensions as large as a couple of microns. Agglomeration of nanoparticles is a common occurrence noted in the literature (Salameh *et al.*, 2012). Nanoparticles in solution are often drawn together by physical long-range forces, such as the van der Waals forces (Section 8.2.3). The relatively high cohesion force experienced by particles in contact (Section 8.2.4), which for nanosized particles is higher than the thermal energy, results in a high probability of the particles remaining in contact for significant periods of time (Salameh *et al.*, 2012).

The metal/metalloid oxide samples were also characterised using zeta potential measurements taken as a function of solution pH, with the results presented in Figure 8.11.



Figure 8.11. Zeta potential as a function of pH image of ground fine particle metal/metalloid oxides: (A) quartz; and (B) TiO₂. A base electrolyte of 10.0 mM NaNO₃ pH-adjusted with 1.00 M NaOH/HCI was used for all samples.

The zeta potential curve of quartz (Figure 8.11A) is negative for the entire pH range investigated (pH 2.75 to 11.5). The charge became more negative, from -25 to -70 mV, with increasing pH from 2.8 to 11.5. These results correlate well with the literature (Burdukova *et al.*, 2010; Yuhua and Jianwei, 2005). Silanol groups (Si-OH) dominate the quartz surface upon hydration (Cao *et al.*, 2013; Clausen *et al.*, 2001). Thus, the increasingly negative surface charge with rising pH (Figure 8.11A) is the result of the dissociation of an increasing number of silanol groups. The presence of the silanol groups on the quartz surface also results in a hydrophilic surface character (Tarasevich, 2007).

The zeta potential of TiO₂ is strongly affected by pH (Figure 8.11B). The zeta potential begins positive in acidic pH before reaching the PZC at around pH 6. At pH>6, the TiO₂ zeta potential is negative, this trend correlates well with zeta potential measurements presented in the literature (Barakat, 2005). The dependence of TiO₂ zeta potential on pH can be explained by the fact that as a hydrous solid, the TiO₂ surface is comprised of Ti-OH groups. At low pH, the Ti-OH groups undergo proton association to form Ti-OH₂⁺ obtaining a positive charge. Conversely, proton dissociation to produce Ti-O⁻ groups and a negative surface charge occurs at high pH (Barakat, 2005).

8.5.2 Effect of pH on adsorption

The core-shell particle – metal/metalloid oxide interaction was examined pH values of 4.0, 7.0 and 10.0 (Section 8.3.1). SEM images, presented in Figures 8.12 and 8.13, were obtained of each sample after magnetic separation and multiple washing steps. As in Section 8.4.2, the interaction with core-shell particles with a raspberry-like morphology are presented in this section due to their superior recyclability performance in Chapter 7,

while the SEM results of the gel-like core-shell particles are presented in Appendix C (Figures C.3 and C.4).



Figure 8.12. SEM images taken of PEI-silica shell (geI-like) – carbonyl iron core particles incubated with (A-C) quartz and (D-F) TiO₂. Core-shell particles and clays were incubated in 100 mM succinic acid buffer at pH 4.0, phosphate buffer (PB) at pH 7.0 and gly-gly buffer at pH 10.0. Images taken with the secondary electron detector.





The quartz fragments can clearly be observed for the samples incubated at pH 4.0 and 7.0 (Figures 8.12A,B and 8.13A,B). In contrast to the small, spherical particles making up the raspberry-like PEI-silica shell, the quartz fragments are sharp edged and boxy (Figure 8.10A). The quartz particles also appear in the backscattered electron detector images (Figures 8.13A,B) as dark grey in colour, in contrast to the light grey of the carbonyl iron cores of the core-shell particles.

As the samples were washed multiple times before SEM imaging, the observance of quartz fragments in the pH 4.0 and 7.0 samples indicates a strong interaction between the quartz and the core-shell carrier particles. At pH 4.0 and 7.0, the quartz is negatively charged (Figure 8. 11A) while the PEI-silica is positively charged (Figure 8.1) resulting in electrostatic attraction. Slightly more quartz appeared to adsorb at pH 4.0 compared to incubation at pH 7.0 (Figures 8.12A,B and 8.13A,B). This can be explained by the

higher charge differential between the PEI-silica and quartz surfaces at pH 4.0 (Figures 8.1 and 8.11A).

The interaction between quartz particulates and amine groups, such as, those found on the PEI-silica coated surface, has been previously explored in industry and in the literature (Filippov *et al.*, 2013; Sahoo *et al.*, 2015; Wang *et al.*, 2014a; Weng *et al.*, 2014). Amine groups, including primary amine salts (dodecylamine) and ether amines, are known to have a high adsorption capacity for quartz and are widely used as cationic collectors in quartz flotation (Filippov *et al.*, 2013; Wang *et al.*, 2014a; Weng *et al.*, 2014). More recently, quaternary ammonium based ionic liquids have also been investigated for the ability to selectively associate with quartz (Sahoo *et al.*, 2015). However, molecular amine collectors do not possess the potential for extraction and reuse that the core-shell particles developed in this project do.

At pH 10.0, no quartz was observed in the SEM images of the sample. The quartz surface is even more negatively charged at pH 10.0, meanwhile, the surface of the PEI-silica shell is approaching the PZC and does not possess a sufficiently positive charge for the electrostatic adsorption the quartz particles to withstand shear forces of the washing process. This effect was also observed for montmorillonite and kaolin adsorption at pH 10.0 in Section 8.4.2.

The TiO₂ nanoparticles can be observed in the secondary electron detector SEM image as a fine powdered texture on the core-shell particle surface (Figures 8.12D-F). In the backscattered electron detector image (Figures 8.13D-F), the TiO₂ particles appear bright compared with the PEI-silica coating due to the higher average atomic number of TiO₂ particles.

TiO₂ nanoparticles adsorbed to the PEI-silica coated particles in all the incubation conditions (pH 4.0, 7.0, 10.0) tested (Figures 8.12D-F and 8.13D-F). The highest amount of TiO₂ was adsorbed at pH 7.0 (Figures 8.12E and 8.13E). Significant TiO₂ adsorption occurs at pH 7.0 and can be explained by the large difference in electrostatic charge between the negative TiO₂ (Figure 8.11B) and the positive PEI-silica surface charge (Figure 8.1) at pH 7.0, compared with pH 4.0 and 10.0.

However, at pH 10.0 the surface charge of PEI approaches neutrality (Figure 8.1) and, thus, electrostatic forces are expected to play a limited role in attachment, as was observed for quartz adsorption and clay adsorption (Section 8.5.2). In addition, at pH 4.0 both the surfaces are positively charged resulting in electrostatic repulsion between the surfaces. Therefore, the adsorption of TiO_2 nanoparticles at pH 4.0 and 10.0 (Figures

8.12D,F and 8.13D,F) likely results from a combination of the van der Waals (Section 8.2.3) and adhesion forces (Section 8.2.4).

VDW forces (Section 8.2.3) are generally attractive forces inherent between all particles in a system. In some cases, the VDW forces can overwhelm electrostatic repulsion allowing particles of the same charge to come into contact (Yuan *et al.*, 2017). This could be the reason for core-shell particle TiO_2 contact at pH 4.0 and 10.0.

The adhesion force (Section 8.2.4) is the force that holds two 'unlike' particles in contact. For nano-sized particles, the energy required to overcome the adhesion force is comparable to, or significantly greater in magnitude than, the thermal energy of the system (Israelachvili, 2011). Thus, for nanoparticles, the adhesion force has a significant effect on the behaviour of the system by extending the average-lifetime of particle-particle contact (under equilibrium conditions). The effect of the cohesion force, the adhesion force between 'like' particles, was evident in the extensive agglomeration of the TiO₂ nanoparticles in Figure 8.10B and in the literature (Salameh *et al.*, 2012). For the TiO₂ nanoparticles the adhesion force is likely to have the effect of making contact between nanoparticles and the surface more stable and less liable to thermal desorption, prolonging any TiO₂ – core-shell particle interaction.

The combination of VDW forces and adhesion effect may explain the attachment of significant amounts of TiO_2 nanoparticles adsorbed onto the PEI-silica surface at pH 4.0 and 10.0 (Figures 8.12D, F and 8.13D, F) despite of the lack of electrostatic and/or hydrophobic driving forces.

8.5.3 Adsorption-desorption cycle

The potential reusability of the PEI-silica shell – carbonyl iron core particles magnetic carrier separation system is dependent on the ability to desorb and re-adsorb the target fine particle, i.e. quartz and TiO₂. As in Section 8.5.2, the raspberry-like PEI-silica shell was chosen for the adsorption – desorption – re-adsorption cycle due to its superior performance over multiple adsorption – desorption cycles as demonstrated in Chapter 7. The adsorption and re-adsorption processes were undertaken in pH 4.0 and 7.0 for quartz and TiO₂, respectively, as these were the conditions that produced the best adsorption in Section 8.5.2. After washing, each sample was imaged by SEM using the secondary electron detector (Figure 8.14) and backscattered electron detector (Figure 8.15).



Figure 8.14. SEM images taken of PEI-silica shell (raspberry-like) – carbonyl iron core particles after adsorption of quartz at pH 4.0, desorption at pH 11.5 with 2000 rpm vortex mixing and re-adsorption at pH 4.0 (A-C) and after adsorption of TiO₂ at pH 7.0, desorption at pH 11.5 with 2000 rpm vortex mixing and re-adsorption at pH 7.0 (D-F). For adsorption and re-adsorption, core-shell particles and quartz were incubated in 100 mM succinic acid buffer at pH 4.0, while core-shell particles and TiO₂ were incubated in 100 mM phosphate buffer at pH 7.0. Incubation in 3.00 mM NaOH at pH 11.5 was used for desorption for both systems. Images taken with the secondary electron detector.



Figure 8.15. SEM images taken of PEI-silica shell (raspberry-like) – carbonyl iron core particles after adsorption of (A-C) quartz at pH 4.0, desorption at pH 11.5 with 2000 rpm vortex mixing and re-adsorption at pH 4.0 and after adsorption (D-F) TiO₂ at pH 7.0, desorption at pH 11.5 with 2000 rpm vortex mixing and re-adsorption at pH 7.0. For adsorption and re-adsorption, core-shell particles and quartz were incubated in 100 mM succinic acid buffer at pH 4.0, while core-shell particles and TiO₂ were incubated in 100 mM phosphate buffer at pH 7.0. Incubation in 3.00 mM NaOH at pH 11.5 was used for desorption for both systems. Images taken with the backscattered electron detector.

In Figures 8.14A-C and Figure 8.15A-C, samples from the adsorption – desorption – readsorption cycle of quartz were imaged. The images show both successful adsorption – re-adsorption of quartz at pH 4.0 and desorption of quartz at pH 11.5. In addition, as with Section 8.4.3, the SEM images of the core-shell particles show no disruption to the coreshell structure after the high pH and vortex mixing utilised during desorption. These results are positive indicators for the possibility of reusing the core-shell carrier separation method over multiple cycles. A similar amount of quartz was detected in the first adsorption and re-adsorption stages. In Figures 8.14D-F and 8.15D-F, TiO₂ nanoparticles appear successfully adsorbed, desorbed and re-adsorbed at pH 7.0, 11.5 and 7.0, respectively, and were magnetically separated from solution. To support the SEM results, EDX spectra were taken of the particles after adsorption at pH 7.0 and after desorption at pH 11.5. In the adsorption EDX spectrum (Figure 8.16A), a characteristic energy emission peak at 4.51 keV (Crawford *et al.*, 2011) can be observed indicating the presence of Ti following adsorption. Another characteristic emission signal for Ti is expected at 0.45 keV (Crawford *et al.*, 2011). However, this signal appears weaker and more difficult to distinguish due to its overlap with the strong core-shell particle signals of O and Fe, occurring at 0.53 and 0.71 keV, respectively (Crawford *et al.*, 2011).



Figure 8.16. EDX spectra of the raspberry-like PEI-silica shell – carbonyl iron core particles after (A) adsorption of TiO₂ at pH 7.0 and (B) desorption of TiO₂ at pH 11.5 with 2000 rpm vortex mixing. For adsorption and re-adsorption, core-shell particles and quartz were incubated in 100 mM succinic acid buffer at pH 4.0, while core-shell particles and TiO₂ were incubated in 100 mM phosphate buffer at pH 7.0. Incubation in 3.00 mM NaOH at pH 11.5 was used for desorption for both systems. The corresponding SEM image of the area analysed by EDX is given in the top right corner of each spectrum.

After TiO₂ desorption, Figure 8.16B, the Ti signal at 0.45 keV appeared extremely weak and was not identified by the EDX autodetection system. Thus, the EDX spectrum after desorption (Figure 8.16B) indicates that the majority of the TiO₂ was removed during the desorption process. Correlating with the SEM image of the desorbed core-shell particles, where a small amount of TiO₂ particles appeared to remain after adsorption.

8.6 Interaction with colloidal Au

Au nanoparticles have been found to possess a large number of advantageous properties, including a well-defined structure, facile synthesis, self-assembly, an ability to be functionalised and high stability (Mehdinia *et al.*, 2014). Thus, Au nanoparticles, among other metal nanoparticles, have attracted considerable interest as catalysts, sorbents, drug delivery agents and biosensors (Mehdinia *et al.*, 2014; Zhao *et al.*, 2013b). Au nanoparticles have also found use in the fields of electronics and optics (Mehdinia *et al.*, 2014; Zhao *et al.*, 2013b).

Through attachment to magnetic carrier particles, the applications of Au nanoparticles can be further developed. The magnetic support offers a facile method for placement and extraction of the Au nanoparticles. For example, Mehdinia *et al.* (2014) immobilised Au nanoparticles on the surface of amine functionalised mesoporous silica coated magnetite carrier support particles (final diameters <150 nm). These Au nanoparticle-coated magnetic particles were utilised as sorbents for the extraction of a key group of organic pollutants, polycyclic aromatic hydrocarbons. In Mehdinia and coworkers' (2014) study, the magnetic carrier particles allowed the Au nanoparticle sorbent to be extracted, regenerated and reused. Similarly, Ahmadi *et al.* (2014) adsorbed Au nanoparticles onto citrate ion coated Fe₃O₄ nanoparticles. Ahmadi and coworkers' Au modified Fe₃O₄ nanoparticles were designed as facile, low cost and sensitive biological sensors for the detection of the common cardiac medication, Digoxin. In addition, Fang *et al.* (2014) attached Au nanoparticles (5 nm) to thiol functionalised mesoporous silica shell – magnetite core particles (130 nm) in an effort to develop an efficient and recoverable catalyst for the oxidation of olefins.

As the applications for engineered nanomaterials, such as, Au nanoparticles, expands, so too does commercial interest in these products. Adaption of these nanomaterials for commercial use, however, results in an increased amount of these materials finding their way into the environment through various waste disposal pathways (Meisterjahn *et al.*, 2016). The increasing presence of nanomaterials in the ecosystem has raised issues relating to their possible toxicity for humans and the environment (Meisterjahn *et al.*, 2016). In the case of Au nanoparticles, several studies have brought attention to their unintentional release into the environment and related environmental toxicity (Mahapatra *et al.*, 2015; Moreno-Garrido *et al.*, 2015). Despite these worries, only a small number of studies so far have focused on the removal of disposed nanomaterials. Meisterjahn *et al.* (2016) demonstrated the removal of gold and silver nanoparticles using a Field Flow Fractionation technique where hydrodynamic principles were combined with an ultrafiltration membrane to recover nanosized particles. In contrast, Mwilu *et al.* (2014)

developed functionalised magnetic nanoparticles for the capture and removal of silica nanoparticles.

8.6.1 Interaction of PEI-silica and PEI-thiol silica shell – carbonyl iron core particles with colloidal Au

Colloidal Au nanoparticles (10 nm diameter) were investigated for their interaction with the magnetic core-shell carrier particles developed in Chapter 6. As gold possesses a well-known affinity for thiol functional groups (Fang *et al.*, 2014; Neville *et al.*, 2009), both the gel-like PEI-thiol silica and PEI-silica coated carbonyl iron particles were investigated for their interaction with Au nanoparticles.

Backscattered electron detector SEM images of the core-shell particles after the Au incubation, magnetic separation and washing steps are presented in Figure 8.17. Backscattered electron detection was chosen for this experiment as it enables the Au nanoparticles to be clearly observed. The atomic gradient contrast, available through backscattered electron detection, results in the Au nanoparticles appearing as very bright spots against the Fe and SiO₂ core shell particles. Also presented in Figure 8.17, are the EDX spectra taken of the core-shell particles to further confirm the presence of adsorbed Au nanoparticles on the core-shell particle surface.



Figure 8.17. SEM images taken of the (A) PEI-thiol silica and (C) PEI-silica coated carbonyl iron particles following incubation at pH 8.0 (100 mM phosphate buffer (PB)) with Au nanoparticles. Images were taken with the backscattered electron detector. EDX spectra of the (B) PEI-thiol silica and (D) PEI-silica coated carbonyl iron particles following incubation at pH 8.0 (100 mM phosphate buffer (PB)) with Au nanoparticles. The corresponding SEM image of the area analysed by EDX is given in the top right corner of each spectrum.

At 10 \pm 2 nm diameter (according to the manufacturer, Sigma-Aldrich), the Au nanoparticles were too small for individual detection due to the resolution limits of the SEM (Section 3.7.1). However, in Figures 8.17A,C, Au nanoparticles could be identified as bright spots on the PEI-thiol silica and PEI-silica coated surfaces. The Au nanoparticles appeared to adsorb as clusters on the PEI-thiol silica and PEI-silica surfaces, possibly signifying aggregation of the nanoparticles prior to adsorption. Overall, the clusters appeared to adsorb evenly throughout the surfaces of the core-shell particles indicating the more adsorption sites are available for higher concentrations of Au nanoparticles. In the literature, both -NH₂ and -SH surface groups have displayed strong affinity to metal nanoparticles (Fang *et al.*, 2014; Mehdinia *et al.*, 2014; Neville *et al.*, 2009). Thus, Au nanoparticle adsorption in this study likely arises due to the

nanoparticle's interaction with the amine and thiol surface groups on the PEI-thiol silica coating; and the amine surface groups on the PEI-silica coating.

Comparing the two types of shell, PEI-thiol silica (Figure 8.17A) and PEI-silica (Figure 8.17B), the PEI-thiol silica coated particles were observed to have adsorbed a slightly higher amount of Au nanoparticles. The higher adsorption of Au nanoparticles on PEI-thiol silica coating can be explained by its dual thiol/amine functionalisation, in comparison with the singular amine functionalisation available for the PEI-silica coated carrier particles. However, quantitative measurements of the amount of adsorbed Au will be required to determine how significant the difference in adsorption between the two coating types is.

The presence of Au nanoparticles was confirmed by the EDX spectra in Figures 8.17B and 8.17D for PEI-thiol silica and PEI-silica coated carbonyl iron samples, respectively. In both figures, elemental Au was identified by a strong characteristic peak at 0.22 keV accompanied by a weaker peak at 2.12 keV (Crawford *et al.*, 2011). The other characteristic Au x-ray energy peak at 9.71 keV (Crawford *et al.*, 2011) was not observed. This is because the electron beam energy selected was below the threshold level needed to excite the 9.71 keV energy band. A lower energy for the electron beam had to be selected due to the fact the sample experienced charging at higher electron beam energy.

In comparison with earlier studies (Fang et al., 2014; Mehdinia et al., 2014), the advantage of the core-shell carrier particle system for Au nanoparticle adsorption is down to the facile synthesis technique of the core-shell particles (Chapter 6). In the literature, Fang et al. (2014) introduced a thiol functionalisation to mesoporous silica-magnetite particles for Au nanoparticle adsorption. In Fang and coworkers' (2014) study, the thiol functionalisation introduced via 3was post-synthesis precipitation of mercaptopropyltrimethoxysilane (3mPTMOS). However, for the core-shell particles developed in this project, 3mPTMOS was used as the principal reactant silane for coating. Thus, this project produced a thiol-functionalisation silica coating using a single one-pot reaction. Similarly, Mehdinia et al. (2014) produced amine functionalised mesoporous silica shell for Au adsorption through the development of a post-shell synthesis, reflux polymerisation reaction utilising 3-aminopropyltriethoxysilane (APTS). For both the PEI-thiol silica and PEI-silica coated carbonyl iron particles developed in this work, the amine functionalisation was a consequence of the biomimetic silication catalyst, PEI, and required no additional functionalisation reactions. Thus, the core-shell synthesis methods developed in this project offer reductions in complexity, reagents and reaction time compared with other similar studies for the development of Au nanoparticle carriers. However, similarly to these previous studies (Fang *et al.*, 2014; Mehdinia *et al.*, 2014), no Au nanoparticle desorption was attempted due to the strength of the gold-thiol covalent bond (Jain *et al.*, 2006), especially compared to the reversibility of electrostatic/hydrophobic fine particle adsorption demonstrated in Sections 8.4 and 8.5.

8.7 Conclusions

A preliminary study was conducted to determine the suitability of the core-shell particles (developed in Chapter 6) as magnetic carrier particles for colloidal solids. Magnetic coreshell carrier particles can be developed to specifically adsorb to target materials imparting non-magnetic particles with magnetic properties. Non-magnetic materials augmented with magnetic carrier particles are then able to be separated via low cost, facile magnetic separation techniques. Magnetic carrier systems have applications in waste management, catalyst regeneration and mineral beneficiation. In this study, a large range of different target materials were investigated including clays, metal/metalloid oxides and metal nanoparticles.

Amine functionalised PEI-silica coated carbonyl iron carrier particles were investigated for their interaction with common clays (talc, montmorillonite and kaolin) and metal/metalloid oxides (quartz and TiO₂). Control over the incubation pH was observed as paramount to the successful adsorption of the target particles. Thus, at an optimum incubation pH, all target materials examined in this study were able to be successfully adsorbed onto the core-shell carrier particles and separated magnetically with the carrier particles. Desorption through vortex mixing in highly basic conditions was also successful, indicating the potential for carrier particle reusability. The results from this study indicate that for micron-sized (>100 nm) target particles both electrostatic and hydrophobic forces played a vital role in particle adsorption and desorption. While for the TiO₂ nanoparticles (diameter 21 nm), van der Waals and adhesion forces appeared to govern the adsorption behaviour.

The adsorption of Au nanoparticles was also investigated in this chapter. Au nanoparticles were successfully adsorbed onto the surface of amine and amine/thiol functionalised carrier particles (PEI-silica and PEI-thiol silica coated carbonyl iron, respectively). Of these coating types, the dual functionalised PEI-thiol silica coated carbonyl iron particles were observed to adsorb Au nanoparticles more effectively, indicating that both the amine and thiol groups were active in the Au nanoparticle adsorption process.

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This chapter has provided a way to effectively attach fine particles of various materials onto the surfaces of magnetic core - silica shell carriers which were fabricated using a one pot synthesis. Therefore, the relative simplicity of the synthesis process opens up the possibility to scale up production and, thus, utilisation of these carrier particles on a commercial scale.

CHAPTER NINE

Conclusions and future work

9.1 Conclusions

In this thesis, biomimetic fabrication of functionalised core-shell particles and their subsequent utilisation as reusable magnetic carriers was demonstrated. Prior to the experimental studies, an extensive literature review was conducted on the silica fabrication and functionalisation processes and the applications of silica coated magnetic carrier particles. Through the detailed literature review, a number of gaps in the literature were identified. These included: a lack of facile, mild surface modification techniques to functionalise the silica surface; the omission of works adapting biomimetic particle silication methods for coating; and a deficiency in non-complex, low temperature and scalable fabrication processes described for the production functionalised magnetic core – silica shell with demonstrated applicability as magnetic carrier particles.

The initial set of studies focused on the development of facile methods of silica synthesis and functionalisation, with the objective to facilitate the specific and reversible adsorption of target materials, such as, ion or mineral particles, onto the silica surface. With this focus in mind, Chapter 4 begun with the development of a novel method of silica particle synthesis, requiring only two reactants, TMOMS and NaOH, and mild reaction conditions. Characterisation of the NaOH-silica particles, found this synthesis method to be robust, producing consistent particle sizes (from DLS and SEM data) and yields, while requiring fewer reactants than previously published methods. As such, the NaOH-silica synthesis method reported in this thesis is a promising alternative to current silica particle synthesis techniques.

Chapter 4 also investigated the surface modification of the NaOH-silica particles. In this study, control over the particles' surface charge was achieved via the rapid electrostatic adsorption and acidic desorption of the branched polyamine, polyethylenimine (PEI). Successful adsorption and desorption of PEI was supported by ATR-FTIR spectral analysis, an adsorption isotherm and zeta-potential curves. PEI adsorption above a threshold PEI concentration was determined to categorically change the topography of the silica particles' zeta potential curve. Thus, the surface modification method detailed in Chapter 4, conveys a reversible, reliable method of silica particle surface charge control, which may be of particular use in tailoring surface interactions of silica or silica-coated particles.

Chapter 5 investigated another method of silica surface modification, this time focusing on biomimetically synthesised PEI-thiol silica particles. In previous studies, covalent/irreversible surface modification commonly required an intermediate stage, through which the silica surface was pretreated with a silane coupling agent. This silane

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coupling agent pretreatment was necessary to covalently link the surface and surface modifier due to the relative inertness of the silica surface. However, the pretreatment of the surface may result in an increase in cost and synthesis time. The modification method presented in Chapter 5 acted to bypass the pretreatment stage by utilising the intrinsic thiol surface groups to covalently attach various surface modifiers to the particle surface. The modified particles were characterised via zeta potential measurements and FTIR spectroscopy to assess changes surface charge and confirm the presence of the added surface functional groups. The results clearly demonstrated the capacity for one-pot modification of the biomimetic silica particles.

The second objective of this thesis was to adapt the biomimetic silication process method as a shell fabrication technique to coat magnetic carbonyl iron core particles. This process enabled the physico-chemical properties of the silica shell to be combined with the magnetic properties of the core, thus, allowing the core-shell particles to be used as magnetic carrier particles for waste recovery later in the project. In Chapter 6, the biomimetic PEI-silica and PEI-thiol silica synthesis techniques were successfully developed as coating methods. Unfortunately, the adaption of the NaOH-silica synthesis process has so far resulted in only poor coverage, with continuing development recommended for future work.

For the PEI-silica coating technique, seven possible particle coating methods were investigated as were multiple silane concentrations with a total fabrication time of less than 60 min. The PEI-silica coated carbonyl iron particles were characterized via SEM, EDX and FTIR spectroscopy. Varying the fabrication method and silane concentration successfully tuned the shell characteristics. Methods using sonication produced a smooth, evenly distributed PEI-silica shell (referred to as a gel-like coating). In contrast, a rough raspberry-like PEI-silica coating was produced via the slow addition, one- and two-pot methods. Applying similar procedures for the PEI-thiol silica reactants also produced gel-like and raspberry-like coating morphologies. Both the PEI-silica and PEI-thiol silica shell fabrication processes were successfully scaled up using batch experiments, which was a promising indicator for further scale up in future work.

The final major aim of this thesis study was to demonstrate the applicability of the coreshell particles developed in Chapter 6 as magnetic carrier particles for the recovery of target heavy metal ions (Chapter 7) and fine particle species (Chapter 8). The biomimetic fabrication of the PEI-silica shell imparted the particles with an amine surface functionalisation without the disadvantages of complex/multi-step procedures, harsh
conditions, long synthesis times and/or high temperatures which were required in previous core-shell synthesis methods.

In Chapter 7, the PEI-silica coated core-shell particles were utilised for magnetic removal of Cu(II) ions from aqueous solutions. EDX and UV-vis spectroscopic analysis of the particles and supernatant, respectively, confirmed and quantified Cu(II) adsorption and magnetic removal at pH 6.0 via the core-shell particle system. Core-shell particles with a raspberry-like PEI-silica shell exhibited superior adsorptive capacity, compared to those with a smooth gel-like shell. For the raspberry-like core-shell particles a maximum adsorption capacity of 160 ± 10 mg Cu(II) per g core-shell particles was observed, which compared favourably with other literature studies. In addition to adsorption capacity, reuse of the core-shell particles was identified as another key aspect for the core-shell recovery technology. To this aim, Cu(II) desorption at pH ~3 and re-adsorption at pH 6 were demonstrated over five cycles. Once again, the core-shell particles possessing the raspberry-like PEI-silica shell morphology were observed to perform better overall, with a small initial decrease in adsorption capacity over the first couple of cycles before stabilising. The high adsorption capacities and ability to be regenerated, demonstrate the applicability of the biomimetically synthesised core-shell particles, especially with the raspberry-like shell morphology, for use as magnetic carrier particles for heavy metal removal.

In Chapter 8, the core-shell particles developed in Chapter 6 were applied as magnetic carrier particles for the recovery of fine particle species. In this study, the amine functionalised PEI-silica coated core-shell carrier particles were investigated for their interaction with common clays (talc, montmorillonite and kaolin) and metal/metalloid oxides (quartz and TiO₂). Adsorption was determined through qualitative measurements made through SEM imaging and EDX analysis (where applicable). Successful adsorption of the target particles onto the core-shell particles was observed to be dependent on incubation pH. Thus, at optimum incubation pH, all target materials examined in this study were able to be successfully adsorbed onto the core-shell carrier particles and separated magnetically with the carrier particles. Desorption through vortex mixing in basic conditions was also successful, indicating the potential for carrier particle reusability.

Chapter 8 also examined the adsorption of Au nanoparticles onto the amine and amine/thiol functionalised carrier particles, possessing PEI-silica and PEI-thiol silica shells, respectively. Comparison of the coating types showed dual functionalised PEI-thiol silica coated core-shell particles were observed to adsorb Au nanoparticles more

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effectively, indicating that both the amine and thiol groups were active in the Au nanoparticle adsorption process. Overall, Chapter 8 demonstrated the successful adsorption and magnetic removal of fine particles utilising biomimetically fabricated PEI-silica shell – magnetic core carrier particles.

In conclusion, a rapid, facile process, utilising mild reaction conditions, was developed to synthesise and functionalise the silica shell of magnetic core-shell carrier particles. The potential for scale up was also successfully demonstrated. To demonstrate the coreshell particles suitability as magnetic carrier particles, the core-shell particles were effectively utilised for the magnetic recovery of heavy metal ion and fine particle species.

9.2 Future work

In this project, biomimetic fabrication of the functionalised core-shell particles was demonstrated, and the core-shell particles implemented as magnetic carrier particles. As an innovative work in this area, the study reported in this thesis has paved the way for a number of long- and short-term future projects. Recommendations for future projects that could be undertaken as an extension of this thesis are detailed below.

- The surface modification methods, developed in Chapters 4 and 5, describe processes for facile reversible and irreversible functionalisation of the NaOH-silica and PEI-thiol silica particle surfaces, respectively. However, these surface modification methods have not yet been implemented to functionalise the coreshell particle surface. Utilising the methodologies developed in Chapters 4 and 5 to modify the core-shell particles may act to further optimise the specificity and adsorption capacity of the core-shell particles for heavy metal ion and fine particle recovery. Future work could involve adapting and optimising the modification methods developed in Chapters 4 and 5 to functionalise the surfaces of the coreshell particles. An investigation into how surface modifications effect the performance of core-shell particles as magnetic carrier particles recovering heavy metal ions and fine particles, would also be useful.
- In Chapter 5, PEI-thiol silica particles were characterised, and the particle's thiol surface groups were utilised to covalently bond to surface modifiers through the formation of disulfide bonds. An investigation quantifying the number of thiol groups on the PEI-thiol silica particle surface in a future study will allow for further characterisation of the PEI-thiol silica particles. Moreover, this characterisation study will also determine the maximum amount of thiol groups available to form disulfide bonds during surface modification. Sahaf *et al.* (2003) utilised

fluorescent dyes to stain free surface thiol groups and spectroscopically measure the thiol groups available on the surface of cells. A similar methodology could be utilised to determine the free thiol groups present on the PEI-thiol silica surface. In addition, a comparison of the free thiol surface groups available before and after surface modification through disulfide bond formation, would useful in determining the percentage of thiol groups forming disulfide bonds and, thus, the extent to which the particle surfaces were modified using the covalent modification technique described in Chapter 5.

- PEI-silica and PEI-thiol silica syntheses methods were adapted as shell fabrication techniques used to coat carbonyl iron cores in Chapter 6. The optimisation of the shell fabrication process utilised qualitative measurements of the PEI-silica shell thickness made by comparing the EDX ratio of Si to Fe peaks. Future work building upon this study may investigate methods to quantitatively determine the thickness of the silica shells. One method that could be used to quantify silica shell thickness is as follows: (1) freeze a suspension of core-shell particles in resin, (2) polish the resin to reveal cross-sections of the core-shell particles entrapped, (3) use SEM to image the polished resin and, thus, image the cross-sectioned core-shell particles from the SEM images, (5) calculate an average shell thickness from the measurements taken.
- Through variation in the fabrication method it was observed in Chapter 6 that silica shells could be produced with two distinct morphologies: (1) a rough raspberry-like shell and (2) a smooth gel-like shell. Previous studies (Du et al., 2009a; Rubio and Hoberg, 1993) have observed surfaces with rough, raspberrylike morphologies possess hydrophobic properties. Future work investigating the hydrophobicity of the core-shell particles with raspberry-like shells produced in Chapter 6, especially in comparison to the gel-like smooth shells, will help to further characterise the core-shell particles. Furthermore, the interaction between fine particles and the core-shell particle surface investigated in Chapter 8 indicated that hydrophobicity of the core-shell particles may play a major role in the adsorption of fine particle materials onto the core-shell particle surface. Examining the hydrophobicity of the core-shell particle surface will assist in elucidating the mechanism by which targeted fine particles interact with the coreshell particle surface. Neville et al. (2016) investigated the hydrophobicity of PEIsilica and NaOH-silica particles by first pressing the particles into tablets and then measuring the contact angle of a water droplet placed on the tablet. This

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methodology could be adapted to determine the hydrophobicity of the core-shell particles fabricated in Chapter 6.

- In Chapter 7, core-shell particles were demonstrated to effectively recover Cu(II) ions from solution. The core-shell carrier particles were also able regenerated for multiple recovery cycles. Reusability could be improved by studying the stability PEI-silica carbonyl iron particles against aggregation, first through an investigation into particle aggregation using dynamic light scattering techniques, and then through examining processes to improve suspension stability of the core-shell particles. Possible methods to counter core-shell suspension instability that could be investigated include surface modification of the silica shell and introduction of stabilising additives. Investigating any degradation of the silica shell during acid desorption could also be a pathway to improving core-shell particle reusability.
- Another extension of heavy metal ion recovery work conducted in Chapter 7 • would involve the recovery of other heavy metal ions, such as, Co(II), Sn(II), Zn(II), Pb(II), Hg(II) and Mn(II), from solution. Therefore, expanding the applicability of the core-shell particles system for waste recovery applications. Techniques, such as, atomic absorption (AA) spectroscopy, could be used in conjunction with the UV-vis spectroscopy measurements (employed in Chapter 7) to quantify the concentration of heavy metal ions remaining in solution after utilising the core-shell particles for recovery. Moreover, Bao et al. (2017) demonstrated the use of dual thiol/amine functionalised core-shell for the reusable recovery of Hg(II) and Pb(II) ions. Thus, investigating the ability of thiol/amine functionalised PEI-thiol silica coated particles to adsorb and recover heavy metal ions would be an interesting future study. The results could then be contrasted with the current work which developed amine functionalised PEI-silica coated particles for recovery. Early work with the PEI-thiol silica coated particles using EDX analysis has been promising, demonstrating the successful adsorption and acidic desorption of Cu(II) (Appendix B.3).
- Chapter 8 detailed a preliminary study examining the recovery potential of the core-shell particles for fine particles. In this study, a large selection of fine particle materials were examined for their adsorption and magnetic recovery using the core-shell particles. Desorption and re-adsorption of the fine particles was also investigated to demonstrate the reusability of the particles. However, the preliminary study reported in this thesis was focused on qualitative measurements made through SEM imaging and EDX analysis (where applicable). An expansion of this work is needed in order to determine the

quantity of fine particles able to be removed by the core-shell particles and to quantify how successful fine particle recovery is over multiple adsorption – desorption cycles. Measuring the yield of recovered fine particles and/or the mass of material not recovered could be used to create a mass balance over the system and, therefore, produce a quantifiable measure of the recovery potential of the core-shell particle carrier system for each of the fine particle materials examined.

- The study in Chapter 8 could also be extended by investigating the specificity of fine particle adsorption onto the core-shell particles. In previous studies (Anastassakis, 1999; Gray *et al.*, 1994; Prakash *et al.*, 1999; Raitani *et al.*, 2012; Singh *et al.*, 2014), selectivity of fine mineral separation was demonstrated by recovering the target fine particles from a mixture of competing adsorbents. Similarly, future extensions of the work in Chapter 8 could use the core-shell particles to recover fine mineral particles from mixtures of materials created to emulate typical industrial environments, therefore, working to demonstrate and optimise the selective recovery of the targeted fine particle materials.
- Taking a more long-term approach, a number of scale up studies will be needed to prepare the core-shell particle system developed in this thesis for possible commercial use. The successful scale up of the core-shell particle fabrication process was demonstrated in this thesis for 10 and 50 times the original reaction volume. Continuation of the scale up progression, with a focus on exchanging the original batch methodology for a continuous reaction process, will be useful in producing the quantities of core-shell particles required for feasible commercial use. In addition, on the application side, an examination on how high reaction volumes and shifting to a continuous process over the original batch method would affect the surface chemistry of the core-shell particles would be necessary. In particular, an investigation on the effect of any changes to core-shell particle surface chemistry will have on the ability of the carrier particles to recover target ion and fine particle materials would also be vital to industrial scale application of this process.

In conclusion, the work of this thesis has resulted in the development of a novel fabrication process to produce functionalised silica coated magnetic particles, utilising mild reaction conditions. Moreover, Cu(II) ions and fine particle species have been successfully adsorbed and magnetically separated from aqueous solutions using the core-shell particles fabricated in this thesis project. However, future work is required to further optimise these processes, through further characterisation studies and the broadening of the core-shell particles' applications. In addition, work

is required to develop these processes for large scale production and for application as a real-world waste management solution.

CHAPTER TEN

References

Abarkan, I., Doussineau, T., Smaïhi, M. (2006). Tailored macro/microstructural properties of colloidal silica nanoparticles via microemulsion preparation. *Polyhedron, 25*, 1763-1770.

Abou El-Reash, Y.G. (2016). Magnetic chitosan modified with cysteine-glutaraldehyde as adsorbent for removal of heavy metals from water. *JECE*, *4* (4A), 3835-3847.

Ahmadi, A., Shirazi, H., Pourbagher, N., Akbarzadeh, A., Omidfar, K. (2014). An electrochemical immunosensor for digoxin using core-shell gold coated magnetic nanoparticles as labels. *Mol. Biol. Rep., 41*, 1659-1668.

Aizawa, M., Nosaka, Y., Fujii, N. (1991). FT-IR liquid attenuated total reflection study of TiO₂-SiO₂ sol-gel reaction. *J. Non-Cryst. Solids, 128* (1), 77-85.

Akurati, K.K., Dittmann, R., Vital, A., Klotz, U., Hug, P., Graule, T., Winterer, M. (2006). Silica-based composite and mixed oxide nanoparticles from atmospheric pressure flame synthesis. *J. Nanopart. Res.*, 8, 379-393.

Alcántar-Vázquez, B., Diaz, C., Romero-Ibarra, I.C., Lima, E., Pfeiffer, H. (2013). Structural and CO₂ chemisorption analyses on Na₂($Zr_{1-x}AI_x$)O₃ solid solutions. *J. Phys. Chem. C*, *117* (32), 16483-16491.

Al-Hussaini, A.S., Zoromba, M.S., El-Ghamaz, N.A. (2013). *In situ* polymerization and characterization of aniline and o-anthranilic acid copolymer/pyrogenic silica nanocomposites. *Polym. Plast. Technol. Eng.*, *5*2, 1089-1096.

Almeida, C.A.P., Debacher, N.A., Downs, A.J., Cottet, L., Mello, C.A.D. (2009). Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. *J. Colloid Interface Sci.*, 332 (1), 46-53.

Anastassakis, G.N. (1999). A study on the separation of magnesite fines by magnetic carrier methods. *Colloids Surf., A, 149* (1-3), 585-593.

Anastassakis, G.N. (2002). Separation of fine mineral particles by selective magnetic coating. *J. Colloid Inter. Sci., 256* (1), 114-120.

Anbia, M., Kargosha, K., Khoshbooei, S. (2015). Heavy metal ions removal from aqueous media by modified magnetic mesoporous silica MCM-48. *Chem. Eng. Res. Des.*, *93*, 779-788.

Anfinsen, C., Haber, E. (1961). Studies on reduction and re-formation of protein disulfide bonds. *J. Biol. Chem., 236*, 1361-1363.

Annenkov, V.V., Pal'shin, V.A., Verkhozina, O.N., Larina, L.I., Danilovtseva, E.N. (2015). Composite nanoparticles: a new way to siliceous materials and a model of biosilica synthesis. *Materials Chem. Phys.*, *165*, 227-234.

Aplan, F. (1997). The historical development of coal flotation in United States. In B.K. Parekh, J.D. Miller (Eds.), *Advances in flotation technology*. Littleton, CO: SME.

Arias, J.L., López-Viota, M., Ruiz, M.A., López-Viota, J., Delgado, A.V. (2007). Development of carbonyl iron/ethylcellulose core/shell nanoparticles for biomedical applications. *Int. J. Pham.*, 339 (1-2), 237-245.

Arriagada, F.J., Osseo-Asare, K. (1992). Phase and dispersion stability effects in the synthesis of silica nanoparticles in a non-ionic reverse microemulsion. *Colloids Surf., 69* (2-3), 105-115.

Arriagada, F.J., Osseo-Asare, K. (1995). Synthesis of nanosize silica in aerosol OT reserve microemulsions. *J. Colloid Interface Sci., 170*, 8-17.

Arriagada, F.J., Osseo-Asare, K. (1999a). Controlled hydrolysis of tetraethoxysilane in a non-ionic water-in-oil microemulsion: a statistical model of silica nucleation. *Colloids Surf., A, 154* (3), 311-326.

Arriagada, F.J., Osseo-Asare, K. (1999b). Synthesis of nanosize silica in a non-ionic water-in-oil microemulsion effects of the water/surfactant molar ratio and ammonia concentration. *J. Colloid Interface Sci.*, 211, 210-220.

Arseguel, D., Babouléne, M. (1994). Removal of phenol from coupling of talc and peroxidase. Application for depollution of waste water containing phenolic compounds. *J. Chem. Tech. Biotechnol.*, *61*, 331-335.

Ashik, U.P.M., Wan Daud, W.M.A. (2016). Stabilization of Ni, Fe, and Co nanoparticles through modified Stöber method to obtain excellent catalytic performance: preparation, characterization, and catalytic activity for methane decomposition. *J. Taiwan Inst. Chem. Eng.*, *16*, 247-260.

Ashtiani, M., Hashemabadi, S.H., Ghaffari, A. (2015). A review on the magnetorheological fluid preparation and stabilization. *J. Magn. Magn. Mater.*, 374, 716-730.

Aslan, K., Pérez-Luna, V.H. (2002). Surface modification of colloidal gold by chemisorption of alkanethiols in the presence of a non-ionic surfactant. *Langmuir, 18*, 6059-6065.

Atik, M., Zarzycki, J. (1994). Protective TiO₂-SiO₂ coatings on stainless steel sheets prepared by dip coating. *J. Mater. Sci. Letters*, *13* (17), 1301-1304

Atkins, P., de Paula, J. (2009). *Elements of physical chemistry* (5th ed.). New York, NY: Oxford University Press Inc.

Avadiar, L., Leong, Y.K. (2011). Interactions of PEI (polyethylenimine)-silica particles with citric acid in dispersions. *Colloid Polym. Sci.*, 289, 237-245.

Badertscher, M., Bühlman, P., Pretsch, E. (2009). *Structure determination of organic compounds* (4th ed.). Berlin, Germany: Springer.

Bae, D.H., Choi, H.J., Choi, K., Nam, J.D., Islam, M.S. (2017). Microcrystalline cellulose added carbonyl iron suspension and its magnetorheology. *Colloids Surf., A, 514*, 161-167.

Bagwe, R.P., Hilliard, L.R., Tan, W. (2006). Surface modification of silica nanoparticles to reduce aggregation and nonspecific binding. *Langmuir, 22*, 4357-4362.

Bai, A., Song, H., He, G., Li, Q., Yang, C., Tang, L., Yu, Y. (2016). Facile synthesis of core-shell structured ZrO₂@SiO₂ via a modified Stöber method. *Ceram. Int., 42*, 7583-7592.

Baig, R.B.N., Varma, R.S. (2014). Magnetic silica-supported palladium catalyst: synthesis of allyl aryl ether in water. *Ind. Eng. Chem. Res., 53*, 18625-18629.

Balarak, D., Jaafari, J., Hassani, G., Mahdavi, Y., Tyagi, I., Agarwal, S., Gupta, V.K. (2015). The use of low-cost adsorbent (Canola residues) for the adsorption of methylene blue from aqueous solution: isotherm, kinetic and thermodynamic studies. *Colloid Interface Sci. Communications*, *7*, 16-19.

Baldwin, D.H., Sandahl, J.F., Labenia, J.S., Scholz, N.L. (2003). Sublethal effects of copper on coho salmon: impacts on nonoverlapping receptor pathways in the peripheral olfactory nervous system. *Environ. Toxicol. Chem., 22* (10), 2266-2274.

Bao, Y., Li, Q., Xue, P., Huang, J., Wang, J., Guo, W., Wu, C. (2011). Tailoring the morphology of raspberry-like carbon black/polystyrene composite microspheres for fabricating superhydrophobic surface. *Mater. Res. Bull.*, *46*, 779–785.

Bao, Y., Shi, C., Wang, T., Li, X., Ma, J. (2016). Recent progress in hollow silica: template synthesis, morphologies and applications. *Micropor. Mesopor. Mat., 227*, 121-136.

Bao, S., Li, K., Ning, P., Peng, J., Jin, X., Tang, L. (2017). Highly effective removal of mercury and lead ions from wastewater by mercaptoamine-functionalised silica-coating magnetic nano-adsorbents: behaviours and mechanisms. *Appl. Surf. Sci.*, 393, 457-466.

Barakat, M.A. (2005). Adsorption behaviour of copper and cyanide ions at TiO₂-solution interface. *J. Colloid Inter. Sci.*, 291, 345-352.

Barrera, E.G., Livotto, P.R., dos Santos, J.H.Z. (2016). Hybrid silica bearing different organosilanes produced by the modified Stöber method. *Powder Technol., 301*, 486-492.

Battino, R., Rettich, T.R., Tominaga, T. (1983), The solubility of oxygen and ozone in liquids. *J. Phys. Chem. Ref. Data, 12* (2), 163-178.

Bazula, P.A., Arnal, P.M., Galeano, C., Zibrowius, B., Schmidt, W., Schüth, F. (2014). Highly microporous monodisperse silica spheres synthesized by the Stöber process. *Micropor. Mesopor. Mat., 200*, 317-325.

Becuwe, M., Cazier, F., Delattre, F., Landy, D., Ruellan, S., Woisel, P. (2011). Internal structure investigation of pyrogenic modified silica by fluorescent labelling. *Colloids Surf., A*, 384, 248-253.

Becuwe, M., Danjou, P.-E., Cazier, F., Woisel, P., Delattre, F. (2015). Immobilization of fluorescent chemosensor on pyrogenic silica: a promising device for gaseous detection. *J. Colloid Interface Sci., 450*, 62-67.

Belikov, S.I., Kaluzhnaya, O.V., Schöder, H.C., Krasko, A., Müller, I.M., Müller, W.E.G. (2005). Expression of silicatein in spicules from the Baikalian sponge *Lubomiroskia baicalensis*. *Cell Biol. Int.*, *29*, 943-951.

Belton, D.J., Patwardhan, S.V., Annenkov, V.V., Danilovtseva, E.N., Perry, C.C. (2008). From biosilication to tailored materials: optimizing hydrophobic domains and resistance to protonation of polyamines. *PNAS*, *105*, 5963-5968.

Bergna, H. E. (2006). Colloid science. In H.E. Bergna, W.O. Roberts (Eds.), *Colloidal silica fundamentals and applications* (pp. 575-588). Boca Raton, FL: CRC Press.

Bernecker, A., Wieneke, R., Riedel, R., Seibt, M., Geyer, A., Steinem, C. (2010). Tailored synthesis polyamines for controlled biomimetic silica formation. *J. Am. Chem. Soc., 132*, 1023-1031.

Bérubé, F., Khadhraoui, A., Janicke, M.T., Kleitz, F., Kaliaguine, S. (2010). Optimizing silica synthesis for the preparation of mesoporous Ti-SBA-15 epoxidation catalysts. *Ind. Eng. Chem. Res., 49*, 6977-6985.

Betancor, L., Luckarift, H.R. (2008). Bioinspired enzyme encapsulation for biocatalysis. *Trends Biotechn., 26*, 566-572.

Bharali, D., Klejbor, I., Stachowiak, E.K., Dutta, P., Roy, I., Kaur, N., Bergey, E.J., Prasad, P.N., Stachoiwiak, M.K. (2005). Organically modified silica nanoparticles: a nonviral vector for in vivo gene delivery and expression in the brain. *Proceedings of the PNAS*, *102* (32), 11539-11544.

Bhatta, L.K.G., Subramanyam, S., Chengala, M.D., Olivera, S., Venkatesh, K. (2015). Progress in hydrotalcite like compounds and metal-based oxides for CO₂ capture: a review. *J. Clean Prod., 103*, 171-196.

Bigui, W., Qing, C., Caixia, B., Liang, D., Guozhen, Z., Fuping, W. (2013). Surface modification of filter medium particles with silane coupling agent KH550. *Colloids Surf., A*, *434*, 276-280

Biradar, A.V., Biradar, A.A., Asefa, T. (2011). Silica-dendrimer core-shell microsphere with encapsulation ultrasmall palladium nanoparticles: efficient and easily recyclable heterogeneous nanocatalysts. *Langmuir, 27* (23), 14408-14418.

Bitar, A., Ahmad, N.M., Fessi, H., Elaissari, A. (2012). Silica-based nanoparticles for biomedical applications. *Drug Discov. Today, 17*, 1147-1154.

Bloemacher, D.I. (1990). Carbonyl iron powders: its production and new developments. *Met. Powder Rep., 45*, 117–119.

Bogush, G.H., Tracy, M.A., Zukoski, C.F. (1988). Preparation of monodisperse silica particles: control of size and fraction. *J. Non-Cryst. Solids, 104*, 95-106.

Bogush, G.H., Zukoski, C.F. (1991). Studies of the kinetics of the precipitation of uniform silica particles through the hydrolysis and condensation of silicon alkoxides. *J. Colloid Interface Sci.*, 142, 1-18.

Boldridge, D. (2010). Morphological characterization of fumed silica aggregates. *Aerosol Sci. Technol., 44*, 182-186.

Bonenfant, D., Mimeault, M., Hausler, R. (2003). Determination of the structural features of distinct amines important for the adsorption of CO₂ and regeneration in aqueous solution. *Ind. Eng. Chem. Res., 42* (14), 3179-3184.

Bonoiu, A.C., Mahajan, S.D., Ding, H., Roy, I., Yong, K., Kumar, R., Hu, R., Bergey, E.J., Schwartz, S.A., Prasad, P.N. (2009). Nanotechnology approach for drug addiction therapy: Gene silencing using delivery of golf nanorod-siRNA nanoplex in dopaminergic neurons. *PNAS*, *106*, 5546-5550.

Bootz, A., Vogel, V., Schubert, D., Kreuter, J. (2004). Comparison of scanning electron microscopy, dynamic light scattering and analytical ultracentrifugation for the sizing of poly(butyl cyanoacrylate) nanoparticles. *Eur. J. Pharm. Biopharm.*, *57*, 369-375.

Borm, P., Klaessig, F.C., Landry, T.D., Moudgil, B., Pauluhn, J. (2006). Research strategies for safety evaluation of nanomaterials, part V: role of dissolution in biological fate and effects of nanoscale particles. *Toxicol. Sci., 90* (1), 23-32.

Brinkmann, U., Ettlinger, M., Kernerm, D., Schmoll, R. (2006). Synthetic amorphous silicas. In H.E. Bergna, W.O. Roberts (Eds.), *Colloidal silica fundamentals and applications* (pp. 575-588). Boca Raton, FL: CRC Press.

Broomberg, J., Gélinas, S., Finch, J.A., Xu, Z. (1999). Review of magnetic carrier technologies for metal ion removal. *Magnetic and Electrical Separation*, *9* (3), 169-188.

Brott, L.L., Naik, R.R., Pikas, D.J., Kirkpatrick, S.M., Tomlin, D.W., Whitlock, P.W., Clarson, S.J., Stone, M.O. (2001). Ultrafast holographic nanopatterning of biocatalytically formed silica. *Letters to Nature*, *413*, 291-293.

Brunink, J.A.J., Di Natale, C., Bungaro, F., Davide, F.A.M., D'Amico, A., Paolesse, R., Boschi, T., Faccio, M., Ferri, G. (1996). The application of metalloporphyrins as coating material for quartz microbalance-based chemical sensors. *Analytica Chimica Acta, 325*, 53-64.

Brunner, E., Lutz, K., Sumper, M. (2004). Biomimetic synthesis of silica nanospheres depends on the aggregation and phase separation of polyamines in aqueous solution. *Phys. Chem. Chem. Phys.*, *6*, 854-857.

Brunner, E., Richthammer, P., Ehrlich, H., Paasch, S., Simon, P., Ueberlein, S., van Pée, K.-H. (2009). *Angew. Chem. Int. Ed., 48*, 9724-9727.

Brunner, S., Wakili, K.G. (2014). Hints for an additional aging factor regarding the thermal performance of vacuum insulation panels with pyrogenic silica core. *Vacuum, 100*, 4-6.

Burdukova, E., Bradshaw, D., Franks, G. (2010, September 6-10). *Temperature sensitive polymers as efficient and selective flotation collectors*. Paper presented at the XXV International Mineral Processing Congress (IMPC), Brisbane, Australia.

Cabot Corporation. (2011). General guide: CAB-O-SIL® fumed silica and SpectrAl® fumed alumina, 2011. Carbot Corporation website. Retrieved October 18, 2017, from http://cdn.inoxia.co.uk/documents/product-documents/CabOSil-guide.pdf

Canevari, T.C., Vinhas, R.C., Landers, R., Gushikem, Y. (2011). SiO₂/SnO₂/Sb₂O₅ microporous ceramic material for immobilization of Meldola's blue: application as an electrochemical sensor for NADH. *Biosens. Bioelectron., 26* (5), 2402-2406.

Canton, G., Riccò, R., Marinello, F., Carmignato, S., Enrichi, F. (2011). Modified Stöber synthesis of highly luminescent dye-doped silica nanoparticles. *J. Nanopart. Res., 13*, 4349-4356.

Cao, Z., Zhang, Y., Cao, Y. (2013). Reverse flotation of quartz from magnetite ore with modified sodium oleate. *Mineral Processing & Extractive Metall. Rev., 34*, 320-330.

Capozzi, C.A., Pye, L.D., Condrate, R.A. (1992). Vibrational spectral/structural changes form the hydrolysis/polycondensation of methyl-modified silicates. I. Comparisons for single monomer condensates. *Mater. Lett.*, *15*, 130-136.

Cardoso, W.S., Francisco, M.S.P., Lucho, A.M.S., Gushikem, Y. (2004). Synthesis and acidic properties of the SiO₂/SnO₂ mixed oxides obtained by the sol-gel process. Evaluation of immobilized copper hexacyanoferrate as an electrochemical probe. *Solid State Ionics, 167*, 165-173

Cassidy, P.E., Yager, B.J. (1971). Coupling agents as adhesion promoters. *J. Macromol. Sci. D, 1* (1), 1-49

Cha, J.N., Shimizu, K., Zhou, Y., Christiansen, S.C., Chmelka, B.F., Stucky, G.D., Morse, D.E. (1999). Silicatein filaments and subunits from a marine sponge direct the polymerization of silica and silicones *in vitro. PNAS*, *96*, 361-365.

Cha, J.N., Stucky, G.D., Morse, D.E., Deming, T.J. (2000). Biomimetic synthesis of order silica structures mediated by block copolypeptides. *Nature, 403*, 289-292.

Chang, C.L., Fogler, H.S. (1996). Kinetics of silica particle formation in non-ionic W/O microemulsions from TEOS. *AIChE Journal, 42*, 3153-3163.

Chattopadhyay, P., Gupta, R.B. (2003). Supercritical CO₂-based formation of silica nanoparticles using water-in-oil microemulsions. *Ind. Eng. Chem. Res.*, *4*2, 465-472.

Chen, J.W., Kalback, W.M. (1967). Effect of ultrasound on chemical reaction rate. *Ind. Eng. Chem. Fundam., 6* (2) 175–178.

Chen, M., Zhou, S., You, B., Wu, L. (2005). A novel preparation method of raspberry-like PMMA/SiO₂ hybrid microspheres. *Macromolecules*, *38* (15), 6411–6417.

Chen, L., Hu, J., Qi, Z., Fang, Y., Richards, R. (2011). Gold nanoparticles intercalated into the walls of mesoporous silica as a versatile redox catalyst. *Ind. Eng. Chem. Res., 50*, 13642-13649.

Chen, H.S., Huang, S.H., Perng, T.P. (2012). Preparation and characterization of molecularly homogeneous silica-titatia film by sol-gel process with different synthesis strategies. *ACS Appl. Mater. Interfaces, 4* (10), 5188-5195.

Chen, G., Shan, R., Li, S., Shi, J. (2015). A biomimetic silicification approach to synthesize CaO-SiO₂ catalyst for the transesterification of palm oil into biodiesel. *Fuel*, *153*, 48-55.

Chen, H., Sui, X., Zhou, C., Wang, C., Liu, F. (2016). Preparation and characterization of monolithic Al₂O₃-SiO₂ aerogel. *J. Ceram. Soc. Jpn., 124* (4), 442-447.

Chen, T., Zhao, Y., Li, H., Song, S. (2017). Effects of colloidal montmorillonite particles on froth flotation of graphite, galena and fluorite. *Physicochem. Probl. Miner. Process.*, *53* (2), 699-713.

Chermahini, A.N., Omran, M.K., Dabbagh, H.A., Mohammadnezhad, G., Teimouri, A. (2015). Application of a functionalized mesoporous silica catalyst to the synthesis of tetrazoles. *New J. Chem.*, *39*, 4814-4820.

Chevallier, Y., Prat, E. (2002). Precipitated silica. US Patent No. 6335396 B1.

Chin, C.-J.M., Chang, Y.-J., Weng, G.-J., Shen, C.-Y. (2010). Synthesis of magnetic TiO₂ nanoparticles as bactericidal photocatalyst. *Adv. Mater. Res., 123-125*, 260-263.

Chiu, S.J., Wang, S.Y., Chou, H.C., Liu, Y.L., Hu, T.M. (2014). Versatile synthesis of thiol- and amine-bifunctionalized silica nanoparticles based on the ouzo effect. *Langmuir, 30*, 7676-7686.

Choi, O., Kim, B.C., An, J.H., Min, K., Kim, Y.H., Um, Y., Oh, M.K., Sang, B.I. (2011). A biosensor based on the self-entrapment of glucose oxidase within biomimetic silica nanoparticles induced by a fusion enzyme. *Enzyme Microb. Technol., 49*, 441-445.

Chomoucka et al. (2010). Magnetic nanoparticles and targeted drug delivering. *Pharmacological Research*, *62*, 144-149.

Chung, S.H., Lee, D.W., Kim, M.S., Lee, K.Y. (2011). The synthesis of silica and silicaceria, core-shell nanoparticles in a water-in-oil (W/O) microemulsion composed of heptane and water with the binary surfactants AOT and NP-5. *J. Colloid Interface Sci.,* 355, 70-75.

Clark, B.J., Frost, T., Russell, M.A. (1993). UV spectroscopy techniques, instrumentation data handling. In *Techniques in visible and ultraviolet spectrometry* (vol. 4). Suffolk, UK: UV Spectrometry Group.

Clausen, L., Fabricius, I., Madsen, L. (2001). Adsorption of pesticides onto quartz, calcite, kaolinite, and α -alumina. *J. Environ. Qual., 30* (3), 846-857.

Coradin, T., Roux, C., Livage, J. (2002a). Biomimetic self-activated formation of multiscale porous silica in the presence of arginine-based surfactants. *J. Mater. Chem.*, *12*, 1242-1244.

Coradin, T., Durupthy, O., Livage, J. (2002b). Interactions of amino-containing peptides with sodium silicate and colloidal silica: a biomimetic approach of silicification. *Langmuir, 18*, 2331-2336.

Crawford, J., Cohen, D., Doherty, G., Atanacio, A. (2011). Calculated K, L and M-shell X-ray line intensities for light ion impact on selected targets from Z=6 to 100. ANSTO/E-774, Australian Government. Retrieved October 21, 2017, from http://www.ansto.gov.au/__data/assets/pdf_file/0016/51424/JagodaKLMabRatiosERep ortE774-ver3-07Sep11.pdf

Cui, J., Feng, Y., Yue, S., Zhao, Y., Li, L., Liu, R., Lin, T. (2016). Magnetic mesoporous enzyme-silica composites with high activity and enhanced stability. *J. Chem. Technol. Biotechnol.*, *91* (6), 1905-1913.

Dagan, G., Sampath, S., Lev, O. (1995). Preparation and utilization of organically modified silica-titania photocatalysts for decontamination of aquatic environments. *Chemical Matters*, *7*, 446-453.

Das, B., Mondal, N.K. (2011). Calcareous soil as new adsorbent to removal lead from aqueous solution: equilibrium, kinetic and thermodynamic study. *Universal Journal of Environmental Research and Technology, 1* (4), 515-530.

Deakin, M.R., Buttry, D.A. (1989). Electrochemical applications of the quartz crystal microbalance. *Anal. Chem.*, *61* (20), 1147-1154.

Delgado, A., González-Caballero, F., Bruque, J.M. (1986). On the zeta potential and surface charge density of montmorillonite in aqueous electrolyte solutions. *J. Colloid Interface Sci., 113*, 203-211.

Delgado, A.V. (2002). *Interfacial electrokinetics and electrophoresis.* New York, NY: Marcel Dekker, Inc.

Derjaguin, B.V., Muller, V.M., Toporov, Y.P. (1975). Effect of contract deformations on the adhesion of particles. *J. Colloid Inter. Sci.*, *53* (2), 314-326.

Deutsche Forschungsgemeinschaft (DFG). (1991). Silica, amorphous. In *MAK Collection for Occupational Health and Safety* (vol. 2, pp. 158-179). Germany: Wiley-VCH Verlag GmbH & Co. KGaA.

Dev, S., Bhunia, A., Boldog, I., Janiak, C. (2017). A mixed-linker approach towards improving covalent triazine-based frameworks for CO₂ capture and separation. *Microporous Mesoporous Mater.*, *241*, 303-315.

Diao, S., Zhang, S., Yang, Z., Feng, S., Zheng, C., Wang, Z., Wang, G. (2011). Effect of tetraphenylphenyl-modified fumed silica on silicone rubber radiation resistance. *J. Appl. Polym. Sci.*, *120*, 2440-2447.

Dieter, H.H., Schimmelpfennig, W., Meyer, E., Tabert, M. (1999). Early childhood cirrhoses (ECC) in Germany between 1982 and 1994 with special consideration of copper etiology. *Eur. J. Med. Res., 4* (6), 233-242.

Dingsøyr, E., Christy, A.A. (2001). Effect of reaction variables on the formation of silica particles by hydrolysis of tetraethyl orthosilicate using sodium hydroxide as a basic catalyst. *Prog. Colloid Polym. Sci.*, *116*, 67-73.

Donnet, J.B., Vrisakis, G., Coudurier, M., Baudru, B. (1981). *Processes for the manufacturing of precipitated silica*. US Patent No. US 4243428 A.

Drummond, C., McCann, R., Patwardhan, S.V. (2014). A feasibility study of the biologically inspired green manufacturing of precipitated silica. *Chem. Eng. J., 244*, 483-492.

Du, X., Liu, X., Chen, H., He, J. (2009a). Facile fabrication of raspberry-like composite nanoparticles and their application as building blocks for constructing superhydrophilic coatings. *J. Phys. Chem.*, *113*, 9063–9070.

Du, H., Hamilton, P.D., Reilly, M.A., d'Avignon, A., Biswas, P., Ravi, N. (2009b). A facile synthesis of highly water-soluble, core-shell organo-silica nanoparticles with controllable size via sol-gel process. *J. Colloid Interface Sci.*, *340* (2), 202-208.

Du, Y.-J., Jiang, N.-J., Liu, S.-Y., Jin, F., Singh, D.N., Puppala, A.J. (2014). Engineering properties and microstructural characteristics of cement-stabilized zinc-contaminated kaolin. *Can. Geotech. J.*, *51* (4), 289-302.

Dung, T.H., Kim, J., Kim, M.S., Kim, J.S., Yoo, H. (2008). Preparation and biophysical characterization of pluronic F127-dendrimer conjugate as a delivery agent of antisense oligonucleocleotides. *J. Nanosci. Nanotechnol.*, *8* (10), 5326-5330.

Durkin, C.A., Mock, T., Armbrust, E.V. (2009). Chitin in diatom and its association with cell wall. *Eukaryot. Cell, 8*, 1038-1050.

Dutcher, B., Fan, M., Russell, A.G. (2015). Amine-based CO₂ capture technology development from the beginning of 2013 – a review. *ACS Appl. Mater. Interfaces*, *7*, 2137-2148.

Dutz, S., Clement, J.H., Gelbrich, T., Hergt, R., Müller, R., Wotschadlo, J., Zeisberger, M. (2009). Ferrofluids of magnetic multicore nanoparticles for biomedical applications. *J. Magn. Magn. Mater.*, *321* (10), 1501-1504.

Elia, A., Aispuro, M., Quaranta, N., Martín-Martínez, J.M., Vázquez, P. (2011). Synthesis and characterization of new silica-titatnia mixed oxides obtained by sol-gel technique. *Macromolecular Symposia*, 301 (1), 136-145.

Erim, F.B., Cifuentes, A., Poppe, H., Kraak, J.C. (1995). Performance of a physically adsorbed high-molecular-mass polyethyleneimine layer as coating for the separation of basic proteins and peptides by capillary electrophoresis. *J. Chromatogr. A, 708* (2), 356-361.

Esch, H., Kuhlmann, R., Neumueller, M., Otto, K., Rausch, R. (1996). *Process for the production of precipitated silica*. US Patent No. US 5484581 A.

Esmaeili-Shahri, E., Es'haghi, Z. (2015). Superparamagnetic Fe₃O₄@SiO₂ core-shell composite nanoparticles for the mixed hemimicelle solid-phase extraction of benzodiazepines from hair and wastewater samples before high-performance liquid chromatography analysis. *JSS*, *38* (23), 4095-4104.

Esmaeilpour, M., Javidi, J., Zahmatkesh, S. (2016). One-pot synthesis of 1- and 5substituted 1*H*-tetrazoles using 1,4-dihydroxyanthraquinone-copper(II) supported on superparamagnetic $Fe_3O_4@SiO_2$ magnetic porous nanospheres as a recyclable catalyst. *Appl. Organomet. Chem., 30* (11), 897-904.

Esquena, J., Tadeos, T.F., Kostarelos, K., Solans, C. (1997). Preparation of narrow size distribution silica particles using microemulsions. *Langmuir, 13*, 6400-6406.

ESRL (2015). ESRL's global monitoring division, trends in atmospheric carbon dioxide 2015. Retrieved October 18, 2017, from www.esrl.noaa.gov/

Evonik Industries. (1967). Technical bulletin fine particles 11: basic characteristics of AEROSIL® fumed silica. Retrieved October 18, 2017, from aerosil.com/product/aerosol

Evonik Industries. (2015). Brazil & Germany: Evonik - Precipitated Silica. *Focus Pigm.* No. 7, 5.

Fang, Y., Chen, Y., Li, X., Zhou, X., Li, J., Tang, W., Huang, J., Jin, J., Ma, J. (2014). Gold on thiol-functionalized magnetic mesoporous silica sphere catalyst for the aerobic oxidation of olefins. *J. Mol. Catal. A, 392*, 16-21.

Faramawy, S., El-Naggar, A.Y., El-Fadly, A.M., El-Sabagh, S.M., Ibrahim, A.A. (2011). Silica, alumina and aluminosilicates as solid stationary phases in gas chromatography. *Arab. J. Chem.,* DOI: 10.1016/j.arabjc.2011.08.015.

Feng, B., Lu, Y., Feng, Q., Zhang, M., Gu, Y. (2012). Talc-serpentine interaction and implication for talc depression. *Miner. Eng.*, *3*2, 68-73.

Feng, B., Peng, J., Guo, W., Zhu, X., Huang, W. (2017). The stimulus response of chitosan and its depression effect on talc flotation. *Miner. Process. Extr. Metall.*, DOI: 10.1080/03719553.2017.1288358

Ferch, H.K. (2006). Industrial synthetic silicas in powder form. In H.E. Bergna, W.O. Roberts (Eds.), *Colloidal silica fundamentals and applications* (pp. 187-199). Boca Raton, FL: CRC Press.

Fernandes, J.C., Henriques, F.S. (1991). Biochemical, physiological, and structural effects of excess copper in plants. *The Botanical Review, 57* (3), 246-273.

Fernandes, M.T.C., Garcia, R.B.R., Leite, C.A.P., Kawachi, E.Y. (2013). The competing effect of ammonia in the synthesis of iron oxide/silica nanoparticles in microemulsion/sol-gel system. *Colloids Surf., A, 422*, 136-142.

Figeys, D., Aebersold, R. (1997). Capillary electrophoresis of peptides and proteins at neutral pH in capillaries covalently coated with polyethyleneimine. *J. Chromatogr. B, 695* (91), 163-168.

Filipović, R., Obrenović, Z., Stijepović, I., Nikolić, L.M., Srdić, V.V. (2009). Synthesis of mesoporous silica particles with controlled pore structure. *Ceram. Int., 35*, 3347-3353.

Filippov, L.O., Severov, V.V., Filippova, I.V. (2013). An overview of the beneficiation of iron ores via reverse cationic flotation. *Int. J. Miner. Process.*, *127*, 62-69.

Finnie, K.S., Bartlett, J.R., Barbé, C.J.A., Kong, L. (2007). Formation of silica nanoparticles in microemulsions. *Langmuir, 23*, 3017-3024.

Flagan, R.C., Mori, Y. (2006). Generation of particle by reaction. In H. Masuda, K. Higashitani, H. Yoshida (Eds.), *Powder Technology Handbook* (3rd ed., pp. 413-418). Boca Raton, FL: CRC Press.

Forsyth, C., Yip, T.W.S., Patwardhan, S.V. (2013). CO₂ sequestration by enzyme immobilized onto bioinspired silica. *Chem. Commun.*, *4*9, 3191-3193.

Friedman, G., Yellen, B. (2005). Magnetic separation, manipulation and assembly of solid phase in fluid. *Curr. Opin. Colloid Interface Sci., 10*, 158-166.

Funayama, N., Nakatsukasa, M., Kuraku, S., Takechi, K., Dohi, M., Iwabe, N., Miyata, T., Agata, K. (2005). Isolation of Ef silicatein and Ef lectin as molecular markers sclerocytes and cells involved in innate immunity in the freshwater sponge *Ephydatia Fluviatilis*. *Zool. Sci.*, *22*, 1113-1122.

Funes, A., de Vicente, J., Cruz-Pizarro, L., de Vicente, I. (2014). The influence of pH on manganese removal by magnetic microparticles in solution. *Water Res.*, *53*, 110-122.

Galet, L., Dodds, J. (2009). The importance of surface energy in the dispersion behaviour of talc particles in aqueous media. *Powder Technol., 190*, 242-246.

Gawande, M.B., Goswami, A., Asefa, T., Guo, H., Biradar, A.V., Peng, D.-L., Zboril, R., Varma, R.S. (2015). Core-shell nanoparticles: synthesis and applications in catalysis and electrocatalysis. *Chem. Soc. Rev.*, *44*, 7540-7590.

Geszke-Moritz, M., Moritz, M. (2016). APTES-modified mesoporous silicas as the carriers for poorly water-soluble drug. Modeling of diflunisal adsorption and release. *Appl. Surf. Sci., 368*, 348-359.

Ghosh, P., Han, G., De, M., Kim, C.K., Rotello, V. M. (2008). Gold nanoparticles in delivery applications. *Adv. Drug Deliv. Rev., 60* (11), 1307-1315.

Gill, I., Ballesteros, A. (1998). Encapsulation of biologicals within silicate, siloxane and hybrid sol-gel polymers: an efficient and generic approach. *J. Am. Chem. Soc., 120*, 8587-8598.

Gill, I., Ballesteros, A. (2000). Bioencapsulation within synthetic polymers (part 1): solgel encapsulated biologicals. *TIBTICH, 18*, 282-296. Goeppert, A., Meth, S., Prakash, G.K.S., Olah, G.A. (2010). Nanostructured silica as a support for regenerable high-capacity organoamine-based CO₂ sorbents. *Energy Environ. Sci., 3*, 1949-1960.

González-Ruiz, V., Olives, A.I., Martín, M.A. (2015). Core-shell particles lead the way to renewing high-performance liquid chromatography. *Trends Anal. Chem., 64*, 17-28.

Goodwin, J.W. (2004). *Colloids and interfaces with surfactants and polymers - an introduction*. Portland, Oregon: John Wiley & Sons, Ltd.

Gorbachuk, V.V., Yakimova, L.S., Mostovaya, O.A., Bizyaev, D.A., Bukharaev, A.A., Antipin, I.S., Konovalov, A.I., Zharov, I., Stoikov, I.I. (2011). Silica nanoparticles with proton donor and proton acceptor groups: synthesis and aggregation. *Silicon, 3* (1), 5-12.

Grasset, F., Marchand, R., Marie, A.M., Fauchadour, D., Fajardie, F. (2006). Synthesis of CeO₂@SiO₂ core-shell nanoparticles by water-in-oil microemulsion. Preparation of functional thin firm. *J. Colloid Interface Sci., 299*, 726-732.

Gray, S.R., Langberg, D.E., Gray, N.B. (1994). Fine mineral recovery with hydrophobic magnetite. *Int. J. Miner. Process.*, *41*, 183-200.

Guerrero-Martínez, A., Pérez-Juste, J., Liz-Marzán, L. M. (2010). Recent progress on silica coating of nanoparticles and related nanomaterials. *Adv. Mater.*, *22*, 1182-1195.

Guo, D., Xie, G., Luo, J. (2014). Mechanical properties of nanoparticles: basics and applications. *J. Phys. D: Appl. Phys.*, *47*, 1-25.

Guo, L., Zhao, X., Zhang, R., Chen, C., Chen, J., Chen, A., Liu, X., Hou, Z. (2016). Mesoporous spherical silica encapsulating Pd nanoparticles prepared by CO₂-induced microemulsion and catalytic application in Suzuki coupling reaction. *J. Supercrit. Fluids., 107*, 715-722.

Gutha, Y., Zang, Y., Zhang, W., Jiao, X. (2017). Magnetic-epichlorohydrin crosslinked chitosan schiff's base (m-ECCSB) as a novel adsorbent for the removal of Cu(II) ions from aqueous environment. *Int. J. Biol. Macromol.*, *97*, 85-98.

Gutiérrez, L., Costo, R., Grüttner, C., Westphal, F., Heinke, D., Fornara, A., Pankhurst, Q.A., Johansson, C., Veintemillas-Verdaguer, S., Morales, M.P. (2015). *Dalton Trans., 44*, 2943-2952.

Hagar, W.J., Gallis, K.W. (2011). *Continuous silica production process and silica product prepared from same.* US Patent No. US 20110206746 A1.

Hamaker, H.C. (1937). The London-van der Waals attraction between spherical particles. *Physica, 4* (10), 1058-1072.

Hamade, R., Okahata, Y., Yamamori, N. (1998). *Glucoxide derivatives for enzyme modification, lipid-coated enzymes, method of producing such enzymes and antifouling paint composition.* US Patent No. US 5770188 A.

Han, W., MacEwan, S.R., Chilkoti, A., López, G.P. (2015). Bio-inspired synthesis of hybrid silica nanoparticles templated from elastin-like polypeptide micelles. *Nanoscale, 7*, 12038-12044.

Hao, X., Hu, X., Zhang, C., Chen, S., Li, Z., Yang, X., Liu, H., Jia, G., Liu, D., Ge, K., Liang, X.–J., Zhang, J. (2015). Hybrid mesoporous silica-based drug carrier nanostructures with improved degradability by hydroxyapatite. *ASC Nano, 9*, 9614-9625.

Harbi, R., Derabla, R., Nafa, Z. (2017). Improvement of the properties of a mortar with 5% of kaolin fillers in sand combined with metakaolin, brick waste and glass powder in cement. *Construction and Building Materials, 152*, 632-641.

Harris, D.C. (2010). *Quantitative chemical analysis* (8 ed.). New York, NY: W.H. Freeman and Co.

Hatahet, F., Boyd, D., Beckwith, J. (2014), Disulfide bond formation in prokaryotes: history, diversity and design. *Biochim. Biophys. Acta, 1844*, 1402-1414.

Hayes, W.A., Shannon, C. (1996). Electrochemistry of surface-confined mixed monolayers of 4-aminothiophenol and thiophenol on Au. *Langmuir, 12*, 3688-3694.

He, P., Greenway, G., Haswell, S.J. (2008). The on-line synthesis of enzyme functionalized silica nanoparticles in a microfluidic reactor using polyethyleneimine polymer and R5 peptide. *Nanotechnology*, 19, 315603-315610.

He, P., Greenway, G., Haswell, S.J. (2011). Microfluidic synthesis of silica nanoparticles using polyethylenimine polymers. *Chem. Eng. J., 167*, 694-699.

He, D., Wang, S., Lei, L., Hou, Z., Shang, P., He, X., Nie, H. (2015). Core-shell particles for controllable release of drug. *Chem. Eng. Sci.*, *125*, 108-120.

Hedrich, R., Machill, S., Brunner, E. (2013). Biomineralization in diatoms – phosphorylated saccharides are part of *Stephanopyxis turris* biosilica. *Carbohydr. Res., 365*, 52-60.

Hernández-Pardròn, G., Rodriguez, R., Castañro, V.M. (2004). *In-situ* thiol-modified silica nanoparticles. *The Internet Journal of Nanotechnology, 1* (2).

Hewitt, N. (2007). *Compounding precipitated silica in elastomers: theory and practice*. Norwich, NY: William Andrew Inc.

Hildebrand, M., Kim, S., Shi, D., Scott, K., Subramaniam, S. (2009a). 3D Imaging of diatoms with ion-abrasion scanning electron microscopy. *J. Struct. Biol.*, *166*, 316-328.

Hildebrand, M., Holton, G., Joy, D.C., Doktycz, M.J., Allison, D.P. (2009b). Diverse and conserved nano- and mesoscale structures of diatom silica revealed by atomic force microscopy. *J. Microsc., 235*, 172-187.

Hu, J.-J., Hsieh, Y.-H., Jan, J.-S. (2015). Polyelectrolyte complex-silica hybrid colloidal particles decorated with different polyelectrolytes. *J. Colloid Interface Sci., 438*, 94-101.

Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L., Zhang, Q. (2012). Heavy metal removal from water/wastewater by nanosized metal oxide: a review. *J. Hazard. Mater., 211-212*, 317-3311.

Huang, J., Zhang, K., Wang, K., Xie, Z., Ladewig, B., Wang, H. (2012). Fabrication of polyethersulfone-mesoporous silica nanocomposite ultrafiltration membranes with antifouling properties. *J. Membr. Sci., 423-424*, 362-370.

Huang, Z., Yao, Y., Che, S. (2014). Design of amphiphilic peptide geometry towards biomimetic self-assembly of chiral mesoporous silica. *Chem. Eur. J., 20*, 3273-3276.

Huang, Y.-T., Shih, M.-C. (2016). Effect of linearized expressions of Langmuir equations on the prediction of the adsorption of methylene blue on rice husk. *IJSRP, 6* (4), 549-554.

Huber, D.L. (2005). Synthesis, properties, and applications of iron nanoparticles. *Small, 1* (5), 482-501.

Huber Engineered Materials. (2012). Huber's Expansion of Its Precipitated Silica Plant in India on Track for Completion in 2012. Published Atlanta, March 12, 2012. Retrieved October 18, 2017, from http://www.hubermaterials.com/news/

Huo, Q., Feng, J., Schüth, F, Stucky, G.D. (1997). Preparation of hard mesoporous silica spheres. *Chem. Mater.*, *9*, 14-17.

Hurd, A.J., Flower, W.L. (1987). *In situ* growth and structure of fractal silica aggregates in a flame. *J. Colloid Interface Sci., 122*, 178-192.

Ibrahim, I.A.M., Zikry, A.F.F., Sharaf, M.A. (2010). Preparation of spherical silica nanoparticles: Stöber silica. *J. Am. Sci.*, *6*, 985-989.

Idrus, S.S., Ismail, H., Palaniandy, S. (2011). Study of the effect of different shapes of ultrafine silica as fillers in natural rubber compounds. *Polym. Test.*, *30*, 251-259.

IEAGHG. (2010). Environmental impacts of amine emissions during post combustion capture workshop, 2010/11, June 2010. Cheltenham, UK: IEA Environmental Projects Ltd. (IEAGHG).

Iler, R.K. (1979). The chemistry of silica. New York, NY: John Wiley & Sons, Inc.

Isobe, H., Kaneko, K. (1999). Porous silica particles prepared from silicon tetrachloride using ultrasonic spray method. *J. Colloid Interface Sci., 212*, 234-241.

Israelachvili, J.N. (2011). *Intermolecular and surface forces* (3rd ed.). Santa Barbara, CA: Academic Press.

Issa, B., Obaidat, I.M., Albiss, B.A., Haik, Y. (2013). Magnetic nanoparticles: surface effects and properties related to biomedicine applications. *Int. J. Mol. Sci., 14* (11), 21266-21305.

Jacobs, J.F., van de Poel, I., Osseweijer, P. (2010). Sunscreens with titanium dioxide (TiO₂) nano-particles: a societal experiment. *NanoEthics, 4* (2), 103-113.

Jaganathan, H., Godin, B. (2012). Biocompatibility assessment of Si-based nano- and micro-particles. *Adv. Drug Delivery Rev., 64*, 1800-1819.

Jain, P.K., Qian, W., El-Sayed, M.A. (2006). Ultrafast cooling of photoexcited electrons in gold nanoparticles-thiolated DNA conjugated involves the dissociation of the gold-thiol bond. *J. Am. Chem. Soc.*, *128*, 2426-2433.

Jal, P.K., Patel,S., Mishra, B.K. (2004). Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. *Talanta, 62*, 1005-1028.

Jan, J.-S., Lee, S., Carr, C.S., Shantz, D.F. (2005). Biomimetic synthesis of inorganic nanospheres. *Chem. Mater.*, *17*, 4310-4317.

Javidi, J., Esmaeilpour, M. (2016). Fe₃O₄@SiO₂-imid-PMAn magnetic porous nanosphere as recyclable catalyst for green synthesis of quinoxaline derivatives at room temperature and study of their antifungal activities. *Mater. Res. Bull.*, *73*, 409–422.

Jensen, K.A., Saber, A.T. (2015). Case study: paints and lacquers with silica nanoparticles. In W. Wohlleben, T.A.J. Kuhlbusch, J. Schnekenburger, C.M. Lehr (Eds.), *Safety of nanomaterials along their lifecycles: release, exposure and human hazard* (pp. 381-398). Boca Raton, FL: CRC Press.

Jesionowski, T., Krysztafkiewicz, A. (2001). Influence of silane coupling agents on surface properties of precipitated silicas. *Appl. Surf. Sci., 172*, 18-32.

Ji, H.F., Hansen, K.M., Hu, Z., Thundat, T. (2001). Detection of pH variation using modifier microcantilever sensors. *Sens. Actuators, B, 72*, 233-238.

Jiang, F., Fu, Y., Zhu, Y., Tang, Z., Sheng, P. (2012). Fabrication of iron oxide/silica coreshell nanoparticles and their magnetic characteristics. *J. Alloys Compd.*, *543*, 43-48.

Jiang, K., Dickinson, J.E., Galvin, K.P. (2016). Two-stage fast flotation of coal tailings using reflux flotation. *Miner. Eng.*, *98*, 151-160.

Jiles, D.C. (1998). Introduction to magnetism and magnetic materials (2nd ed.). Boca Raton, FL: CRC Press.

Jin, R.-H., Yuan, J.-J. (2005). Poly(ethyleneimine) aggregates pre-organized by media modulation. *Macromol. Chem. Phys., 206*, 2160-2170.

Jin, R.-H., Yuan, J.-J. (2007). One-pot and rapid synthesis of uniformed silica spheres via mediation of linear poly(ethyleneimine)s and dyes. *Polym. J.,* 39, 822-827.

Jin, C., Wang, Y., Wei, H., Tang, H., Liu, X., Lu, T., Wang, J. (2014). Magnetic iron oxide nanoparticles coated by hierarchically structured silica: a highly stable nanocomposite system and ideal catalyst support. *J. Mater. Chem. A*, *2*, 11202-11208.

Jo, K., Ishizuka, M., Shimabayashi, K., Ando, T. (2014). Development of new mineral oilbased antifoams containing size-controlled hydrophobic silica particles for gloss paints. *J. Oleo Sci., 63*, 1303-1308.

Johnson, K.L., Kendall, K., Roberts, A.D. (1971). Surface energy and the contact of elastic solids. *Proc. R. Soc. Lond. A., 324*, 301-313.

Joo, S.H., Park, J.Y., Tsung, C.-K., Yamada, Y., Yang, P., Somorjai, G.A. (2009). Thermally stable Pt/mesoporous silica core-shell nanocatalysts for high-temperature reactions. *Nat. Mater.*, *8*, 126-131.

Jung, H.S., Kwon, S.H., Choi, H.J., Jung, J.H., Kim, Y.G. (2016). Magnetic carbonyl iron/natural rubber composite elastomer and its magnetorheology. *Composite Structures*, *136*, 106-112.

Kalantari, M., Kazemeini, M., Arpanaei, A. (2013). Facile fabrication and characterization of amino-functionalized Fe_3O_4 cluster@SiO_2 core/shell nanocomposites spheres. *Mater. Res. Bull., 48* (6), 2023-2028.

Kalantari, K., Ahmad, M.B., Fard Masoumi, H.R., Shameli, K., Basri, M., Khandanlou, R. (2015). Rapid and high capacity adsorption of heavy metals by Fe₃O₄/montmorillonite nanocomposite using response surface methodology: preparation, characterization, optimization, equilibrium isotherms, and adsorption kinetics. *Engineers, 49,* 192-198.

Kawachi, Y., Kugimiya, S., Nakamura, H., Kato, K. (2014). Enzyme encapsulation in silica gel prepared by polylysine and its catalytic activity. *Appl. Surf. Sci., 314*, 64-70.

Kawaguchi, T., Ono, K. (1990). Spherical silica gels precipitated from acid catalyzed TEOS solutions. *J. Non-Cryst. Solids, 121*, 383-388.

Kciuk, M., Kciuk, S., Turczyn, R. (2009). Magnetorheological characterisation of carbonyl iron based suspension. *JAMME*, *33* (2), 135-141.

Kempen, P.J., Greasley, S., Parker, K.A., Campbell, J.L., Chang, H.Y., Jones, J.R., Sinclair, R., Gambhir, S.S., Jokerst, J.V. (2015). Theranostic mesoporous silica nanoparticles biodegrade after pro-survival drug delivery and ultrasound/magnetic resonance imaging of stem cells. *Theranostics*, *5*, 631-642.

Khakharia, P., Brachert, L., Mertens, J., Huizinga, A., Schallert, B., Schaber, K., Vlugt, T.J.H., Goetheer, E. (2013). Investigation of aerosol based emission of MEA due to sulphuric acid aerosol and soot in a post combustion CO₂ capture process. *Int. J. Greenh. Gas Control, 19*, 138-144.

Khan, S.A., Güther, A., Schmidt, M.A., Jensen, K.F. (2004). Microfluidic synthesis of colloidal silica. *Langmuir, 20*, 8604-8611.

Khodadadi, M., Malekpour, A., Ansaritabar, M. (2017). Removal of Pb(II) and Cu(II) from aqueous solutions by NaA zeolite coated magnetic nanoparticles and optimization of method using experimental design. *Microporous Mesoporous Mater.*, *248*, 256-265.

Ki, M.-R., Jang, E.-K., Pack, S.P. (2014). Hypothetical cathepsin-like protein from *Nematostella vectensis* and its silicatein-like cathepsin mutant for biosilica production. *Process Biochem., 49*, 95-101.

Kim, J.K., Park, J.K., Kim, H.K. (2004). Synthesis and characterization of nanoporous silica support for enzyme immobilization. *Colloids Surf., A, 241*, 113-117.

Kim, J., Grate, J.W., Wang, P. (2008). Nanobiocatalysis and its potential applications. *Trends Biotechnol.*, *26*, 639-646.

Kindler, W.A., Sawnson, J.W. (1971). Adsorption kinetics in the polyethyleneiminecellulose fiber system. *J. Polym. Sci., Part B: Polym. Phys., 9* (5), 853-865. Klopfer, H. (1952). Verfahren zum Reinigen von hochdispersen Oxyden von Metallen bzw. Metalloiden. German Patent No. DE 762723 C.

Knecht, M.R., Wright, D.W. (2003). Functional analysis of the biomimetic silica precipitating activity of the R5 peptide from *Cylindrotheca fusiformis*. *Chem. Commun., 2003* (24), 3038-3039.

Knecht, M.R., Wright, D. W. (2004) Amine-Terminated Dendrimers as Biomimetic Templates for Silica Nanosphere Formation. *Langmuir, 20*, 4728-2732.

Knecht, M.R., Sewell, S.L., Wright, D.W. (2005). Size control of dendrimer-templated silica. *Langmuir*, *21*, 2058-2061.

Kneuer, C., Sameti, M., Bakowsky, U., Schiestel, T., Schirra, H., Schmidt, H., Lehr, C. (2000a). A nonviral DNA delivery system based on surface modified silica-nanoparticles can efficiently transfect cells *in vitro*. *Bioconjugate Chem.*, *11*, 926-932.

Kneuer, C., Sameti, M., Haltner, E.G., Schiestel, T., Schirra, H., Schmidt, H., Lehr, C. (2000b). Silica nanoparticles modified with aminosilanes as carriers for plasmid DNA. *Int. J. Pharm.*, *196*, 257-261.

Knopp, D., Tang, D., Niessner, R. (2009). Review: bioanalytical applications of biomolecule-functionalized nanometer sized doped silica particles. *Anal. Chim. Acta, 647*, 14-30.

Kobayashi, Y., Katakami, H., Mine, E., Nagao, D., Konno, M., Liz-Marzán, L.M. (2005). Silica coating of silver nanoparticles using a modified Stöber method. *J. Colloid Interface Sci.*, 283, 392-396.

Kobler, J., Möller, K., Bein, T. (2008). Colloidal suspensions of functionalized mesoporous silica nanoparticles. *ASC Nano*, *2*, 791-799.

Kolesar, G.B., Siddiqui, W.H., Geil, R.G., Malczewski, R.M., Hobbs, E.J. (1989). Subchronic inhalation toxicity of tetramethoxysilane in rats. *Toxicol. Sci.*, *13*, 285-295.

Kopp, W., Silva, F.A., Lima, L.N., Masunaga, S.H., Tardioli, P.W., Giodano, R.C., Araugo-Moreira, F.M., Giordanoo, R.L.C. (2015). Synthesis and characterization of robust magnetic carriers for bioprocess applications. *Mater. Sci. Eng. B*, *193*, 217-228.

Krasko, A., Lorenz, B., Batel, R., Schröder, H.C., Müller, I.M., Müller, W.E.G. (2000). Expression of silicatein and collagen genes in the marine sponge *Suberites domuncula* is controlled by silicate and myotrophin. *Eur. J. Biochem., 267*, 4878-4887.

Kröger, N., Deutzmann, R., Sumper, M. (1999). Polycationic peptides from diatom biosilica that direct silica nanosphere Formation. *Science*, *286* (5442), 1129-1132.

Kröger, N., Deutzmann, R., Bergsdorf, C., Sumper, M. (2000). Species-specific polyamines from diatoms control silica morphology. *PNAS*, *97*, 14133-14138.

Kröger, N., Deutzmann, R., Sumper, M. (2001). Silica-precipitating peptides from diatoms: the chemical structure of silaffin-1A from Cylindrotheca fusiformis. J. Biol. Chem., 276, 26066-26070.

Kröger, N., Lorenz, S., Brunner, E., Sumper, M. (2002). Self-assembly of highly phosphorylated silaffins and their function in biosilica morphogenesis. *Science*, *298*, 584-586.

Kröger, N. (2007). Prescribing diatom morphology: toward genetic engineering of biological nanomaterials. *Curr. Opin. Chem. Biol.*, *11*, 662-669.

Kröger, N., Poulsen, N. (2008). Diatoms – from cell wall biogenesis to nanotechnology. *Annu. Rev. Genet.*, *4*2, 83-107.

Kröger, N., Poulsen, N. (2013). Diatoms – from cell wall biogenesis to nanotechnology. *Annu. Rev. Genet.*, *4*2, 83-107.

Kuan, I.-C., Wu, J.-C., Lee, S.-L., Tsai, C.-W., Chuang, C.-A., Yu, C.-Y. (2010). Stabilization of D-amino acid oxidase from *Rhodosporidium toruloides* by encapsulation in polyallylamine-mediated biomimetic silica. *Biochem. Eng. J., 49*, 408-413.

Kuan, I.-C., Lee, C.-C., Tsai, B.-H., Lee, S.-L., Lee, W.-T., Yu, C.-Y. (2013). Optimizing the production of biodiesel using lipase entrapped in biomimetic silica. *Energies, 6*, 2052-2064.

Kumari, M., Pittman Jr., C.U., Mohan, D. (2015). Heavy metals [chromium (VI) and lead (II)] removal from water using mesoporous magnetite (Fe₃O₄) nanospheres. *J. Colloid Interface Sci., 44*2, 120-132.

Lai, J.-K., Chuang, T.-H., Jan, J.-S., Wang, S.S.-S. (2010). Efficient and stable enzyme immobilization in a block copolypeptide vesicle-templated biomimetic silica support. *Colloids Surf., B, 80*, 51-58.

Launer, P.J. (1987). Infrared analysis of organosilicon compounds: spectra-structure correlations. In *Silicone compounds register and review*. Bristol, PA: Petrarch Systems.

Laurent, S., Forge, D., Port, M., Roch, A., Robic, C., Elst, L.V., Muller, R.N. (2008). Magnetic iron oxide nanoparticles: synthesis stabilization, vectorization, physiochemical characterizations, and biological applications. *Chem. Rev., 108*, 2064-2110.

Lavelle, P., Spain, A.V. (2003). *Soil ecology*. New York, NY: Kluwer Academic Publishers.

Lawrance, G.A. (2010). *Introduction to coordination chemistry*. West Sussex, UK: John Wiley & Sons Ltd.

Leblanc, J.L. (2010). *Filled polymers: science and industrial applications*. Boca Raton, FL: CRC Press.

Lechner, C.C., Becker, C.F.W. (2012). Exploring the effect of native and artificial peptide modifications on silaffin induced silica precipitation. *Chem. Sci., 3*, 3500-3504.

Lechner, C.C., Becker, C.F.W. (2015). Silaffins in silica biomineralization and biomimetic silica precipitation. *Mar. Drugs, 13*, 5297-5333.

Lee, Y.G., Park, J.H., Oh, C., Oh, S.G., Kim, Y.C. (2007). Preparation of highly monodispersed hybrid silica spheres using one-step sol-gel reaction in aqueous solution. *Langmuir, 23* (22), 10875-10878.

Lee, J., Lee, Y., Youn, J.K., Na, H.B., Yu, T., Kim, H., Lee, S.-M., Koo, Y.-M., Kwak, J.H., Park, H.G., Chang, H.N., Hwang, M., Park, J.-G., Kim, J., Hyeon, T. (2008). Simple synthesis of functionalized superparamagnetic magnetite/silica core/shell nanoparticles and their application as magnetically separable high-performance biocatalysts. *Small, 4*, 143-152.

Lee, Y.-C., Kim, J.-Y., Shin, H.-J. (2012). Removal of malachite green (MG) from aqueous solutions by adsorption, precipitation, and alkaline fading using talc. *Sep. Sci. Technol., 48* (7), 1093-1101.

Li, Y., Benicewicz, B.C. (2005). Synthesis of well-defined polymer brushes grafted onto silica nanoparticles via surface reversible addition-fragmentation chain transfer polymerization. *Macromolecules, 38* (14), 5929-5936.

Li, Y., Benicewicz, B.C. (2008). Functionalization of silica nanoparticles via the combination of surface-initiated RAFT polymerization and click reactions. *Macromolecules, 41* (21), 7986-7992.

Li, X., Yang, T., Gao, Q., Yuan, J., Cheng, S. (2009a). Biomimetic synthesis of copolymer-silica nanoparticles with tunable compositions and surface properties. *J. Colloid Interface Sci.*, 338, 99-104.

Li, J.H., Hong, R.Y., Li, H.Z., Ding, J., Zheng, Y., Wei, D.G. (2009b). Simple synthesis and magnetic properties of Fe₃O₄/BaSO₄ multi-core/silica particles. *Mater. Res. Phys., 113*, 140–144.

Li, H., Xiao, D.-L., He, H., Lin, R., Zuo, P.-L. (2013a). Adsorption behavior and adsorption mechanism of Cu(II) ions on amino-functionalized magnetic nanoparticles. *Trans. Nonferrous Met. Soc. China, 23*, 2657-2665.

Li, X., Niitsoo, O., Couzis, A. (2013b). Electrostatically driven adsorption of silica nanoparticles on functionalized surfaces. *J. Colloid Interface Sci., 394*, 26-35.

Li, J., Xu, L., Yang, B., Bao, Z., Pan, W., Li, S. (2015). Biomimetic synthesized chiral mesoporous silica: structures and controlled release functions as drug carriers. *Mater. Sci. Eng. C, 55*, 367-372.

Li, W., Wu, J., Lee, S.S., Fortner, J.D. (2017). Surface tunable magnetic nano-sorbents for carbon dioxide sorption and separation. *Chem. Eng. J., 313*, 1160-1167.

Lian, J., Xu, Y., Lin, M., Chan, Y. (2012). Aqueous-phase reactions on hollow silicaencapsulated semiconductor nanoheterostructures. *J. Am. Chem. Soc., 134*, 8754-8757.

Liberman, A., Mendez, N., Trogler, W.C., Kummel, A.C. (2014). Synthesis and surface functionalization of silica nanoparticles for nanomedicine. *Surf. Sci. Rep., 69*, 132-158.

Lin, J., Siddiqui, J.A., Ottenbrite, R.M. (2001). Surface modification of inorganic oxide particles with silane coupling agent and organic dyes. *Polym. Adv. Technol., 12* (5), 285-292.

Lin, C.-H., Chang, J.-H., Yeh, Y.-Q., Wu, S.-H., Liu, Y.-H., Mou, C.-Y. (2015). Formation of hollow silica nanospheres by reverse microemulsion. *Nanoscale, 7*, 9614-9626.

Lin, J., Ye, W., Zhong, K., Shen, J., Jullok, N., Sotto, A., der Bruggen, B.V. (2016). Enhancement of polyethersulfone (PES) membrane doped by monodisperse Stöber silica for water treatment. *Chem. Eng. Process. Process Intensif.*, *107*, 194-205.

Lindquist, G.M., Stratton, R.A. (1976). The role of polyelectrolyte charge density and molecular weight on the adsorption and flocculation of colloidal silica with polyethylenimine. *J. Colloid Interface Sci.*, *55*, 45–59.

Liu, Q., Friedlaender, F.J. (1994). Fine particle processing by magnetic carrier methods. *Mineral Engineering*, *7* (4), 449-463.

Liu, X., He, J. (2007). Hierarchically structured superhydrophilic coatings fabricated by self-assembling raspberry-like silica nanospheres. *J. Colloid Interface Sci., 314*, 341–345.

Liu, J.-F., Zhao, Z.-S., Jiang, G.-B. (2008a). Coating Fe₃O₄ magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. *Environ. Sci. Technol., 42* (18), 6949-6954.

Liu, Q., Zhang, Y., Xu, H. (2008b). Properties of vulcanized rubber nanocomposites filled with nanokaolin and precipitated silica. *Appl. Clay Sci., 442*, 232-237.

Liu, Y.D., Fang, F.F., Choi, H.J. (2011). Core-shell-structured silica-coated magnetic carbonyl iron microbead and its magnetorheology with anti-acidic characteristics. *Colloid Polym. Sci.*, *289* (11), 1295-1298.

Liu, Y., Chen, M., Yongmei, H. (2013). Study of the adsorption of Cu(II) by EDTA functionalized Fe₃O₄ magnetic nano-particles. *Chem. Eng. J., 218*, 46-54.

Liu, S. (2015a). Cooperative adsorption on solid surfaces. *J. Colloid Inter. Sci., 450*, 224-238.

Liu, J., Detrembleur, C., De Pauw-Gillet, M.-C., Mornet, S., Jérôme, C., Duguet, E. (2015b). Gold nanorods coated with mesoporous silica shell as drug delivery system for remote near infrared light-activated release and potential phototherapy. *Small, 11* (19), 2323-2332.

Liu, Y.D., Choi, H.J. (2015c). Magnetorheology of core–shell type dual coated carbonyl iron particle fabricated by a sol-gel and self-assembly process. *Mater. Res. Bull., 69*, 92–97.

Liu, L., Yue, S., Zhang, Y., Qin, R., Liu, L., Zhang, D., Sun, R., Chen, L. (2015d). Onepot reverse microemulsion synthesis of core-shell structured YVO₄:Eu³⁺@SiO₂ nanocomposites. *Opt. Mater.*, *39*, 207-210.

Liz-Marzán, L.M., Giersig, M., Mulvaney, P. (1996). Synthesis of nanosized gold-silica core-shell particles. *Langmuir, 12* (18), 4329-4335.

Lloyd, G.E. (1987). Atomic number and crystallographic contrast images with the SEM: a review of backscattered electron techniques. *Mineralogical Magazine, 51*, 3-19.

Lo, S.-F., Wang, S.-Y., Tsai, M.-J., Lin, L.-D. (2012). Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons. *Chem. Eng. Res. Des., 90*, 1397-1406.

Lopez, P.J., Desclés, J., Allen, A.E., Bowler, C. (2005). Prospects in diatom research. *Curr. Opin. Biotechnol.*, *16*, 180-186.

Luckarift, H., Spain. J.C., Naik, R.R., Stone, M.O. (2004). Enzyme immobilization in a biomimetic silica support. *Nat. Biotechnol.*, *22*, 211-213.

Luckarift, H.R., Dickerson, M.B., Sandhage, K.H., Spain, J.C. (2006). Rapid, roomtemperature synthesis of antibacterial bionanocomposites of lysozyme with amorphous silica or titania. *Small*, *2*, 640-643.

Lundin, J.G., McGann, C.L., Daniels, G.C., Streifel, B.C., Wynne, J.H. (2017). Hemostatic kaolin-polyurethane foam composites for multifunctional wound dressing applications. *Mater. Sci. Eng. C., 79*, 702-709.

Lutz, K., Gröger, C., Sumper, M., Brunner, E. (2005). Biomimetic silica formation: analysis of the phosphate-induced self-assembly of polyamines. *Phys. Chem. Phys. Chem.*, *7*, 2812-2815.

Lv, G., Li, Z., Hoeppner, N., Wu, L., Liao, L. (2014). Interaction between sulfa drug sulfadiazine and hydrophobic talc surfaces. *Colloids Surf., A, 446*, 172-178.

Lv, X., Zhang, L., Xing, F., Lin, H. (2016). Controlled synthesis of monodispersed mesoporous silica nanoparticles: particle size tuning and formation mechanism investigation. *Micropor. Mesopor. Mat.*, *225*, 238-244.

Ma, F., Zhou, L., Tang, J., Wei, S., Zhou, Y., Zhou, J., Wang, F., Shen, J. (2012). A facile method for haemoglobin encapsulation in silica nanoparticles and applications in biosensors. *Micropor. Mesopor. Mat., 160*, 106-113.

Ma, K., Werner-Zwanziger, U., Zwanziger, J., Weisner, U. (2013). Controlling growth of ultrasmall sub-10 nm fluorescent mesoporous silica nanoparticles. *Chem. Mater., 25*, 677-691.

Ma, M., Zheng, S., Chen, H., Yao, M., Zhang, K., Jia, X., Mou, J., Xu, H., Wu, R., Shi, J. (2014). A combination "RAFT" and "graft from" polymerisation strategy for surface modification of mesoporous silica nanoparticles: towards enhanced tumor accumulation and cancer therapy efficacy. *J. Mater. Chem.*, *2*, 5828-5836.

Mahapatra, I., Sun, T.Y., Clark, J.R.A., Dobson, P.J., Hungerbuehler, K., Owen, R., Nowack, B., Lead, J. (2015). Probabilistic modelling of prospective environmental concentrations of gold nanoparticles from medical applications as a basis for risk assessment. *J. Nanobiotechnol., 13*, 93-107.

Mahmood, A., Malik, R.N. (2014). Human health risk assessment of heavy metals via consumption of contaminated vegetables collected from difference irrigation sources in Lahore, Pakistan. *Arabian Journal of Chemistry*, *7*(1), 91-99.

Makaraviciute, A., Ruzgas, T., Ramanavicius, A., Ramanaviciene, A. (2014). Antibody fragment immobilization on planar gold and gold nanoparticle modified quartz crystal microbalance with dissipation sensor surfaces for immunosensor applications. *Anal. Methods, 6*, 2134-2140.

Malik, M.A., Wani, M.Y., Hashim, M.A. (2012). Microemulsion method: a novel route to synthesize organic and inorganic nanoparticles. *Arabian J. Chem.*, *5*, 397-417.

Malvern Instruments Ldt. (2004). *Zetasizer nano series user manual*. Worcestershire, UK: Malvern Instruments Ltd.

Margelefsky, E.L., Zeidan, R.K., Davis, M.E. (2008). Cooperative catalysis by silicasupported organic functional groups. *Chem. Soc. Rev.,* 37, 1118-1126.

Marner, W.D., Shaikh, A.S., Muller, S.J. (2009). Enzyme immobilization via silaffinmediated autoencapsulation in a biosilica support. *Biotechn. Prog., 25*, 417-423.

Matsoukas, T., Gulari, E. (1988). Dynamics of growth of silica particles from ammoniacatalyzed hydrolysis of tetra-ethyl-orthosilicate. *J. Colloid Interface Sci., 124*, 252-261.

Matsunaga, S., Sakai, R., Jimbo, M., Kamiya, H. (2007). Long-chain polyamines (LCPAs) form marine sponge: possible implication in spicule formation. *ChemBioChem, 8*, 1729-1735.

Maugis, D. (1992). Adhesion of spheres: The JKR-DMT transition using a dugdale model. *J. Colloid Inter. Sci., 150* (1), 243-269.

McBain, S.C., Yui, H.H.P., El Haj, A., Dobson, J. (2007). Polyethyleneimine functionalized iron oxide nanoparticles as agents for DNA delivery and transfection. *J. Mater. Chem.*, *17*, 2561-2565.

McKenna, B.J., Birkedal, H., Bartl, M.H., Deming, T.J., Stucky, G.D. (2004). Micrometersized spherical assemblies of polypeptides and small molecules by acid-base chemistry. *Angew. Chem., 116*, 5770-5773. McMahon, G. (2007). Analytical instrumentation: a guide to laboratory, portable and miniaturized instruments. Chinchester, UK: John Wiley & Sons, Ltd.

Mehdinia, A., Khojasteh, E., Kayyal, T.B., Jabbari, A. (2014). Magnetic solid phase extraction using gold immobilized magnetic mesoporous silica nanoparticles coupled with dispersive liquid-liquid microextraction for determination of polycyclic aromatic hydrocarbons. *J. Chromatogr. A, 1364*, 20-27.

Meisterjahn, B., Wagner, S., von der Kammer, F., Hennecke, D., Hofmann, T. (2016). Silver and gold nanoparticle separation using asymmetrical flow-field flow fractionation: Influence on run conditions and of particle and membrane changes. *J. Chromatogr. A, 1440*, 150-159.

Melnyk, I.V., Gdula, K., Dabrowski, A., Zub, Y.L. (2016). Magneto-sensitive adsorbents modified by functional nitrogen-containing groups. *Nanoscale Res. Lett.*, *11* (61).

Memon, M.Z., Zhao, X., Sikarwar, V.S., Vuppaladadiyam, A.K., Milne, S.J., Brown, A.P., Li, J., Zhao, M. (2017). Alkali metal CO₂ sorbents and the resulting metal carbonates: potential for process intensification of sorption-enhanced steam reforming. *Environ. Sci. Technol.*, *51* (3), 12-27.

Meng, Z., Xue, C., Zhang, Q., Yu, X., Xi, K., Jia, X. (2009). Preparation of highly monodisperse hybrid silica nanospheres using a one-step emulsion reaction in aqueous solution. *Langmuir, 25* (14), 7879-7883.

Mertens, J., Knudsen, J., Thielens, M.-L., Andersen, J. (2012). On-line monitoring and controlling emissions in amine post combustion carbon capture: a field test. *Int. J. Greenh. Gas Control, 6,* 2-11.

Mészáros, R., Thompson, L., Bos, M., de Groot, P. (2002). Adsorption and electrokinetic properties of polyethyleneimine on silica surfaces. *Langmuir, 18*, 6164-6169.

Mezey, E.J. (1966). Pigments and reinforcing agents. In C.F. Powell, J.H. Oxley, J.M. Blocher Jr (Eds.), *Vapor deposition*. New York, NY: John Wiley and Sons.

Mihaly, M., Lacatusu, I., Olteanu, N.L., Maghea, A. (2014). A systematic methodology to design silica templates: silica microemulsion formulation and nanodroplet type and size estimation. *Comptes Rendus Chimie, 17*, 342-351.

Miller, J.B., Johnston, S.T., Ko, E.I. (1994). Effect of prehydrolysis on the textural and catalytically properties of titani-silica aerogels. *J. Catal., 150* (2), 311-320

Mine, E., Yamada, A., Kobayashi, Y., Konno, M., Liz-Marzán, L.M. (2003). Direct coating of gold nanoparticles with silica by seeded polymerization technique. *J. Colloid Interface Sci., 264*, 385-390.

Misra, V.N., Reddy, P.S.R., Mohapatra, B.K. (Eds.) (2004). *Mineral characterisation and processing*. Mayapuri, New Delhi: Allied Publishers Pvt. Ltd.

Miyake, Y., Yumoto, T., Kitamura, H., Sugimoto, T. (2002). Solubilization of organic compounds into As-synthesized spherical mesoporous silica. *Phys. Chem. Chem. Phys., 4*, 2680-2684.

Miyake, Y., Hanaeda, M., Asada, M. (2007). Separation of organic compounds by spherical mesoporous silica prepared from W/O microemulsions of tetrabutoxysilane. *Ind. Eng. Chem. Res., 46*, 8152-8157.

Moayedi, H., Huat, B.B.K., Kazemian, S., Daneshmand, S., Moazami, D., Niroumand, H. (2011). Electrophoresis of suspended kaolinite in multivalent electrolyte solution. *Int. J. Electrochem. Sci., 6*, 6514-6524.

Moffart, G., Williams, R.A., Webb, C., Stirling, R. (1994). Selective separations in environmental and industrial processes using magnetic carrier technology. *Miner. Eng.,* 7 (8), 1039-1056.

Moftakhar, M.K., Dousti, Z., Yaftian, M.R., Ghorbanloo, M. (2016). Investigation of heavy metal ions adsorption behavior of silica-supported Schiff base ligands. *Desalination and Water Treatment*, *57*(56).

Möller, K., Kobler, J., Bein, T. (2007). Colloidal Suspensions of Nanometer-Sized Mesoporous Silica. *Adv. Funct. Mater.*, *17*, 605-612.

Moradi, O., Mirza, B., Norouzi, M., Fakhri, A. (2012). Removal of Co(II), Cu(II) and Pb(II) ions by polymer based 2-hydroxyethyl methacrylate: thermodynamics and desorption studies. *Iranian J. Environ. Health Sci. Eng.*, *9* (1), 31-40.

Moreland, C. (1978). *Handbook of fillers and reinforcements for plastics*. New York, NY: Van Nostrand Reinhold Co.

Moreno, Y.P., Cardoso, M.B., Ferrão, M.F., Moncada, E.A., dos Santos, J.H.Z. (2016). Effect of SiCl₄ on the preparation of functionalized mixed-structure silica from monodisperse sol-gel silica nanoparticles. *Chem Eng. J., 292*, 233-245.

Moreno-Garrido, I., Perez, S., Blasco, J. (2015). Toxicity of silver and gold nanoparticles on marine microalgae. *Marine Environ. Res., 111*, 60-73.
Morris, G.E., Fornasiero, D, Ralston, J. (2002). Polymer depressants at the talc-water interface: adsorption isotherm, microflotation and electrokinetic studies. *Int. J. Miner. Process.,* 67, 211-227.

Morse, D.E. (1999). Silicon biotechnology: harnessing biological silica production to construct new materials. *Trends Biotechn.*, *17*, 230-232.

Mugica, L.C., Rodríguez-Molina, B., Ramos, S., Kozina, A. (2016). Surface functionalization of silica particles for their efficient fluorescent and stereo selective modification. *Colloids Surf., A, 500*, 79-87.

Müller, W.E.G., Boreiko, A., Schloβmacher, U., Wang, X., Tahir, M.N., Tremel, W., Brandt, D., Kanndorp, J.A., Schröder, H.C. (2007). Fractal-related assembly of the axial filament in the demosponge *Suberites domuncula*: relevance to biomineralization and the formation of biogenic silica. *Biomaterial, 28*, 4501-4511.

Müller, A.K., Ruppel, J., Drexel, C.P., Zimmermann, I. (2008). Precipitated silica as flow regulator. *Eur. J. Pharm. Sci.*, *34*, 303-308.

Müller, C., Kraushaar, K., Doebbe, A., Mussgnug, J.H., Kruse, O., Kroke, E., Patel, A.V. (2013). Synthesis of transparent aminosilane-derived silica based networks for entrapment of sensitive materials., *Chem. Commun. 49*, 10163-10165.

Müller, W.E.G., Link, T., Schröder, H.C., Korzhev, M., Neufurth, M., Brandt, D., Wang, X. (2014). Dissection of the structure-forming activity from the structure-guiding activity of silicatein: a biomimetic molecular approach to print optical fibers. *J. Mater. Chem. B, 2*, 5368-5377.

Murthy. Y.R., Tripathy, S.K., Kumar, C.R. (2011). Chrome ore beneficiation challenges & opportunities – a review. *Miner. Eng., 24*, 375-380.

Mwilu, S.K., Siska, E., Baig, R.B.N., Varma, R.S., Heightmar, E., Rogers, K.R. (2014). Separation and measurements of silver nanoparticles and silver ions using magnetic particles. *Sci. Total Environ.*, *47*2, 316-323.

Naik, R.R., Whitlock, P.W., Rodriguez, F., Brott, L.L., Glawe, D.D., Clarson, S.J., Stone, M.O. (2003). Controlled formation of biosilica structures *in vitro. Chem. Commun., 9*, 238-239.

Nair, B.P., Pavithran, C. (2009). Bifunctionalized hybrid silica spheres by hydrolytic cocondensation of 3-aminopropyltriethoxysilane and vinyltriethyoxysilane. *Langmuir, 26* (2), 730-735.

Nakahara, Y., Motohashi, K., Tanaka, Y., Miyata, K. (1978). Preparation of the spherical silica particles and their properties. *Journal of the Japan Society of Colour Material, 51*, 521-527.

Neville, F., Pchelintsev, N.A., Broderick, M.J.F., Gibson, T., Millner, P.A. (2009). Novel one-pot synthesis and characterization of bioactive thiol-silicate nanoparticles for biocatalytic and biosensor applications. *Nanotechnology*, *20*, 055612.

Neville, F., Broderick, M.J.F., Gibson, T., Millner, P.A. (2010). Fabrication and activity of silicate nanoparticles and nanosilicate-entrapped enzymes using polyethyleneimine as a biomimetic polymer. *Langmuir, 27* (1), 279-285.

Neville, F., Broderick, M.J.F., Gibson, T., Millner, P.A. (2011a). Fabrication and activity of silicate nanoparticles and nanosilicate-entrapped enzymes using polyethyleneimine as a biomimetic polymer. *Langmuir, 27*, 279-285.

Neville, F., Millner, P. (2011b). Fabrication and characterization of bioactive thiol-silicate nanoparticles. In P. Wang (Ed.), *Nanoscale biocatalysis, methods in molecular biology* (pp. 131-145). New Jersey, CA: Humana Press Inc.

Neville, F., Moreno-Atanasio, R. (2012, September 23-26). *Magnetic interactions of core–shell composite particles: a combined experimental and simulation approach.* Paper presented at the Chemeca 2012: Quality of Life Through Chemical Engineering (pp. 727–737), Wellington, New Zealand.

Neville, F., Murphy, T., Wanless, E.J. (2013a). The formation of polyethyleneiminetrimethoxysilane organic-inorganic hybrid particles. *Colloids Surf., A, 431*,42-50.

Neville, F., Seyfaee, A. (2013b). Real-time monitoring of *in situ* polyethyleneimine-silica particle formation. *Langmuir, 29*, 14681-14690.

Neville, F., Dixon, L., Hyde, E.D.E.R. (2016). A comparative study on hydrophobic silica particle synthesis. *Adv. Powd. Techn.*, *27* (6), 3217-2323.

Ngomsik, A.-F., Bee, A., Draye, M., Cote, G., Cabuil, V. (2005). Magnetic nano- and microparticles for metal removal and environmental applications: a review. *C. R. Chiimie, 8*, 963-970.

Nguyen, T., Hilliard, M. Rochelle, G. (2011). Volatility of aqueous amines in CO₂ capture. *Energy Procedia, 4*, 1624-1630.

Nguyen, N.-T. (2012). Micro-magnetofluidics: interactions between magnetism and fluid flow on the microscale. *Microfluid Nanofluidics*, *12* (1-4), 1-16.

Noll, F., Sumper, M., Hampp, N. (2002). Nanostructure of diatom silica surfaces and of biomimetic analogues. *Nano Letters*, *2*, 91-95.

Nooney, R., O'Connell, C., Roy, S., Boland, K., Keegan, G., Kelleher, S., Daniels, S., McDonagh. (2015). Synthesis and characterisation of far-red fluorescent cyanine dye doped silica nanoparticles using a modified microemulsion method for application in bioassays. *Sensor. Actuat. B-Chem., 221*, 470-479.

Nsami, J.N., Mbadcam, J.K. (2013). The adsorption efficiency of chemically prepared activated carbon from cola nut shells by ZnCl₂ on methylene blue. *J. Chem.,* doi.org/10.1155/2013/469170

Oats, W.J., Ozdemir, O., Nguyen, A.V. (2010). Effect of mechanical and chemical clay removals by hydrocyclone and dispersants on coal flotation. *Miner. Eng.*, *23*, 413-419.

O'Donohue, J., Reid, M., Vanghese, A., Portmann, B., Williams, R. (1999). A case of adult chronic copper self-intoxication resulting in cirrhosis. *Eur. J. Med. Res.*, *4* (6), 252.

Oertel, T., Helbig, U., Hutter, F., Kletti, H., Sextl, G. (2014). Influence of amorphous silica on the hydration in ultra-high performance concrete. *Cement and Concrete Res., 58*, 121-130.

Oh, C., Lee, Y.G., Choi, T.S., Jon, C.U., Oh, S.G. (2009). Facile synthesis of PEG-silica hybrid particles using one-step sol-gel reaction in aqueous solution. *Colloids Surf., A, 349* (1-3), 145-150.

Ojemaye, M.O., Okoh, O.O., Okoh, A.I. (2017). Adsorption of Cu²⁺ from aqueous solution by novel material; azomethine functionalized magnetic nanoparticles. *Sep. Purif. Technol., 183*, 204-215.

Okel, T.A. *Microporous precipitated silica*. US Patent No. US 8114935 B2.

Ong, S., Zhao, X., Eisenthal, K.B. (1992). Polarization of water molecules at a charged interface: second harmonic studies of the silica/water interface. *Chem. Phys. Lett., 191*, 327-335.

Osei-Prempeh, G., Ingles, J., Keffer, M., Dunlap, D., Thomas, G., Davari, A. (2015). Influence of the polymer surface charge on the synthesis and properties of polymer-silica composites. *Ind. Eng. Chem. Res., 54*, 11295-11301.

Osseo-Asare, K., Arriagada, F.J. (1990). Preparation of SiO₂ nanoparticles in a non-ionic reverse micellar system. *Colloid Surf.*, *50*, 321-339.

Osseo-Asare, K., Arriagada, F.J. (1999). Growth kinetics of nanosized silica in a nonionic water-in-oil microemulsion: a reverse micellar pseudophase reaction model. *J. Colloid Interface Sci., 218*, 69-76.

Padmavathy, K.S., Madhu, G., Haseena, P.V. (2016). A study on the effects of pH, adsorbent dosage, time, initial concentration and adsorption isotherm study for the removal of hexavalent chromium (Cr(IV)) from wastewater by magnetite nanoparticles. *Procedia Technology*, *24*, 585-594.

Pamirsky, I.E., Golokhvast, K.S. (2013). Silaffin of diatoms: from applied biotechnology to biomedicine. *Mar. Drugs, 11*, 3155-3167.

Park, J.S., Kim, D.S., Lim, H.M., Kim, D.H., Jeong, J.H., Lee, S.H. (2007). Preparation of TiO₂/SiO₂ hybrid hardcoatings on stainless steel and its photocatalytic effect. *Materials Science Forum*, *544-545*, 127-130

Park, H.K., Park, K.Y. (2008). Vapor-phase synthesis of uniform silica spheres through two-stage hydrolysis of SiCl₄. *Mater. Res. Bull.*, *43*, 2833-2839.

Pattanawanidchai, S., Loykulnant, S., Sae-oui, P., Maneevas, N., Sirisinha, C. (2014). Development of eco-friendly coupling agent for precipitated silica filled natural rubber compounds. *Polym. Test., 34*, 58-63.

Patwardhan, S.V., Mukherjee, N., Clarson, S.J. (2002a). Effect of process parameters on the polymer mediated synthesis of silica at neutral pH. *Silicon Chemistry*, *1*, 47-55.

Patwardhan, S.V., Mukherjee, N., Clarson, S.J. (2002b). Formation of fiber-like amorphous silica structures by externally applied shear. *J. Inorg. Organomet. Polym. Mater., 11*, 117-121.

Patwardhan, S.V., Mukherjee, N., Clarson, S.J. (2002c). Silication and biosilication. *Silicon Chemistry*, *1*, 207-214.

Patwardhan, S.V., Mukherjee, N., Clarson, S.J. (2002d). The use of poly-L-lysine to form novel silica morphologies and the role of polypeptides in biosilication. *J. Inorg. Organomet. Polym. Mater.*, *11*, 195-198.

Patwardhan, S.V., Mukherjee, N., Steinitz-Kannan, M., Clarson, S.J. (2003). Bioinspired synthesis of new silica structures. *Chem. Comm.*, 2003 (10), 1122-1123.

Patwardhan, S.V., Maheshwari, R., Mukherjee, N., Kiick, K.L., Clarson, S.J. (2006). Conformation and assembly of polypeptide scaffolds in templating the synthesis of silica: an example of a polylysine macromolecular "switch". *Biomacromolecules*, *7*, 491-497. Patwardhan, S.V. (2011). Biomimetic and bioinspired silica: recent developments and applications. *Chem. Commun., 47*, 7567-7582.

PerkinElmer, Inc. (2005). *FT-IR spectroscopy attenuated total reflectance (ATR)*. Shelton, CT: PerkinElmer, Inc.

Perry, C.C., Belton, D., Shafran, K. (2003). Studies of biosilicas; structural aspects, chemical principles, model studies and the future. *Progr. Mol. Subcell. Biol.*, *33*, 269-299.

Petruk, W. (2000). *Applied mineralogy in the mining industry*. Amsterdam, The Netherlands: Elsevier Science B.V.

Philipse, A.P., Vrij, A. (1989). Preparation and properties of nonaqueous model dispersions of chemically modified, charged silica spheres. *J. Colloid Interface Sci., 128* (1), 121-136.

Piniazkiewicz, R.J., McCarthy, E.F., Genco, N.A. (1994). Talc. In D.D. Carr (Ed.), *Industrial minerals and rocks* (6th ed.). Littleton, CO: SME

Pires, J., Fernandes, A.C., Avó, R. (2014). Bio-inspired synthesis of mesoporous silicas using large molecular weight poly-L-lysine at neutral pH. *J. Mater. Sci.*, *49*, 6087-6092.

Plumeré, N., Ruff, A., Speiser, B., Feldmann, V., Mayer, H.A. (2012). Stöber silica particles as basis for redox modifications: particle shape, size, polydispersity and porosity. *J. Colloid Interface Sci., 368*, 208-219.

Polshettiwar, V., Cha, D., Zhang, X., Basset, J.M. (2010). High-surface-area silica nanospheres (KCC-1) with a fibrous morphology. *Angew. Chem. Int. Ed., 49*, 9652–9656.

Popova, L., Djulgerova, R., Beshkov, G., Mihailov, V., Szytula, A., Gondek, L., Petrovic, Z.J. (2004). SnO₂ thin films for gas sensors modified by hexamethyldisilanzane after rapid thermal annealing. *Sens. Actuators, B, 100*, 352-358.

Pouget, E., Dujardin, E., Cavalier, A., Moreac, A., Valéry, C., Marchi-Artzner, V., Weiss, T., Renault, A., Paternostre, M., Artzner, F. (2007). Hierarchical architectures by synergy between dynamic template self-assembly and biomineralization. *Nat. Mater.*, *6*, 434-439.

Poulsen, N., Sumper, M., Kröger, N. (2003). Biosilica formation in diatoms: characterization of native siliaffin-2 and its role in silica morphologenesis. *PNAS, 100*, 12075-12080.

Poulsen, N., Kröger, N. (2004). Silica morphogenesis by alternative processing of silaffins in the diatom *Thalassiosira pseudonana*. *J. Biol. Chem., 279*, 42993-42999.

Poulsen, N., Berne, C., Spain, J., Kröger, N. (2007). Silica immobilization of an enzyme through genetic engineering of the diatom *Thalassiosira pseudonana*. *Angew. Chem. Int. Ed., 46*, 1943-1846.

Poulsen, N., Scheffel, A., Sheppard, V.C., Chesley, P.M., Kröger, N. (2013). Pentalysine clusters mediate silica targeting of silaffins in *Thalassiosira pseudonana*. *J. Biol. Chem., 288*, 20100-20109.

Pozzolini, M., Sturla, L., Cerrano, C., Bavestrello, G., Camardella, L., Parodi, A.M., Raheli, F., Benatti, U., Müller, W.E.G., Giovine, M. (2004). Molecular cloning of silicatein gene from marine sponge *Petrosia ficiformis* (porifera, demospongiae) and development of primmorphs as a model for biosilication studies. *Mar. Biotechnol., 6*, 594-603.

PPG Industries. (2016). PPG to increase precipitated silica production capacity in North America. Published Pittsburgh, February 7, 2016. Retrieved October 18, 2017, from http://corporate.ppg.com/Media/Newsroom/2016/PPG-to-increase-North-America-precipitated-silica/

Prakash, S., Das, B., Mohanty, J.K., Venugopal, R. (1999). The recovery of fine iron minerals from quartz and corundum mixtures using selective magnetic coating. *Int. J. Miner. Process.*, *57*, 87-103.

Prasertsri, S., Rattanasom, N. (2012). Fumed and precipitated silica reinforced natural rubber composites prepared from latex system: mechanical and dynamic properties. *Polym. Test., 31*, 593-603.

Pratsinis, S.E. (1998). Flame aerosol synthesis of ceramic powders. *Prog. Energy Combust. Sci., 24*, 197-219.

Pratsinis, S.E. (2006, May 7-11). *Overview – Nanoparticulate dry (flame) synthesis & application*. Paper presented at the NSTI Nanotechnology Conference and Trade Show, Boston, MA.

Puig, M., Cabedo, L., Gracenea, J.J., Jiménez-Morales, A., Gámez-Pérez, J., Suay, J.J. (2014). Adhesion enhancement of powder coatings on galvanised steel by addition of organo-modified silica particles. *Prog. Org. Coat.*, *77*, 1309-1315.

Qiao, B., Liang, Y., Wang, T.-J., Jiang, Y. (2016). Surface modification to produce hydrophobic nano-silica particles using sodium dodecyl sulfate as a modifier. *Appl. Surf. Sci.*, *2016*, 103-109.

Quang, D.V., Sarawade, P.B., Hilonga, A., Park, S.D., Kim, J.-K., Kim, H.T. (2011). Facile route for preparation of silver nanoparticle-coated precipitated silica. *Appl. Surf. Sci.*, 257, 4250-4256.

Rafferty, J.P. (2012). *Minerals*. New York, NY: Britannica Educational Publishing.

Rahman, I.A., Padavettan, V. (2012). Synthesis of silica nanoparticles by sol-gel: sizedependent properties, surface modifications and applications in silica-polymer nanocomposites – a review. *J. Nanomater., 2012*, doi: 10.1155/2012/132424.

Raitani, R., Jiang, S., Bhatnagar, A., Ravishankar, S.A. (2012). Chemically enhanced magnetic separation technologies for kaolin processing. *Miner. Metall. Proc.,* 29 (1), 20-26.

Rajanna, S.K., Kumar, D., Vinjamur, M., Mukhopadhyay, M. (2015). Silica aerogel microparticles from rice husk ash for drug delivery. *Ind. Eng. Chem. Res., 54*, 949-956.

Ramón, M.E., Movva, H.C.P., Chowdhury, S.F., Parrish, K.N., Rai, A., Magnuson, C.W., Ruoff, R.S., Akinwande, D., Banerjee, S.K. (2014). Impact of contact and access resistances in graphene field-effect transistors on quartz substrates for radio frequency applications. *Appl. Phys. Lett.*, *104* (7), 073115.

Reetz, M.T., Zonta, A., Simpelkamp, J. (1996). Efficient immobilization of lipases by entrapment in hydrophobic sol-gel materials. *Biotechnol. Bioeng., 49*, 527-534.

Ren, Y., Abbood, H.A., He, F., Peng, H., Huang, K. (2013). Magnetic EDTA-modified chitosan/SiO₂/Fe₃O₄ adsorbent: preparation, characterization, and application in heavy metal adsorption. *Chem. Eng. J., 226*, 300-311.

Ren, Y., Zhao, Y., Zhang, Y., Tang, W., Xin, X., Shen, J., Wang, L. (2015). Facile synthesis of Au@SiO₂ core-shell nanoparticles with multiple Au nanodots by a reverse microemulsion (water-in-oil) method. *Colloids Surf., A, 486*, 14-20.

Reshmi, G., Kumar, P.M., Malathi, M. (2009). Preparation, characterization and dielectric studies on carbonyl iron/cellulose acetate hydrogen phthalate core/shell nanoparticles for drug delivery applications. *Int. J. Pham., 365* (1-2), 131-135.

Ribeiro, T., Baleizão, C., Farinha, J.P.S. (2017). Artefact-free evaluation of metal enhanced fluorescence in silica coated gold nanoparticles. *Scientific Reports*, 7 (1), 2440.

Richthammer, P., Börmel, M., Brunner, E., van Pée, K.-H. (2011). Biomineralization in diatoms: the role of silacidins. *ChemBioChem*, *12*, 1362-1366.

Rochelle, G.T. (2009). Amine scrubbing for CO₂ capture. *Science, 325* (5948), 1652-1654.

Rodriguez, F., Glawe, D.D., Naik, R.R., Hallinan, K.P., Stone, M.O. (2004). Study of the chemical and physical influences upon *in vitro* peptide-mediated silica formation. *Biomacromolecules*, *5*, 261-265.

Roto, R., Yusran, Y., Kuncaka, A. (2016). Magnetic adsorbent of Fe₃O₄@SiO₂ core-shell nanoparticles modified with thiol group for chloroauric ion adsorption. *Appl. Surf. Sci., 377*, 30-36.

Ruan, S., Yuan, M., Zhang, L., Hu, G., Chen, J., Cun. X., Zhang, Q., Yang, Y., He, Q., Gao, H. (2015). Tumor microenvironment sensitive doxorubicin delivery and release to glioma using angiopep-2 decorated gold nanoparticles. *Biomaterials*, *37*, 425-435.

Rubio, J., Hoberg, H. (1993). The process of separation of fine mineral particles by flotation with hydrophobic polymeric carrier. *Int. J. Miner. Process.*, *37* (1–2), 109–122.

Rutledge, R.D., Wright, D.W. (2008). Biomineralization: peptide mediated synthesis of materials. In C.M. Lukehart and R.A. Scott (Eds.), *Nanomaterials: inorganic and bioinorganic perspectives*. Chichester, UK: John Wiley & Sons Ltd.

Saadi, R., Saadi, Z., Fazaeli, R., Fard, N. E. (2015). Monolayer and multilayer adsorption isotherm models for sorption from aqueous media. *Korean J. Chem. Eng., 32* (5), 787-799.

Sacanna, S., Rossi, L., Pine, D. J. (2012). Magnetic click colloidal assembly. *J. Am. Chem. Soc.*, *134*, 6112-6115.

Sacristán, J., Reinecke, H., Mijangos, C. (2000). Surface modification of PVC films in solvent-non-solvent mixture. *Polymer, 41*, 5577-5582.

Saevarsdottir, G., Bakken, J.A. (2010, June 6-9). *Current distribution in submerged arc furnaces for silicon metal/ferrosilicon production*. Paper presented at the Twelfth International Ferroalloys Congress Sustainable Future, Helsinki, Finland.

Safdarnejad, S.M., Hedengren, J.D., Baxter, L.L. (2015). Plant-level dynamic optimization of cryogenic carbon capture with conventional and renewable power sources. *Appl. Ener.*, *149*, 354-366.

Sahaf, B., Heydari, K., Herzenberg, L.A., Herzenberg, L.A. (2003). Lymphocyte surface thiol levels. *PNAS*, *100* (7), 4001-4005.

Sahoo, H., Sinha, N., Rath, S.S., Das, B. (2015). Ionic liquids as novel quartz collectors: insights from experiments and theory. *Chem. Eng. J., 273*, 46-54.

Saka, E.E., Güller, C. (2006). The effects of electrolyte concentration, ion species and pH on the zeta potential and electrokinetic charge density of montmorillonite. *Clay Minerals*, *41*, 853-861.

Salameh, S., Schneider, J., Laube, J., Alessandrini, A., Facci, P., Seo, J.W., Ciacchi, L.C., Madler, L. (2012). Adhesion mechanisms of the contact interface of TiO₂ nanoparticles in films and aggregates. *Langmuir, 28*, 11457-11464.

Schaefer, D.W., Kohls, D., Feinblum, E. (2012). Morphology of highly dispersing precipitated silica: impact of drying and sonication. *J. Inorg. Organomet. Polym. Mater.*, *22*, 617-623.

Scheffel, A., Poulsen, N., Shian, S., Kröger, N. (2011). Nanopatterned protein microrings from a diatom that direct silica morphogenesis. *PNAS, 108*, 3175-3180.

Schröder, H.C., Wiens, M., Schloβmacher, U., Brandt, D., Müller, W.E.G. (2012). Silicatein-mediated polycondensation of orthosilicic acid: modelling of a catalytic mechanism involving ring formation. *Silicon*, *4*, 33-38.

Seyfaee, A., Moreno-Atanasio, R., Neville, F. (2014). High-resolution analysis of the influence of reactant concentration on nucleation time and growth of polyethyleneimine-trimethoxymethylsilane particles. *Colloid Polym. Sci., 292*, 2673-2685.

Seyfaee, A., Neville, F., Moreno-Atanasio, R. (2015a). Experimental results and theoretical modeling of the growth kinetics of polyamine-derived silica particles. *Ind. Eng. Chem. Res., 54*, 2466-2475.

Seyfaee, A., Hyde, E.D.E.R., Aubin, J., Moreno-Atanasio, R., Neville, F. (2015b, Sep 27-Oct 1). *Investigation of polymeric nuclei and their role in biomimetic silication: effect of physical conditions*. Paper presented at the Asia Pacific Confederation of Chemical Engineering Congress 2015 (APCChE), incorporating CHEMECA 2015 (pp. 2081-2092), Melbourne, Australia.

Shah, K.W., Sreethawong, T., Liu, S.H., Zhang, S.Y., Tan, L.S., Han, M.Y. (2014). Aqueous route to facile, efficient and functional silica coating of metal nanoparticles at room temperature. *Nanoscale, 6*, 11273-11281

Shahbeig, H., Bagheri, N., Ghorbanian, S.A., Hallajisani, A., Poorkarimi, S. (2013). A new adsorption isotherm model of aqueous solutions on granular activated carbon. *WJMS*, *9* (4), 243-254.

Shaikh, A.M.H., Banerjee, S.S., Dixit, S.G. (1994). Use of magnetic surfactants in the high gradient magnetic separation. *Sep. Technol., 4*, 174-179.

Shapiro, I., Kolthoff, I.M. (1940). Studies on aging of precipitates and coprecipitation. XXXIII. The thermal aging of imperfect barium sulphate. *J. Phys. Chem.*, *44*, 921-935.

Sheppard, V.C., Scheffel, A., Poulsen, N., Kröger, N. (2012). Live diatom silica immobilization of multimeric and redox-active enzymes. *Appl. Environ. Microbiol.*, *78*, 211-218.

Shi, Y.-L. Asefa, T. (2007). Tailored core–shell–shell nanostructures: sandwiching gold nanoparticles between silica cores and tunable silica shells. *Langmuir, 23,* 9455–9462.

Shi, J.-Y., Yao, G.-T., Fu, S.-Q. (2013). Two-dimensional silica sieve plates mimicking the diatom valve. *Chem. Eur. J.*, *19*, 8073-8077.

Shimizu, K., Cha, J., Stucky, G.D., Morse, D.E. (1998). Silicatein α: cathepsin L-like protein in sponge biosilica. *PNAS*, *95*, 6234-6238.

Shindo, D., Oikawa, T. (2002). Energy dispersive x-ray spectroscopy. In *Analytical electron microscopy for materials science* (pp. 81-102). Tokyo, Japan: Springer.

Shiomi, T., Tsunoda, T., Kawia, A., Chiku, H., Mizukami, F., Sakaguchi, K. (2005). Synthesis of protein–silica hybrid hollow particles through the combination of protein catalysts and sonochemical treatment. *Chem. Commun., 2005* (42), 5325-5327.

Shiomi, T., Tsunoda, T., Kawia, A., Mizukami, F., Safaguchi, K. (2007). Biomimetic synthesis of lysozyme – silica hybrid hollow particles using sonochemical treatment: influence of pH and lysozyme concentration on morphology. *Chem. Mater., 19*, 4486-4493.

Shirzad-Siboni, M., Farrokhi, M., Soltani, R.D.C., Khataee, A., Tajassosi, S. (2014). Photocatalytic reduction of hexavalent chromium over ZnO nanorods immobilized on kaolin. *Ind. Eng. Chem. Res.*, *53* (3), 1079-1087.

Sierra, L., Guth, J.L. (1999). Synthesis of mesoporous silica with tunable pore size from sodium silicate solutions and a polyethylene oxide surfactant. *Micropor. Mesopor. Mat., 27*, 243-253.

Sierra, L., Lopez, B., Guth, J.L. (2000). Preparation of mesoporous silica particles with controlled morphology from sodium silica solutions and a non-ionic surfactant at pH values between 2 and 6. *Micropor. Mesopor. Mat., 39*, 519-527.

Simpson, T.L. (1984). *The cell biology of sponges*. New York, NY: Springer-Verlag, New York, Inc.

Šimšíková, M., Antalík, M., Kaňuchová, M., Škvarla, J. (2013). Anionic 11mercaptoundecanoic acid capped ZnO nanoparticles. *Appl. Surf. Sci., 282*, 342-347.

Singh, S., Sahoo, H., Rath, S.S., Sahu, A.K., Das, B. (2014). Recovery of iron minerals from Indian iron ore slimes using colloidal magnetic coating. *Powder Technol., 269*, 38-45.

Siwińska-Stefańska, K., Walkowiak, J., Krysztafkeiwicz, A., Jesionowski, T. (2008). Polymer adsorption on the surface of highly disperse silica. *Appl. Surf. Sci., 254*, 3591-3600.

Slowing, I.I., Trewyn, B.G., Giri, S., Lin, V.S.-Y. (2007). Mesoporous silica nanoparticles for drug delivery and biosensing applications. *Adv. Funct. Mater.*, *17*, 1225-1236.

Somasundaran, P. (Ed.) (2006). *Encyclopedia of surface and colloid science* (2nd ed.). Boca Raton, FL: CRC Press

Song, X., Jiang, Z., Li, L., Wu, H. (2014). Immobilization of β -glucuronidase in lysozymeinduced biosilica particles to improve its stability. *Front. Chem. Sci. Eng.*, *8*, 353-361.

Spinde, K., Kammer, M., Freyer, K., Ehrlich, H., Vournakis, J.N., Brunner, E. (2011). Biomimetic silication of fibrous chitin from diatoms. *Chem. Mater.*, *23*, 2973-2978.

Sprynskyy, M., Kowalkowski, T., Tutu, H., Cukrowska, E.M., Buszewski, B. (2011). Adsorption performance of talc for uranium removal from aqueous solution. *Chem. Eng. J.*, 171, 1185-1193.

Srinivasan, S., Datye, A.K., Smith, M.H., Peden, C.H.F. (1994). Interaction of titanium isopropoxide with surface hydroxyls on silica. *J. Catal., 145* (2), 565-573.

Stark, W.J., Kammler, H.K., Strobel, R., Günther, D., Baiker, A., Pratsinis, S.E. (2002). Flame-made titania/silica epoxidation catalysts: toward large-scale production. *Ind. Eng. Chem. Res., 41*, 4921-4927.

Stenzel, O., Uhrlandt, S., Luginsland, H.D., Weheier, A. (2009). *Highly dispersible precipitated silica with a high surface area*. US Patent No. US 20060137575 A1.

Stöber, W., Fink, A., Bohn, E. (1968). Controlled growth of mondisperse silica spheres in the micron size range. *J. Colloid Interfaces Sci., 26*, 62-69.

Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (2013). Climate change 2013: the physical science basis. In *Intergovernmental panel on climate change, working group I contribution to the IPCC fifth assessment report (AR5)*. New York, NY: Cambridge University Press.

Strobel, R., Pratsinis, S.E. (2007). Flame aerosol synthesis of smart nanostructure materials. *J. Mater. Chem.*, *17*, 4743-4756.

Sumper, M. (2002). A phase separation model for the nanopatterning of diatom biosilica. *Science*, *295*, 2430-2433.

Sumper, M., Lorenz, S., Brunner, E. (2003). Biomimetic control of size in the polyaminedirected formation of silica nanosphere. *Angew. Chem. Int. Ed., 42*, 5192-5195.

Sumper, M. (2004a). Biomimetic patterning of silica by long-chain polyamines. *Angew. Chem. Int. Ed., 43*, 2251-2254.

Sumper, M., Kröger, N. (2004b). Silica formation in diatoms: the function of long-chain polyamines and silaffins. *J. Mater. Chem.*, *14*, 2059-2065.

Sumper, M., Brunner, E. (2006). Learning from diatoms: nature's tools for the production of nanostructured silica. *Adv. Funct. Mater.*, *16*, 17-26.

Sun, Z., Bai, C., Zheng, S., Yang, X., Frost, R.L. (2013). A comparative study of different porous silica minerals supported TiO₂ catalysts. *Appl. Catal. A, 458*, 103-110.

Svoboda, J. (2004). *Magnetic techniques for the treatment of materials*. Dordrecht, The Netherlands: Kluwer Academic Publishers.

Szilágyi, I., Rosická, D., Hierrezuelo, J., Borkovec, M. (2011). Charging and stability of anionic latex particles in the presence of linear poly(ethylene imine). *J. Colloid Interface Sci.*, *360*, 580-585.

Szilágyi, I., Trefalt, G., Tiraferri, A., Maroni, P., Borkovec, M. (2014). Polyelectrolyte adsorption, interparticle forces and colloidal aggregation. *Soft Matter, 10*, 2479-2502.

Tahir, H., Hammed, U., Sultan, M., Jahanzeb, Q. (2010). Batch adsorption technique for the removal of malachite green and fast green dyes by using montmorillonite clay as adsorbent. *African Journal of Biotechnology*, *9* (48), 8206-8214.

Taikum, O., Friehmelt, R., Scholz, M. (2010). The last 100 years of fumed silica in rubber reinforcement. *Rubber World, 242*, 35-44.

Takeda, Y., Komori, Y., Yoshitake, H. (2013). Direct Stöber synthesis of monodisperse silica particles functionalized with mercapto-, vinyl- and aminopropylsilanes in alcohol-water mixed solvents. *Colloids Surf., A, 422*, 68-74.

Tam, J.P., Wu, C.R., Liu, W., Zhang, J.W. (1991). Disulfide bond formation in peptides by dimethyl sulfoxide. Scope and applications. *J. Am. Chem. Soc.*, *113*, 6657-6662.

Tan, X., Wu, W.G., Wang, Z.M., Tan, X., Liu, H.y. (2014). Experimental study on comprehensive recovery of valuable minerals from flotation tailings in copper-molybdenum mine. *Adv. Mater. Res., 878*, 234-243.

Tang, F., Li, L., Chen, D. (2012). Mesoporous silica nanoparticles: synthesis, biocompatibility and drug delivery. *Adv. Mater., 24*, 1504-1534.

Tang, Y., Song, L., Wang, J., Yu, S., Wang, Y. (2013). Amino-functionalized core-shell magnetic mesoporous composite microspheres for Pb(II) and Cd(II) removal. *J. Environ. Sci.*, *25* (4), 830-837.

Tang, H., Wang, L., Sun, W., Hu, Y., Han, H., Zhai, J. (2017). Electric arc furnace dust as magnetic carrier particles for removal of micro-fine particles from suspensions. *Sep. Purif. Technol.*, *176*, 220-230.

Tarasevich, Y.I. (2007). The surface energy of hydrophilic and hydrophobic adsorbents. *Colloid J.*, 69 (2), 212-220.

Taylor, M.P., Mackay, A.K., Hudson-Edwards, K.A., Holz, E. (2010). Soil Cd, Cu, Pb and Zn contaminants Mount Isa city, Queensland, Australia: potential sources and risks to human health. *Appl. Geochem.*, *25* (6), 841-855.

Taylor, A., Herrmann, A., Moss, D., Sée, V., Davies, K., Williams, S.R., Murray, P. (2014). Assessing the efficiency of nano- and micro-sized magnetic particles as contrast agents for MRI cell tracking. *PLOS ONE, 10* (2), e0118037.

Teoh, W.Y., Amal, R., Mädler, L. (2010). Flame spray pyrolysis: an enabling technology for nanoparticles design and fabrication. *Nanoscale, 2*, 1324-1347.

Teste, B., Malloggi, F., Gassner, A.-L., Georgelin, T., Siaugue, J.-M., Varenne, A., Girault, H., Descroix, S. (2011). Magnetic core shell nanoparticles trapping in a microdevice generating high magnetic gradient. *Lab Chip, 11,* 833-840.

Thakur, R., Gupta, R.B. (2005). Supercritical CO₂ based silica coating of gold nanoparticles using water-in-oil microemulsion. *Ind. Eng. Chem. Res.*, *44*, 3086-3090.

The Freedonia Group. (2014). *World speciality silicas – demand and sales forecasts, market share, market size, market leaders.* Cleveland, OH: The Freedonia Group, Inc.

Tian, L., Li, X., Zhao, P., Chen, X., Ail, Z., Ali, N., Zhang, B., Zhang, H., Zhang, Q. (2015). Generalized approach for fabricating monodisperse anisotropic microparticles via singlehole swelling PGMA seed particles. *Macromolecules*, *48*, 7592–7603.

Tomczak, M.M., Glawe, D.D., Drummy, L.F., Lawrence, C.G., Stone, M.O., Perry, C.C., Pochan, D.J., Deming, T.J., Naik, R.R. (2005). Polypeptide-templated synthesis of hexagonal silica platelets. *J. Am. Chem. Soc., 127*, 12577-12582.

Torimoto, T., Sakata, T., Mori, H., Yoneyama, H. (1994). Effect of surface charge of 4aminothiophenol-modified PbS microcrystal photocatalysts on photoinduced charge transfer. *J. Phys. Chem.*, *98* (11), 3036-3043.

Torney, F., Trewyn, B.G., Lin, V.S.Y., Wang, K. (2007). Mesoporous silica nanoparticles deliver DNA and chemicals into plants. *Nat. Nanotechnol.*, *2*, 295-300.

Towns, J.K., Regnier, F.E. (1990). Polyethyleneimine-bonded phases in the separation of proteins by capillary electrophoresis. *J. Chromatogr. A, 516*, 69-78.

Tricoli, A., Graf, M., Pratsinis, S.E. (2008). Optimal doping for enhanced SnO₂ sensitivity and thermal stability. *Adv. Funct. Mater.*, *18* (13), 1969-1976.

Tsai, C.S. (Ed.) (1990). *Guided-wave acousto-optics: interactions, devices, and applications*. Berlin, Germany: Springer-Verlag.

Ungaro, F., De Rosa, G., Miro, A., Quaglia, F. (2003). Spectrophotometric determination of polyethylenimine in the presence of an oligonucleotide for the characterization of controlled release formation. *J. Pharm. Biomed. Anal.*, 31, 143-149.

Ulrich, G.D. (1984). Special Report. C&EN, 62, 22-29.

Uskokocić, V., Drofenik, M. (2005). Synthesis of materials within reverse micelles. *Surf. Rev. Lett.*, *12*, 239-277.

van Blaaderen, A., Kentgens, A.P.M. (1992). Particle morphology and chemical microstructure of colloidal silica spheres made from alkoxysilanes. *J. Non-Cryst. Solids, 149*, 161-178.

van Helden, A.K., Jansenm, J.W., Vrij, A. (1981). Preparation and characterization of spherical monodisperse silica dispersions in nonaqueous solvents. *J. Colloid Interface Sci.*, *81*, 354-368.

Vakurov, A., Pchelintsev, N.A., Gibson, T., Millner, P. (2012) Development of polymeric nanoparticles showing tuneable pH-responsive precipitation. *J. Nanopart. Res.,* 14, 1302–1311.

Vansant, E.F., van der Voort, P., Vrancken, K.C. (1995). Characterization and chemical modification of the silica surface. In B. Delmon, J.T. Yates (Eds.), *Studies in surface science and catalyst* (vol. 93). Amsterdam, The Netherlands: Elsevier Science B.V.

Vilela, S.O., Soto-Oviedo, M.A., Albers, A.P.F., Faez, R. (2007). Polyaniline and mineral clay-based conductive composites. *Mat. Res., 10* (3), 297-300.

Vogt, C., Toprak, M.S., Muhammed, M., Laurent, S., Bridot, J.-L., Müller, R.N. (2010). High quality and tunable silica shell-magnetic core nanoparticles. *J. Nanopart. Res., 12* (4), 1137-1147.

Wacker Chemical Corporation. (2009). There's more to it than you think HDK®pyrogenic silica, 2009. Retrieved October 18, 2017, from http://www.wacker.com/cms/media/publications/downloads/6174_EN.pdf

Wagner, E., Brünner, H. (1960). Aerosil, Herstellung, Eigenschaften und Verhalten in Organischen Flüssigkeiten. *Angew. Chem., 72*, 744-750.

Wallace, A.F., DeYoreo, J.J., Dove, P.M. (2009). Kinetics of silica nucleation on carboxyland amine-terminated surfaces: insights for biomineralisation. *J. Am. Chem. Soc., 131*, 5244-5250.

Wang, J., Somasundaran, P. (2005). Adsorption and conformation of carboxymethyl cellulose at solid-liquid interfaces using spectroscopic, AFM and allied techniques. *J. Colloid Interface Sci.*, 291, 75-83.

Wang, J., Somasundaran, P. (2006). Mechanisms of ethyl(hydroxyethyl) cellulose-solid interaction: influence of hydrophobic modification. *J. Colloid Interface Sci.*, 293, 322-332.

Wang, L., Neoh, K.G., Kang, E.T., Shuter, B., Wang, S.-, C. (2009). Superparamagnetic hyperbranched polyglycerol-grafted Fe_3O_4 nanoparticles as a novel magnetic resonance imaging contrast agent: an *in vitro* assessment. *Adv. Funct. Mater., 19* (16), 2615-2622.

Wang, J., Zheng, S., Shao, Y., Liu, J., Xu, Z., Zhu, D. (2010a). Amino-functionalized Fe₃O₄@SiO₂ core-shell magnetic nanomaterial as a novel adsorbent for aqueous heavy metals removal. *J. Colloid Interface Sci., 349*, 293-299.

Wang, X.-D., Shen, Z.-X., Sang, T., Cheng, X.-B., Li, M.-F., Chen, L.-Y., Wang, Z.-S. (2010b). Preparation of spherical silica particles by Stöber process with high concentration of tetra-ethyl-orthosilicate. *J. Colloid Interface Sci.*, *341*, 23-29.

Wang, Z., Zong, S., Chen, H., Wu, H., Cui, Y. (2011a). Silica coated gold nanoaggregates prepared by reverse microemulsion method: dual mode probes for multiplex immunoassay using SERS and fluorescence. *Talanta, 86*, 170-177.

Wang, X., Schröder, H.C., Brandt, D., Wiens, M., Lieberwirth, I., Glasser, G., Schloβmacher, U., Wang, S., Müller, W.E.G. (2011b). Sponge biosilica formation involves syneresis following polycondensation *in vivo*. *ChemBioChem*, *12*, 2316-2324.

Wang, X., Schröder, H.C., Wang, K., Kaandorp, J.A., Müller, W.E.G. (2012). Genetic, biological and structural hierarchies during sponge spicule formation: from soft sol-gels to solid 3D silica composite structures. *Soft Matter, 8*, 9501-9518.

Wang, F., Liu, P., Nei, T., Wei, T., Cui, Z. (2013a). Characterization of a polyamine microsphere and its adsorption for protein. *Int. J. Mol. Sci.*, 14, 17-29.

Wang, Q., Yu, J., Zheng, J., Liu, D., Jiang, F., Zhang, X., Li, W. (2013b). Morphologycontrolled synthesis of silica materials template by self-assembled short amphiphilic peptides. *RSC Advances*, *3*, 15955-15965.

Wang, L., Sun, W., Hu, Y.-H., Xu, L.-H. (2014a). Adsorption mechanism of mixed anionic/cationic collectors in Muscovite – quartz flotation system. *Miner. Eng., 64*, 44-50.

Wang, S., Xue, J., Zhao, Y., Du, M., Deng, L., Xu, H., Lu, J.R. (2014b). Controlled silica deposition on self-assembled peptide nanostructures via varying molecular structures of short amphiphilic peptides. *Soft Matter, 10*, 7623-7629.

Wang, K., Liu, P., Ye, Y., Li, J., Zhao, W., Huang, X. (2014c). Fabrication of a novel laccase biosensor based on silica nanoparticles modified with phytic acid for sensitive detection of dopamine. *Sens. Actuator B, 197*, 292-299.

Wang, J., Shah, Z.H., Zhang, S., Lu, R. (2014d). Silica-based nanocomposites via reverse microemulsions: classifications, preparations and applications. *Nanoscale, 6*, 4418-4437.

Wang, D., Wang, X., Ma, X., Fillerup, E., Song, C. (2014e). Three-dimensional molecular basket sorbents for CO₂ capture: effects of pore structure of supports and loading level of polyethylenimine. *Catalysis Today*, 233, 100-107.

Wang, S., Wang, K., Dai, C., Shi, H., Li, J. (2015a). Adsorption of Pb²⁺ on aminofunctionalized core-shell magnetic mesoporous SBA-15 silica composite. *Chem. Eng. J., 262*, 897-903.

Wang, W., Cao, L., Wang, J., Zhao, J., Wu, X., Hao, Y. (2015b). Characterization and adsorptive properties of poly(1-vinylimidazole)/silica nanocomposites synthesized in supercritical carbon dioxide. *e-Polymers*, *15*, 245-254.

Wang, S., Cai, Q., Du, M., Xue, J., Xu, H. (2015c). Synthesis of 1D silica nanostructures with controllable sizes based on short anionic peptide self-assembly. *J. Phys. Chem. B, 119*, 12059-12065.

Wang, Y., Peng, Y., Nicholson, T., Lauten, R.A. (2015d). The different effects of bentonite and kaolin on copper flotation. *Appl. Clay Sci., 114*, 48-52.

Wang, A., Yang, Y., Qi, Y., Qi, W., Fei, J., Ma, H., Zhao, J., Cui, W., Li, J. (2016). Fabrication of mesoporous silica nanoparticle with well-defined multicompartment structure as efficient drug carrier for cancer therapy *in vitro* and *in vivo*. *ACS Appl. Mater. Interfaces, 8*, 8900-8907.

Wang, T., Liu, Y., Wu, C. (2017). Effect of Paclitaxel-mesoporous silica nanoparticles with a core-shell structure on the human lung cancer cell line A549. *Nanoscale Research Letters, 12* (66).

Wason, S.K. (1987). Synthetic silicas. In H.S. Katz, J.V. Milewski (Eds.), *Handbook of fillers for plastics* (pp. 165-201). New York, NY: Van Nostrand Reinhold.

Wen, T., Qu, F., Li, N.B., Luo, H.Q. (2017). A facile, sensitive, and rapid spectrophotometric method for copper(II) ion detection in aqueous media using polyethyleneimine. *Arabian Journal of Chemistry, 10*, S1680-S1685.

Weng, X., Nguyen, A.V., Mei, G., Yu, Y. (2014). Biodegradable quaternary ammonium salts for processing iron ores. *Am. J. Analyt. Chem.*, *5*, 646-654.

Wenzl, S., Hett, R., Richthammer, P., Sumper, M. (2008). Silacidins: highly acidic phosphopeptides from diatom shells assist in silica precipitation *in vitro*. *Angew. Chem. Int. Ed., 47*, 1729-1732.

Werner, P., Blumtritt, H., Zlotnikov, I., Graff, A., Dauphin, Y., Fratzl, P. (2015). Electron microscopy analyses of the bio-silica basal spicule from the *Monorhaphis chuni* sponge. *J. Struct. Biol., 191*, 165-174.

White, L.J., Duffy, G.J. (1959). Staff-industry collaborative report vapor-phase production of colloidal silica. *Ind. Eng. Chem. Res.*, *51*, 232-238.

Wieneke, R., Bernecker, A., Riedel, R., Sumper, M., Steinem, C., Geyer, A. (2011). Silica precipitation with synthetic silaffin peptides. *Org. Biomol. Chem.*, *9*, 5482-5486.

Wiese, J., Becker, M., Yorath, G., O'Connor, C. (2015). An investigation into the relationship between particle shape and entrainment. *Miner. Eng.*, *83*, 211-216.

Williams, D.J.A., Williams, K.P. (1978). Electrophoresis and zeta potential of kaolinite. *J. Coll. Inter. Sci., 65* (1), 79-87.

Wongsasuluk, P., Chotpantarat, S., Siriwong, W., Robson, M. (2014). Heavy metal contamination and human health risk assessment in drinking water from shallow groundwater wells in an agricultural area in Ubon Ratchathani province, Thailand. *Environ. Geochem. Health, 36* (1), 169-182.

Wu, H., Mansouri, J., Chen, V. (2013). Silica nanoparticles as carriers of antifouling ligands for PVDF ultrafiltration membranes. *J. Membrane Sci., 433*, 135-151.

Wu, Z.-C., Wang, Z.-Z., Liu, J., Yin, J.-H., Kuang, S.-P. (2016). Removal of Cu(II) ions from aqueous water by L-agrinine modifying magnetic chitosan. *Colloids Surf., A, 499*, 141-149.

Xia, T., Kovochich, M., Liong, M., Meng, H., Kabehie, S., George, S., Zink, J.I., Nel, A.E. (2009). Polyethyleneimine coating enhances the cellular uptake of mesoporous silica nanoparticles and allows safe delivery of siRNA and DNA constructs. *ASC Nano, 3* (10), 3273-3286.

Xiao, Y., Wang, Y., Luo, G., Bai, S. (2016). Using hydrolysis of silicon tetrachloride to prepare highly dispersed precipitated nanosilica. *Chem. Eng. J.,* 283, 1-8.

Xie, W., Wang, H., Li, H. (2012). Silica-supported tin oxides as heterogeneous acid catalysts for transesterification of soybean oil with methanol. *Ind. Eng. Chem. Res., 51* (1), 225-231.

Xie, W., Hu, L., Yang, X. (2015). Basic ionic liquid supported on mesoporous SBA-15 silica as an efficient heterogeneous catalyst for biodiesel production. *Ind. Eng. Chem. Res., 54*, 1505-1512.

Xing, Y., Xu, X., Gui, X., Cao, Y., Xu, M. (2017). Effect of kaolinite and montmorillonite on fine coal flotation. *Fuel, 195*, 284-289.

Xu, Z., Xia, A., Wang, C., Yang, W., Fu, S. (2007). Synthesis of raspberry-like magnetic polystyrene microspheres. *Mater. Chem. Phys., 103* (2–3), 494–499.

Xu, L., Zhuang, W., Xu, B., Cai, Z. (2011). Fabrication of superhydrophobic cotton fabrics by silica hydrosol and hydrophobization. *Appl. Surf. Sci., 257* (13), 5491-5498

Yamauchi, H., Ishikawa, T., Kondo, S. (1989). Surface characterization of ultramicro spherical particles of silica prepared by W/O microemulsion method. *Colloids Surf.*, *37*, 71-80.

Yan, F., Jiang, J., Chen, X., Tian, S., Li, K. (2014). Synthesis and characterization of silica nanoparticles preparing by low-temperature vapor-phase hydrolysis of SiCl₄. *Ind. Eng. Chem. Res., 53*, 11884-11890.

Yang, C., Wang, G., Lu, Z., Sun, J., Zhuang, J., Yang, W. (2005). Effect of ultrasonic treatment on dispersibility of Fe₃O₄ nanoparticles and synthesis of multicore-core Fe₃O₄/SiO₂ core/shell nanoparticle. *J. Mater. Chem., 14*, 4252–4257.

Yang, P., Gai, S., Lin, J. (2012). Functionalized mesoporous silica materials for controlled drug delivery. *Chem. Soc. Rev., 41*, 3679-3698.

Yang, S.H. (2013). Biomimetic silica nanostructures on the surface, controlled by polyvalent counteranions. *Solid State Sci.*, 23, 1-7.

Yantasee, W., Warner, C.L., Sangvanich, T., Addleman, R.S., Carter, T.G., Wiacek, R.J., Fryxell, G.E., Timchalk, C., Warner, M.G. (2007). Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles. *Environ. Sci. Technol., 41* (14), 5114-5119.

Yao, H., Fan, M., Wang, Y., Luo, G., Fei, W. (2015). Magnetic titanium dioxide based nanomaterials: synthesis, characteristics, and photocatalytic applications in pollutant degradation. *J. Mater. Chem. A*, *3* (34), 17511-17524.

Yi, Y., Yang, Z., Zang, S. (2011). Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. *Environ. Pollut., 159* (10), 2575-2585.

Yi, J., Jang, H.S., Lee, J.S., Park, W.I. (2012). Bioinspired morphologenesis of highly intricate and symmetric silica nanostructures. *Nano Lett., 12*, 3743-3748.

Yu, J., Wang, Q., Zhang, X. (2014). Effects of external force fields on peptide selfassembly and biomimetic silica synthesis. *Appl. Surf. Sci.*, *311*, 799-807. Yuan, J.-J., Jin, R.-H. (2005). Multiply shaped silica mediated by aggregates of linear poly(ethyleneimine). *Adv. Mater., 17*, 885-888.

Yuan, J.-J., Zhu, P.-X., Fukazawa, N., Jin, R.-H. (2006). Synthesis of nanofiber-based silica networks mediated by organized poly(ethyleneimine): structure, properties, and mechanism. *Adv. Funct. Mater.*, *16*, 2205-2212.

Yuan, L., Hyodo, T., Shimizu, Y., Egashira, M. (2011). Preparation of mesoporous and/or macroporous SnO2-based powders and their gas-sensing properties as thick film sensors. *Sensors, 11* (2), 1261-1276.

Yuan, Z.-T., Lu, J.-W., Liu, J.-T, Li, L.-X., Wang, S.-Y. (2017). Enhancement of pentlandite surface magnetism and implications for its separation from serpentine via magnetic separation. *Trans. Nonferrous Met. Soc. China*, *27*, 204-210.

Yuhua, W., Jianwei, R. (2005). The flotation of quartz from iron minerals with a combined quaternary ammonium salt. *Int. J. Miner. Process.*, 77 (2), 116-122.

Zarabadi-Poor, P., Badiei, A., Fahlman, B.D., Arab, P., Ziarani, G.M. (2011). One-pot synthesis of ethanolamine-modified mesoporous silica. *Ind. Eng. Chem. Res., 50*, 10036-10040.

Zelenák, V., Badanicová, M., Halamová, D., Cejka, A., Murafa, N., Goerigk, G. (2008). Amine-modified ordered mesoporous silica: effect of pore size on carbon dioxide capture. *Chem. Eng. J., 144*, 336–342.

Zhang, J., Liu, Z., Han, B., Li, Z., Yang, G., Li, J., Chen, J. (2006). Preparation of silica and TiO₂-SiO₂ core-shell nanoparticles in water-in-oil microemulsion using compressed CO₂ as reactant and antisolvent. *J. Supercrit. Fluids*, *36*, 194-201.

Zhang, Y., Liu, Q., Zhang, Q., Lu, Y. (2010). Gas barrier properties of natural rubber/kaolin composites prepared by melt blending. *Appl. Clay Sci., 50*, 255-259.

Zhang, H., Zhang, H., Longcheng, T., Zhou, L., Egere, C., Zhang, Z. (2011a). Comparative study on the optical, surface mechanical and wear resistant properties of transparent coatings filled with pyrogenic colloidal silica nanoparticles. *Compos. Sci. Technol., 71*, 471-479.

Zhang, L., Chou, C.P., Moo-Young, M. (2011b). Disulfide bond formation and its impact on the biological activity and stability of recombinant therapeutic proteins produced by *escherichia coli* expression system. *Biotechnol. Adv., 29*, 923-929. Zhang, F., Lan, J., Zhao, Z., Yang, Y., Tan, R., Song, W. (2012a). Removal of heavy metal ions from aqueous solution using Fe_3O_4 -SiO_2-poly(1,2-diaminobenzene) core-shell sub-micron particles. *J. Colloid Interface Sci.*, *387*, 205-212.

Zhang, Q., Liu, Q., Zhang, Y., Cheng, H., Lu, Y. (2012b). Silane-grafted silica-covered kaolinite as filler of styrene butadiene rubber. *Appl. Clay Sci., 65-66*, 134-138.

Zhang, S., Zhang, Y., Liu, J., Xu, Q., Xiao, H., Wang, X., Xu, H., Zhou, J. (2013). Thiol modified Fe₃O₄@SiO₂ as a robust, high effective, and recycling magnetic sorbent for mercury removal. *Chem. Eng. J., 226*, 30–38.

Zhang, X., Yao, X., Wang, X., Feng, L., Qu, J., Liu, P. (2014a). Robust hybrid raspberrylike hollow particles with complex structures: a facile method of swelling polymerization towards composite spheres. *Soft Matter, 10*, 873–881.

Zhang, J., Li, B., Yang, W., Liu, J. (2014b). Synthesis of magnetic Fe₃O₄@hierarchical hollow silica nanosphere for efficient removal of methylene blue from aqueous solution. *Ind. Eng. Chem. Res.*, *53*, 10629-10636.

Zhang, T., Wang, Y., Luo, G., Bai, S. (2016). Effects of precipitation and drying processes on the synthesis of silica materials with a large-pore-volume and narrow-pore-diameter distribution. *Ind. Eng. Chem. Res., 55*, 3579-3587.

Zhang, N.-N., Zhou, C.-C., Liu, C., Pan, J.-H., Tang, M.-C., Cao, S.-S., Ouyang, C.-H., Peng, C.-B. (2017). Effects of particle size on flotation parameters in the separation of diaspore and kaolinite. *Powder Techn.*, *317*, 253-263.

Zhao, M., Zheng, L., Li, N., Yu, L. (2008). Fabrication of hollow silica spheres in an ionic liquid microemulsion. *Mater. Lett., 62*, 4591-4593.

Zhao, S., Peng, Y. (2012). The oxidation of copper sulfide minerals during grinding and their interaction with clay particles. *Powder Technol.*, 230, 112-117.

Zhao, W., Fang, Y., Zhu, Q., Wang, K., Liu, M., Huang, X., Shen, J. (2013a). A novel glucose biosensor based on phosphonic acid-functionalized silica nanoparticles for sensitive detection of glucose in real samples. *Electrochimica Acta, 89*, 278-283.

Zhao, P., Li, N., Astruc, D. (2013b). State of the art in gold nanoparticle synthesis. *Coord. Chem. Rev., 257*, 638-665.

Zhao, K., Gu, G., Wang, C., Rao, X., Wang, X., Xiong, X. (2015). The effect of a new polysaccharide on the depression of talc and flotation of a nickel-copper sulfide ore. *Miner. Eng.*, *77*, 99-106

Zhijun, Z., Jiongtian, L., Zhiqiang, X., Liqiang, M. (2013). Effects of clay and calcium ions on coal flotation. *International Journal of Mining Science and Technology*, *23* (5), 689-692.

Zhong, B., Jia, Z., Luo, Y., Jia, D. (2015). Surface modification of silica with N-cyclohexyl-2-benzothiazole sulfenamide for styrene-butadiene rubber composites with dramatically improved mechanical property. *Mater. Lett.*, *145*, 41-43.

Zhou, Y., Shimizu, K., Cha, J.N., Stucky, G.D., Morse, D.E. (1999). Efficient catalysis of polysiloxane synthesis by silicate α requires specific hydroxyl and imidazole functionalities. *Angew. Chem.*, *38*, 779-782.

Zhou, D., Zhang, L., Zhou, J., Gou, S. (2004). Cellulose/chitin beads for adsorption of heavy metals in aqueous solution. *Water Res., 38* (11), 2643-2650

Zhu, Y., Fang, Y., Borchardt, L., Kaskel, S. (2011). PEGylated hollow mesoporous silica nanoparticles as potential drug delivery vehicles. *Micropor. Mesopor. Mat., 141*, 199-206.

Zhu, Y., Jiang, Y., Goa, J., Zhou, L., He, Y., Jia, F. (2013). Immobilization of glucose oxidase in liposome-templated biomimetic silica particles. *Chinese J. Catal., 34*, 741-750.

Zhu, L.J., Zhu, L.P., Jiang, J.H., Yi, Z., Zhao, Y.F., Zhu, B.K., Xu, Y.Y. (2014). Hydrophilic and anti-fouling polyethersulfone ultrafiltration membranes with poly(2-hydroxyethyl methacrylate) grafted silica nanoparticles as additive. *J. Membr. Sci.*, *451*, 157-168.

Zou, Y., Wang, X., Khan, A., Wang, P., Liu, Y., Alsaedi, A., Hayat, T., Wang, X. (2016). Environmental remediation and application of nanoscale zero-valent iron and its composites for the removal of heavy metal ions: a review. *Environ. Sci. Technol., 50*, 7290-7304.

Supplementary data for Chapter 6

A.1 NaOH-silica shell and KOH-silica coated carbonyl iron particles

Fabrication of the NaOH-silica and KOH-silica shells was performed using the all in one method (Method E) whereby 5.0 ± 0.3 mg mL⁻¹ carbonyl iron particles were combined with 25.0 mM NaOH or KOH and 200 mM TMOMS in a 9:1 water:ethanol medium with a final reaction volume of 1.000 mL. The reaction was conducted for 30 min with the reaction tube upended every 5 min to retain the suspension. Core-shell particles were magnetically separated and washed 3 times with ~1 mL water following the reaction. SEM samples were prepared as per Section 3.7.1.2 and carbon coated before imaging. SEM images of the NaOH-silica and KOH-silica coated carbonyl iron particles taken with the secondary electron detector are presented in Figure A.1.



Figure A.1. SEM images of (A) NaOH-silica and (B) KOH-silica coated carbonyl iron particles. NaOH-silica and KOH-silica coating fabricated using the all in one method (Method E) and a TMOMS concentration of 200 mM. Images were taken with the secondary electron detector.

Both the Method E NaOH-silica and KOH-silica shell fabrication procedures resulted in poor shell coverage of the carbonyl iron core, as can be seen in Figure A.1. The poor shell coverages indicate that the polyamine silication-inducing compound PEI, which was absent for NaOH-silica (Chapter 4) and KOH-silica fabrication, plays an important role in the silica coating of the carbonyl iron cores. The role of the PEI was discussed further in Section 6.4 and 6.5 and will form the subject of future work (Chapter 9).

The NaOH-silica shell was also synthesised using the sonication method (Method D). Firstly, 5.0 ± 0.3 mg carbonyl iron particles (final reaction concentration 5.0 ± 0.3 mg mL⁻¹) and 25.0 µL 1.00 M NaOH (final reaction concentration 25.0 mM) were combined and sonicated for 5 min. Next 14.5 µL TMOMS (neat) (final reaction concentration 100 mM) was added followed by another 5 min of sonication. The reaction mixture was then made up to 1.000 mL through the addition of a 9:1 water:ethanol reaction medium and sonicated for a further 5 min. The reaction was conducted for 30 min with the reaction tube upended every 5 min to retain particle suspension. Core-shell particles magnetically separated and washed three times with water following the reaction. Samples of the synthesised particles were prepared for SEM/EDX analysis as per Sections 3.7.1 and 3.7.2, with carbon coating. The SEM images (taken with the secondary electron and backscattered electron detector) of the NaOH-silica shell – carbonyl iron core particles synthesised using the sonication method are presented in Figure A.2.



Figure A.2. SEM images taken with (A) the secondary electron detector and (B) backscattered electron detector of the NaOH-silica coated carbonyl iron particles. NaOH-silica coating fabricated using the sonication method (Method D) and a TMOMS concentration of 100 mM. The EDX spectra of NaOH-silica coated carbonyl iron particles produced using the sonication method (Method D) are presented in Figure A.3.



Figure A.3. EDX spectra of the NaOH-silica coated carbonyl iron particles. NaOH-silica coating fabricated using the sonication method (Method D) and a TMOMS concentration of 100 mM. (A) and (B) are the EDX spectra of different particles in the same sample to confirm reproducibility.

A.2 ATR-FTIR spectra of PEI-silica coated carbonyl iron particles

In Figures A.4 to A.10 are the full set of ATR-FTIR spectra taken of the PEI-silica coated carbonyl iron particles fabricated using Methods A-G and TMOMS concentrations 50 mM to 300 mM. The data from the spectra (Figures A.4-A.10) was summarised in Chapter 6 (Figure 6.4 and Table 6.2).



Figure A.4. ATR-FTIR spectra of PEI-silica coated carbonyl iron particles. PEI-silica shell fabricated by the two tube method (Method A) with TMOMS concentrations 50 mM to 300 M. Data offset for clarity.



Figure A.5. ATR-FTIR spectra of PEI-silica coated carbonyl iron particles. PEI-silica shell fabricated by the two tube method (Method B) with TMOMS concentrations 50 mM to 300 M. Data offset for clarity.



Figure A.6. ATR-FTIR spectra of PEI-silica coated carbonyl iron particles. PEI-silica shell fabricated by the sonication method (Method C) with TMOMS concentrations 50 mM to 300 M. Data offset for clarity.



Figure A.7. ATR-FTIR spectra of PEI-silica coated carbonyl iron particles. PEI-silica shell fabricated by the sonication method (Method D) with TMOMS concentrations 50 mM to 300 M. Data offset for clarity.



Figure A.8. ATR-FTIR spectra of PEI-silica coated carbonyl iron particles. PEI-silica shell fabricated by the all in one method (Method E) with TMOMS concentrations 50 mM to 300 M. Data offset for clarity.



Figure A.9. ATR-FTIR spectra of PEI-silica coated carbonyl iron particles. PEI-silica shell fabricated by the slow addition method (Method F) with TMOMS concentrations 50 mM to 300 M. Data offset for clarity.



Figure A.10. ATR-FTIR spectra of PEI-silica coated carbonyl iron particles. PEI-silica shell fabricated by the slow addition method (Method G) with TMOMS concentrations 50 mM to 300 M. Data offset for clarity.

Supplementary data for Chapter 7

B.1 Buffer selection

In Figure B.1, Cu(II) adsorption onto raspberry-like PEI-silica – carbonyl iron particles in 2-N-morpholinoethanesulfonic acid (MES) buffer (buffered at pH 6.0 with 16.0, 32.0 and 48.0 mM MES buffer) was compared to adsorption in phosphate buffer (PB) (buffered at pH 6.0 with 32.0 mM PB). MES buffer was prepared from solid MES with the pH adjusted to pH 6.0 by additions of 1.00 M NaOH. The Cu(II) adsorption capacity and removal efficiency of the core-shell particles were given as a function of core-shell particle mass for the different buffer types and concentrations (Figure C.1).



Figure B.1. (A) Cu(II) adsorption capacity and (B) Cu(II) removal efficiency of raspberry-like PEI-silica – carbonyl iron particles as a function of particle mass in different buffer solutions (buffered at pH 6.0).

B.2 Cu(II) adsorption onto PEI-silica versus NaOH-silica particles

To confirm that the Cu(II) ions in solution were interacting with the core-shell particles by forming a complex ion with the PEI groups entrapped on the surface of the PEI-silica – carbonyl iron particles, a control test was performed. In Figure B.2, the Cu(II) ion interaction with PEI-silica particles is contrasted with the ion's interaction with NaOH-silica particles, which do not have entrapped PEI.



Figure B.2. (A) PEI-silica and (B) NaOH-silica particles after incubation with Cu(II) to visually assess the effect of entrapped PEI on Cu(II) interaction.

B.3 EDX spectra of PEI-thiol silica coated carbonyl iron particles following Cu(II) adsorption and desorption

In Figure B.3, the EDX spectra of the PEI-thiol silica – carbonyl iron particles following Cu(II) adsorption and magnetic removal, as well as, Cu(II) desorption and magnetic removal are presented. Both the gel-like and raspberry-like PEI-thiol silica shell morphologies identified in Chapter 6 were considered. Core-shell particles were synthesised in 1.000 mL batches for this experiment, as per Chapter 6 and Section 3.5.3. Cu(II) adsorption was conducted by incubating (10 min with constant 1000 rpm vortex mixing) 5.0 ± 0.3 mg mL⁻¹ suspended core-shell particles with 5.0 mM Cu(II) and 32.0 mM PB (pH 6.0) (as per Chapter 7 and Section 3.6.1). Cu(II) desorption from the core-shell particles was performed through incubating particles in 1.00 mM HCl (pH ~ 3) for 10 min with 1000 rpm vortex mixing (as per Chapter 7 and Section 3.6.1). SEM/EDX samples were prepared as per Sections 3.7.1 and 3.7.2, on silicon wafers and with carbon coating.



Figure B.3. EDX spectra of the (A,C) gel-like and (B,D) raspberry-like PEI-silica – carbonyl iron particles (A,B) after Cu (II) adsorption and (C,D) after the acidic desorption of Cu (II).

In Figure B.3, the successful adsorption and desorption of Cu(II) could be observed by the appearance and disappearance of the characteristic Cu peak at 0.93 keV, respectively. The positive results of this preliminary study indicate that Cu(II) adsorption and desorption is possible with the PEI-thiol silica shell which possesses a dual thiol/amine surface functionalisation. A full set of experiments focusing on ion recovery with a PEI-thiol silica – carbonyl iron carrier particle system, including a comparison to the recovery potential of the PEI-silica – carbonyl iron carrier particle system investigated in Chapter 7, will form the basis of a future study.

Supplementary data for Chapter 8

C.1 Interaction of fine particles with gel-like PEI-silica coated carbonyl iron particles

SEM images showing the interaction of clays (talc, montmorillonite and kaolin) with gellike PEI-silica – carbonyl iron particles at pH 4.0, 7.0 and 10.0 are presented in Figures C.1 and C.2.



Figure C.1. SEM images taken of the gel-like PEI-silica – carbonyl iron particles incubated with (A-C) talc; (D-F) montmorillonite; and (G-I) kaolin. Clays and core shell particles were incubated in succinic acid buffer at pH 4.0, phosphate buffer (PB) at pH 7.0 and gly-gly buffer at pH 10.0. Images taken with the secondary electron detector.



Figure C.2. SEM images taken of the gel-like PEI-silica - carbonyl iron particles incubated with (A-C) talc; (D-F) montmorillonite; and (G-I) kaolin. Clays and core shell particles were incubated in succinic acid buffer at pH 4.0, phosphate buffer (PB) at pH 7.0 and gly-gly buffer at pH 10.0. Images taken with the backscattered electron detector.

SEM images showing the interaction of metal/metalloid oxides (quartz and TiO_2) with gel-like PEI-silica – carbonyl iron particles at pH 4.0, 7.0 and 10.0 are presented in Figures C.3 and C.4.



Figure C.3. SEM images taken of the gel-like PEI-silica - carbonyl iron particles incubated with (A-C) quartz; and (D-F) TiO_2 nanoparticles (20 ± 2 nm). Clays and core shell particles were incubated in succinic acid buffer at pH 4.0, phosphate buffer (PB) at pH 7.0 and gly-gly buffer at pH 10.0. Images taken with the secondary electron detector.


Figure C.4. SEM images taken of the gel-like PEI-silica - carbonyl iron particles incubated with (A-C) quartz; and (D-F) TiO_2 nanoparticles (20 ± 2 nm). Clays and core shell particles were incubated in succinic acid buffer at pH 4.0, phosphate buffer (PB) at pH 7.0 and gly-gly buffer at pH 10.0. Images taken with the backscattered electron detector.