REMOVAL OF
GEOSMIN AND 2-METHYLISOBORNEOL
FROM DRINKING WATER
BY UV/TiO$_2$ TREATMENT

A Thesis Submitted for the Degree of
Doctor of Philosophy

by

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The University of Newcastle
Australia

October 2010
I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

______________________________
Hoang Nguyen Tran
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During my PhD I was motivated by one of Henry Ford’s famous quotes:” Whether you think you can or whether you think you can’t, you are right”. Thinking positive was a great way for me to overcome many difficulties. To be able to have positive thoughts throughout my PhD, I am in debt to a number of people.

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ABSTRACT

Geosmin and 2-methylisoborneol (MIB) are taste and odour compounds commonly present in drinking water. Their presence can be detected even at the nanogram-per-litre level, and at such low concentrations they are not readily removed by conventional water treatment processes. Consequently, alternative treatment processes are needed that add significant cost to the water treatment option. Recently, it has been found that UV/TiO₂ photocatalysis is capable of degrading geosmin and MIB, and because TiO₂ is relatively cheap UV/TiO₂ photocatalysis is a possible commercial treatment option. However, the reaction kinetics and mechanisms are not well understood, which limits current development.

This study was aimed at gaining a better understanding of kinetics and mechanisms of the photocatalytic degradation of geosmin and MIB by UV/TiO₂. It sought to undertake an extensive experimental investigation to quantify the influence of TiO₂ type, TiO₂ loading, geosmin and MIB concentration, UV intensity, mixing condition, pH and presence of additives (bicarbonate, alcohols and humic acid) on the removal of geosmin and MIB. Before embarking on the experiments, however, a rapid and cost-effective methodology for the quantification of geosmin and MIB at the nanogram-per-litre level was required. Consequently, a solid phase micro-extraction technique coupled with gas chromatography/mass spectrometry (GC/MS) analysis was developed. Briefly, accurate and reproducible measurements were achieved with biphenyl-d₁₀ as the internal standard and preconditioning the fibre prior to the adsorption stage. Optimum extraction temperature and duration were found to be 270°C and 30 minutes, respectively.
Once the quantitative detection process was in place geosmin and MIB degradation experiments were carried out using various commercial TiO\textsubscript{2} photocatalysts, including Degussa P25 and Millennium PCs with different specific surface areas. All these photocatalyst were found to be effective to remove geosmin and MIB, with Degussa P25 giving the best performance. Interestingly, there was no apparent correlation between the specific surface area of the photocatalyst particle and the degradation rate. A reason for this is possibly related to the agglomeration occurring when the material is suspended in water.

The experiments examining the degradation rate of geosmin and MIB involved both suspended and immobilised TiO\textsubscript{2} systems. Dark adsorption studies showed that there was negligible adsorption of either geosmin or MIB onto the TiO\textsubscript{2} surface. This observation was supported by zeta potential measurements which identified repulsion between the different surfaces. The degradation rate of both geosmin and MIB involving the activation of TiO\textsubscript{2} photocatalyst with UV light followed a first-order kinetic processes with respect to TiO\textsubscript{2} loading, geosmin and MIB concentration, pH, UV intensity and mixing condition. The degradation rates for the suspended Degussa P25 photocatalyst exhibited energy efficiencies comparable to those of existing treatment processes such as hydrogen peroxide/UV.

The mechanistic studies focused on understanding the generation process for hydroxyl radicals. It was found that the presence of bicarbonate and alcohols, that are known hydroxyl radical scavengers, resulted in a decrease in the degradation rates of both geosmin and MIB. The increased negative effect bicarbonate<methanol<ethanol was consistent with corresponding reduction in the amount of available HO\textsuperscript{*} radicals. Humic acid, commonly present in raw water, exhibited both positive and negative influences
on the degradation rate. This was because humic acid can act as both promoter and scavenger of hydroxyl radicals depending on the conditions. At low concentrations, humic acid slightly increased the degradation rate for both geosmin and MIB. However, this effect was quickly reversed as the concentration of humic acid was increased. Similarly, the presence of hydrogen peroxide showed negative influences on the degradation rate of geosmin and MIB. Again, this effect was thought to be related to the availability of hydroxyl radicals in the degradation process.

The GC/MS analyses identified the presence of 1-propanol, 2-(2-hydroxypropoxy)- and 2-butanol, 3,3’-oxybis- as the intermediates of geosmin degradation, and the presence of camphor and borneol as the intermediates of MIB degradation. From the kinetics and the GC/MS analysis results the degradation pathways of geosmin and MIB have been proposed based on the involvement of hydroxyl radicals. Successful application of the Turchi and Ollis kinetic model based on hydroxyl radical attack has further reinforced the likelihood that hydroxyl radicals are the major contributor to geosmin and MIB degradation resulting from UV/TiO₂.

Finally, recommendations for additional research are presented.
1. Tran, H., Evans, G.M., Yan, Y. and Nguyen, A.V. (2008), Photocatalytic removal of geosmin and MIB and its potential applications for drinking water treatment, *Proceedings, Australasia’s Environmental & Sustainability Conference & Exhibition, Environ08, 5-7 May, Melbourne, Australia, paper 46*.


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# ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Electron acceptor</td>
</tr>
<tr>
<td>AOP</td>
<td>Advanced Oxidation Processes</td>
</tr>
<tr>
<td>BAC</td>
<td>Biological activated carbon</td>
</tr>
<tr>
<td>BDOC</td>
<td>Biodegradable dissolved organic carbon</td>
</tr>
<tr>
<td>C</td>
<td>Molar concentration</td>
</tr>
<tr>
<td>cb</td>
<td>Conduction band</td>
</tr>
<tr>
<td>CLS</td>
<td>Close-loop stripping</td>
</tr>
<tr>
<td>D</td>
<td>Electron donor</td>
</tr>
<tr>
<td>e^-</td>
<td>Electron</td>
</tr>
<tr>
<td>e_{cb}^-</td>
<td>Conduction band electron</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>E</td>
<td>Einstein – unit of photon (1E = 1 mole of photon)</td>
</tr>
<tr>
<td>E_{cb}</td>
<td>Conduction band potential</td>
</tr>
<tr>
<td>E_g</td>
<td>Band gap of the semiconductor</td>
</tr>
<tr>
<td>E-R</td>
<td>Eley-Rideal</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron spin resonance</td>
</tr>
<tr>
<td>E_{vb}</td>
<td>Valence band potential</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular activated carbon</td>
</tr>
<tr>
<td>GC/MS</td>
<td>Gas chromatography/mass spectrometry</td>
</tr>
<tr>
<td>GM</td>
<td>Geosmin</td>
</tr>
<tr>
<td>h</td>
<td>Plank’s constant (6.63×10^{-34} J.s)</td>
</tr>
<tr>
<td>h^+</td>
<td>Hole</td>
</tr>
<tr>
<td>h_\nu</td>
<td>Photon energy</td>
</tr>
<tr>
<td>H_2</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HA</td>
<td>Humic acid</td>
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<td>HO^*</td>
<td>Hydroxyl radical</td>
</tr>
<tr>
<td>H_2O_2</td>
<td>Hydrogen peroxide</td>
</tr>
<tr>
<td>h_{vb}^+</td>
<td>Valence band hole (an electron vacancy in the valence band)</td>
</tr>
<tr>
<td>I</td>
<td>Light intensity</td>
</tr>
<tr>
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<td>Photodegradation rate constant</td>
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<td>Normal hydrogen electrode</td>
</tr>
</tbody>
</table>
NOM  Natural organic matter
Num.%  Number percentage
O2  Oxygen
O2·  Superoxide radical
O3  Ozone
OLS  Open-loop stripping
TEM  Transmission electron microscopy
TiO2  Titanium dioxide
P  Radiant power
PAC  Powdered activated carbon
P25  Degussa P25
PC50  Millennium PC50
PC105  Millennium PC105
PC500  Millennium PC500
pKa  Ionization equilibrium constant
pHzpc  pH at zero point of charge
r  Reaction rate
r0  Initial reaction rate
RH  Organic substance
R·  Organic radicals
rpm  Revolution per minute
SBSE  Stir bar sorptive extraction
SEM  Scanning electron microscope
SIM  Selected ion monitoring
SPME  Solid phase micro-extraction
UV  Ultraviolet
UVA  Ultraviolet - wavelengths of 320-400 nm
UVC  Ultraviolet - wavelengths of less than 280 nm
UV-Vis  Ultraviolet-Visible
vb  Valence band
Vol.%  Volume percentage
wt%  Weigh percentage
ε  Molar absorptivity
φ  Quantum yield
λ  Wavelength
θ  Fraction of surface coverage by the substrate
ξ  Photonic efficiency
ζ  Zeta potential
CHAPTER 1

INTRODUCTION

This chapter introduces the reader to the need for an effective treatment process to deal with taste and odour problems caused by geosmin and 2-methylisoborneol (MIB) in drinking water sources. General knowledge about geosmin and MIB and previous work relating to geosmin and MIB removal are briefly reviewed to highlight the need to gain increased understanding of the kinetics and mechanisms of the removal of geosmin and MIB by UV/TiO$_2$. Finally, an outline of the thesis structure is given along with a brief description of each chapter.
1.1 INTRODUCTION

Geosmin and 2-methylisoborneol (MIB) are common compounds causing taste and odour problems in drinking water. They are produced as secondary metabolites of blue-green algae (cyanobacteria) that is often found in warm surface waters with high nutrient levels, such as eutrophic drinking water reservoirs, lakes and rivers (Codd et al., 2005). An illustration of a cyanobacterial bloom in Myponga Reservoir, South Australia is shown in Figure 1.1.

![Cyanobacterial Bloom in Myponga Reservoir, South Australia, Australia](image)

*Figure 1.1  Cyanobacterial Bloom in Myponga Reservoir, South Australia, Australia*

While geosmin and MIB pose no risk to human health, their unpleasant taste and odour have attracted the highest number of reported complaints about drinking water quality (Suffet et al., 1999). For example, a survey in Australia reported that of the total number of reported complaints, the percentage attributed to taste and odour were 60 and 17%, respectively (Year Book Australia, 2003). Geosmin and MIB have been also found to affect fish stocks and quality, as they are easily absorbed by the tissue of fish and other aquatic organisms, making them unfit for sale (Höfer, 1998). Taste and odour problems added an estimated value of $15-23 million annually to catfish production costs in the United States (Hanson, 2003).
The occurrence of taste and odour events caused by geosmin and MIB is mostly seasonal. Their levels vary significantly throughout the year due to season weather change and generally peak in summer when cyanobacterial blooms occur (Boleda et al., 2007). Maximum geosmin and MIB concentrations of 50-500 ng.L\(^{-1}\) have been detected (Boleda et al., 2007; Uwins et al., 2007; Ingleton et al., 2008; Suffet et al., 2008). These levels are well beyond the taste and odour thresholds of 1.3-7.5 and 2.5-6.3 ng.L\(^{-1}\), respectively (Young et al., 1996). Geosmin and MIB are not easily destroyed under natural conditions. Neither are they effectively removed by conventional treatment processes, such as flocculation, filtration and chlorination of drinking water plants because of their low concentrations in water (Bruce et al., 2002).

Additional treatment is required to remove geosmin and MIB from drinking water to values below the thresholds. The most common industry-scale processes are activated carbon dosing (Jung et al., 2004; Liang et al., 2005), ozonation (Rosenfeldt et al., 2005; Li et al., 2007), and biofiltration (Ho et al., 2007; Joe et al., 2007; Persson et al., 2007). Varying degrees of success have been achieved for each of these processes (Westerhoff et al., 2005a). Advanced oxidation processes, that utilise the highly reactive hydroxyl radical, have been used in the treatment of geosmin and MIB. For example, hydrogen peroxide/UV (Rosenfeldt et al., 2005; Royce and Stefan, 2005) and ozone/UV (Collivignrelli and Sorlini, 2004; Meunier et al., 2006) have been used successfully to remove geosmin and MIB to concentrations below the thresholds.

UV/TiO\(_2\) is also an advanced oxidation process and it has not yet been developed to a commercialised state. The TiO\(_2\) surface becomes energetically excited under illumination of a UV light having photons of energy equal to or greater than the band gap energy, corresponding to wavelengths below 380 nm. Electrons are excited, moving
from the valence band to the conduction band and generating electron and hole pairs. The positively charged holes in TiO$_2$ are very strong oxidising agents and can either oxidise directly or react with hydroxyl ions and water molecules to form hydroxyl radicals which then act as oxidising agents.

The use of TiO$_2$ has a number of advantages. Firstly, when properly dispersed it has the potential to produce large quantities of reactive hydroxyl radicals (Legrini et al., 1993). Secondly, it is chemically stable, non-toxic, reusable and available at a relatively modest price (Carp et al., 2004). Finally, it can be activated by UVA (wavelengths of 320-400 nm) which is at a lower energy than UVC (wavelength less than 280 nm) required for both hydrogen peroxide/UV and ozone/UV processes (Legrini et al., 1993).

UV/TiO$_2$ has been used to destroy a wide range of recalcitrant organic pollutants (Hoffmann et al., 1995; Mills and Le Hunte, 1997). It has been demonstrated, at a laboratory-scale at least, that for initial concentrations of 2-1,000 µg.L$^{-1}$ and 1 hour of treatment greater than 99% decomposition of geosmin and MIB can be achieved. While these initial concentrations are at least an order of magnitude greater than those commonly encountered in the field, the results do highlight the potential of UV/TiO$_2$ in removing geosmin and MIB. Given that it has already been shown to be effective against cyanobacterial toxins (Robertson et al., 1997; Antoniou et al., 2009; Liu et al., 2009; Pelaez et al., 2009), UV/TiO$_2$ has real potential to become a commercial-scale treatment process. However, before this can be achieved a greater understanding of the underlying photocatalytic and oxidation processes are required, as well as the influences of process conditions, such as TiO$_2$ type, TiO$_2$ loading, UV intensity, mixing condition, pH, water composition, etc, is required.


1.2 AIMS OF THIS STUDY

The overall purpose of this study was to gain a better understanding of kinetics and mechanisms of the photocatalytic degradation of geosmin and MIB by UV/TiO$_2$. Specifically the aims were:

1. To assess the effectiveness of UV/TiO$_2$ by undertaking an extensive experimental investigation to quantify the influence of TiO$_2$ type, TiO$_2$ loading, geosmin and MIB concentration, UV intensity, mixing condition, pH and presence of additives (bicarbonate, alcohols and humic acid) on the removal of geosmin and MIB for both suspended and immobilised systems.

2. To utilise the experimental information on geosmin and MIB degradation in identifying possible mechanistic models that describe the UV activation of the TiO$_2$ surface, the intermediates formed and the reactions that take place.

In order to achieve these aims it was essential to quantify the concentrations of geosmin and MIB at the nanogram-per-litre level. Such quantifications or measurements are both difficult and expensive\(^1\). It was not practical, both financially and time-wise, to utilise the services of a commercial laboratory, so consequently an additional aim was:

3. To develop a rapid and cost-effective methodology for the quantification of geosmin and MIB at the nanogram-per-litre level.

Moreover, it was essential to achieve aim (3) before commencing with aims (1) and (2).

\(^1\) Cost for a single geosmin and MIB concentration measurement by a National Association of Testing Authorities registered laboratory in Australia is of order AUS200.
The thesis outline is illustrated in Figure 1.2. Chapter 2 provides a critical review of geosmin and MIB removal processes, including a discussion on the advantages and disadvantages for each process. The UV/TiO₂ process is described as well as the mechanistic models reported in the literature. Finally, the effects of major process variables are reported.
Chapter 3 describes the materials and methodologies employed in this study. Results of the characterisation of the TiO₂ photocatalysts are also presented.

Chapter 4 reports on the development of a methodology for the geosmin and MIB quantification. Existing techniques are reviewed as part of the development process. Quantitative analysis of geosmin and MIB for a range of materials and operating conditions are used to optimise the methodology.

Chapter 5 focuses on quantifying the degradation rate as a function of reactor setup. Experiments are carried out to investigate the degradation of geosmin and MIB as a function of TiO₂ type, TiO₂ loading, TiO₂ coating density, geosmin and MIB concentration, UV intensity, mixing condition, pH and water characteristics. Suspended and immobilised TiO₂ systems are used.

Chapter 6 utilises the experimental work from the previous chapter to explore mechanistic models for the degradation process. Proposed theories are tested, where appropriate, with additional experiments involving the addition of hydroxyl radical scavengers, radical promoters and radical scavenger. Finally, an attempt is made to identify and quantify the presence of intermediates as further validation of the proposed mechanisms.

Chapter 7 summarises the main findings, discusses some of the unsolved problems and provides recommendations for further work.
CHAPTER 2

LITERATURE REVIEW

This chapter outlines and reviews the main geosmin and MIB removal processes. In addition, a review of the UV/TiO₂ process is also described.
2.1 GEOSMIN/MIB REMOVAL

Cyanobacteria are known to produce geosmin and MIB that are the two main taste and odour compounds in drinking water (Zaitlin and Watson, 2006). Cyanobacteria blooms can be minimised through: (1) biological controls by minimising nutrient levels, (2) chemical controls by dosing with copper based algicides and (3) physical controls including artificially agitating the water to create turbulence, restricting light onto the water surface, physically removing algal scum, using clays and/or minerals as flocculants or using sonication. In cyanobacteria bloom events when geosmin and MIB have been released treatment processes are required. However, the standard approach of sedimentation and filtration followed by disinfection has been shown to be ineffective, especially at very low concentrations (Peterson et al., 1995). For this reason, alternative treatment processes have been investigated.

Membrane filtration has been used for geosmin and MIB removal with some degrees of success (Teixeira and Rosa, 2005; Gijsbertsen et al., 2006). Smith et al. (2003) using different types of nano-filtration reported 22-95% removal of geosmin and MIB. Reiss et al. (2006) reported 35-50% removal of geosmin and MIB for a cellulose acetate membrane while for polyamide over 99% removal was achieved. Reiss et al. (2006) also discuss the high cost of the different membrane technologies and the need for cheaper alternatives.

Alternative treatment processes can be broadly classified as being either (a) adsorption or (b) oxidation. Adsorption occurs when the geosmin and MIB molecules are adsorbed by an activated material that is then physically separated from the water by a subsequent
filtration stage whereas advanced oxidation specifically utilises hydroxyl radicals (HO•) to break down the geosmin and MIB molecules. The oxidation potential of HO• is 2.80 V, which is much higher than that of chlorine (1.36 V), hypochlorous acid (1.49 V), hydrogen peroxide (1.77 V), ozone (2.07 V) and even nascent ozone (2.42 V). Hydroxyl radicals can oxidise a broad range of organic contaminants, including geosmin and MIB, into carbon dioxide and water. Ideally, advanced oxidation processes are preferred as they destroy the contaminant rather than transfer it from one phase to another, as is the case with activated carbon or air stripping processes (Legrini et al., 1993). The most common adsorption and advanced oxidation processes are presented in Table 2.1.

### Table 2.1  Geosmin/MIB Removal Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Powdered activated carbon (PAC)</td>
</tr>
<tr>
<td></td>
<td>Granular activated carbon (GAC)</td>
</tr>
<tr>
<td></td>
<td>Biological activated carbon (BAC)</td>
</tr>
<tr>
<td>Advanced oxidation</td>
<td>Ozone</td>
</tr>
<tr>
<td></td>
<td>Ozone/Hydrogen peroxide</td>
</tr>
<tr>
<td></td>
<td>Ozone/UV</td>
</tr>
<tr>
<td></td>
<td>Hydrogen peroxide/UV</td>
</tr>
<tr>
<td></td>
<td>UV/TiO₂</td>
</tr>
<tr>
<td>Adsorption/Advanced oxidation</td>
<td>Ozone/BAC</td>
</tr>
</tbody>
</table>

2 Other advanced oxidation processes include ultrasonic radiation (Song and O’Shea, 2007) and UVC radiation (Kutschera et al., 2009) presently remain only at the laboratory scale. For this reason they are not included in Table 2.1.
2.1.1 Powdered and Granulated Activated Carbon

Activated carbon is a material with an exceptionally high surface area (>400 m².g⁻¹). Typically, activated carbon is used to enhance the adsorbing properties of the material in metal extraction, water purification, medicine, sewage treatment and gas purification. Both powdered (PAC) and granular (GAC) activated carbon are used in water treatment (Herzing et al., 1977). Generally, PAC is directly added to the raw water either as a powder or in slurry form prior to the addition of either oxidant or coagulant chemicals. This allows the carbon to adsorb taste and odour generating compounds without losing adsorption ability. Conversely, GAC is used after conventional water treatment operations and in continuous flow through column reactors with adsorption occurring in filters rather than in the sedimentation process (Mallevalle and Suffet, 1987). For both powdered and granulated activated carbon removal performance is a function of: (1) type (Matsui et al., 2002; Yu et al., 2007), (2) contact time (Nowack et al., 2004) and (3) water quality (Cook et al., 1998).

A number of studies have been reported for the removal and geosmin and MIB using PAC. Cook et al. (2001) found that for the water treatment plants of Anstey Hill, Happy Valley, Hope Valley and Myponga in Australia, the minimum PAC doses required to reduce 40 ng.L⁻¹ of geosmin and MIB to 10 ng.L⁻¹ with a contact time of 50 minutes were 21 and 39 mg.L⁻¹, respectively. Jung et al. (2004) using PAC for the taste and odour treatment of Lake Paldang in Korea water found that for a dosage of 30 mg.L⁻¹, 70.4-87.3% of geosmin (initial concentration of 106-220 ng.L⁻¹) and 38.5-51.2% of MIB (initial concentration of 112-158 ng.L⁻¹) was removed. Moreover, they found that over 50 mg.L⁻¹ was required to achieve 70% MIB removal. Liang et al. (2005) used both wood and coal-based PAC and found that for initial MIB concentration of 100
ng.L\(^{-1}\) after a contact time of 1 hour and 20 mg.L\(^{-1}\) PAC dosage, the wood-based PAC removed 53.16% of the MIB, while for coal-based PAC achieved a removal of 74.68%. Generally, it was found that with PAC doses of 20-40 mg.L\(^{-1}\) and contact times of 20-50 minutes, maximum removal achieved was about 90% (Kim et al., 1997; Gillogly et al., 1999; Cook et al., 2001) with geosmin being more easily removed than MIB (Jung et al., 2004).

Granular activated carbon has a longer functional time and higher adsorptive capacity than PAC. It also provides the ability to regenerate the carbon for reuse and easy process control (Sugiura et al., 1997; Svrcek and Smith, 2004). Like PAC, type of carbon source and water quality greatly influences removal efficiency (Chestnutt et al., 2007; Drikas et al., 2009). Kim et al. (1997) reported removal efficiencies of 63-74%, with initial geosmin and MIB concentrations of 15.6 and 82 ng.L\(^{-1}\), respectively. Ndiongue et al. (2006) reported that within a 5 minutes contact time frame in filters with 25 centimetres of new GAC, 78% of geosmin (initial concentrations of 70-110 ng.L\(^{-1}\)) was removed. However, removal efficiency decreased gradually to 10-38% over time. Similarly, Ridal et al. (2001) reported that GAC filters removed on average 80% of geosmin and 60% of MIB (initial concentrations of 5-60 ng.L\(^{-1}\)). However, after 24 successive times of operation, the removal efficiency was reduced to 54% for geosmin and 15% for MIB.

Geosmin and MIB removal efficiencies for both PAC and GAC are influenced by adsorption of natural organic matter (NOM) present in the water. NOM competes with geosmin and MIB for adsorption sites on the activated carbon surface and leads to a decrease in the longevity of the activated carbon (Newcombe et al., 1997) and reduces removal efficiency with time (Ridal et al., 2001; Ndiongue et al., 2006).
2.1.2 Biological Activated Carbon

Biological activated filtration (BAC) processes involve the use of micro-organisms to convert contaminated substances into less toxic substances. Geosmin and MIB are susceptible to biological degradation as their molecular structures are similar to biodegradable alicyclic alcohols and ketones (Rittmann et al., 1995). However, micro-organisms must have appropriate enzymes to biodegrade geosmin and MIB. Since the taste and odour thresholds of geosmin and MIB are very low, these compounds in raw water do not support the growth of micro-organisms in a biofilter as primary substrates (primary substrates maintained biofilm micro-organisms). Hence, geosmin and MIB behave as secondary substrates. Secondary substrates can be only biodegraded when the primary substrate concentration falls below its minimum level to sustain biological growth. Several organisms are capable of biotransforming MIB into innocuous forms, including Candida sp. (yeast), Bacillus subtilis, Enterobacter sp., Pseudomonas putida, and Pseudomonas fluorescens (Sumitomo, 1992; Tanaka et al., 1996).

The efficiency of a BAC process is determined by its surface area and the amount of water passing over it. The efficiency is strongly influenced by the type of micro-organisms used and the media such as water quality and its dynamic parameters, including temperature, pH and dissolved oxygen content (Lorio et al., 1992). BAC processes usually combine with other materials used as a filter such as sand or GAC. Studies of geosmin and MIB removal using different filter types are summarised in Table 2.2.
Table 2.2  Removal of Geosmin/MIB in Biofilter Studies

<table>
<thead>
<tr>
<th>Reactor Type/Media</th>
<th>Contact Time (min)</th>
<th>Initial Conc. (ng.L⁻¹)</th>
<th>GM/MIB Removal (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seeding sand</td>
<td>8-17 days</td>
<td>100 (GM)</td>
<td>75-80 (GM)</td>
<td>McDowall et al., 2009</td>
</tr>
<tr>
<td>GAC biofilter</td>
<td>30</td>
<td>n/a</td>
<td>&gt;96</td>
<td>Persson et al., 2007</td>
</tr>
<tr>
<td>Batch sand biofilter</td>
<td>35 days</td>
<td>120 (GM)</td>
<td>96-100</td>
<td>Ho et al., 2007</td>
</tr>
<tr>
<td>Fresh GAC biofilter</td>
<td>n/a</td>
<td>100</td>
<td>76-96 (GM)</td>
<td>Elhadi et al., 2004</td>
</tr>
<tr>
<td>Rapid GAC biofilter</td>
<td>14.4-20.2</td>
<td>9-17</td>
<td>26-64</td>
<td>Nerenberg et al., 2000</td>
</tr>
<tr>
<td>Bench-scale bioreactor with glass beads</td>
<td>n/a</td>
<td>32</td>
<td>43-56</td>
<td>Huck et al., 1995</td>
</tr>
<tr>
<td>Granular ceramic biofilter</td>
<td>12.7</td>
<td>50-750</td>
<td>60-80</td>
<td>Terauchi et al., 1995</td>
</tr>
<tr>
<td>Lab slow sand</td>
<td>480</td>
<td>50</td>
<td>&gt;95</td>
<td>Lundgren et al., 1988</td>
</tr>
<tr>
<td>Lab GAC biofilter</td>
<td>n/a</td>
<td>360 (GM)</td>
<td>98</td>
<td>Yagi et al., 1988</td>
</tr>
<tr>
<td>Lab honeycomb tube biofilter</td>
<td>120</td>
<td>90 (GM)</td>
<td>83</td>
<td>Hattori, 1988</td>
</tr>
<tr>
<td>Rapid sand biofilter</td>
<td>8.3</td>
<td>20-120</td>
<td>8-54</td>
<td>Ashitani et al., 1988</td>
</tr>
</tbody>
</table>

Yagi et al. (1988) utilised a bio-activated carbon filter seeded with a particular strain of *Bacillus subtilis* to obtain 88-100% MIB removal with the initial concentrations of 25-69 ng.L⁻¹. They also obtained 98% geosmin removal with the initial concentration of 360 ng.L⁻¹. Lundgren et al. (1988) used slow sand bio-filters to obtain success rates
greater than 95% removal of geosmin and MIB with the initial concentration of 50 ng.L\(^{-1}\). Hattori (1988) used a honeycomb tube bio-filter to obtain 63 and 83% removal of MIB (160 ng.L\(^{-1}\) and geosmin (90 ng.L\(^{-1}\)), respectively. Ho et al. (2002) found that the effectiveness of the BAC was strongly influenced by the presence of NOM at much higher concentrations than geosmin and MIB.

2.1.3 Ozone

Ozonation is used to disinfect water supplies. Oxidation processes may occur directly through oxidation of dissolved compounds with molecular ozone, or indirectly through oxidation with hydroxyl radicals (HO•), which are formed by ozone decomposition as described by Reactions 2.1-2.4 (Hoigne and Bader, 1976).

\[
\begin{align*}
O_3 + HO^- & \rightarrow HO_2^- + O_2 \\ O_3 + HO_2^- & \rightarrow HO^+ + O_2^- + O_2 \\ O_3 + O_2^- & \rightarrow O_5^- + O_2 \\ O_5^+ + H_2O & \rightarrow HO^+ + HO^- + O_2
\end{align*}
\] (2.1) (2.2) (2.3) (2.4)

While ozone is considered as a selective oxidant, hydroxyl radicals are highly reactive non-selective oxidants (Meunier et al., 2006). Ozone is one of the strongest oxidants, being capable to degrade taste and odour compounds.

The efficiency of the ozonation process strongly depends on solution pH, water quality and ozone dose (Meunier et al., 2006). The increase of solution pH increases the degradation rate of both ozonation alone and the combined ozone processes (Beltran et al., 1997), which was explained by the reaction of ozone with the hydroxyl ion (Reaction 2.1) that was considered as a first step of radical mechanism leading to the
formation of hydroxyl radicals (Beltran et al., 1997; Von Gunten, 2003). High pH of 9-11 was reported to be the optimum value for oxidation by ozone (Beltran et al., 1997). It was agreed by Duguet et al. (1989), who observed that geosmin and MIB removal by ozonation was significantly influenced by solution pH. At pH 5.6 and 7.5 the concentration of geosmin or MIB was reduced from 350-500 ng.L\(^{-1}\) to 100 ng.L\(^{-1}\) (71-80% removal) in 30 minutes using an ozone dose of 2 mg.L\(^{-1}\). The reaction rate increased by a factor of 5-6 at pH 11, reducing geosmin or MIB concentration to less than 10 ng.L\(^{-1}\) (98% removal) in 20 minutes.

Geosmin and MIB removal is also influenced by water media. Lalezary et al. (1986) found that the optimum ozone dose of 4 mg.L\(^{-1}\) achieved highest destruction of only 30% of geosmin and MIB (initial concentration of 100 ng.L\(^{-1}\)) in organic-free water. Terashima (1988), however, reported that doses between 2 and 5 mg.L\(^{-1}\) of ozone led to 75-100% destruction of MIB (initial concentrations of 55-250 ng.L\(^{-1}\)) and geosmin (initial concentrations of 33-89 ng.L\(^{-1}\)) in natural water. Jung et al. (2004) found that at an ozone dose of 3.8 mg.L\(^{-1}\), 84.8% MIB removal efficiency (initial concentrations of 66-291 ng.L\(^{-1}\) from Lake Paldang water in Korea) was achieved. Similarly, Glaze et al. (1990) reported that an ozone dose of 0.2 mg.L\(^{-1}\) resulted in 73-83% of MIB removal and 86-92% of geosmin removal from Colorado River water. Different results of the destruction of geosmin and MIB obtained can be attributed to the nature of water used, as natural waters contain variable constituents, such as NOM, which affect the ozonation process (Ho et al., 2002). Table 2.3 summarises geosmin and MIB removal in different water media with different ozone doses.
## Table 2.3  Summary of Geosmin/MIB Removal by Ozone

<table>
<thead>
<tr>
<th>Water Source</th>
<th>Ozone Dose (mg.L⁻¹)</th>
<th>Contact Time (min)</th>
<th>Initial Conc. (ng.L⁻¹)</th>
<th>GM / MIB removal (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Paldang water in Korea</td>
<td>3.8</td>
<td>6.4</td>
<td>66-291</td>
<td>84.8 (MIB)</td>
<td>Jung <em>et al.</em>, 2004</td>
</tr>
<tr>
<td>Detroit source raw water</td>
<td>0.5-2</td>
<td>n/a</td>
<td>40 (GM)</td>
<td>30-95 (GM)</td>
<td>Atasi <em>et al.</em>, 1999</td>
</tr>
<tr>
<td>California surface water</td>
<td>0.2</td>
<td>20</td>
<td>n/a</td>
<td>98 (GM)</td>
<td>Glaze <em>et al.</em>, 1990</td>
</tr>
<tr>
<td>Colorado River water</td>
<td>0.2</td>
<td>20</td>
<td>n/a</td>
<td>73-82 (GM)</td>
<td>Glaze <em>et al.</em>, 1990</td>
</tr>
<tr>
<td>Pure water</td>
<td>2</td>
<td>30</td>
<td>350-500</td>
<td>71-80</td>
<td>Duguet <em>et al.</em>, 1989</td>
</tr>
<tr>
<td>Osaka municipal water</td>
<td>2-5</td>
<td>10</td>
<td>55-250</td>
<td>75-100</td>
<td>Terashima, 1988</td>
</tr>
</tbody>
</table>

Ozone dose is another important factor. Atasi *et al.* (1999) reported an increase from 30 to over 95% removal of geosmin (initial concentration of 40 ng.L⁻¹) when the ozone dose was increased from 0.5 to 2.0 mg.L⁻¹. For MIB (initial concentration of 26 ng.L⁻¹), 80% removal was achieved with an ozone dose of 2 mg.L⁻¹.

High removal efficiencies can be achieved at high ozone doses. However, at these levels bromate (OBr⁻) is produced, and these are known carcinogens (Meunier *et al.*, 2006; Sagehashi *et al.*, 2005). After 20 minutes of contact time with an ozone dosage of 1 mg.L⁻¹, the concentrations of bromates formed were between 3 and 6 μg.L⁻¹, which is close to the European Union and the USEPA (USEPA, 1998) drinking water standard of 10 μg.L⁻¹. There are three strategies to reduce levels of bromates in water: (1) reducing
pH, which shifts the equilibrium from OBr\(^-\) to HOBr, (2) adding ammonia before ozonation that allows HOBr/OBr\(^-\) available in water to react with ammonia and form bromanines, rather than being oxidised further by ozone and hydroxyl radicals to form bromates and (3) minimising the ozone dosage required (less than 1 mg.L\(^{-1}\)) by combining ozonation with other processes such as BAC, hydrogen peroxide and UV treatment (Meunier et al., 2006).

### 2.1.4 Ozone/Hydrogen Peroxide

The benefit of introducing hydrogen peroxide in the ozonation process lies in the formation of hydroxyl radicals (Beltran et al., 1997). Hydroxyl peroxide reacts very slowly with ozone, suggesting that the reactive species are in their ionised form (HO\(_2\)^-) as described by Reaction 2.5. Hydroxyl radicals are formed by the reaction of these ions with ozone (Reaction 2.6), which helps to increase the oxidation rate (Duguet et al., 1989).

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{HO}_2^- \\
\text{O}_3 + \text{HO}_2^- & \rightarrow \text{HO}^+ + \text{O}_2^+ + \text{O}_2
\end{align*}
\]

The addition of hydrogen peroxide in the ozonation process has been found to increase the degradation rate of various compounds (Beschkov et al., 1997; Mokrini et al., 1997; Ormad et al., 1997; Beltran et al., 1999; Berger et al., 1999; Akmehehmet and Otker, 2003; Rosenfeldt et al., 2006; Chu and Lau, 2007; Lee et al., 2007; Oguz and Keskinler, 2007; Pi et al., 2007; Wert et al., 2007). Similar results have been found for geosmin and MIB. The addition of hydrogen peroxide (at 6 ppm) has been shown to increase the removal rate of geosmin or MIB. With an ozone dose of 2 mg.L\(^{-1}\) and at a pH of 7.5, the
concentration of geosmin or MIB was reduced from 500 ng.L$^{-1}$ to less than 10 ng.L$^{-1}$ in just less than 5 minutes (Duguet et al., 1989); which is about 10 fold faster than that obtained with ozone alone. Similarly, Bablon et al., (1991) reported that the addition of hydrogen peroxide increased geosmin and MIB removal by up to 35% compared to ozone alone (ozone dosages of 1, 2 and 4 mg.L$^{-1}$; the ratio of O$_3$/H$_2$O$_2$=2). Atasi et al. (1999) and Glaze et al. (1990) observed that the presence of hydrogen peroxide helped to increase 10% and about 5%, respectively, in geosmin removal at low ozone dosages (less than 2 mg.L$^{-1}$). Ozone coupled with hydrogen peroxide has been reported as one of the most effective processes for geosmin and MIB removal (Bruchet et al., 2004).

2.1.5 Ozone/Ultraviolet Radiation

By itself, UVA radiation is not effective in removing geosmin and MIB. However, it can combine with ozone to produce hydrogen peroxide (Peyton and Glaze, 1988) as described in Reaction 2.7.

$$\text{O}_3 + \text{H}_2\text{O} \xrightarrow{\text{hv}} \text{H}_2\text{O}_2$$  \hspace{1cm} (2.7)

This can then lead to an increase in the concentration of hydroxyl radicals. Glaze et al. (1990) found that with an ozone dosage of 0.2 mg.L$^{-1}$ and a UVA radiation 75-83% MIB and 99% reduction of geosmin reduction were obtained within 20 minutes. Collivignarelli and Sorlini (2004) found that the combination of ozone (1.5-3 mg.L$^{-1}$) and UV radiation (5,000-6,000 J.m$^{-2}$) completely removed geosmin and MIB within 2-3 minutes and the concentration of bromate formation was 40-50% lower than that of using the ozone process alone. Meunier et al. (2006) reported that combining with UV
50% removal of geosmin and 40% removal of MIB were achieved at an ozone dose of 0.5 mg.L⁻¹.

2.1.6 Hydrogen Peroxide/Ultraviolet Radiation

The UV radiation of hydrogen peroxide generates hydroxyl radicals. The mechanism most commonly accepted is the cleavage of the hydrogen peroxide molecule into hydroxyl radicals at UV wavelengths below 300 nm (Rosenfeldt et al., 2005):

\[
\text{H}_2\text{O}_2 + \text{hv, } \lambda < 300 \text{ nm} \rightarrow 2\text{HO}^* \quad (2.8)
\]

Any un-reacted hydroxyl radicals can be subsequently consumed by hydrogen peroxide (Rosenfeldt et al., 2006):

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{HO}^* & \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \quad (2.9) \\
\text{HO}_2^* + \text{HO}^* & \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (2.10)
\end{align*}
\]

The H₂O₂/UV process has advantages of (1) no inhibition of light transmittance and (2) no need for H₂O₂ removal after treatment, thus making the process very promising to remove contaminants from water. The H₂O₂/UV process has been applied in a number of plants and it has been the subject of numerous studies (e.g.: Shemer and Linden, 2006; Abdullah et al., 2007; Chiou, 2007; Coleman et al., 2007; Daneshvar et al., 2007; Mamane et al., 2007; Sanchez-Polo et al., 2007; Schrank et al., 2007; Toor and Mohseni, 2007; Xu et al., 2007).

Geosmin and MIB have been successfully removed to a level below their odour threshold by the H₂O₂/UV process. Rosenfeldt et al. (2005) reported that 10-50% of geosmin and MIB were removed by direct UVC photolysis with an energy consumption
of 1,000 mJ.cm\(^{-2}\). The removal efficiency, however, was greatly improved by adding 2.3 mg.L\(^{-1}\) of hydrogen peroxide, and more than 70% removal efficiencies were achieved with 7.2 mg.L\(^{-1}\) of hydrogen peroxide. At the pilot-scale, Korategere et al. (2004) reported that with UVC photolysis the geosmin and MIB removal efficiencies were 20-50%. With the addition of hydrogen peroxide the corresponding removal efficiencies were increased to 40-99%. Romain et al. (2003) found that up to 98% geosmin removal (initial concentration of 120 ng.L\(^{-1}\)) was achieved with a UV dose of 458 mJ.cm\(^{-2}\) and 2.2 mg.L\(^{-1}\) hydrogen peroxide. Royce and Stefan (2005) also reported that UV and hydrogen peroxide could remove geosmin and MIB (initial concentration of 200 ng.L\(^{-1}\)) to levels below their taste and odour thresholds.

H\(_2\)O\(_2\)/UV has been found to be cost effective in removing geosmin and MIB. Rosenfeldt et al. (2005) reported UV energy consumption of less than 5 kWh to remove 90% of geosmin and MIB in 1,000 gallons (3,785 litres) of clear-well or raw blend water, corresponding to a cost of less than US$ 0.35 per 1,000 gallons. In contrast, Trojan Technologies Inc (Royce and Stefan, 2005) report a much lower cost at US$ 0.05-0.07 per 1,000 gallons for a combined oxidation and disinfection system.

### 2.1.7 Ultraviolet Radiation/ TiO\(_2\)

TiO\(_2\) activated with ultraviolet radiation has been found to destroy a wide range of organic contaminants including a number of toxic cyanobacteria metabolites (Shephard et al., 1998; Senogles et al., 2001; Cornish et al., 2000; Liu et al., 2002; Shephard et al., 2002; Lawton et al., 2003a; Lee et al., 2004a; Lee et al., 2004b; Liu et al., 2005a; Antoniou et al., 2008; Antoniou et al., 2009; Liu et al., 2009; Pelaez et al., 2009). For geosmin and MIB removal, Lawton et al. (2003b) reported over 99% removal (initial
concentrations of 2 ng.L⁻¹) after 30 and 60 minutes of treatment using suspended (Degussa P25) TiO₂. Bellu et al. (2008), using a pellet form of TiO₂ (Hombikat K01/C) obtained complete removal of geosmin (with initial concentration of 1,000 μg.L⁻¹) after 25 minutes treatment. Both the work of Lawton et al. (2003b) and Bellu et al. (2008) use initial concentrations that are at least an order of magnitude greater than those commonly encountered in taste and odour events in drinking water sources.

2.1.8 Ozone/Biological Activated Carbon

Ozonation followed by BAC includes both oxidation and the adsorption stages of treatment. The ozone breaks down the larger geosmin and MIB molecules into other (lower molecular weight) compounds, namely biodegradable dissolved organic carbon (BDOC), that are more readily utilised in a fixed biologically activated carbon filter. Nerenberg et al. (2000) reported 65-100% removal of MIB with combined ozone/BAC process compared to 26-64% removal was achieved with biofiltration alone. Joe et al. (2007) successfully removed MIB from Han River water (Korea) to levels below its threshold by using ozone/BAC.

2.1.9 Summary of Geosmin/MIB Removal Processes

In summary, for adsorption processes removal efficiencies of up to 90% can be regularly achieved. When biological activated carbon is combined with ozonation, the removal efficiency can be further increased. Advanced oxidation processes show better removal efficiencies of up to 100% removal of geosmin and MIB. A listing of previous studies involving geosmin and MIB removal by advanced oxidation processes is reviewed and presented in Table 2.4. Ozonation can also be combined with hydrogen peroxide and UV treatment to enhance geosmin and MIB removal. The operating cost
for all these treatment processes, however, can be substantially high precluding their wide-scale application. A possible low cost alternative is UV activation of TiO₂.

### Table 2.4 Geosmin/MIB Removal by AOP

<table>
<thead>
<tr>
<th>Compound</th>
<th>C&lt;sub&gt;in&lt;/sub&gt; (ng.L⁻¹)</th>
<th>Removal Process</th>
<th>R. (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM</td>
<td>10</td>
<td>H₂O₂/UV (1,000 mJ.cm⁻²)</td>
<td>&gt;70</td>
<td>Rosenfeldt et al., 2005</td>
</tr>
<tr>
<td>MIB</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GM - MIB</td>
<td>200</td>
<td>H₂O₂ (0-11 mg.L⁻¹)/UV</td>
<td>&gt;95</td>
<td>Royce and Stefan, 2005</td>
</tr>
<tr>
<td>GM</td>
<td>300</td>
<td>H₂O₂ (3-4 mg.L⁻¹)/UV</td>
<td>40-99</td>
<td>Korategere et al., 2004</td>
</tr>
<tr>
<td>MIB</td>
<td>150</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GM</td>
<td>120</td>
<td>H₂O₂ (2.2 mg.L⁻¹)/UV (458 mJ.cm⁻²)</td>
<td>85-98</td>
<td>Romain et al., 2003</td>
</tr>
<tr>
<td>GM - MIB</td>
<td>25</td>
<td>H₂O₂ (2 mg.L⁻¹)/UV (3,000 - 10,000 mJ.cm⁻²)</td>
<td>100%</td>
<td>Linden et al., 2002</td>
</tr>
<tr>
<td>GM - MIB</td>
<td>100</td>
<td>H₂O₂ (5-25 mg.L⁻¹)/UV</td>
<td>&gt;90</td>
<td>Andrews et al., 1995</td>
</tr>
<tr>
<td>GM</td>
<td>n/a</td>
<td>O₃/UV (40 mJ.cm⁻²)</td>
<td>50</td>
<td>Meunier et al., 2006</td>
</tr>
<tr>
<td>MIB</td>
<td>n/a</td>
<td></td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>GM</td>
<td>22</td>
<td>O₃ (4 mg.L⁻¹)/</td>
<td>100</td>
<td>Collivignarelli and Sorlini, 2004</td>
</tr>
<tr>
<td>MIB</td>
<td>130</td>
<td>UV (500-600 mJ.cm⁻²)</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>MIB</td>
<td>120</td>
<td>O₃ (1-4 mg.L⁻¹)/UV (270-1,400 mJ.cm⁻²)</td>
<td>25-75</td>
<td>Bablon et al., 1991</td>
</tr>
<tr>
<td>MIB</td>
<td>n/a</td>
<td>O₃ (0.2 mg.L⁻¹)/</td>
<td>75-83</td>
<td>Glaze et al., 1990</td>
</tr>
<tr>
<td>GM</td>
<td>n/a</td>
<td>UV (flux of 0.56 W.L⁻¹)</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>GM</td>
<td>40</td>
<td>O₃ (0.5-2 mg.L⁻¹)/H₂O₂</td>
<td>40-100</td>
<td>Atasi et al., 1999</td>
</tr>
<tr>
<td>MIB</td>
<td>n/a</td>
<td>O₃ (1-4 mg.L⁻¹)/H₂O₂ (0.2-2 mg.L⁻¹)</td>
<td>75-95</td>
<td>Bablon et al., 1991</td>
</tr>
<tr>
<td>GM</td>
<td>n/a</td>
<td>O₃ (0.2 mg.L⁻¹)/H₂O₂ (0.1 mg.L⁻¹)</td>
<td>95</td>
<td>Glaze et al., 1990</td>
</tr>
<tr>
<td>MIB</td>
<td>n/a</td>
<td></td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>GM - MIB</td>
<td>500</td>
<td>O₃ (2 mg.L⁻¹)/H₂O₂ (6 mg.L⁻¹)</td>
<td>&gt;98</td>
<td>Duguet et al., 1989</td>
</tr>
<tr>
<td>GM</td>
<td>1,000,000</td>
<td>UV/TiO₂ (Hobikat K01/C)</td>
<td>100</td>
<td>Bellu et al., 2008</td>
</tr>
<tr>
<td>GM - MIB</td>
<td>2,000</td>
<td>UV/TiO₂ (Degussa P25)</td>
<td>99</td>
<td>Lawton et al., 2003b</td>
</tr>
</tbody>
</table>
2.2 ULTRAVIOLET RADIATION/ TiO₂

2.2.1 Introduction

Heterogeneous photocatalysis is a process based on the radiation of a photocatalyst, usually a semiconductor, such as TiO₂, ZnO or CdS. The energy band and the electrical conductivity of semiconductors compared to insulators and metals, is illustrated in Figure 2.1. For a metal there is no band gap, so electrons (e⁻) can move freely, giving rise to conductivity. For an insulator the band gap is so large that an electron cannot cross the distance. For a semiconductor the electrons in the valance band can be excited by light energy equal to or greater than its band gap, moving it to the conduction band, thereby creating electron vacancies called holes (h⁺) in the valence band (Hoffmann et al., 1995).

![Energy Bands in Insulators, Semiconductors and Metals](image)

**Figure 2.1** Energy Bands in Insulators, Semiconductors and Metals
The excited electrons and holes can either get trapped in the surface defect state or react with electron donors and electron acceptors that are either adsorbed onto the semiconductor surface or within the surrounding electrical double layer of the charged particles. In the absence of electron and hole scavengers, the stored energy is released within a few nanoseconds through the recombination of electrons and holes. If a suitable scavenger or surface defect state is available to trap electrons or holes, the electron-hole recombination reaction is prevented and subsequent reduction-oxidation (redox) reactions may occur (Hoffmann et al., 1995).

A schematic illustration of the processes involving $e^-$ and $h^+$ at the surface of a semiconductor photocatalyst (Mills and Le Hunte, 1997) is shown in Figure 2.2.

**Figure 2.2**  Processes Occurring on a Semiconductor Particle under Illumination

\[ h = \text{Planck's constant} \ (6.63 \times 10^{-34} \ J.s), \ \nu \text{ is the radiation frequency, } E_g \text{ is the band gap, } CB \text{ is the conduction band, } VB \text{ is the valence band} \]

Photo-generated electrons can reduce an electron acceptor, A, as indicated by reaction (a); while photo-generated holes can oxidise an electron donor, D, as indicated by
reaction (b). Electron-hole recombination can occur either at the surface, via reaction (c), or in the bulk, via reaction (d).

Some semiconductors commonly used as photocatalysts include titanium dioxide (TiO₂), zinc oxide (ZnO), tungsten oxide (WO₃), hematite (α-Fe₂O₃), strontium titanate (SrTiO₃), cadmium sulphide (CdS), and zinc sulphide (ZnS). Figure 2.3 illustrates band gaps and band-edge positions in aqueous media at pH 0 for a number of semiconductor materials and the relevant redox couples. Table 2.5 lists the corresponding threshold wavelengths needed to activate photocatalysts (Chen et al., 2000).

**Figure 2.3  Band Gap Edge Positions for Different Semiconductors at pH = 0**

If the reduction of a given electron acceptor species, A, is to occur, its redox level must be positioned below the conduction band of the semiconductor. Similarly, if oxidation of an electron donor species, D, is to occur its redox level needs to be located above the valence band of the semiconductor. When the redox levels of A or D are located
between the valance and conduction bands of the semiconductor, both reduction of A and oxidation of D can occur (Serpone, 1995).

Table 2.5 Band Gap Energies and Corresponding Threshold Wavelengths for Different Semiconductors at pH = 0

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Band gap (eV)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ (rutile)</td>
<td>3.0</td>
<td>413</td>
</tr>
<tr>
<td>TiO₂ (anatase)</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.6</td>
<td>335</td>
</tr>
<tr>
<td>CdS</td>
<td>2.4</td>
<td>516</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.2</td>
<td>539</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>WO₃</td>
<td>2.7</td>
<td>443</td>
</tr>
</tbody>
</table>

2.2.2 Reaction Sequence

The heterogeneous photocatalytic process using TiO$_2$ as the photocatalyst is a complex sequence of reactions that can be expressed by the following set of simplified reactions:

\[
\text{TiO}_2(h^\ast_{vb}) + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + \text{HO}^\ast + \text{H}^+ \quad (2.11)
\]

\[
\text{TiO}_2(h^\ast_{vb}) + \text{HO}^- \rightarrow \text{TiO}_2 + \text{HO}^\ast \quad (2.12)
\]

\[
\text{TiO}_2(h^\ast_{vb}) + \text{D} \rightarrow \text{TiO}_2 + \text{D}^+ \quad (2.13)
\]

\[
\text{HO}^\ast + \text{D} \rightarrow \text{D}' \quad (2.14)
\]

\[
\text{TiO}_2(e^-_{cb}) + \text{A} \rightarrow \text{TiO}_2 + \text{A}^- \quad (2.15)
\]

Generally, dissolved oxygen is the electron acceptor which is transformed into the superoxide radical anion (O$_2$\(^{\ast -}\)) and can lead to the formation of oxidising HO\(^\ast\):

\[
e^-_{cb} + \text{O}_2 + \text{H}^+ \rightarrow \text{HO}_2^\ast \rightarrow \text{O}_2^{\ast -} + \text{H}^+ \quad (2.16)
\]

\[
\text{HO}_2^\ast + e^-_{cb} + \text{H}^+ \rightarrow \text{H}_2\text{O} \quad (2.17)
\]

\[
2\text{HO}_2^\ast \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (2.18)
\]

\[
\text{H}_2\text{O}_2 + \text{O}_2^{\ast -} \rightarrow \text{HO}^\ast + \text{O}_2 + \text{HO}^- \quad (2.19)
\]

\[
\text{H}_2\text{O}_2 + e^-_{cb} \rightarrow \text{HO}^\ast + \text{HO}^- \quad (2.20)
\]

In order to make photocatalyst processes efficient, electron-hole pair recombination must be suppressed. This can be accomplished by trapping the photo-generated electrons and/or holes. Since the recombination of an electron-hole pair in TiO$_2$ occurs within a fraction of a nanosecond (Rothenberger et al., 1985), the rate of interfacial carrier trapping must be rapid if efficient conversion of the absorbed photon to a chemically stored redox equivalent is to be achieved. The required rate for carrier trapping needs to be faster than diffusion, so the species acting as the carrier trap must
be pre-associated with the photocatalyst surface before the arrival of the acting photon (Fox and Dulay, 1993).

Hole trapping is usually achieved by either degradable adsorbates or a sacrificial reagent. For example, triethylamine and hydroquinone have been successfully used as sacrificial electron donors (Shiragami et al., 1989). These compounds function as the hole traps so that conduction band electrons can be transferred at slower rates without significant electron-hole recombination.

Electron trapping suppresses electron-hole recombination. The conduction band of TiO₂ is nearly iso-energetic with the reduction potential of oxygen in an inert solvent. Adsorbed oxygen serves as a trapping agent for the conduction band electrons in many heterogeneous photocatalytic reactions. It is often found that photocatalytic activity is nearly completely suppressed in the absence of oxygen possibly because of back interfacial electron transfer from active species present on the TiO₂ surface. Similarly, the steady-state concentration of oxygen has a significant effect on the relative rate of photocatalytic degradation occurring under ambient conditions (Fox and Dulay, 1993).

### 2.2.3 Mechanistic Model

The effective scavenging of conduction band electrons by dissolved oxygen, or any other electron acceptor, makes valance band holes available for the photocatalytic oxidation of both organics and inorganics in water. The exact nature of the oxidising species and the mechanism involved in TiO₂ photocatalysis is still not clearly understood since the two species, i.e. holes and hydroxyl radicals, are spectroscopically indistinguishable. In general, either direct or indirect oxidation (Turchi and Ollis, 1990, Serpone et al., 1993; Ilisz et al., 1999) mechanisms have been adopted in the
photocatalytic degradation of contaminants in drinking and wastewater. In the direct process, the adsorbed contaminant molecules on the TiO₂ surface are oxidised primarily by holes. The photo-generated holes can be trapped by surface hydroxyl groups or adsorbed water molecules as shown in Reactions 2.11 and 2.12 to form hydroxyl radicals. In the indirect process, the contaminants are oxidised indirectly by hydroxyl radicals either on the TiO₂ surface or in the solution at a certain distance away from the TiO₂ surface.

The oxidation potential of holes of 3.1 V is above that for most organic compounds thus making the direct reaction of holes thermodynamically feasible. Evidence (Turchi and Ollis, 1990; Serpone et al., 1993; Ilisz et al., 1999) to support this possibility includes:

(1) No hydroxylated intermediates or isomer ring hydrocarbon detected, that would be expected if HO’ reactions occurred.
(2) Absence of negative effects when hydroxyl radical scavengers are added.
(3) Direct electron transfer reactions of holes with strongly adsorbed organic compounds such as formate and acetate.
(4) Photocatalytic reactions of organic compounds, such as trichloroacetic acid and oxalic acid that lack hydrogen atoms - these organic compounds could not be abstracted by hydroxyl radicals.

Evidence (Turchi and Ollis, 1990; Serpone et al., 1993; Ilisz et al., 1999) supporting the involvement of hydroxyl radicals in the indirect process includes:

(1) Detection of hydroxylated intermediates during the degradation of organic compounds.
(2) Similarity between the by-products in photocatalytic reactions and in Fenton-type reactions, where hydroxyl radicals are known to be the primary oxidants.

(3) Detection of hydroxyl radicals in photocatalytic reaction systems by electron spin resonance (ESR) spectroscopy.

(4) Lower concentrations of hydroxyl radicals generated in the presence of D$_2$O, which could be due to lower concentration of H$_2$O for the oxidation of holes.

Both hydroxyl radicals and holes have been shown to be involved in photocatalytic reactions. For example, the oxidation of phenol, and other aromatic alcohols, the intermediates detected were similar to supposed intermediates when holes and hydroxyl radicals were involved (Richard and Boule, 1995; Richard et al., 1997).

There is no rule to state which organic compound is oxidised by holes and/or hydroxyl radicals. Generally, it is accepted that for organic compounds that adsorb well onto the TiO$_2$ surface, photocatalytic reactions are a combination of hole and hydroxyl radical attack, whereas for compounds that do not adsorb onto the TiO$_2$ surface photocatalytic degradation is related to hydroxyl radical attack only (Pichat, 2007). The location of hydroxyl radicals during reactions can be either at the TiO$_2$ surface or up to several hundred Angstroms into the solution (Turchi and Ollis, 1990; Minero et al., 1992).

Understanding where the reaction takes place, either at or at some distance from the TiO$_2$ surface, is important for optimising the removal process. For example, adsorption of contaminant molecules may be a crucial step if the contaminant is to be oxidised on the TiO$_2$ surface by holes. The promotion of radical formation, on the other hand, may be a crucial step if the contaminant is to be oxidised near the TiO$_2$ surface by hydroxyl
radicals. The addition of radical promoters could enhance the overall oxidation efficiency.

While UV/TiO₂ is widely known to degrade a number of contaminants, the mechanisms by which this is achieved have not been conclusively identified. Several mechanistic models for photocatalytic oxidation of organic compounds have been published, including: the Langmuir-Hinshelwood (L-H) model, the Eley-Rideal (E-R) model (Matthews, 1990; Mills and Morris, 1993), and hydroxyl radical related models (Turchi and Ollis, 1990).

2.2.4 Langmuir-Hinshelwood Model

The L-H model can be described simply in Figure 2.4.

![Figure 2.4 Illustration of L-H Model](image-url)

The assumptions are:

1. At equilibrium, the number of surface adsorption sites is fixed.
2. Only one substrate may bind at each surface site.
3. The heat of adsorption by the substrate is identical for each site and is independent of surface coverage.
4. There is no interaction between adjacent adsorbed molecules.
(5) The rate of surface adsorption of the substrate is greater than the rate of any subsequent chemical reactions.

(6) No irreversible blocking of active sites by binding to product occurs.

The surface coverage $\theta$ is related to the initial concentration of the substrate $C$ and to the observed (apparent) adsorption equilibrium constant $K_{obs}$ by the expression:

$$\theta = \frac{K_{obs}C}{1 + K_{obs}C}.$$  \hspace{1cm} (2.21)

The rate of formation for a single product can be written as a kinetic rate expression:

$$rate(r) = -\frac{dC}{dt} = k\theta = \frac{k_{obs}K_{obs}C}{1 + K_{obs}C},$$ \hspace{1cm} (2.22)

where $k_{obs}$ is the observed (apparent) reaction rate constant.

For reactions involving competition between two or more species for a single adsorption site, the following expression has been suggested:

$$rate(r) = -\frac{dC}{dt} = k\theta = \frac{k_{obs}K_{obs}C}{1 + K_{obs}C + \sum_i K_iC_i},$$ \hspace{1cm} (2.23)

where $i$ is a competitively adsorbed species. At very low concentration of substrate ($K_{obs}C<<1$), the reaction becomes mass transfer limited and the kinetic of the photocatalytic oxidation varies proportionally to the substrate concentration with a first-order rate constant being equal to $k_{obs}K_{obs}$. Similarly, at a high substrate concentration ($K_{obs}C>>1$) where all the available adsorption sites are occupied by the substrate molecules, the observed oxidation rate becomes independent of substrate concentration.
and reaction limited with a zero-order rate constant of $k_{obs}$. For this case, a plot of $1/r$ versus $1/C$ yields a straight line with slope of $1/k_{obs}k_{obs}$ and y-interception of $1/k_{obs}$.

The weakness of the L-H model is the differences between the adsorption constants, $K$, obtained mathematically from equation (2.22) with those obtained experimentally from dark equilibrium adsorption tests. The disagreement becomes greater when the contaminant is present at low concentrations in the ppm or lower levels (Turchi and Ollis, 1990).

### 2.2.5 Eley-Rideal Model

The Eley-Rideal (E-R) model assumes that surface-generated redox intermediates undergo secondary reactions with the non-adsorbed substrate as illustrated in Figure 2.5. Generally, the E-R model is considered applicable to the photocatalytic oxidation of contaminants in the gas phase (Pichat and Herrmann, 1989).

![Illustration of E-R Model](image)

**Figure 2.5 Illustration of E-R Model**

The difference between the L-H and E-R models is that for the E-R model the reaction rate will increase with increasing coverage until the surface is completely covered by redox intermediates, while for the L-H model the rate will go through a maximum before returning to zero (see Figure 2.6).
Neither the L-H nor E-R models offer insight into why degradation rates are similar for a number of organic compounds which have different adsorption characteristics. In these instances it is likely that hydroxyl radicals (HO\(^\cdot\)), either at or near the photocatalyst surface, control the rate at which degradation takes place (Turchi and Ollis, 1990).

2.2.6 Hydroxyl Radical Reaction Mechanisms

Turchi and Ollis (1990) have proposed four mechanisms involving HO\(^\cdot\) attack, namely:

(1) An adsorbed radical reacts with an adsorbed organic compound.
(2) A free hydroxyl radical reacts with the adsorbed organic compound.
(3) Adsorbed hydroxyl radical reacts with a free organic compound passing the catalyst surface.
(4) A free hydroxyl radical reacts with a free organic compound.
Turchi and Ollis (1990) have stated that the average distance HO• can diffuse into a solution before reacting is inversely related to the concentration of the organic compound. For organic compound concentrations of $1 \times 10^{-3}$-$1 \times 10^{-6}$ M this distance would be in the range of $1 \times 10^{-8}$-$1 \times 10^{-6}$ m. In addition, they have also stated that the kinetic rate expression for all four cases is similar to the L-H rate expression:

$$rate(r) = -\frac{dC}{dt} = \frac{k_{obs} K_{obs} C}{1 + K_{obs} C},$$

(2.24)

where $K_{obs}$ is the observed (apparent) adsorption equilibrium constant, and $k_{obs}$ is the observed (apparent) reaction rate constant, which is only a function of catalyst properties and reaction conditions. Experimentally it was found that $k_{obs}$ was directly proportional to the light intensity, $I$, at high intensities, and proportional to $I^{0.5}$ at low intensities.

In more detail, Legrini et al. (1993) has proposed that HO• degradation can take place through hydrogen abstraction, electrophilic addition or electron transfer reaction mechanisms.

2.2.6.1 Hydrogen Abstraction

In hydrogen abstraction, the hydroxyl radical reacts with an organic compound (HRH) to produce an organic radical (HR•) as described in Reaction 2.25. The organic radical then reacts quickly with dissolved oxygen to yield an organic peroxyl radical (HROO•) (Reaction 2.26), initiating subsequent thermal oxidation reactions.

HRH + HO• $\rightarrow$ HR• + H$_2$O

(2.25)
Peyton (1990) has proposed three different reaction paths: (1) heterolysis and generation of organic cations as well as superoxide anions (Reaction 2.27), (2) 1,3-hydrogen shift and homolysis into hydroxyl radicals and carbonyl compounds (Reaction 2.28) and (3) reverse reaction to RH\(^{\cdot}\) and O\(_2\) (Reaction 2.29).

\[
\begin{align*}
HR^{\cdot} + O_2 & \rightarrow HROO^{\cdot} \\
HROO^{\cdot} & \rightarrow RH^{\cdot} + O^{\cdot} \\
HROO^{\cdot} & \rightarrow RO + HO^{\cdot} \\
HROO^{\cdot} & \rightarrow HR^{\cdot} + O_2 \\
\end{align*}
\]

Hydrogen abstraction by RHO\(_2^{\cdot}\) (Reaction 2.30) is also considered.

\[
HROO^{\cdot} + HRH \rightarrow RH^{\cdot} + HROOH
\]  

Destruction reactions (Reactions 2.31-2.33) then take place by converting carbon aldehydes (RO or R’CHO) into carboxylic acids before decarboxylation to form shorter hydrocarbons.

\[
\begin{align*}
R’CHO + HO^{\cdot} & \rightarrow R’CO^{\cdot} + H_2O \\
R’CO^{\cdot} + HO^{\cdot} & \rightarrow R’COOH \\
R’COOH & \rightarrow R’H + CO_2
\end{align*}
\]

Finally, non-productive radical reactions occur when hydrocarbons are completely degraded into carbon dioxide and water (Blake \textit{et al.}, 1991).

\[
\begin{align*}
HO^{\cdot} + HO^{\cdot} & \rightarrow H_2O_2
\end{align*}
\]
\[ \text{HO}^* + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \quad (2.35) \]
\[ \text{HO}^* + \text{HO}_2^* \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (2.36) \]
\[ \text{HO}^* + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^* \quad (2.37) \]

2.2.6.2 Electrophilic Addition

*Electrophilic addition* of HO\(^*\) radicals to an organic \(\pi\)-system leads to organic radicals:

\[ \text{R=R}^* + \text{HO}^* \rightarrow \text{R}^* - \text{ROH} \quad (2.38) \]

For dechlorination of chlorinated compounds yielding chloride ions the reaction is:

\[ \text{RHCl} + \text{HO}^* \rightarrow \text{HORH}^*\text{Cl} \rightarrow \text{ROH} + \text{HCl} \quad (2.39) \]

For the electrophilic addition of the hydroxyl radical to the arene system this would result on the subsequent fragmentation of the intermediate chlorohydrol, i.e.:

\[ \text{Cl} \quad \text{OH} \quad \text{HO} \quad \text{Cl} \quad \text{O} \quad \text{OH} \quad \text{OH} \quad \text{OH} \] (2.40)

2.2.6.3 Electron Transfer

*Electron transfer* from an organic substrate can result in the reduction of hydroxyl radicals to hydroxide anions, i.e.:
when either hydrogen abstraction or electrophilic addition reactions are limited by multiple halogen substitution or steric hindrance.

2.3 FACTOR INFLUENCING UV/TiO₂ PERFORMANCE

2.3.1 Suspended or Immobilised TiO₂ Surfaces

_Suspended Reactors:_ The main advantage is the relatively high photocatalyst surface area for photon absorption, while the main disadvantage is difficulty in the separation of the photocatalyst from the water after treatment (Hoffmann et al., 1995). Typically, suspensions in the range 0.1-3.0 g.L⁻¹ are used.

_Immobilised reactors:_ The main advantage is that the TiO₂ is fixed in a substrate and a particle-free water product is produced. The main disadvantage is the decreased surface area for photon absorption (Jiang et al., 2001, Jiang et al., 2003).

2.3.2 Type of TiO₂

Anatase and rutile are the most commonly used crystalline forms of photocatalytic TiO₂ (Carp et al., 2004). Even though the band gaps of anatase (3.2 V) and rutile (3.0 V) are similar, anatase has typically shown a better photocatalytic activity than rutile (Sclafani et al., 1990). This has been attributed to the slower charge carrier recombination rates and more negative conduction band position of anatase as well as the better adsorption of oxygen, which can act as an electron acceptor.
It has been shown that mixtures of anatase and rutile are more active than pure anatase and rutile (Gumy et al., 2008). Degussa P25 (Degussa AG) commercial TiO$_2$, consisting of an amorphous state with a mixture of anatase (70-75%) and rutile (25-30%), is widely considered as the industry benchmark because of its photoactivity. Millennium Inorganic Chemicals have also introduced a range of pure anatase (>99% TiO$_2$) photocatalysts, namely, PC10-500, where the numerical value is an indication of the specific surface area (m$^2$.g$^{-1}$). Other commercially available TiO$_2$ materials that have been mentioned in the literature include: Hombikat UV100 (Hufschmidt et al., 2002), Hombikat K01/C (Bellu et al., 2008), Tioxides (Sclafani and Herrmann, 1996) and Ishihara ST-01 (Almquist and Biswas, 2002).

Commercial photocatalysts are produced by very different routes. For example, Degussa P25 is produced by flame hydrolysis of TiCl$_4$ in the presence of hydrogen and oxygen, whereas Millennium PCs are prepared by the sol-gel method at different sintering temperatures (Mills and Le Hunte, 1997). These photocatalysts have been used in degradation experiments for a number of organic compounds, but as yet no order of performance has been found. For example, Degussa P25 has shown higher photocatalytic activities than Millennium PCs for the degradation of phenol, nitrophenol (Gumy et al., 2008), metaboluron (Amine-Khodja et al., 2005), 4-chloro-2-methylphenoxycetic acid (Zertal et al., 2004), imazapyr (Pizarro et al., 2005), 4,4’-dinitrostilbene-2,2’-disulfonate (Rachel et al., 2002a), 3-nitrobenenesulfonic acid (Rachel et al., 2002b), phenoxyacetic acid (Singh et al., 2007a), 2,4,5-trichlorophenoxyacetic acid (Singh et al., 2007a), 4-chlorophenolxyacetic acid (Singh et al., 2007b), uracil (Singh et al., 2007c), 5-bromouracil (Singh et al., 2007c), 2-napthol (Qourzal et al., 2008) and orange II (Bassaid et al., 2009) whereas Millennium PCs
have exhibited better performance for the degradation of benzoic acid (Gumy et al., 2008), 4-hydroxybenzoic acid (Gumy et al., 2008), 2,5-anilinedisulfonic acid (Rachel et al., 2002b) and 4-chlorophenol (Herrmann et al., 2002). This suggests that both the type of photocatalyst and the organic compound itself may affect the degradation efficiency.

2.3.3 TiO₂ Loading

TiO₂ loading has a strong influence on the reaction rate. When the TiO₂ loading is increased, there is a proportional increase in the reaction rate. This is due to the increase in the available surface area and in the number of active sites for reactions to occur (Mathews, 1990). As the TiO₂ loading is increased further to a certain value known as the optimum loading, the rate of reaction reaches a constant value. This corresponds to the complete adsorption of the UV light potentially absorbable by the TiO₂ photocatalyst (Stafford et al., 1996). When the TiO₂ is increased beyond the optimum loading aggregation takes place causing a reduction in the amount of UV impinging on the photocatalyst surface (Augugliaro et al., 1988; Augugliaro et al., 1995). The optimum TiO₂ loading depends on the geometry and working conditions of the reactor. The optimum TiO₂ loadings are 0.5-2.5 g.L⁻¹ for a suspended reactor and 0.5-1.5 mg.cm⁻² for an immobilised reactor (Herrmann, 1999).

2.3.4 Surface Area and Particle Size

An increase in the surface area per mass of photocatalyst generally leads to an increase in the degradation rate of organic compounds that adsorb well onto the photocatalyst surface. This is due to an increase in the number of active surface sites per mass (Chen et al., 2000). Increasing surface area per mass is unlikely to influence the degradation
rate of organic compounds that do not adsorb well on the photocatalyst surface (Pichat, 2007).

Particle size specific surface areas are directly related, with a decrease in particle size resulting in an increase in the specific surface area. The change in number of defects in nanocrystalline particles due to manufacture conditions to produce smaller particle sizes may increase the hole-electron recombination rate. This can offset the benefits of the increase in the specific surface area (Zhang et al., 1998). For example, Millennium PC50, with a particle diameter of approximately 25 nm, was found to be more active than Millennium PC500 which had a particle diameter of around 5 nm for the degradation of phenol, anisole (Agrios and Pichat, 2006) and 4-chloro-2-methylphenoxyacetic acid (Zertal et al., 2004).

Specific surface area and diameter of TiO$_2$ photocatalyst particles in suspension can be different to that for the powder (Nguyen et al., 2005). For example, Degussa P25 and Millennium PC50 TiO$_2$ have comparable specific surface areas and particle sizes in the powder form, but in suspension the reported average radii are 370 and 700 nm, respectively (Gumy et al., 2008).

2.3.5 Initial Organic Compound Concentration

In photocatalysis systems the reaction rate can be controlled by either the generation and migration of the photo-generated electron-hole pairs or the reaction between the organic compounds and either the hydroxyl radicals or electron-hole pair (Chen et al., 2000). At low organic compound concentrations degradation is controlled by the reaction process and the rate is likely to be directly proportional to concentration. Conversely, at high organic compound concentrations the generation/migration process
is likely to be the controlling step (Chen et al., 2000). At high concentrations, the formation of intermediates is also likely to adversely impact on the degradation rate due to the increased competition for active sites (Parent et al., 1996).

### 2.3.6 Solution pH

Solution pH can influence the surface charge, band edge position, and the particle size of TiO₂. Surface charge is governed by the ionisation reaction of the surface-adsorbed HO⁻ groups. Depending on the solution pH, these surface groups can either remove (Reaction 2.42) or add protons (Reaction 2.43), resulting in either a negatively or positively charged surface:

\[
\text{Ti-OH} \leftrightarrow \text{TiO}⁻ + H_{aq}⁺ (pK₁) \tag{2.42}
\]

\[
\text{Ti-OH} + H_{aq}⁺ \leftrightarrow \text{Ti-OH}_2⁺ (pK₂) \tag{2.43}
\]

The pH value at which the TiO₂ surface carries no charge is defined as the zero point charge (pHzpc), and it is calculated by Equation 2.44.

\[
pH_{zpc} = \frac{1}{2} (pK₁ + pK₂) \tag{2.44}
\]

The pHzpc of various TiO₂ photocatalysts are typically in the range of 4-7 (Hoffmann et al., 1995). At pH<pHzpc the surface charge of the TiO₂ particles is positive and, conversely, at pH>pHzpc the surface charge of the TiO₂ particles is negative.

The surface charge can alter the dissociation state of organic compounds with an acid or base and thus likely changing the adsorption property of organic compounds. The competition for adsorption sites between organic compounds and HO⁻/H₂O at various
pH values can influence reaction rates and degradation pathways (O’Shea and Cardona, 1995).

Solution pH influence depends on the adsorptivity of the organic compound onto the TiO₂ surface. For example, the decrease in pH from 9.5 to 4.0 increased the adsorption of salicylic acid that resulted in a three fold increase in the degradation rate (Fox and Dulay, 1993). Conversely, the degradation rate of phenolic compounds was found to be independent of the solution pH (Tunesi and Anderson, 1991). Solution pH can also influence the flat band edge potentials of TiO₂, following a Nernstian pH dependence. The potential decreases by 59 mV with increasing pH. Hence, the reduction power of conduction band electrons is increased while the oxidation potential of valence band holes is decreased with increasing pH (Litter, 1999). Changes in rate of photocatalytic activity from one end of the pH range to the other due to changes in flat band edge are usually small, often less than 1 order of magnitude (Fox and Dulay, 1993). Finally, solution pH can influence the average radii of TiO₂ suspensions through aggregation, especially at pHₑₑₑₑ (Mills and Le Hunt, 1997).

2.3.7 Temperature

Photocatalytic reactions are relatively insensitive to temperature and can be carried out at room temperature, and as such are well suited for water treatment (Herrmann, 1999). It is due to the low activation energies of reactions between holes and/or hyroxyl radicals and organic compounds. For example, low activation energies for photocatalytic degradation of 4-chlorophenol (Hofstadler et al., 1993), dichloroacetic acid (Bahnemann et al., 1993) and salicylic acid (Mills et al., 1994) have been found to be 20.6, 16.2 and 4.6 kJ.mol⁻¹, respectively.
2.3.8 UV Intensity

The light intensity determines the concentration of photogenerated electron-hole pairs, thus greatly influencing the degradation rate of organic compounds (Chen et al., 2000). At low light intensities the degradation rate is proportional to the light intensity (Zhang et al., 1996). This is explained by the first-order dependence of the rates of production of holes and hydroxyl radicals on the light intensity. At medium light intensities (~$4\times10^{15}$ photons.sec$^{-1}$.cm$^{-2}$ or ~$0.398\times10^{-5}$ E.min$^{-1}$.cm$^{-2}$) the degradation rate is proportional to the square root of the light intensity. This is due to the recombination reaction of electrons and holes and the self-reaction of hydroxyl radicals, which competes with the degradation reaction (Stafford et al., 1996). At high light intensities the degradation rate is independent of the light intensity as a result of the domination of the electron-hole recombination reactions and the self-reaction of hydroxyl radicals (Mills et al., 1994).

2.3.9 Presence of Bicarbonates

Bicarbonate reacts with hydroxyl radicals to form $\text{CO}_3^{•-}$ (Morioka et al., 1993):

$$\text{HCO}_3^- + \text{HO}^- \rightarrow \text{CO}_3^{•-} + \text{H}_2\text{O} \quad (2.45)$$

resulting in a reduction of concentration of hydroxyl radicals and a corresponding decrease in the degradation rate. This has been observed for nitrobenzene, 1,4-benzoquinone, 4-nitrophenol (Vione et al., 2009), naphthalene (Lair et al., 2008) and aniline (Kumar and Mathur, 2006).
Bicarbonate can also adsorb onto the TiO₂ surface, thereby competing with other adsorbing molecules. Consequently, for these systems the degradation rate is also likely to decrease, as observed for humic acid (Wiszniowski et al., 2004) and acid orange 7 (Wang et al., 2004).

### 2.3.10 Presence of Alcohols

Alcohols are degraded by hydroxyl radicals (Chen et al., 1999a,b; Hatipoglu and Cinar, 2003) and their presence in photocatalytic reaction systems is likely to result in a decrease in the degradation rate. This has been observed for molecules that are not readily adsorbed onto the TiO₂ surface. Examples include: (1) ethanol (Sojic et al., 2009) on the photocatalytic degradation of herbicide clopyralid, (2) methanol, isopropanol and n-butanol on the photocatalytic degradation of phenol (Wang et al., 2007; Zhang et al., 2009) and (3) tert-butanol on the photocatalytic degradation of nitrobenzene and atrazine (Ma and Graham, 2000; Yang et al., 2007). For strongly adsorbing molecules, such as acid orange 7 and antibiotic flumequine with the addition of isopropanol (Chen et al., 2005; Palominos et al., 2009), the effect of alcohol is much less. This is possibly due to the degradation process taking place through direct electron transfer (reaction of holes).

### 2.3.11 Presence of Humic Acid

Often pre-treated drinking water contains a complex mixture of different species including solids, salts and NOM. Humic acid is one of the common components of NOM, and is usually at 0-10 mg.L⁻¹ in pre-treated drinking water. The presence of humic acid can either positively (e.g. Zhang et al., 2007; Zhang et al., 2008) or
negatively (Marinas et al., 2001; Lin and Lin, 2007) influence the photocatalytic degradation process.

The positive influence of humic acid can be attributed to its sensitisation affect. Humic acids are electron-rich compounds, capable of absorbing visible light, producing electrons from their excited state (Reaction 2.46). Under UV light, which has higher energy than visible light, electrons are produced via photoionisation processes (Aguer and Richard, 1999):

\[ \text{HA} \xrightarrow{h\nu} \text{HA}^* + e^- \]  

(2.46)

In oxygenated solutions, these electrons are found to be transformed into hydroxyl radicals (Reactions 2.47-2.49):

\[ e^- \xrightarrow{O_2} O_2^*- \xrightarrow{HO_2^*} H_2O_2 \]  

(2.47)

\[ H_2O_2 \xrightarrow{h\nu} 2HO^* \]  

(2.48)

\[ e^- + H_2O_2 \rightarrow HO^* + HO^- \]  

(2.49)

The additional radicals would lower the radical induction period in the UV/TiO₂ process and increase the radical reaction rate, thus increasing the overall degradation rate.

The negative effects of humic acid, normally occurring at high concentrations, can be explained by the hole scavenger role of humic acids. It has been reported that humic acids adsorb on the TiO₂ surface at pH 5-7 (Selli et al., 1999; Li and Li, 2002; Liu et al., 2008). The electrons produced via photo-ionisation processes behave as scavengers of valance band holes. Addition of high concentrations of humic acid may decrease significantly the number of holes available for generating hydroxyl radicals, thus reducing the degradation rates of organic compounds (Fox and Dulay, 1993).
2.3.12 Presence of Hydrogen Peroxide

Recent studies on the potential of using hydrogen peroxide to enhance the degradation rate of organic compounds have been summarised in Table 2.6. It can be seen that hydrogen peroxide addition mostly resulted in an increase in the degradation rate.

Enhancement of the degradation rate by hydrogen peroxide is due to (1) the electron acceptor role of hydrogen peroxide (the reduction potential of hydrogen peroxide is higher than oxygen ($E_{0(H_2O_2)} = +1.35V$ compared to $E_{0(O_2)} = -0.28 V$), thus making hydrogen peroxide a better electron acceptor than oxygen and (2) the formation of hydroxyl radicals (Fujishima et al., 2000):

\[
H_2O_2 + e^- \rightarrow HO^+ + HO^-
\]  
\[
H_2O_2 \rightarrow 2HO^-
\]

Excess hydrogen peroxide can react (scavenge) with hydroxyl radicals according to Reactions 2.9 and 2.10, resulting in a decrease in the degradation rate (Malato et al., 2000; Dionysiou et al., 2004). The excess can also scavenge the photo-generated holes on the TiO$_2$ surface (Wang and Hong, 1999).

2.3.13 Others

There are other effects of interest that may exert an influence on the photocatalytic degradation process of the pollutants, which include wavelength of the UV light, presence of dissolved oxygen and metallic ions or anions in the aqueous solutions (Kabra et al., 2004; Mascolo et al., 2008; Chong et al., 2010).
<table>
<thead>
<tr>
<th>Compound</th>
<th>Source of TiO₂</th>
<th>[H₂O₂]</th>
<th>( r_{H₂O₂}/r₀ )</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI Fast Green PCP</td>
<td>Hombikat UV 100</td>
<td>10 mM</td>
<td>0.2</td>
<td>Saquid et al., 2008</td>
</tr>
<tr>
<td>CI Acid Blue</td>
<td>Degussa P25</td>
<td>10 mM</td>
<td>3.5</td>
<td>Saquid et al., 2008</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>Degussa P25</td>
<td>3 ppm</td>
<td>1.2</td>
<td>Coleman et al., 2007</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>Degussa P25</td>
<td>30 ppm</td>
<td>0.6</td>
<td>Coleman et al., 2007</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>Lab-made magnetic</td>
<td>30 ppm</td>
<td>3</td>
<td>Coleman et al., 2007</td>
</tr>
<tr>
<td>Terbacil</td>
<td>Degussa P25</td>
<td>10 mM</td>
<td>0.7</td>
<td>Bahnemann et al., 2007</td>
</tr>
<tr>
<td>4-chlorobenzoic acid</td>
<td>Degussa P25</td>
<td>248 ppm</td>
<td>1.2</td>
<td>Dionysiou et al., 2000</td>
</tr>
<tr>
<td>Norfloxacin</td>
<td>Degussa P25</td>
<td>10 mM</td>
<td>1.2</td>
<td>Haque and Muneer, 2007</td>
</tr>
<tr>
<td>Black table olive</td>
<td>Lab-made S-TiO₂</td>
<td>0.1 g.L⁻¹</td>
<td>2</td>
<td>Chatzisymeon et al., 2008</td>
</tr>
<tr>
<td>Maxoline Navy 2 RM</td>
<td>Anatase</td>
<td>1.5 mL.L⁻¹</td>
<td>1.4</td>
<td>Ghaly et al., 2007</td>
</tr>
<tr>
<td>Phenol</td>
<td>Degussa P25</td>
<td>1.77 mM</td>
<td>3</td>
<td>Chiou, 2007</td>
</tr>
<tr>
<td>Cyanosine</td>
<td>Anatase</td>
<td>1.2 mM</td>
<td>2</td>
<td>Jain and Shrivastava, 2008</td>
</tr>
<tr>
<td>Disperse blue 1</td>
<td>Hombikat UV 100</td>
<td>0.4 mL.mL⁻¹</td>
<td>1</td>
<td>Saquid et al., 2007</td>
</tr>
<tr>
<td>Disperse blue 1</td>
<td>Degussa P25</td>
<td>0.4 mL.mL⁻¹</td>
<td>1.7</td>
<td>Saquid et al., 2007</td>
</tr>
<tr>
<td>Phenol</td>
<td>Degussa P25</td>
<td>1-20 vol.%</td>
<td>2-1</td>
<td>Kabir et al., 2006</td>
</tr>
<tr>
<td>Triclosan</td>
<td>Degussa P25</td>
<td>0.005 wt.%</td>
<td>7.3</td>
<td>Yu et al., 2006</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>TiO₂/SiO₂</td>
<td>29.1 mM</td>
<td>3</td>
<td>Adan et al., 2006</td>
</tr>
<tr>
<td>Phenol</td>
<td>Self-made TiO₂</td>
<td>0.05-0.2 mM</td>
<td>2.9-1.4</td>
<td>Ling et al., 2004</td>
</tr>
<tr>
<td>Dicamba</td>
<td>Degussa P25</td>
<td>4.49 mmol.L⁻¹</td>
<td>2.4</td>
<td>Chu and Wong, 2004</td>
</tr>
<tr>
<td>Imazaquin</td>
<td>Degussa P25</td>
<td>0.0001-0.001 mol.L⁻¹</td>
<td>5-6</td>
<td>Garcia and Takashima, 2003</td>
</tr>
<tr>
<td>Microcystin-LR</td>
<td>Degussa P25</td>
<td>0.05 vol.%</td>
<td>1.8</td>
<td>Cornish et al., 2000</td>
</tr>
<tr>
<td>Microcystin-LR</td>
<td>Degussa P25</td>
<td>0.005 vol.%</td>
<td>2.0</td>
<td>Cornish et al., 2000</td>
</tr>
<tr>
<td>Microcystin-LR</td>
<td>Degussa P25</td>
<td>0.5 vol.%</td>
<td>0.8</td>
<td>Cornish et al., 2000</td>
</tr>
</tbody>
</table>
2.4 SUMMARY

The UV/TiO₂ process now appears to be one of the most promising advanced oxidation technologies for drinking water and wastewater treatment since many refractory water contaminants, either inorganic or organic, at very low concentrations (μg.L⁻¹ - ng.L⁻¹) can be mineralised completely or converted into harmless substances. With the recent engineering development of pilot-scale solar reactors and the success of treating contaminated drinking water and wastewater, it indicates that the technology is reaching a pre-industrialised stage. With the advances in nano-particle technologies, and development in molecular probes, highly effective UV/TiO₂ processes can be obtained. Many principles governing the complex photocatalytic kinetics and mechanism established in earlier work can be rectified and further developed. Continuous effort must be made in order to understand the fundamental kinetics and mechanism. It is essential to improve the quantum yield of the photocatalytic reactions, develop easily separable photocatalysts or stable film photocatalysts.

The review highlighted the potential use of UV/TiO₂ for the degradation of geosmin and MIB, resulting in a need for a closer examination of the quantitative degradation and the mechanistic degradation pathway. Geosmin and MIB are chosen in this study because they are one of the big concerns in the drinking water industry and they can influence the water quality at very low concentrations. In the following Chapters, the quantitative degradation of geosmin and MIB is first carried out in order to assess the effectiveness of the UV/TiO₂ process. Results obtained from such studies would provide developers of photocatalytic technologies with data for deciding what factors are important for determining degradation rates.
CHAPTER 3

EXPERIMENTAL

This chapter describes the materials and methodologies used to investigate the degradation of geosmin and MIB in a photocatalytic reactor. Firstly, the materials are reported, including physical and chemical properties and supply sources. Secondly, details of the bench-scale experimental apparatus including information on UV intensity generated by the lamps and reactor vessel dimensions are given. Thirdly, experimental procedures for test solution preparation and degradation experiment preparation are given in detail. Finally, characterisation techniques used to study photocatalyst properties and characterisation results are reported.
3.1 MATERIALS

3.1.1 Photocatalysts

Two TiO₂ photocatalyst brands were used, namely:

- Degussa P25 (Degussa AG, Dusseldorf, Germany)
- Millennium PC50, PC105 and PC500 (Millennium Inorganic Chemicals, Seoul, South Korea).

Compositions, particle diameters and specific surface areas (S_{BET}), as certified by the respective manufacturers, are given in Table 3.1.

\textit{Table 3.1 Photocatalyst Properties}

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>P25</th>
<th>PC50</th>
<th>PC105</th>
<th>PC500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>~70% anatase</td>
<td>&gt;99.0%</td>
<td>&gt;99.0%</td>
<td>&gt;99.5%</td>
</tr>
<tr>
<td></td>
<td>~30% rutile</td>
<td>anatase</td>
<td>anatase</td>
<td>anatase</td>
</tr>
<tr>
<td>Particle diameter (nm)</td>
<td>30</td>
<td>20-30</td>
<td>15-25</td>
<td>5-10</td>
</tr>
<tr>
<td>ρ (kg.m⁻³)</td>
<td>3.7</td>
<td>2.8</td>
<td>2.8</td>
<td>2.7</td>
</tr>
<tr>
<td>S_{BET} (m².g⁻¹)</td>
<td>48.0</td>
<td>50.1</td>
<td>86.0</td>
<td>345.0</td>
</tr>
</tbody>
</table>
3.1.2 Geosmin/MIB

The geosmin and MIB standard, containing both geosmin and MIB at concentrations of 100 mg.L\(^{-1}\) each dissolved in 2 mL methanol vial, was sourced from Supelco (Bellefonte, PA, USA). Physical properties and molecular structures of geosmin and MIB are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Property and Structure</th>
<th>Geosmin</th>
<th>MIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C(<em>{12})H(</em>{22})O</td>
<td>C(<em>{11})H(</em>{20})O</td>
</tr>
<tr>
<td>Molecular weight (g.mol(^{-1}))</td>
<td>182.31</td>
<td>168.28</td>
</tr>
<tr>
<td>Molecular structure</td>
<td><a href="image">Molecular structure image</a></td>
<td><a href="image">Molecular structure image</a></td>
</tr>
<tr>
<td>Form</td>
<td>Colourless/yellow oil</td>
<td>White solid</td>
</tr>
<tr>
<td>Aqueous solubility (mg.L(^{-1}))</td>
<td>150</td>
<td>194.5</td>
</tr>
<tr>
<td>Vapour pressure (atm)</td>
<td>5.49\times10^{-5}</td>
<td>6.68\times10^{-5}</td>
</tr>
<tr>
<td>Density (kg.m(^{-3}))</td>
<td>949</td>
<td>929</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.47</td>
<td>1.47</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>165.1</td>
<td>196.7</td>
</tr>
</tbody>
</table>
3.1.3 Additives

The following additives were sourced from Sigma-Aldrich:

- Sodium hydroxide (SigmaUltra, ≥98%): to adjust pH;
- Hydrochloric acid (ACS reagent, 37%): to adjust pH;
- Hydrogen peroxide solution (30 g.L⁻¹ stabilised with 200 ppm acetanilide, density: 1 g.mL⁻¹ at 25°C);
- Humic acid in powder (technical grade);
- Sodium bicarbonate in powder (SigmaUltra, ≥99.5%);
- Methanol and ethanol solutions (absolute, density: 0.791 g.mL⁻¹ at 25°C).

Milli-Q (Millipore Corp., Bedford, MA, USA) water was used in all preparations.

3.2 APPARATUS

The photocatalytic reactor system arrangement is shown in Figure 3.1, and consisted of:

1. UV absorbing chamber (31 cm width × 29 cm height × 25 cm length) sourced from Extech Equipment (Melbourne, Victoria, Australia);
2. Magnetic stirrer with a controller to set speeds of 0-700 rpm and magnetic stirrer bar (10 mm length × 3 mm diameter);
3. 6-Watt UV lamps (Cole-Parmer). The distance between UV lamps and the top of reactor vessel was 180 mm;
4. 365 nm UV filters (Extech Equipment). After the filter, each lamp had a UV (λ=365 nm) radiation intensity of 7.41×10⁻⁵ E.min⁻¹ as measured by ferrioxalate actinometry (Hatchard and Parker, 1956; Murov et al., 1993). The
corresponding intensity at the top of the reactor vessel was 610 and 1,220 μW.cm⁻², respectively, for single and dual lamp operation;

5. Reactor vessel (Figure 3.2) comprised a Petri dish, with 100 mm outer diameter and 15 mm height, and a glass cover. An O-ring was inserted to seal the gap between the dish and the cover.

Figure 3.1 Reactor System Arrangement

[1: UV chamber, 2: magnetic stirrer, 3: UV lamps, 4: UV filters, 5: reactor vessel]

Figure 3.2 Reactor Vessel
3.3 EXPERIMENTAL PROCEDURE

3.3.1 Test solution preparation

Test solutions were prepared in 500 mL volumetric flasks as follows:

1. Add weighed amount of TiO$_2$ (for suspended TiO$_2$ experiments only);
2. Add measured volume of stock geosmin and MIB solution (Section 3.3.1.2);
3. Add measured volume of stock solution of additives (for immobilised TiO$_2$ experiments only);
4. Fill to 500 mL with Milli-Q water;
5. Sonicate and mix for 30 minutes;
6. 60 mL of test solution was used for each experiment.

The test solution was used either directly in the suspended TiO$_2$ reactor system or to prepare the immobilised TiO$_2$.

3.3.1.1 Immobilised TiO$_2$

The immobilised TiO$_2$ was prepared by depositing TiO$_2$ onto the inner wall of the Petri-dish (reactor vessel) using the dip-coating method. The preparation method was described as follows:

1. Empty Petri-dish was weighed;
2. Reactor vessel was filled with 60 mL of the 1 g.L$^{-1}$ TiO$_2$ suspension, which was prepared by sonicating 0.5 g of TiO$_2$ in 500 mL of Milli-Q water for 30 minutes;
3. TiO$_2$ suspension was kept still in the dish for 30 minutes;
4. TiO₂ suspension was drained;
5. Petri-dish was placed in an oven at 80°C for 1 hour;
6. Petri-dish was reweighed to obtain the mass of TiO₂ deposited.

The procedure described above produced a single layer of the immobilised TiO₂ with an average coating density of ~0.1 mg.cm⁻² (the mass of 1 layer TiO₂ deposited was 7.8 mg covering 78 cm² of the reactor vessel inner surface). The procedure was repeated to add additional layers to increase the coating density, as reported in Table 3.3.

Table 3.3  Coating Layer Density of the Immobilised TiO₂

<table>
<thead>
<tr>
<th>Number of Layers Deposited</th>
<th>Coating Density (mg.cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
</tr>
<tr>
<td>5</td>
<td>0.51</td>
</tr>
<tr>
<td>7</td>
<td>0.71</td>
</tr>
</tbody>
</table>

3.3.1.2 Geosmin/MIB

Geosmin and MIB solutions were prepared as follows:

1. Standard vial of geosmin and MIB was stored in a freezer at 4°C for 1 day prior to use of the vial. This minimised the escape of volatile material when the vial was broken;
2. Standard vial was broken and poured quickly into a 500 mL volumetric flask containing 400 ml of Milli-Q water;
3. Volumetric flask was filled to the 500 ml mark. Nominal concentration of geosmin and MIB, based on stated vial concentration, was 400 μg.L⁻¹;
4. Magnetic stirrer bar was added and flask was sealed;
5. Solution was stirred for 4 hours before storing in a freezer at 4°C prior to use;
6. 5 mL of the solution was diluted into a 500 mL volumetric flask and then sent to the Australian Water Quality Centre in Adelaide, South Australia, Australia for quantitative analysis. The reported concentrations for geosmin and MIB were both 3,200 ng.L\(^{-1}\).

### 3.3.1.3 Additives

Solutions of sodium hydroxide, hydrochloric acid, hydrogen peroxide, sodium bicarbonate, methanol and ethanol were used as listed in Table 3.4.

<table>
<thead>
<tr>
<th>Additive Solution</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydroxide (NaOH)</td>
<td>0.1 M</td>
</tr>
<tr>
<td>Hydrochloric acid (HCl)</td>
<td>0.1 M</td>
</tr>
<tr>
<td>Hydrogen peroxide (H(_2)O(_2))</td>
<td>30 g.L(^{-1})</td>
</tr>
<tr>
<td>Sodium bicarbonate (NaHCO(_3))</td>
<td>30 g.L(^{-1})</td>
</tr>
<tr>
<td>Methanol (CH(_3)OH)</td>
<td>7.86 g.L(^{-1})</td>
</tr>
<tr>
<td>Ethanol (C(_2)H(_5)OH)</td>
<td>7.86 g.L(^{-1})</td>
</tr>
</tbody>
</table>

Humic acid solution (14 mg.L\(^{-1}\)), which was difficult to dissolve, was prepared as follows:
1. 7 mg of humic acid powder was dissolved into 500 mL (volumetric flask) of water;

2. Solution was mixed for 3 days before filtering through a 2 nm Millipore membrane;

3. Humic acid concentrations in filtrates were then measured at Hunter Water Laboratories (Newcastle, New South Wales, Australia). A humic acid concentration of 14 mg.L\(^{-1}\) was reported for both total and dissolved organic carbon.

### 3.3.2 Degradation Experiment

Degradation experiments using a variety of test solutions were carried out in the UV chamber as illustrated in Figure 3.1. The experimental procedure was as follows:

1. 60 mL of test solution plus a magnetic stirrer bar were added to the Petri-dish, which was then quickly sealed and placed on a magnetic stirrer. Test solution was stirred at 600 rpm;

2. Petri-dish was illuminated with UV light at a given intensity and duration time;

3. Lamps were turned-off and samples removed. For suspended TiO\(_2\) experiments the solution was filtered through a 0.22 μm Millipore filter;

4. Two 20 mL samples were taken for gas chromatography/mass spectrometry (GC/MS) analysis to determine geosmin and MIB concentrations.

The experimental conditions using both suspended and immobilised TiO\(_2\) are summarised in Tables 3.5 and 3.6, respectively.
### Table 3.5  Summary of Experiment Conditions using the Suspended TiO₂

<table>
<thead>
<tr>
<th>Test</th>
<th>Study Effect of</th>
<th>TiO₂ Type</th>
<th>Conc. (g.L⁻¹)</th>
<th>Geosmin/MIB Conc. (ng.L⁻¹)</th>
<th>UV Intensity (μW.cm⁻²)</th>
<th>pH</th>
<th>Monitored Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Different TiO₂</td>
<td>P25</td>
<td></td>
<td>1</td>
<td>250</td>
<td>1,220</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PC50</td>
<td></td>
<td></td>
<td></td>
<td>4.2</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PC105</td>
<td></td>
<td></td>
<td></td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>PC500</td>
<td></td>
<td></td>
<td></td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Concentration of suspended TiO₂</td>
<td>P25</td>
<td>0.01, 0.1, 0.2, 0.5, 1, 1.5</td>
<td>250</td>
<td>1,220</td>
<td>4.2-6.0</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>Geosmin/MIB initial concentration</td>
<td>P25</td>
<td>1</td>
<td>250</td>
<td>1,220</td>
<td>4.6</td>
<td>Until completion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>UV intensity</td>
<td>P25</td>
<td>1</td>
<td>250</td>
<td>610</td>
<td>4.6</td>
<td>Until completion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1,220</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 3.6 Summary of Experiment Conditions using the Immobilised TiO$_2$

<table>
<thead>
<tr>
<th>Test</th>
<th>Study Effect of</th>
<th>TiO$_2$ (No. of Layers)</th>
<th>Geosmin/MIB Conc. (ng.L$^{-1}$)</th>
<th>Additive (mg.L$^{-1}$)</th>
<th>pH</th>
<th>Mixing Condition (rpm)</th>
<th>Monitored Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Number of layer</td>
<td>1, 3, 5, 7</td>
<td>250</td>
<td>-</td>
<td>6.6</td>
<td>600</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Geosmin/MIB initial concentration</td>
<td>5</td>
<td>250, 500</td>
<td>-</td>
<td>6.6</td>
<td>600</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>Mixing</td>
<td>5</td>
<td>250</td>
<td>-</td>
<td>6.6</td>
<td>0-700</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>pH</td>
<td>5</td>
<td>250</td>
<td>-</td>
<td>3.5-9.1</td>
<td>600</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>Addition of NaHCO$_3$</td>
<td>5</td>
<td>250</td>
<td>0-50</td>
<td>6.6-7.5</td>
<td>600</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>Addition of methanol</td>
<td>5</td>
<td>250</td>
<td>0-35</td>
<td>6.6</td>
<td>600</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>Addition of ethanol</td>
<td>5</td>
<td>250</td>
<td>0-50</td>
<td>6.6</td>
<td>600</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>Addition of humic acid</td>
<td>5</td>
<td>250</td>
<td>0-9.3</td>
<td>6.6-6.8</td>
<td>600</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>Addition of H$_2$O$_2$</td>
<td>5</td>
<td>250</td>
<td>0-300</td>
<td>4.8-6.6</td>
<td>600</td>
<td>30</td>
</tr>
</tbody>
</table>
3.4 CHARACTERISATION AND ANALYSIS

3.4.1 Characterisation of Suspended TiO₂

3.4.1.1 TEM Imaging

Transmission electron microscopy (TEM) images of the suspended TiO₂ were obtained using a Jeol 1200-EX II. Samples for the TEM measurement were prepared by suspending small amounts of photocatalysts in ethanol. They were then sonicated in an ultrasonic bath for 30 minutes before two droplets of the suspensions were placed on carbon-coated copper grids. TEM images for all four TiO₂ types are given in Figure 3.3.

Figure 3.3   TEM Images, (a) P25, (b) PC50, (c) PC105 and (d) PC 500
It can be seen that for all four samples individual particle sizes correspond approximately with the mean diameter values given in Table 3.1. Aggregation has taken place in all cases, with more open structures forming in the case of the P25 photocatalyst. If it is assumed that there is no influence of the drying process needed for TEM imaging, then for the suspended photocatalyst system compactness of the TiO₂ clusters is increased in the order: P25<PC50<PC105<PC500. It is quite possible that the drying process does influence the bulk density and size of the clusters; and to overcome this limitation direct measurement of the suspended particles was undertaken.

3.4.1.2 Size Distribution

The size distribution of TiO₂ particles in suspension was measured with a nano-series Zetasizer (Malvern Instruments Ltd.). The sample volume was 60 cm³ at 1 g.L⁻¹ photocatalyst concentration and the sample was kept at the natural suspension pH of between 4.2 and 6.0 depending on the type of photocatalyst (see Table 3.5). The sample was sonicated for 30 minutes and then left to settle while the size distribution measurement was being undertaken. The resultant volume percentage size distribution is shown in Figure 3.4 for each of the four TiO₂ types. Also included are the volume and number diameter values for each of the peak values.

It can be seen that for each photocatalyst there were two peaks: (1) at average radii of less than 800 nm and (2) at average radii of over 2,000 nm. In all instances the peak values were much greater than the single particle diameters of approximately 10-30 nm reported for each photocatalyst. Clearly, the suspended TiO₂ particles were undergoing an aggregation process.
Figure 3.4  Size Distribution of TiO$_2$ Suspensions

$[[TiO_2] = 1 \text{ g.L}^{-1}, \text{pH} = 4.2-6.0]$
The effect of TiO₂ concentration on the Peak 1 average radius ($R_{av}$) is shown in Figure 3.5. It can be seen that there was little influence of concentration on the size of the aggregates contributing to Peak 1. P25 had a smallest average aggregation size of 390 nm whereas PC500 had the highest average aggregation size of more than 650 nm. The average aggregation sizes of PC50 and PC105 were similar of around 520 nm.

![Graph showing the relationship between TiO₂ concentration and Peak 1 radius](image)

**Figure 3.5** Average Radius (Vol.%) of Peak 1 vs TiO₂ Concentration

[pH = 4.2-6.0]

In Figures 3.4 and 3.5 the pH was at the natural pH for each suspension, ranging from 4.2-6.0 as listed in Table 3.5. The influence of adjusting the suspension pH in the 3.5-9.1 range is shown in Figure 3.6. It can be seen that the suspension pH only influenced the average radius of the aggregation in the range of 6.0-7.0. The aggregation size is possibly maximum at the pH when the TiO₂ particle charge is neutral ($pH_{zpc}$). The $pH_{zpc}$
of the four photocatalysts should therefore lie between 6.0 and 7.0. The values $\text{pH}_{\text{zpc}}$ of the P25, PC50, PC105 and PC500 were obtained by zeta potential measurements shown in the next section.

![Figure 3.6](image)

**Figure 3.6** Average Radius (Vol.%) of Peak 1 vs Suspension pH

$[[\text{TiO}_2] = 1 \text{ g.L}^{-1}]$

### 3.4.1.3 Zeta Potential

A nano-series Zetasizer was used to measure the zeta potential ($\zeta$) of 1 g.L$^{-1}$ of the suspended TiO$_2$ at different pH values. The results are shown in Figure 3.7 for each of the different photocatalysts. It can be seen that in all cases the zeta potential decreased gradually from more than 30 mV to around -10 mV when the suspension pH increased from 3.5 to 9.1.
Figure 3.7  Zeta Potential vs Suspension pH

\[ \text{[TiO}_2\text{]} = 1 \text{ g.L}^{-1} \]

The pH_{zpc} of the P25 and the PC50 was measured to be 6.8, which was higher than that of PC105 (6.5) and PC500 (6.2). These pH_{zpc} are similar to those that have been reported (Kaur and Sing, 2007; Gumy et al., 2008).

3.4.1.4 UV Absorption

UV absorbance, A, is defined as (Harris, 1999):

\[ A = \log \left( \frac{P_0}{P} \right), \]  \hspace{1cm} (3.1)

where \( P_0 \) is the radiant power of the monochromatic light entering the sample and \( P \) is the radiant power of the beam exiting from the other side of the sample.
UV absorption for the immobilised and suspended TiO$_2$ was conducted using a Shimadzu UV Spectrophotometer model UV-1800 (Shimadzu Scientific Instruments Inc.). Measurements were carried out at a single wavelength of 365 nm only, which corresponded to the output wavelength of the UV lamps used for the degradation experiments.

Firstly, the UV reflectance analysis was carried out by comparing the intensity of the light scattered at a single wavelength of 365 nm from an infinitely thick with the intensity of scattered light from an infinitely thick layer of a non-absorbing white standard of BaSO$_4$. The measurements were then converted to absorbance using the Kubelka-Munk function (Delgass et al., 1979).

\[
A(R_\infty) = \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty},
\]

where $R_\infty$ is the diffuse reflectance, and K and S are absorption and scattering coefficients, respectively.

Absorbance measurements can be normalised for concentration and path length of the light through the sample. Molar absorptivity, $\varepsilon$, is defined as:

\[
\varepsilon = \frac{A}{cl},
\]

where $c$ is concentration (mol.L$^{-1}$) and $l$ is length of light path through the cuvette (cm).

In Figure 3.8 molar absorptivity has been plotted as a function of photocatalyst concentration. It was found that for all photocatalysts types the maximum $\varepsilon$ value
occurred at a concentration of approximately 0.1 g.L⁻¹, with P25 reaching a maximum at about 1,800 L.mol⁻¹.cm⁻¹. In the 0-0.5 g.L⁻¹ concentration range, molar absorptivity followed the order P25>PC105>PC500≈PC50. Beyond 0.5 g.L⁻¹, ε values were similar for all four photocatalysts.

![Figure 3.8 Molar Absorptivity vs TiO₂ Concentration](image)

**Figure 3.8 Molar Absorptivity vs TiO₂ Concentration**

\([l = 1 \text{ cm}, \text{pH} = 4.2-6.0, \lambda = 365 \text{ nm}]\)

![Figure 3.9 Absorption Efficiency vs TiO₂ Concentration](image)

**Figure 3.9 Absorption Efficiency vs TiO₂ Concentration**

\([l = 1 \text{ cm}, \text{pH} = 4.2-6.0, \lambda = 365 \text{ nm}]\)
The reason for the trends shown in Figure 3.8 can be found in Figure 3.9, where percentage absorbance efficiency, A (%), defined as:

\[
A(\%) = 100 \left( \frac{P_0 - P}{P_0} \right) = 100 \left[ 1 - 10^{-A} \right],
\]

has been plotted as a function of photocatalyst concentration. It can be seen that for all four photocatalysts A (%) reached the maximum value of 100% at suspension concentration 0-0.5 g.L\(^{-1}\).

### 3.4.2 Characterisation of Immobilised TiO\(_2\)

#### 3.4.2.1 SEM Imaging

Only P25 was used to prepare the immobilised TiO\(_2\). A FEC/Philips XC 30 scanning electron microscope (SEM) was used to examine the immobilised TiO\(_2\) deposited onto the bottom of the reactor vessel. Gold coating was used for obtaining the surface structure while carbon coating was used when determining the thickness of the layer. Figure 3.10 shows the surface structure for five layers of TiO\(_2\). It can be seen that the layer was non-uniform in area coverage and deposition height, with an average thickness of less than 5 μm.
3.4.2.2 UV Absorption

Molar absorptivity, at wavelength of 365 nm, of 1, 3, 5 and 7 layers of the immobilised TiO₂ was measured using a Shimadzu UV Spectrophotometer. Suspended P25 TiO₂, at 1 g.L⁻¹, was used to coat one side (4 cm high x 1 cm wide) of a UV absorption cuvette. The same deposition procedure as used for the Petri-dish was employed, and resulted in the same coating weight of the cuvette surface 0.1 mg.cm⁻².

Figure 3.11 shows the low molar absorptivity of the immobilised TiO₂ of P25 (ε ≤110 L.mol⁻¹.cm⁻¹). In particular, the molar absorptivity was about 70 L.mol⁻¹.cm⁻¹ at a coating density of 0.1 mg.L⁻¹. The molar absorptivity peaked at about 110 L.mol⁻¹.cm⁻¹ at a coating density of 0.3 mg.L⁻¹. The molar absorptivity decreased gradually to less than 70 L.mol⁻¹.cm⁻¹ at a coating density of 0.5 mg.L⁻¹ and to about 50 L.mol⁻¹.cm⁻¹ at 0.7 mg.L⁻¹.
Figure 3.11  *Molar Absorptivity vs TiO$_2$ Coating Density*  

\[P25, l = 1 \text{ cm}, c = 1 \text{ g.L}^{-1}, \lambda = 365 \text{ nm}\]

Figure 3.12 shows the absorption efficiency as a function of the number of immobilised TiO$_2$ layers. It can be seen that the efficiency increased gradually with increasing of coating density before reaching 100% efficiency at coating densities of 0.3-0.7 mg.L$^{-1}$.

Figure 3.12  *Absorption Efficiency vs TiO$_2$ Coating Density*  

\[P25, l = 1 \text{ cm}, c = 1 \text{ g.L}^{-1}, \lambda = 365 \text{ nm}\]
3.4.3 Geosmin/MIB Analysis

A methodology combining GC/MS and solid phase micro-extraction technique was developed for identification and quantification of geosmin and MIB at the nanogram-per-litre level. Details of the methodology are given in Chapter 4.

3.5 SUMMARY

Materials, apparatus and experimental procedures used in the current study have been described in detail. Various characterisation techniques including TEM, SEM, particle sizing, zeta potential measurements and UV absorption measurements have been discussed. Using these techniques, the characteristics of the photocatalysts have been obtained.

In the following two Chapters, details of the methodology for identification and quantification of geosmin and MIB at the nanogram-per-litre level are given in Chapter 4 and the linkage between the characteristics of the photocatalysts and their photocatalytic activities is discussed in Chapter 5.
CHAPTER 4

GEOSMIN/MIB QUANTIFICATION

This chapter presents the methodology for quantifying geosmin and MIB. Firstly, extraction techniques used to pre-concentrate geosmin and MIB and gas chromatography operating conditions used to analyse geosmin and MIB are critically reviewed and on that basis, an extraction technique is chosen. Secondly, parameters related to the chosen extraction technique and corresponding gas chromatography operating conditions are reviewed. Thirdly, a range of extraction parameters and gas chromatography operating conditions are investigated to optimise the methodology for quantitative analysis of geosmin and MIB. The calibration curves are then constructed and used to examine the reproducibility, detection limit and precision of the methodology. Finally, the influence of solution pH on the quantification of geosmin and MIB is investigated.
4.1 INTRODUCTION

Before applying any process for geosmin and MIB removal, it is important to have a methodology that allows for the quantitative analysis of geosmin and MIB at the nanogram-per-litre level, i.e. the normal level found during taste and odour events in drinking water supply sources. Different methodologies with a wide range of operating parameters have been developed in literature to meet the different needs for the quantification of geosmin and MIB. However, having many methodologies with a wide range of operating parameters makes the choice of a suitable method a daunting task.

In this chapter a suitable methodology for the quantitative analysis of geosmin and MIB at the nanogram-per-litre level was developed. In particular, the following questions have been considered:

- What methodology can be used for the quantitative analysis of geosmin and MIB at the nanogram-per-litre level, which is inexpensive, rapid and applicable for a laboratory-scale analysis?
- What are the optimum operating parameters of the methodology?
- What is the sensitivity of the methodology in terms of its reproducibility, detection limit and precision?

To address these questions a literature review of various methodologies for geosmin and MIB quantitative analysis is presented. A critical comparison of these methodologies is then given. The objective of the review was to have an overall understanding of available methodologies for geosmin and MIB quantitative analysis and then to identify the most suitable methodology. Once the methodology is chosen, related parameters and operating conditions are then reviewed, chosen and/or optimised. Important
requirements of the methodology including reproducibility, detection limit and precision are then determined.

4.2 LITERATURE REVIEW ON METHODOLOGIES FOR GEOSMIN/MIB QUANTIFICATION

Most methodologies available for the quantitative analysis of geosmin and MIB involve three main steps: (1) an extraction technique to enrich geosmin and MIB concentrations on an adsorbent material, (2) a desorption process to separate geosmin and MIB from the adsorbent material and (3) analysis by GC/MS. These common steps are presented in the following sections.

4.2.1 Extraction

A variety of extraction techniques have been applied to the analysis of trace amounts of taste and odour compounds such as geosmin and MIB from water samples. Traditional extraction techniques include closed-loop stripping, open-loop stripping, liquid-liquid extraction, steam distillation and purge and trap (Watson et al., 2000; Ikai et al., 2003). Of these traditional techniques, closed-loop stripping and open-loop stripping were the most frequently used techniques for the extraction of geosmin and MIB in water (Palmentier and Taguchi, 2001). Two modern techniques, namely stir bar sorption extraction (SBSE) and solid phase micro-extraction (SPME), have been introduced. Since the early 1990s SBSE and SPME have received much better attention due to their high efficiencies for the extraction of organic compounds with different polarity, volatility and solubility from water samples. Selected extraction techniques including
closed-loop stripping, open-loop stripping, SBSE and SPME are described in the following sections.

4.2.1.1 Closed-Loop Stripping and Open-Loop Stripping

Closed-loop stripping technique developed by Grob and co-workers has been used for the extraction of a large number of organic compounds in water since 1973 (Grob, 1973; Grob and Grob, 1974; Grob et al., 1975; Grob and Zurcher, 1976; Korth et al., 1991; Hassett and Rohwer, 1999). A closed-loop stripping unit consists of a pump (1), a gas inlet (2), a flask containing sample solution (3), a thermostatic water bath (4), an activated carbon adsorbent (5) and an oven (6) (Figure 4.1a).

A complete closed-loop stripping technique involves three steps. In the first step air is required to be bubbled through the sample solution. Volatile geosmin and MIB that transfer into the air stream are captured on a carbon trap with temperature control by an oven in the second step. The air is then recirculated through the sample solution resulting in a closed air loop.

Open-loop stripping technique, an alternative technique to closed-loop stripping, has been applied to improve the adsorption on the adsorbent material and to reduce contaminations in closed-loop stripping technique (Boren et al., 1985; Cotsaris et al., 1995). Compounds that are not adsorbed when passing through carbon adsorbents for the first time are believed to be adsorbed later in closed-loop stripping technique whereas in open-loop stripping technique almost all compounds are expected to adsorb for the first time (Boren et al., 1982) (Figure 4.1b). Generally, purging is undertaken at higher temperatures using open-loop stripping technique than using closed-loop
stripping technique. This has been reported to be able to increase the purging efficiency (Boren et al., 1985).

![Diagram of Striping Techniques](image)

**Figure 4.1** Schematic of the Setup of Closed- (a) and Open- (b) Loop Stripping Techniques


4.2.1.2 Stir Bar Sorptive Extraction

SBSE was first introduced in 1999 (Baltussen et al., 1999) and since then it has gained wide acceptance as a highly efficient micro-extraction technique for enrichment of solutes from sample solutions. The technique has been employed for the determination of aromatic compounds (Kawaguchi et al., 2004a,b,c; Kawaguchi et al., 2005a; Kawaguchi et al., 2006a), pesticides (Liu et al., 2005b; Zuin et al., 2006), estrogens (Kawaguchi et al., 2004d; Kawaguchi et al., 2005b; Kawaguchi et al., 2006b) and endocrine disrupting chemicals (Penalver et al., 2003; Basheer et al., 2005). A SBSE unit consists of a stir bar coated with layers of polydimethylsiloxane (PDMS), (1) a vial
(2) containing sample solution (3), a thermostatic water bath (4) and a heater/magnetic stirrer (5) (Figure 4.2).

![Schematic of the Setup of SBSE](image)

**Figure 4.2  Schematic of the Setup of SBSE**

[1: vial, 2: magnetic stir bar, 3: sample solution, 4: thermostatic water bath, 5: heater/magnetic stirrer]

The SBSE extraction procedure involves the addition of a stir bar into the sample solution. The bar is stirred for certain time, thus allowing the direct adsorption of geosmin and MIB on PDMS layers of the stirred bar from the sample solution.

### 4.2.1.3 Solid Phase Micro-Extraction

The SPME technique, developed in the 1990s, has been used in the analysis of various organic compounds in aqueous samples including volatile organic compounds (Ezquerro *et al.*, 2003a,b; Nakamura and Daishima, 2005; Antoniou *et al.*, 2006; Hippelein, 2006; Cai *et al.*, 2006), herbicides (Krutz *et al.*, 2003; Berrada *et al.*, 2004; Prosen *et al.*, 2007), pesticides (Tsoukali *et al.*, 2005; Dong *et al.*, 2005; Sauret-Szczepanski *et al.*, 2006) and endocrine disrupting chemicals (Santos *et al.*, 2002; Yang *et al.*, 2006). A SPME unit consists of a holder (1) with a needle (2) and an adsorbent fibre (3), a vial (4) containing sample solution (6), a thermostatic water bath (7), a stirrer bar (5) and a heater/magnetic stirrer (Figure 4.3). A fused silica fibre is coated with a polymer material and in some cases mixed with a solid adsorbent such as
divinylbenzene polymer or porous carbon. The fibre is attached to a stainless steel plunger sheathed by a protective needle.

![Figure 4.3 Schematic of the Setup of SPME

[1: holder, 2: needle, 3: fibre, 4: vial, 5: magnetic stir bar, 6: sample solution, 7: thermostatic water bath, 8: heater/magnetic stirrer]

The SPME extraction procedure involves the adsorption of geosmin and MIB onto the fibre, which is directly immersed into the sample solution or placed in the headspace of the vial above the sample solution. The quantification of geosmin and MIB is normally performed using the headspace mode.

4.2.2 Desorption

Geosmin and MIB extracted from sample solutions by different extraction techniques are often adsorbed on a particular adsorption material. The adsorbed geosmin and MIB then need to be desorbed for input into a GC/MS for quantitative analysis. The desorption procedures of the various methodologies are different.
Whether using the closed-loop stripping or open-loop stripping technique, the activated carbon absorbent is removed from the trap and the adsorbed geosmin and MIB are extracted from the activated carbon absorbent by a solvent. Carbon disulfide or dichloromethane are most common solvents used for this purpose (Boren et al., 1985; Hassett and Rohwer, 1999). A measured volume of the extracted solvent is then injected into the heated port of the injector of GC/MS for analysis.

Using SBSE, the stir bar after extraction is removed from the sample solution. It is then placed in a glass tube and transferred into a thermal desorption instrument connected to the injection port of a gas chromatograph. The thermal desorption attachment is temperature programmed, thus allowing geosmin and MIB to thermally desorb from the stirrer bar and go into the heated port of the injector of GC/MS for analysis.

Using SPME, the fibre is retracted into the needle. The fibre is then inserted and exposed directly into the heated injection port of GC/MS for the thermal desorption and analysis.

4.2.3 Analysis by GC/MS

The analysis of geosmin and MIB by GC/MS is similar for different extraction and desorption techniques. Geosmin and MIB are thermally desorbed and transferred into the head of a capillary column for subsequent separation and detection. Separation by GC/MS is based on the difference in partition coefficients between the mobile phase (carrier gas) and the stationary phase (column packing).
4.2.3.1 Geosmin/MIB Identification

Geosmin and MIB are identified by their retention times and their mass spectra. The retention times of geosmin and MIB are determined based on the times of sample injection in the column and the times when the peak of the compound is detected. A comparison of the retention time and the mass spectrum of suspected compounds with those of geosmin and MIB standards under the same conditions would confirm whether suspect compounds are geosmin or MIB. The mass spectra of geosmin and MIB standards can be tentatively determined from good matches with the library mass spectra or can be confirmed by comparing with the mass spectra of standards of geosmin and MIB. A full scan (total ion) mode of geosmin and MIB standards is carried out for that purpose.

The column temperature is programmed in order to have identifiable peaks of geosmin and MIB. Generally, the column temperature is raised to ~120°C and hold for 2-5 minutes to release MIB completely. The column temperature is then raised slowly to ~150°C and hold for 2-5 minutes to release geosmin completely. The column temperature is finally raised quickly to ~280°C to release unwanted impurities from the column, which makes the column available for subsequent measurements.

4.2.3.2 Geosmin/MIB Quantification

When the retention times of geosmin and MIB are determined, only maximum ions of each compound (m/z 95 for MIB and m/z 112 for geosmin) are selected and monitored. Selected ion monitoring (SIM) mode is generally used to quantify geosmin and MIB and one ion is monitored in a time window for each compound. The peaks of the ions coming out at the retention times of geosmin and MIB are proportional to their
concentrations. The peak areas are used to determine the concentrations of geosmin and MIB.

4.2.4 Critical Comparison of Methodologies for Geosmin/MIB Analysis

As outlined above, quantification of geosmin and MIB involves three stages: extraction, desorption and analysis by GC/MS. A summary of the advantages and disadvantages of the extraction and desorption techniques is given in Table 4.1.
Table 4.1 Advantages and Disadvantages of Geosmin/MIB Extraction and Desorption Techniques

<table>
<thead>
<tr>
<th>Stage</th>
<th>Technique</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction</td>
<td>CLS-OLS</td>
<td>Simple and low cost (Hassett and Rohwer, 1999).</td>
<td>Requires a large volume sample. Time and labour intensive (Bao et al., 1997).</td>
</tr>
<tr>
<td></td>
<td>SBSE</td>
<td>Fast, simple and adaptable for automation (Bauld et al., 2007). Does not require heat, salt or solvent.</td>
<td>Requires expensive stir bar (Bauld et al., 2007).</td>
</tr>
<tr>
<td>Desorption</td>
<td>CLS-OLS</td>
<td>Does not require expensive equipment.</td>
<td>Requires solvent (Hassett and Rohwer, 1999).</td>
</tr>
<tr>
<td></td>
<td>SBSE</td>
<td>Simple and quick.</td>
<td>Requires an expensive thermal desorption attachment (Bauld et al., 2007).</td>
</tr>
<tr>
<td></td>
<td>SPME</td>
<td>Simple and quick.</td>
<td>Limited lifetime and fragility of the fibre (Nakamura et al., 2005).</td>
</tr>
</tbody>
</table>
Table 4.1  (Continue)

<table>
<thead>
<tr>
<th>Stage</th>
<th>Technique</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis by</td>
<td>CLS-OLS</td>
<td>MDL of 1 ng.L(^{-1}). Detected range: 1-1,000 ng.L(^{-1}).</td>
<td>Low sample throughput and difficult to extract multiple samples (Brownlee et al., 1988). May require expensive high resolution mass spectrometers and may not be suitable for non-volatile compounds (Bao et al., 1997; Palmentier et al., 1998).</td>
</tr>
<tr>
<td>GC/MS</td>
<td>SBSE</td>
<td>MDL is 0.1ng.L(^{-1}). Detected range: 0.1-500 ng.L(^{-1}).</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SPME</td>
<td>MDL is 1 ng.L(^{-1}). Detected range: 1-1,000 ng.L(^{-1}).</td>
<td></td>
</tr>
</tbody>
</table>

*CLS = Closed-loop stripping; OLS = Open-loop stripping.*
4.3 ADOPTED METHODOLOGY

In this study SPME was chosen as the extraction technique for geosmin and MIB quantification due to the following reasons:

1. SPME is reported to have the detection limit of ~1 ng. L\(^{-1}\), which is low enough to evaluate the efficiency of UV/TiO\(_2\);
2. SPME does not require expensive equipment and large sample volumes;
3. SPME is relatively simple and fast.

The performance of the SPME methodology is a function of a number of variables including type of fibre, solubility of geosmin and MIB, solution pH, extraction time and temperature, source of internal standard and desorption time and temperature, which significantly influence the limitation and precision of geosmin and MIB analysis (McCallum et al., 1998; Supelco, 2007-2008). The following section reviews the parameters involved in the three main steps of the SPME methodology, i.e. extraction, desorption and analysis by GC/MS.

4.3.1 Extraction Parameters

Extraction parameters including type of fibre (type of material coated on the adsorbent fibre), solubility of geosmin and MIB, solution pH, extraction time and temperature, sample volume and internal standard greatly influence the detection and quantification of geosmin and MIB. These are discussed below.
4.3.1.1 Fibre Type

The type of fibre is chosen according to the molecular weight and polarity of the analytes. The fibre selection guide is shown in Table 4.2 (Supelco, 2005-2006).

Table 4.2 Fibre Selection Guide for SPME

<table>
<thead>
<tr>
<th>Analyte Type (MW* g.mol⁻¹)</th>
<th>Recommended Fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases and low MW compounds (30-225)</td>
<td>75-μm/85-μm Carboxen/Polydimethylsiloxane (CAR/PDMS)</td>
</tr>
<tr>
<td>Volatiles (60-275)</td>
<td>100-μm Polydimethylsiloxane (100-PDMS)</td>
</tr>
<tr>
<td>Volatiles, amines and nitro-aromatic compounds (50-300)</td>
<td>65-μm Polydimethylsiloxane/Divinylbenzene (PDMS/DVB)</td>
</tr>
<tr>
<td>Polar semi-volatiles</td>
<td>85-μm Polyacrylate (PA)</td>
</tr>
<tr>
<td>Non-polar semi-volatiles (80-500)</td>
<td>7-μm Polydimethylsiloxane (7-PDMS)</td>
</tr>
<tr>
<td>Alcohols and polar compounds (40-275)</td>
<td>30-μm Polydimethylsiloxane (30-PDMS)</td>
</tr>
<tr>
<td>Flavour compounds: volatiles and semi-volatiles (40-275)</td>
<td>65-μm/70-μm Carbowax/Divinylbenzene (CW/DVB)</td>
</tr>
<tr>
<td>Trace compounds (40-275)</td>
<td>Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS)</td>
</tr>
</tbody>
</table>

*MW = molecular weight.
Different fibres have been investigated for the quantification of geosmin and MIB. In general, DVB/CAR/PDMS has been reported to be the most suitable for the extraction of geosmin and MIB. Watson et al. (2000) compared four fibres, namely, 100-PDMS, PA, PDMS/DVB, and DVB/CAR/PDMS, for the extraction of geosmin and MIB, and reported that PDMS and PA were similar but their response was substantially lower than PDMS/DVB and DVB/CAR/PDMS. Zhang et al. (2005) and Sung et al. (2005) investigated six commercial fibres, namely, PDMS, PDMS/DVB, PA, CAR/PDMS, CW/DVB and DVB/CAR/PDMS and found similar results that revealed the extraction efficiency for geosmin and MIB followed the order: DVB/CAR/PDMS>PDMS>PDMS/DVB>CW/DVB>PA. In particular, the extraction efficiency by DVB/CAR/PDMS was found to be 2.5-5 times greater than those by PDMS/DVB or PDMS. DVB/CAR/PDMS was also suggested for the geosmin and MIB extraction by Supelco (2007-2008).

The better performance of DVB/CAR/PDMS compared to other materials is explained by its wide range of polarities and pore sizes, which are suitable for extracting volatile compounds such as geosmin and MIB (Kuwayama et al., 2006). Other materials such as CW/DVB and PA are highly polar materials that may not be suitable for polar compounds such as geosmin and MIB (Zhang et al., 2005). CAR is not suitable for geosmin and MIB extraction due to the smaller pores of carboxen particles, making CAR only effective for extracting small sized molecules (Nakamura et al., 2005).

4.3.1.2 Solubility of Geosmin/MIB

In order to increase the extraction efficiency of geosmin and MIB, sodium chloride has been added to the sample solution in order to change the solubility of geosmin and MIB
in the sample solution. The addition of sodium chloride has increased the ionic strength of the media, which may lead to a decrease in the number of water molecules available surrounding the geosmin and MIB molecules and thus lowering their solubilities (Salemi et al., 2006). The lower solubilities of geosmin and MIB in water are believed to increase their vaporisation and adsorption on adsorbent fibre, thus increasing their extraction efficiencies (Salemi et al., 2006). Geosmin and MIB have very low solubilities (150.2 and 194.5 mg.L⁻¹ for geosmin and MIB at 20°C, respectively) and their vapour pressures are very low (5.49×10⁻⁵ and 6.68×10⁻⁵ atm, respectively). Therefore, a large addition of salt is required to enhance analytical responses.

The effect of adding sodium chloride on the geosmin and MIB extraction efficiencies has been investigated. In general, 25 wt% has been reported to be the optimum level of sodium chloride added. Salemi et al. (2006) studied four different levels of sodium chloride (0 g, 5 g, 10 g and 15 g) in the extraction of 100 ng.L⁻¹ geosmin and MIB in 20 mL samples and found that the highest extraction efficiencies for geosmin and MIB were reached at sodium chloride levels of 25 wt%. Nakamura and Daishima (2005) reported that an increase in sodium chloride additions from 0 to 30 wt% led to an increase in the extraction efficiencies of geosmin and MIB by 3.6 and 5.1 times, respectively. Similarly, Watson et al. (2000) reported that the addition of 6 grams of sodium chloride to 25 mL samples (24 wt%) increased the extraction efficiencies of geosmin and MIB by 1.6 and 3 times, respectively.

4.3.1.3 Solution pH

The influence of solution pH on the extraction efficiencies of geosmin and MIB has been studied. The results obtained for the influence of solution pH on the extraction
efficiencies of geosmin and MIB were not consistent. Saito et al. (2008) mentioned that the extraction efficiency was low at a pH lower than 4 and was constant in the pH range of 4-8. Sung et al. (2005) reported that there were no significant variations in the extraction efficiency of geosmin and MIB in the pH range of 5-9. Alternatively, Boutou and Chatonner, (2007) found that the extraction efficiency of geosmin and MIB was constant in the pH range 4-7, but decreased when the pH was raised. Since large variations in pH conditions (from 4 to 9) may sometimes be encountered in water treatment applications (Sumitomo, 1995; Sumitomo, 1998), further studies on the effect of solution pH needs to be performed.

4.3.1.4 Extraction Time

Ideally, the extraction time \( t_{\text{ext}} \) should be minimised to reduce sample processing time but long enough to extract a sufficient quantity of geosmin and MIB to ensure accuracy, reproducibility and method detection limit. Extraction times of 1, 2 and 3 hours on the extraction efficiency of geosmin and MIB were studied and it was found that there was about a 5% increase in the extraction efficiency of geosmin, but no difference in the extraction efficiency of MIB when the extraction time exceeded 1 hour (Watson et al., 2000). Also, geosmin and MIB were reported to have increasing extraction efficiencies when the extraction time was increased from 0 to 50 minutes (Nakamura et al., 2005). Alternatively, the 30 minute extraction time has often been used in literature (Sung et al., 2005; Zhang et al., 2005; Supelco, 2007-2008). This highlights the need for further studies to optimise the extraction time.
4.3.1.5 Extraction Temperature

Under non-equilibrium conditions, increasing the extraction temperature ($T_{\text{ext}}$) can provide more rapid transfer of analytes from liquid to vapour phase, thus reducing the extraction time (Watson et al., 2000). Very high temperatures, however, may not be applied due to the potential for volatilisation loss. Hence, there should be an optimum temperature for a certain extraction condition.

Different extraction temperatures have been investigated for the quantification of geosmin and MIB. In general, 65°C was reported to be the most suitable for extraction efficiency of geosmin and MIB. For example, the extraction efficiencies of geosmin and MIB at 65°C were reported to be 4 and 3 times, respectively, greater compared to room temperature (20°C) (Watson et al., 2000). Working at higher temperatures (60, 70 and 80°C), Nakamura and Daishima (2005) reported that the extraction efficiencies of both geosmin and MIB decreased with an increase in extraction temperature. On the other hand, Lloyd et al. (1998) compared the peak areas of geosmin and MIB extracted at 20, 40, 60 and 80°C and reported that the extraction efficiency of geosmin and MIB was greatest at 60°C.

4.3.1.6 Sample Volume

The extraction efficiency was not influenced by sample volume when no sodium chloride was added (Salemi et al., 2006). However, the extraction efficiency has been found to be dependent on the sample volume when sodium chloride is added. For example, with the addition of 5 grams sodium chloride the extraction efficiency increased with increasing sample volume from 5 mL to 20 mL for both geosmin and MIB (Salemi et al., 2006). With the addition of 6 grams sodium chloride, a sample
volume of 25 mL was suggested (Watson et al., 2000). Hence, the sample volume should be selected first and then the amount of sodium chloride added can be correspondingly selected or vice versa.

4.3.1.7 Internal Standard

Internal standards are generally required for the quantification analysis of geosmin and MIB in order to adjust obtained results for the possible variability in detection conditions between samples from time to time. Biphenyl-d₁₀ (Watson et al., 2000), naphthalene (Watson et al., 2000), 2,4,6-trichloroanisole (2,4,6-TCA) (Supelco, 2007-2008), n-decyl chloride (Ikai et al., 2003), 2-isobutyl-3-methoxy pyrazine (IBMP) (Sung et al., 2005; Westerhoff et al., 2005b; Westerhoff et al., 2006), cis-decahydro-1-naphthol (Salemi et al., 2006), methyl-4-pentan-2-ol (Boutou and Chatonnet, 2007) d₅-geosmin and d₃-MIB (Palmentier and Taguchi, 2001) have been used for this purpose. However, naphthalene is a source of carcinogen, whereas d₅-geosmin and d₃-MIB are expensive and their usage requires GC coupled with chemical ionisation/electron impact ionisation - ion trap mass spectrometry, which is not readily available in most laboratories (Watson et al., 2000).

4.3.2 Desorption

The desorption of geosmin and MIB from adsorbent fibres is a function of both temperature (Tₜₐₖ) and time (tₜₐₖ). Low desorption temperatures may require longer desorption times and vice versa to obtain sufficient release of geosmin, MIB and internal standard.
4.3.2.1 Desorption Time

Desorption time in the range of 1-5 minutes was reported (McCallum et al., 1998; Watson et al., 2000; Nakamura and Daishima, 2005; Sung et al., 2005; Zhang et al., 2005). Using a desorption time of 1 minute (Watson et al., 2000), it was reported to require an additional fibre cleaning step to remove geosmin, MIB, and the internal standard (biphenyl-d10), thus eliminating the reproducibility issue before the fibre could be used for subsequent measurements. A desorption time of 3 minutes has been often reported in the literature (Sung et al., 2005; Supelco, 2007-2008).

4.3.2.2 Desorption Temperature

Generally, lowering the desorption temperature prolongs the lifetime of the adsorbent material but the temperature should be high enough to obtain good release of geosmin, MIB and the internal standard. The desorption temperature should be lower than the maximum temperature of 325°C recommended for the operation of a GC column. The desorption temperature can be greatly influenced by the internal standard chosen. Using biphenyl-d10 as the internal standard, Watson et al. (2000) found that the desorption temperature of 250°C was not high enough and an additional fibre cleaning step was therefore required. Further studies are required to optimise the desorption temperature.

4.3.3 Analysis by GC/MS

A similar GC/MS operating condition as reported in Watson et al. (2000) was used in this study. In particular, the column temperature was programmed as follows: the column temperature, generally kept at low temperature (50°C), is raised to 120°C to release MIB and then 150°C to release geosmin before it is raised to 280°C to release
unwanted impurities from the column, which makes the column available for subsequent measurements.

4.3.4 Summary

Reported conditions for geosmin and MIB detection using the SPME methodology were summarised in Table 4.3. The following SPME parameters and GC/MS operating conditions were selected:

- Fibre: dual layer 50/30-μm (DVB/CAR/PDMS);
- Solubility: 6 grams of sodium chloride added to 25 mL sample (24 wt%);
- Extraction temperature: 65°C;
- Volume sample: 25 mL in 40 mL capacity vials;
- Internal standard: biphenyl-d10;
- Desorption time: 3 minutes.

There are some uncertainties in the influence of extraction time, desorption temperature and pH solution. Consequently, their influences were undertaken to obtain reliable calibration curves, detection limits and detection precision of the geosmin and MIB quantification. In particular, the influence of extraction time (30 and 60 minutes), desorption temperature (270 and 300°C) and solution pH (3.5-9.1) on extraction efficiency (here-on referred to as recovery) and detection precision of the geosmin and MIB quantification was investigated.
Table 4.3  Summary of Reported Conditions Used for the Detection of Geosmin/MIB Using the SPME Methodology

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Detection Condition</th>
<th>Performance</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/30-μm</td>
<td>IS (^a): 2-isobutyl-3-methoxy pyrazine; 60 mL vial containing 45 mL sample</td>
<td>Linearity 1-500 ng.L(^{-1}); MDL (^b) 0.34-0.59 ng.L(^{-1}); RSD (^c) 5-10%; R(^d) 0.9999 (geosmin) and 0.9990 (MIB)</td>
<td>Sung et al., 2005</td>
</tr>
<tr>
<td>(DVB/CAR/PDMS) **</td>
<td>with 30% NaCl;  t(<em>{ext}) = 30 min, T(</em>{ext}) = 50°C; t(<em>{des}) = 3 min, T(</em>{des}) = 265°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50/30-μm</td>
<td>IS: 2,4,6-trichloroanisole; 40 mL vial containing 25 mL sample with 25% NaCl</td>
<td>Linearity 1-10 ng.L(^{-1}); MDL 1 ng.L(^{-1}); RSD not mentioned; R(^d) 0.9988 (geosmin) and 0.9983 (MIB)</td>
<td>Supelco, 2007-2008</td>
</tr>
<tr>
<td>(DVB/CAR/PDMS)</td>
<td>T(<em>{ext}) = 30 min, T(</em>{des}) = 65°C, T(_{des}) = 65°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50/30-μm</td>
<td>No IS mentioned; 22 mL vial containing 10 mL sample with 4 g NaCl; t(<em>{ext}) = 30 min, T(</em>{ext}) = 60°C; t(<em>{des}) = 5 min, T(</em>{des}) = 265°C using PTV (^e)</td>
<td>Linearity 0.5-50 ng.L(^{-1}); MDL 0.15 ng.L(^{-1}); RSD 1-5.5%; R(^d) 0.9940 (geosmin) and 0.9930 (MIB)</td>
<td>Zhang et al., 2005</td>
</tr>
<tr>
<td>(DVB/CAR/PDMS)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65-μm ***</td>
<td>IS: geosmin-d(<em>5) and MIB-d(<em>3); 40 mL vial containing 30 mL sample with saturated NaCl; t(</em>{ext}) = 20 min, T(</em>{ext}) = 60°C; t(<em>{des}) = 4 min, T(</em>{des}) = 250°C</td>
<td>Linearity 5-40 ng.L(^{-1}); MDL 0.8-0.9 ng.L(^{-1}); RSD &lt;10%; R(^d) 0.9950 (geosmin) and 0.9920 (MIB)</td>
<td>McCallum et al., 1998</td>
</tr>
<tr>
<td>PDMS/DVB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65-μm PDMS/DVB</td>
<td>IS: naphthalene-d(<em>8) and biphenyl-d(</em>{10}); 40 mL vial containing 25 mL sample with 6 g NaCl; t(<em>{ext}) = 60 min, T(</em>{ext}) = 65°C; t(<em>{des}) = 1 min, T(</em>{des}) = 250°C</td>
<td>Linearity 1-80 ng.L(^{-1}) for geosmin, MDL 3.3 ng.L(^{-1}); RSD 1.9%; R(^d) 0.9930; Linearity 1-100 ng.L(^{-1}) for MIB; MDL 1.2 ng.L(^{-1}); RSD 5.3%; R(^d) 0.9840</td>
<td>Watson et al., 2000</td>
</tr>
</tbody>
</table>
Table 4.3  (Continue)

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Detection Condition</th>
<th>Performance</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>65-μm PDMS/DVB</td>
<td>No IS used; 4 mL vial containing 2 ml sample with 0.75 g NaCl; t&lt;sub&gt;ext&lt;/sub&gt; = 30 min, T&lt;sub&gt;ext&lt;/sub&gt; = 70°C; t&lt;sub&gt;des&lt;/sub&gt; = 10 min, T&lt;sub&gt;des&lt;/sub&gt; = 280°C</td>
<td>Linearity 0-500 ng.L&lt;sup&gt;-1&lt;/sup&gt;; MDL &lt;1 ng.L&lt;sup&gt;-1&lt;/sup&gt;; RSD 3.7% (MIB) and 8.0% (geosmin); R&lt;sup&gt;2&lt;/sup&gt; 0.9977 (MIB) and 0.9992 (geosmin)</td>
<td>Saito et al., 2008</td>
</tr>
<tr>
<td>100-μm PDMS</td>
<td>IS: geosmin-d&lt;sub&gt;3&lt;/sub&gt;; 30% NaCl; t&lt;sub&gt;ext&lt;/sub&gt; = 50 min, T&lt;sub&gt;ext&lt;/sub&gt; = 60°C; t&lt;sub&gt;des&lt;/sub&gt; = 1 min, T&lt;sub&gt;des&lt;/sub&gt; = 270°C</td>
<td>Linearity 1-100 ng.L&lt;sup&gt;-1&lt;/sup&gt;; MDL 0.3-0.6 ng.L&lt;sup&gt;-1&lt;/sup&gt;; RSD 3.9-6.9%; R&lt;sup&gt;2&lt;/sup&gt; 0.9988 (geosmin) and 0.9976 (MIB)</td>
<td>Nakamura and Daishima, 2005</td>
</tr>
<tr>
<td>100-μm PDMS</td>
<td>No IS mentioned; 21.5 mL vial containing 15 mL sample with saturated NaCl; t&lt;sub&gt;ext&lt;/sub&gt; = 5 min, T&lt;sub&gt;ext&lt;/sub&gt; = 40°C; t&lt;sub&gt;des&lt;/sub&gt; = 0.5 min, T&lt;sub&gt;des&lt;/sub&gt; = 250°C</td>
<td>Linearity 0.1-30 μg.L&lt;sup&gt;-1&lt;/sup&gt;; MDL 0.1 μg.L&lt;sup&gt;-1&lt;/sup&gt;; RSD 6-14%; R&lt;sup&gt;2&lt;/sup&gt; 0.9787 (geosmin) and 0.9854 (MIB)</td>
<td>Lloyd et al., 1998</td>
</tr>
<tr>
<td>50/30-μm &lt;sup&gt;*&lt;/sup&gt; (DVB/CAR/PDMS) &lt;sup&gt;**&lt;/sup&gt;</td>
<td>IS &lt;sup&gt;;&lt;/sup&gt; 2-isobutyl-3-methoxy pyrazine; 60 mL vial containing 45 mL sample with 30% NaCl; t&lt;sub&gt;ext&lt;/sub&gt; = 30 min, T&lt;sub&gt;ext&lt;/sub&gt; = 50°C; t&lt;sub&gt;des&lt;/sub&gt; = 3 min, T&lt;sub&gt;des&lt;/sub&gt; = 265°C</td>
<td>Linearity 1-500 ng.L&lt;sup&gt;-1&lt;/sup&gt;; MDL &lt;sup&gt;b&lt;/sup&gt; 0.34-0.59 ng.L&lt;sup&gt;-1&lt;/sup&gt;; RSD &lt;sup&gt;c&lt;/sup&gt; 5-10%; R&lt;sup&gt;d&lt;/sup&gt; 0.9999 (geosmin) and 0.9990 (MIB)</td>
<td>Sung et al., 2005</td>
</tr>
</tbody>
</table>
* Dual coat thickness; ** DVB = divinylbenzene, CAR = carboxen, and PDMS = polydimethylsiloxan; *** Coat thickness

$T_{\text{ext}}$ = extraction temperature, $t_{\text{ext}}$ = extraction time; $T_{\text{des}}$ = desorption temperature, $t_{\text{des}}$ = desorption time

$^a$ IS = internal standard, $^b$ MDL = method detection limit, $^c$ RSD = relative standard deviation, $^d$ R$^2$ = determination coefficient from the linear regression line for response ratio (analyte/IS) vs amount ratio (analyte/IS), $^e$ PTV = programmable temperature vapouriser
4.4 EXPERIMENTAL

4.4.1 Material

Standard solutions of geosmin and MIB (100 μg.mL⁻¹ in methanol) were sourced from Supelco (Bellefonte, PA, USA). Biphenyl-d₁₀ was sourced from Isotec (Miamisburg, Ohio, USA). Sodium chloride (Reagent, >99.0%), sodium hydroxide (SigmaUltra, ≥98%) and hydrochloric acid (ACS reagent, 37%) were sourced from Sigma-Aldrich. The dual layer 50/30-μm (DVB/CAR/PDMS) fibre assemblies and manual holders for SPME were sourced from Sigma-Aldrich. Regent water (Milli-Q, Millipore Corp., Bedford, MA, USA) was used in all preparations.

4.4.2 Apparatus

A manual holder with a dual layer 50/30-μm (DVB/CAR/PDMS) fibre protected in a needle was sourced from Supelco (Sydney, Australia). A 40 ml capacity vial (O.D. × H 29 mm × 82 mm, thread 24-400) with a screw cap and a silicone-teflon septum was sourced from Supelco. The vial was kept at the constant temperature of 65°C in a water bath. The sample solution was mixed using a heater and magnetic stirrer and a stirrer bar (10 mm long x 3 mm diameter).

Geosmin and MIB adsorbing on fibres in the SPME was desorbed from fibres in a 1177 glass injector fitted with 0.75 mm internal diameter glass liner of a Varian CP-3800 gas chromatograph (Varian Inc., Melbourne, Victoria, Australia). The gas chromatograph using a VF-5ms 30m × 0.25mm × 0.25μm film column (Varian Inc.) was coupled with a Varian 1200 Quadrupole mass spectrometer (Varian Inc.) used for the identification and quantification of geosmin and MIB.
4.4.3 Solution Preparation

Geosmin and MIB stock solutions at known concentrations of 2,000 and 3,550 ng.L\(^{-1}\), respectively were first prepared. They were then used to prepare a geosmin concentration of 160 ng.L\(^{-1}\) and MIB concentration of 284 ng.L\(^{-1}\) to study the effect of extraction time, desorption temperature and time, and solution pH. The geosmin and MIB stock solutions were also used to make known concentrations of 1, 4, 8, 16, 32, 80, 120, 160, 240, 400, 800 and 1,200 ng.L\(^{-1}\) of geosmin, and 1.8, 7.1, 14.2, 28.4, 56.8, 142, 213, 284, 426, 710, 1,420 and 2,130 ng.L\(^{-1}\) of MIB for the construction of calibration curves. A biphenyl-d\(_{10}\) solution was prepared by dissolving 0.0254 g biphenyl-d\(_{10}\) in 500 mL ethanol. 1 mL of the solution was then diluted with 499 mL of Milli-Q water to produce a biphenyl-d\(_{10}\) concentration of 100 μg.L\(^{-1}\), which was finally diluted 100 times to produce a stock solution of 1,000 ng.L\(^{-1}\). Sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M) were used to adjust pH of the geosmin and MIB solutions (when required).

4.4.4 Procedures

4.4.4.1 Headspace Solid Phase Micro-Extraction

The SPME extraction procedure used is described below:

- Geosmin and MIB solutions were first pH adjusted (where required);
- A total of 25 mL solution, consisting of 20 mL of measured volumes of geosmin and MIB stock solutions and Milli-Q water, 6 grams (24%) of sodium chloride and 5 mL of internal standard stock solution (making up a biphenyl-d\(_{10}\) concentration of 200 ng.L\(^{-1}\)) and a magnetic stirrer bar, was added into a 40 mL capacity vial;
• The vial was quickly sealed with a silicone-teflon septum cap and placed in a hot water bath at 65°C above a magnetic stirrer;

• The solution was premixed for 3 minutes at 600 rpm before piercing the septum with a syringe needle of the SPME device and extending the dual layer 50/30-μm DVB/CAR/PDMS fibre in the headspace of the vial;

• After 30 or 60 minute extraction time the fibre was retracted back into the syringe and withdrawn from the vial.

4.4.4.2 Gas Chromatography/Mass Spectrometry

The quantitative measurement of geosmin and MIB after extraction was performed by GC/MS. For identifying geosmin and MIB, full scan mode was used at an m/z range of 70-500 u. For quantifying geosmin and MIB, selected ion monitoring (SIM) mode was used and three ions were monitored (m/z 112 for geosmin, 95 for MIB and 164 for biphenyl-d10). A dwell time of 0.5 ms for each ion was selected.

The desorption temperature was set at either 270 or 300°C. The column temperature program used was as follows: Hold at 50°C for 2.5 minutes; raise to 120°C (20°C.min⁻¹) and hold for 4 minutes; raise to 150°C (20°C.min⁻¹) and hold for 4 minutes; finally raise to 250°C (50°C min⁻¹) and hold for 2.5 minutes. The carrier gas was helium at a flow rate of 1 mL.min⁻¹. The split mode was used for full scan mode (for identifying) with the split ratio of 100. The splitless mode was used for SIM mode (for quantifying) and the split line (split ratio of 100) was opened after 1 minute. A 1177 glass injector was fitted with a 0.75 mm internal diameter glass liner. The electron impact (EI)-MS conditions were: transfer line temperature of 250°C, ion-trap temperature of 180°C and ionising voltages of 1,000 eV (for full scan mode) and 1,500 eV (for SIM mode).
4.4.4.3 Fibre Conditioning

New dual layer 50/30-μm DVB/CAR/PDMS fibres were first conditioned by placing the injector of the GC/MS at 270°C for 1 hour as recommended by the manufacturer. The fibres were then used for SPME and GC/MS detection of a given number of blank samples (containing no geosmin and MIB but 200 ng.L⁻¹ biphenyl-d₁₀) to achieve an equilibrium amount of the internal standard on the fibres. This was carried out as biphenyl-d₁₀ did not desorb totally at 270°C. It can be seen from Figure 4.4 that at desorption temperatures of 270 and 300°C the fibre required 3 and 2 blank samples, respectively, to reach the equilibrium condition of the internal standard adsorbed. This condition regime was adopted for all new fibres prior to use.

Figure 4.4  Recovery Rates of Biphenyl-d₁₀ versus Sample Order

\[ t_{ext} = 30 \text{ min}, \ T_{des} = 270^\circ C, \ t_{des} = 3 \text{ min}, \ pH = 6.0 \]
4.5 RESULTS AND DISCUSSION

4.5.1 Influence of Extraction Time

The recovery and reproducibility of the geosmin and MIB quantification for the extraction times of 30 and 60 minutes are shown in Table 4.4. It can be seen that the recovery of geosmin, MIB and biphenyl-d₁₀ increased significantly from 61, 33 and 59% to 98, 95 and 80%, respectively, when the extraction time was increased from 30 to 60 minutes. Conversely, the reproducibility of the geosmin and MIB detection decreased when the extraction time increased. For the extraction time of 30 minutes, the measured concentrations ($C$) for both geosmin and MIB were 7-8% lower than the actual concentrations ($C₀$). The measured concentrations were over 10% higher than the actual concentrations, for the extraction time of 60 minutes. Hence, there is no benefit, in terms of reproducibility of the measurement, to run at the longer extraction time.

Table 4.4 Replicate Analyses (n=5) Using Extraction Time of 30 and 60 Minutes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$t_{\text{ext}}$ (min)</th>
<th>Recovery (%)</th>
<th>$C^*$ (ng.L⁻¹)</th>
<th>$(C-C₀)/C₀$ (%)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geosmin</td>
<td>30</td>
<td>60.9</td>
<td>147.4</td>
<td>-8.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Geosmin</td>
<td>60</td>
<td>98.0</td>
<td>177.3</td>
<td>+10.8</td>
<td>4.0</td>
</tr>
<tr>
<td>MIB</td>
<td>30</td>
<td>33.2</td>
<td>263.0</td>
<td>-7.4</td>
<td>4.0</td>
</tr>
<tr>
<td>MIB</td>
<td>60</td>
<td>95.0</td>
<td>319.5</td>
<td>+12.5</td>
<td>9.5</td>
</tr>
<tr>
<td>Biphenyl-d₁₀</td>
<td>30</td>
<td>58.8</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
</tr>
<tr>
<td>Biphenyl-d₁₀</td>
<td>60</td>
<td>80.0</td>
<td>-</td>
<td>-</td>
<td>9.8</td>
</tr>
</tbody>
</table>

* Based on calibration curves obtained at $T_{\text{des}} = 270°C$, $t_{\text{des}} = 3$ min, pH = 6.0, $C₀$ (geosmin) = 160 ng.L⁻¹, $C₀$ (MIB) = 284 ng.L⁻¹, $C₀$ (biphenyl-d₁₀) = 200 ng.L⁻¹.
In general, increasing the extraction time would only be beneficial for very low concentrations as it allows more geosmin and MIB to be recovered. It was also confirmed that the extraction time of 30 minutes was sufficient for detecting geosmin and MIB concentrations of \( \sim 1 \text{ ng.L}^{-1} \) (see Section 4.5.4). Therefore, an extraction time of 30 minutes was used in all subsequent investigations in this thesis.

### 4.5.2 Influence of Desorption Temperature

Desorption temperatures of 270 and 300\(^{\circ}\)C were chosen for this investigation as they are above the boiling point of biphenyl-d\(_{10}\) (255\(^{\circ}\)C) but below the maximum temperature recommended for the GC column used (325\(^{\circ}\)C). The effect of desorption temperatures of 270 and 300\(^{\circ}\)C on component recovery and measurement accuracy is shown in Table 4.5.

| Table 4.5 | Replicate Analyses (n=5) for Desorption Temperatures of 270 and 300\(^{\circ}\)C |
|-----------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Compound  | \(T_{\text{des}}\) (\(^{\circ}\)C) | Recovery (%) | \(C^*\) (ng.L\(^{-1}\)) | \((C-C_0)/C_0\) (%) | RSD (%) |
| Geosmin   | 270                         | 60.9           | 156.2                      | -2.4                       | 2.0     |
| \((C_0 = 160 \text{ ng.L}^{-1})\) | 300                         | 66.4           | 145.9                      | -8.8                       | 0.2     |
| MIB       | 270                         | 33.2           | 307.0                      | +8.1                       | 2.1     |
| \((C_0 = 284 \text{ ng.L}^{-1})\) | 300                         | 35.5           | 273.2                      | -3.8                       | 7.8     |
| Biphenyl-d\(_{10}\) | 270                         | 58.8           | -                           | -                           | 2.2     |
| \((C_0 = 200 \text{ ng.L}^{-1})\) | 300                         | 87.6           | -                           | -                           | 3.3     |

* Based on calibration curves obtained at \(t_{\text{ext}} = 30 \text{ min, pH} = 6.0, C_0\) (geosmin) =160 ng.L\(^{-1}\), \(C_0\) (MIB) = 284 ng.L\(^{-1}\), \(C_0\) (biphenyl-d\(_{10}\)) =200 ng.L\(^{-1}\).
It can be seen from Table 4.5 that increasing the desorption temperature increased the recovery of geosmin and MIB. The recoveries of geosmin and MIB at the desorption temperature of 270°C were 61 and 33%, respectively, and increased to 66 and 36% at 300°C. However, the accuracy of the geosmin and MIB quantification was similar in both cases. At a desorption temperature of 270°C, the measured concentrations of geosmin and MIB were 2-8% different from their actual concentrations. The concentration difference was in the range of 3-9% at a desorption temperature of 300°C. However, a lower reproducibility (i.e., higher RSD value of 7.8%) was observed at the desorption temperature of 300°C than at the lower desorption temperature (RSD value of 2%).

There seems to be of little or no benefit, in terms of recovery, accuracy and reproducibility, to operate at the higher desorption temperature. Operating at the lower desorption temperature would help prolong the lifetime of the fibre. Moreover, the desorption temperature of 270°C lies within the recommended temperature range of 230-270°C by the fibre manufacturer. Hence, a desorption temperature of 270°C was used in all subsequent investigations in this thesis.

### 4.5.3 Calibration

Calibration curves were constructed based on the relative response of analyte to an internal standard versus the concentration of analyte, where the analyte was geosmin or MIB and the internal standard was biphenyl-d10. The relative response was defined as the ratio of the detected peak area of the analyte to that of the internal standard. Calibration curves for geosmin and MIB over the concentration ranges of 1-1,200 ng.L⁻¹ and 2-2,130 ng.L⁻¹, respectively, were investigated and given in Figure 4.5.
It was found that the calibration curves for geosmin and MIB over the concentration ranges of 1-1,200 ng.L\(^{-1}\) and 2-2,130 ng.L\(^{-1}\) were not linear with \(R^2\) values (i.e. line of best fit) of 0.917 and 0.967, respectively. Consequently, two separate calibration curves of low concentrations and high concentrations for both geosmin and MIB were constructed.

\[
y = 0.0062x \quad R^2 = 0.9166
\]

\[
y = 0.0023x \quad R^2 = 0.9673
\]

The calibrations curves for low concentrations of geosmin and MIB are shown in Figure 4.6. It can be seen that both geosmin and MIB showed highly significant linear responses over the ranges of 1-240 and 2-426 ng.L\(^{-1}\) (\(R^2 = 0.990\) and 0.997, respectively). The slopes of geosmin and MIB were 0.0110 and 0.0036, respectively.

**Figure 4.5  Calibration Curves for Geosmin/MIB**

\[t_{ext} = 30\ \text{min},\ t_{des} = 3\ \text{min},\ T_{des} = 270^\circ\text{C},\ \text{pH} = 6.0\]
This is consistent with the standard curves provided by Supelco (2005-2006) for a smaller concentration range of 1-10 ng.L⁻¹ under similar operating conditions. Moreover, using the same operating condition except the fibre (65-μm PDMS/DVB), Watson et al. (2000) also observed similar results over the concentration range of 1-100 ng.L⁻¹.

![Figure 4.6 Calibration Curves for Low Concentrations of Geosmin/MIB](image)

**Figure 4.6** Calibration Curves for Low Concentrations of Geosmin/MIB

\[
y = 0.0110x \\
R^2 = 0.990 \\
y = 0.0036x \\
R^2 = 0.997
\]

[t_{ext} = 30 \text{ min}, \ t_{des} = 3 \text{ min}, \ T_{des} = 270^\circ\text{C}, \ pH = 6.0]

The calibrations curves for high concentrations of geosmin and MIB are shown in Figure 4.7. Both geosmin and MIB showed significant linear responses over the ranges of 240-1,200 and 426-2,130 ng.L⁻¹ (\(R^2 = 0.993\) and 0.990, respectively).
4.5.4 Detection Limits and Precision

The full scan of geosmin and MIB is shown in Figure 4.8. The retention times for geosmin and MIB from water samples were 13.8 and 8.9 minutes, respectively, which were the same with those from standards of geosmin and MIB. The spectra of geosmin and MIB in water samples also matched well with >95% probability and with the corresponding spectra of 250 ng.L\(^{-1}\) geosmin and MIB standards (Figure 4.9) with detected maximum ions of 112 and 95, respectively.
Figure 4.8  Total Ion Chromatogram of Geosmin, MIB and Biphenyl-d10

Figure 4.9  Comparison of Mass Spectra, (A) Geosmin in Standard Solution, (B) MIB in Standard Solution, (C) Geosmin 250 ng.L⁻¹ in Sample Solution, (D) MIB 250 ng.L⁻¹ in Sample Solution
The detection limits of geosmin and MIB found in this study were 1 ng.L\(^{-1}\) with RSD of 3.1\% (n=5) and 1.8 ng.L\(^{-1}\) with RSD of 1.9\% (n=5), respectively, as can be seen in SIM chromatograms (Figure 4.10A and B). The variability among replicate measurements (RSD) ranged from 1 to 12\% for different working days. The variability among measured concentrations and prepared concentrations was less than 8\%.

The detection limit of geosmin and MIB and the range of variability found in this study were similar to those of earlier studies using similar operating conditions. For example, Sung et al. (2005) reported detection limits of ~0.5 ng.L\(^{-1}\), with RSD ranging from 5 to 10\% and Zhang et al. (2005) showed the detection limit of 0.15 ng.L\(^{-1}\), with RSD ranging from 1.0 to 5.5\%. Similarly, Watson et al. (2000) using a different fibre also reported a similar result of the detection limits of 1 ng.L\(^{-1}\), with RSD ranging from 2-12\%.

![SIM Chromatograms of Geosmin/MIB](image)

**Figure 4.10** SIM Chromatograms of Geosmin/MIB, (A) SIM: Geosmin (1 ng.L\(^{-1}\)), \(m/z=112, S/N = 9\), (B) SIM: MIB (1.8 ng.L\(^{-1}\)), \(m/z=95, S/N = 3\)

\[t_{ext} = 30 \text{ min}, T_{des} = 270^\circ \text{C}, t_{des} = 3 \text{ min}, pH = 6.0\]
4.5.5 Influence of Solution pH

The effect of solution pH in the range 3.5-9.1 on the detection of geosmin and MIB is shown in Figure 4.11. The measured concentrations were determined using a calibration curve obtained at pH 6.0. It can be seen that the measured concentrations of geosmin ranged from 160 to 190 ng.L\(^{-1}\) (up to 18% difference from the prepared concentration) over the entire pH range studied. The measured concentrations of MIB were in the range of 280-290 ng.L\(^{-1}\) (up to 2% difference from the prepared concentration) over the pH range of 4.0-7.7. However, the measured concentrations of MIB varied substantially from the prepared concentration of 284 ng.L\(^{-1}\) over pH values outside the range of 4.0-7.7. For example, at pH 3.5 and pH 9.1 the measured concentrations of MIB were 56 and 394 ng.L\(^{-1}\) (80% lower and 39% higher than the prepared concentration), respectively.

\[C_0 (\text{geosmin}) = 160 \text{ ng.L}^{-1}, \ C_0 (\text{MIB}) = 284 \text{ ng.L}^{-1} \text{ and } C_0 (\text{biphenyl-d}_{10}) = 200 \text{ ng.L}^{-1}, \]
\[t_{\text{ext}} = 30 \text{ min}, T_{\text{des}} = 270^\circ \text{C}, t_{\text{des}} = 3 \text{ min, and } pH = 6.0 \text{ used for the calibration curves}\]
The results presented highlight the importance of obtaining the correct calibration curve using conditions that are relevant to the actual sample to be analysed. It was observed that once the samples at pH of 3.5 and 9.1 were pH adjusted back to 6.0, the correct MIB as well as geosmin concentration was again obtained. It is therefore essential for geosmin and especially MIB that if the sample has a pH lower than 4.0 or higher than 8.0, the calibration curve needs to be measured at the corresponding pH of that sample. Otherwise, false readings may result.

Reason for the observed pH effect is unclear. Possible explanations for the reported trends in the geosmin and MIB concentrations as a function of solution pH are the strong interaction between proton and MIB and the weak interaction between proton and geosmin due to their different alcoholic molecular structures (Figure 4.12A and B). These explanations are consistent with the findings of Yoon et al. (2007) who reported that MIB adsorbed better onto acidic surfaces than on non-acidic surfaces. Although not presented here, our observations showed that the peak area of biphenyl-d_{10} was not influenced by pH as can be reasonably expected, since bonding effects between biphenyl-d_{10} and protons based on its molecular structure are unlikely (Figure 4.12C).

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Figure 4.12  Molecular Structures, (A) Geosmin, (B) MIB and (C) Biphenyl-d_{10}
Natural water samples typically have pH values in the neutral range, so pH is generally not expected to interfere with the quantification of geosmin and MIB. There are some specific water treatment applications where pH might become a problem. For example, in some biological water treatment applications, pH values higher than 8 were encountered (Sunitomo, 1995; Sunitomo, 1998) and samples of water at these pH values would falsely report higher than actual MIB concentrations unless the correct calibration curves were used. Similarly, for acidic photocatalysts used to remove geosmin such as that reported by Yoon et al. (2007) it would be important to either adjust the pH of the sample back to the 4.0-7.7 range or prepare calibration curves with the same pH as the sample to ensure correct measurement of removal efficiencies. Our work involving UV/TiO₂ based photocatalytic removal of geosmin and MIB at pH 3.5 suggests that without proper account of the pH effect one would have believed that UV/TiO₂ had resulted in a significant drop in the concentration of MIB within a few minutes of oxidation treatment. Rather, this performance was simply due to low MIB recovery at that pH with the quantification methodology used.

4.6 CONCLUSIONS

A suitable methodology for the quantitative analysis of geosmin and MIB at the nanogram-per-litre level has been developed:

1. SPME was used to extract geosmin and MIB from sample solution before analysing in a GC/MS. SPME parameters chosen included: dual layer fibre 50/30-μm DVB/CAR/PDMS with an appropriate pre-conditioning of the fibre, sodium chloride of 6 grams (24 wt%), extraction temperature of 65°C, volume sample of 25 mL in 40 mL capacity vials and internal standard of biphenyl-d₁₀.
2. Over the range of values investigated an extraction time of 30 minutes and a desorption temperature of 270°C were found to be optimal for the quantification of geosmin and MIB, yielding accurate and reproducible results.

3. Detection limits of 1 and 1.8 ng.L\(^{-1}\) were found for geosmin and MIB, respectively. The variability among replicate measurements (RSD) was less than 12% and the variability among measured concentrations and prepared concentrations was less than 8%.

4. The influence of pH in the range of 3.5-9.1 on the quantification of geosmin and MIB was studied. It was found that extraction of geosmin was slightly influenced by pH >8, whereas for MIB recovery was reduced significantly at pH <4 and increased markedly at pH >8. Consequently, under- or over-prediction in MIB concentration can occur if a calibration curve obtained at a different pH is used. Hence, it would be important to either adjust the pH of the sample back to the 4.0-7.7 range or prepare calibration curves at the investigated pH to ensure correct measurement of geosmin and MIB.
Kinetics of the degradation of geosmin and MIB by UV/TiO$_2$ is presented in this chapter. Firstly, the photocatalytic degradation of geosmin and MIB by different TiO$_2$ photocatalysts is investigated. Secondly, Degussa P25 TiO$_2$, the most photoactive catalyst available on the market, is examined in detail both in the immobilised and suspended forms. The degradation of geosmin and MIB as a function of experimental parameters including TiO$_2$ loading, TiO$_2$ coating density, geosmin and MIB concentrations, UV intensity, mixing condition and pH is studied. Finally, the energy efficiency and the photonic efficiency are compared to other geosmin and MIB treatment processes.
5.1 INTRODUCTION

Advanced oxidation processes (AOP) based on UV radiation such as O$_3$/UV, H$_2$O$_2$/UV and UV/TiO$_2$ have attracted a great deal of interest in the drinking water industry since these processes are capable of providing simultaneous disinfection as well as complete oxidation of a variety of micro-contaminants. UV/TiO$_2$ has been demonstrated to be able to destroy a wide range of organic contaminants including a number of toxic cyanobacterial metabolites (Shephard et al., 1998; Senogles et al., 2001; Cornish et al., 2000; Liu et al., 2002; Shephard et al., 2002; Lawton et al., 2003a; Lee et al., 2004a; Lee et al., 2004b; Liu et al., 2005a; Antoniou et al., 2008; Antoniou et al., 2009; Liu et al., 2009; Pelaez et al., 2009). However, as mentioned in Chapter 2, very few studies have been reported for the removal of geosmin and MIB.

In this chapter the kinetics of the degradation of geosmin and MIB by UV/TiO$_2$ were investigated. In particular, the following questions were addressed:

- What is the most suitable TiO$_2$ photocatalysts for the degradation of geosmin and MIB?
- How do UV/TiO$_2$ reaction parameters influence the degradation of geosmin and MIB?
- How effective is the UV/TiO$_2$ process in removing geosmin and MIB compared to other treatment processes?

To address these questions, a series of experiments were conducted. Firstly, four commercially available TiO$_2$ photocatalysts were investigated. The most effective TiO$_2$
photocatalyst was then chosen. Two typical reactor systems (suspended and immobilised TiO$_2$) were used. The influence of TiO$_2$ loading, initial concentrations of geosmin and MIB and UV intensity were studied for the suspended TiO$_2$ system. The influence of TiO$_2$ coating density, initial concentrations of geosmin and MIB, mixing condition and solution pH were studied for the immobilised TiO$_2$ system. Finally, the energy and photonic efficiencies of the degradation process were calculated and compared to other geosmin and MIB treatment processes.

5.2 EXPERIMENTAL

5.2.1 Adsorption, Characterisation and Analysis

The equilibrium adsorption experiment of geosmin and MIB on the TiO$_2$ photocatalysts was carried out in 500 mL volumetric flasks under the dark condition for 24 hours. Two sets of the adsorption of geosmin and MIB on different TiO$_2$ photocatalysts, i.e., P25, PC50, PC105 and PC500, in the suspended form were conducted. The first set was carried out under the same conditions as those used in the geosmin and MIB photocatalytic experiments (for the suspended form), i.e., 250 ng.L$^{-1}$ each of geosmin and MIB in 1 g.L$^{-1}$ suspensions of P25, PC50, PC105 and PC500, respectively. The second set was undertaken using varying concentrations of geosmin (256, 824, and 1,352 ng.L$^{-1}$) and MIB (512, 1,343 and 2,545 ng.L$^{-1}$) in more concentrated suspensions (2 g.L$^{-1}$) of two representative TiO$_2$ photocatalysts (i.e., P25 and PC50).

These adsorption experiments were carried out at unadjusted pH of 4.2-6.0. TiO$_2$ suspension and geosmin and MIB were mixed and equilibrated for 24 hours under the dark condition. They were then filtered through 0.22 µm Millipore filters. The concentrations of geosmin and MIB in the filtrate were measured in duplicate.
The zeta potential of P25 (representing rutile-anatase TiO₂) and PC50 (representing anatase TiO₂) for a 1 g.L⁻¹ suspension before and after geosmin and MIB additions at 250 ng.L⁻¹ each (for 1 hour) and 2.50 mg.L⁻¹ each (for 4 hours) was measured using a nano-series Zetasizer at pH 4.2 to add further information to the adsorption behaviour of geosmin and MIB on the TiO₂ surface.

The TiO₂ photocatalysts were characterised using TEM, SEM, Zetasizer and UV Spectrophotometer as described in Chapter 3. The geosmin and MIB quantification methodology was described in detail previously in Chapter 4.

5.2.2 Photocatalytic Degradation Experiments

The geosmin and MIB photocatalytic degradation experiments were conducted using the materials, apparatus and procedures described in Chapter 3. Control experiments confirmed that in the absence of either UV illumination or TiO₂ photocatalysts the concentrations of geosmin and MIB remained constant throughout the experimental duration.

5.3 RESULTS AND DISCUSSION

5.3.1 Adsorption Study

The percentage of geosmin and MIB adsorbed on different TiO₂ photocatalysts at 250 ng.L⁻¹ each of geosmin and MIB is reported in Table 5.1. It can be seen that for both geosmin and MIB the adsorbed percentage remained in a small narrow range of 0-5.5%. The percentages of geosmin and MIB adsorbed on P25 and PC105 were around 5.0% whereas they were zero on PC50 and PC500. It is worth noting that these percentages
were always lower than the errors associated with the geosmin and MIB quantification method.

**Table 5.1** Adsorption of Geosmin/MIB ($C_0 = 250$ ng.L$^{-1}$ each) on the Suspended TiO$_2$ Photocatalysts (1 g.L$^{-1}$) after 24 Hours under the Complete Dark Condition

<table>
<thead>
<tr>
<th>Compound</th>
<th>TiO$_2$ Photocatalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P25</td>
</tr>
<tr>
<td>Geosmin</td>
<td></td>
</tr>
<tr>
<td>Adsorption (%)</td>
<td>5.0</td>
</tr>
<tr>
<td>Error (%)</td>
<td>7.1</td>
</tr>
<tr>
<td>MIB</td>
<td></td>
</tr>
<tr>
<td>Adsorption (%)</td>
<td>5.1</td>
</tr>
<tr>
<td>Error (%)</td>
<td>6.8</td>
</tr>
</tbody>
</table>

The adsorption study using higher initial concentrations of geosmin (256, 824 and 1,352 ng.L$^{-1}$) and MIB (521, 1,343 and 2,545 ng.L$^{-1}$) and a higher suspended TiO$_2$ concentration of 2 g.L$^{-1}$ is shown in Table 5.2. It can be seen that geosmin and MIB adsorption remained in the range of 0-7.0%. Moreover, the adsorption percentages of both geosmin and MIB were higher on P25 than PC50, which is consistent with the adsorption study using the 1 g.L$^{-1}$ suspended TiO$_2$ photocatalysts. Again, in the majority of the concentrations studied the adsorption percentages of geosmin and MIB were always lower than the errors associated with the detection of geosmin and MIB, except for geosmin ($C_0 = 256$ ng.L$^{-1}$) and MIB ($C_0 = 512$ ng.L$^{-1}$) on P25.
Table 5.2  
\textit{Adsorption of Geosmin/MIB on Suspended TiO}_2\textsubscript{2} Photocatalysts (2 g.L\textsuperscript{-1}) 
\textit{after 24 Hours under the Complete Dark Condition}

| TiO\textsubscript{2} | \(C_0\) of Geosmin (ng.L\textsuperscript{-1}) | \(C_0\) of MIB (ng.L\textsuperscript{-1}) |
|----------------------|------------------------------------------|
|                      | 256                                      | 512                                      |
|                      | 824                                      | 1,343                                    |
|                      | 1,352                                    | 2,545                                    |

<table>
<thead>
<tr>
<th>TiO\textsubscript{2}</th>
<th>Adsorption (%)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>7.0</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TiO\textsubscript{2}</th>
<th>Adsorption (%)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC50</td>
<td>2.7</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>8.1</td>
</tr>
</tbody>
</table>

The adsorption results obtained suggest geosmin and MIB had negligible adsorption on the TiO\textsubscript{2} photocatalysts. This was further supported by data from the zeta potential measurement before and after adding geosmin and MIB as shown in Table 5.3.

Table 5.3  
\textit{Zeta Potentials (\(\zeta\)) of Suspended TiO}_2\textsubscript{2} Photocatalysts (1 g.L\textsuperscript{-1}) at pH 4.2

<table>
<thead>
<tr>
<th>TiO\textsubscript{2} Photocatalyst</th>
<th>(\zeta)</th>
<th>P25</th>
<th>PC50</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\zeta) before adding geosmin and MIB (mV)</td>
<td>+39</td>
<td>+11</td>
<td></td>
</tr>
<tr>
<td>(\zeta) after adding 250 ng.L\textsuperscript{-1} each geosmin/MIB (mV)</td>
<td>+39</td>
<td>+11</td>
<td></td>
</tr>
<tr>
<td>(\zeta) after adding 2.50 mg.L\textsuperscript{-1} each geosmin/MIB (mV)</td>
<td>+39</td>
<td>+11</td>
<td></td>
</tr>
</tbody>
</table>

The zeta potential of both the P25 and PC50 samples before and after adding geosmin and MIB remained unchanged with a zeta potential of P25 (+39 mV) and PC50 (+11 mV) particles in suspension. It has been widely reported in literature (Tran et al., 2006;
Lam et al., 2007; Liu et al., 2008) that no significant change in zeta potential of TiO$_2$ was recorded from the interaction of weakly adsorbed organic compounds such as sucrose, resorcinol and methanol. On the contrary, highly adsorbed organic compounds such as maleic acid and oxalic acid interacted with the TiO$_2$ surface at low pH and the zeta potential of TiO$_2$ exhibited a negative shift. Therefore, zeta potential results support the adsorption data that negligible amounts of geosmin and MIB adsorbed on P25 or PC50.

5.3.2 Type of TiO$_2$ Photocatalysts

The photocatalytic degradation of geosmin and MIB using P25, PC50, PC105 and PC500 in the suspended form was investigated. The TiO$_2$ loading of 1 g.L$^{-1}$ was chosen as a result of: (1) the UV absorption results reported in Chapter 3, which concluded that the UV absorption efficiency of P25, PC50, PC105 and PC500 increased significantly with increasing TiO$_2$ loadings and reached 100% when the TiO$_2$ loading was 1 g.L$^{-1}$ and (2) the TiO$_2$ loading of 1 g.L$^{-1}$ has been reported to be the optimal loading of P25 and PC photocatalysts in many other studies (Rachel et al., 2002b; Pizarro et al., 2005; Singh et al., 2007a).

The percentage of geosmin remaining as a function of degradation time is shown in Figure 5.1. Of the photocatalysts investigated, P25 was found to be the most efficient, resulting in the shortest complete removal time of 10 minutes for geosmin. PC50 was the second best with a complete removal time of 30 minutes. Finally, PC105 and PC500 had similar photocatalytic efficiencies, i.e., less than 10% remaining after 45 minutes degradation time.
The percentage of MIB remaining as a function of degradation time is shown in Figure 5.2. Similarly to the case of geosmin, P25 was the most effective, resulting in the shortest complete removal time of 20 minutes for MIB. Among the PC photocatalysts investigated, PC50 exhibited a relatively high degree of photoactivity, with complete MIB degradation being achieved within 45 minutes. In comparison PC105 and PC500 were much less active, with approximately 20% MIB still remaining after 45 minutes degradation time.
Figure 5.2 Degradation of MIB by UV/TiO₂

[The insert shows the degradation kinetics on -ln(C/C₀) versus time]

\[ C₀ = 250 \text{ ng.L}^{-1}, [\text{TiO}_2] = 1 \text{ g.L}^{-1}, \text{UV intensity} = 14.82 \times 10^{-5} \text{ E.min}^{-1}, \text{pH} = 4.2-6.0 \]

It can be seen from the inserts in Figures 5.1 and 5.2 that geosmin and MIB degradation profiles between P25 and PC photocatalysts appeared to be quite different. P25 showed a single stage of a quick and steady fall in concentration whereas PCs seemed to exhibit two stages, i.e., a quick fall in the early stage (0-5 minutes) and a gradual and slow decrease in the late stage (from the 5th minute onwards). The results are likely to be related to the aggregation behaviour of P25 and PCs in suspension as described in Chapter 3. P25 had the smallest average aggregation size of 390 nm, which is much smaller than those of PC50 (520 nm), PC105 (520 nm) and PC500 (650 nm). This may
have allowed the P25 particles to remain suspended for a longer period of time in solution than for PCs. Sedimentation did not appear to be a significant issue for P25, but this was expected to have significant impact on the performance of PCs. To eliminate the effects of sedimentation when comparing the photocatalytic activities of P25 and PC photocatalysts, only data points in the first 5 minutes were used. Plots of $\ln \left( \frac{C}{C_0} \right)$ vs time within the first 5 minutes of geosmin and MIB degradation are shown in Figures 5.3 and 5.4, respectively.

Figure 5.3  First-order Kinetics of the Degradation of Geosmin by UV/TiO$_2$

$[C_0 = 250 \text{ ng.L}^{-1}, [\text{TiO}_2] = 1 \text{ g.L}^{-1}, \text{ UV intensity} = 14.82 \times 10^{-5} \text{ E.min}^{-1}, \text{ pH} = 4.2-6.0]$
Figure 5.4  First-order Kinetics of the Degradation of MIB by UV/TiO₂

\[ [C_0 = 250 \text{ ng.L}^{-1}, [\text{TiO}_2] = 1 \text{ g.L}^{-1}, \text{UV intensity} = 14.82 \times 10^{-5} \text{ E.min}^{-1}, \text{pH} = 4.2-6.0] \]

It can be seen in Figures 5.3 and 5.4 that in all cases \( \ln(C/C_0) \) vs time produced straight lines. This indicates that the degradation of geosmin and MIB follows the first-order kinetics in accordance with Equation 5.1:

\[
\frac{-\ln C}{C_0} = kt, \quad (5.1)
\]

where \( C_0 \) and \( C \) are the remaining concentrations of geosmin or MIB at reaction time zero and \( t \), respectively, and \( k \) is the rate constant (min\(^{-1}\)).

The first-order rate constant for geosmin and MIB degradation and their corresponding coefficients of determination are shown in Table 5.4. It can be seen that the rate constant of geosmin degradation using P25 was the highest (0.346 min\(^{-1}\)). The rate
constant with PC50 came second at 0.308 min\(^{-1}\) and then PC105 and PC500 at 0.284 and 0.272 min\(^{-1}\), respectively. The rate constants of MIB degradation were similar (0.177 min\(^{-1}\)) using P25 and PC50, and were slightly lower (0.152-0.156 min\(^{-1}\)) using PC105 and PC500.

Table 5.4  
First-order Rate Constant (k) of Geosmin/MIB Degradation and Their Corresponding Coefficients of Determination (R\(^2\))

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Geosmin</th>
<th>MIB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (min(^{-1}))</td>
<td>R(^2)</td>
</tr>
<tr>
<td>P25</td>
<td>0.346</td>
<td>0.975</td>
</tr>
<tr>
<td>PC50</td>
<td>0.308</td>
<td>0.988</td>
</tr>
<tr>
<td>PC105</td>
<td>0.284</td>
<td>0.982</td>
</tr>
<tr>
<td>PC500</td>
<td>0.272</td>
<td>0.974</td>
</tr>
</tbody>
</table>

The overall better performance of P25 as compared to PCs for the degradation of geosmin and MIB could be closely related to their compositions. P25 is a mixed phase TiO\(_2\) consisting of ~70% anatase and ~30% rutile whereas PCs are single phase TiO\(_2\) containing 100% anatase. It has been hypothesised by Agrios and Pichat (2006) that the mixed phase anatase-rutile TiO\(_2\) photocatalysts have a higher photoactivity than single phase TiO\(_2\) photocatalysts. The electronic interactions between anatase and rutile phases can lead to formation of highly active sites at the interfaces, which enhances the electron-holes separation and increases the number of holes and/or HO\(^*\) radicals available for the degradation of geosmin and MIB. The existence of synergistic effects when anatase and rutile are in contact has been confirmed by Ohno et al. (2001).
Among the three PC photocatalysts studied here the degradation performance of both geosmin and MIB was found to follow the order: PC50>PC105≈PC500. The difference in the sintering temperature between the PCs could be a dominant factor. Agrios and Pichat (2006) have argued that the increased sintering temperature to produce a bigger particle size (or lower $S_{\text{BET}}$) photocatalyst from PC500 to PC50 inversely produces a better crystallised material with reduced number of defects. Consequently, this decreases the rate of electron-hole recombination, i.e., increases the lifetime for photo-generated electrons and holes, thus improving the photocatalytic activity of the photocatalysts as there are more electrons and holes available for reactions to occur.

The observed trend among the PC photocatalysts is unexpected as far as the $S_{\text{BET}}$ is concerned; the $S_{\text{BET}}$ increases significantly from PC50 to PC500. Nevertheless, it has been shown in numerous studies that photocatalysts with a higher $S_{\text{BET}}$ showed a lower degradation performance for compounds having a weak adsorption on the TiO$_2$ surface (Agrios and Pichat, 2006; Enriquez et al., 2007; Gumy et al., 2008). The adsorption study previously showed negligible adsorbed amounts of geosmin and MIB on all the TiO$_2$ photocatalysts investigated. Therefore, the observation is consistent with literature findings, although the reasons are not clearly understood. This suggests that a large $S_{\text{BET}}$ is not necessarily advantageous to the degradation of geosmin and MIB.

As mentioned previously, the degradation performance of geosmin and MIB at the late stage (from the 5th minute onwards as shown in Figures 5.1 and 5.2) was very likely influenced by the aggregation behaviour of the TiO$_2$ particles in suspension. It may be reasonable to compare P25 and PC50 due to their similarity in $S_{\text{BET}}$ and individual particle size in powder form. As described in Chapter 3, P25 in suspension showed a much smaller average aggregate radius than PC50. At various concentrations of TiO$_2$
the average radii of P25 and PC50 were seen to be constant, being 390 nm and 520 nm, respectively. TEM images show that both P25 and PC50 in suspension had a structural morphology that reflects the clusters present and P25 clusters were much more open than those of PC50. If it can be assumed that the TEM data reflects the nature of particles in suspension, the total particle surface area available for direct UV exposure would be much larger for P25 than for PC50. This is similar to what has been reported elsewhere (Nguyen et al., 2005; Gumy et al., 2008).

In summary P25 has proved to have an overall better photoactivity than PCs for the degradation of geosmin and MIB. P25 was therefore chosen for further study in all subsequent investigations.

5.3.3 Suspended TiO$_2$ System

5.3.3.1 Influence of TiO$_2$ Loading

The degradation of geosmin and MIB using TiO$_2$ at a loading of 0.01, 0.1, 0.2, 0.5, 1.0 and 1.5 g.L$^{-1}$ in suspension could be described by first-order kinetic processes. The first-order rate constants calculated based on the first 5 minutes of reaction and the entire degradation period were found to be very similar (<1% difference), which was expected due to negligible sedimentation of the P25 particles as discussed previously. Therefore, all data points over the entire degradation period were used to calculate the first-order rate constants.

Figure 5.5 shows the influence of TiO$_2$ loading on the rate constants of geosmin and MIB degradation. It can be seen that the rate constant of geosmin degradation increased significantly from 0.10 to 0.26 min$^{-1}$ when the TiO$_2$ loading was increased from 0.01 to
It then increased gradually and slowly to 0.35 min⁻¹ when TiO₂ was increased to 1 g.L⁻¹. There was no difference in the rate constants using 1.0 and 1.5 g.L⁻¹ TiO₂. Similarly, to the case of geosmin, the rate constant of MIB degradation increased significantly from 0.06 to 0.18 min⁻¹ when the TiO₂ loading was increased from 0.01 to 1.0 g.L⁻¹ but the rate constant became constant at 0.18 min⁻¹ when TiO₂ loading exceeded 1.0 g.L⁻¹. Therefore, 0.5-1 g.L⁻¹ was considered to be the optimum TiO₂ loadings for the degradation of geosmin and MIB using the suspended TiO₂ system.

![Figure 5.5 Influence of TiO₂ Loading on Rate Constants of Geosmin/MIB Degradation Using the Suspended TiO₂](image)

The above observation was supported by the UV absorption results of the suspended TiO₂ shown in Chapter 3. The UV absorption efficiency of P25 increased significantly with increasing TiO₂ loadings. It increased from 41.3% at a TiO₂ loading of 0.01 g.L⁻¹ to 99.4% at 0.1 g.L⁻¹, then to nearly 100% at 1 g.L⁻¹ or above. The existence of an
optimum TiO₂ loading for the degradation of organic compounds was mentioned in Chapter 2. Unless stated otherwise, a TiO₂ loading of 1 g.L⁻¹ was used for further study in this thesis whenever the suspended TiO₂ system was used.

5.3.3.2 Influence of Initial Pollutant Concentration

The influence of initial concentration in the 0-500 ng.L⁻¹ range on geosmin and MIB degradation was investigated. Figure 5.6 shows the percentage of geosmin and MIB remaining as a function of degradation time and initial concentrations of 250 and 500 ng.L⁻¹.

![Figure 5.6](image)

**Figure 5.6**  Influence of Initial Concentration on the Degradation of Geosmin/MIB Using the Suspended TiO₂

[The insert shows the first-order degradation kinetics on -ln(C/C₀) versus time]

[C₀ = 250 and 500 ng.L⁻¹, [TiO₂] = 1 g.L⁻¹, UV intensity = 14.82 × 10⁻⁵ E.min⁻¹]
It can be seen that for all four curves the percentage remaining decreased in an approximately steady rate. For the initial concentration of 250 ng.L\(^{-1}\), geosmin and MIB were completely degraded within 10 and 20 minutes, respectively. For the higher initial concentration of 500 ng.L\(^{-1}\), geosmin and MIB were completely degraded within 20 and 30 minutes, respectively.

Figure 5.6 (inset) shows that ln(C/C\(_0\)) vs time produced a straight line with \(R^2>0.97\) (Table 5.5), indicating that the photocatalytic degradation of geosmin and MIB could be described by a first-order kinetic process in accordance with Equation 5.1. The first-order rate constants and the coefficients of determination are listed in Table 5.5. It can be seen that the first-order rate constant decreased when the initial concentration of geosmin and MIB was raised. The first-order rate constant of geosmin degradation decreased from 0.342 to 0.269 min\(^{-1}\) when the initial concentration of geosmin was increased from 250 to 500 ng.L\(^{-1}\). Similarly, the first-order rate constant of MIB degradation decreased from 0.178 to 0.135 min\(^{-1}\) when the initial concentration of MIB was increased from 250 to 500 ng.L\(^{-1}\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(C_0) (ng.L(^{-1}))</th>
<th>(k) (min(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geosmin</td>
<td>250</td>
<td>0.342</td>
<td>0.979</td>
</tr>
<tr>
<td>Geosmin</td>
<td>500</td>
<td>0.269</td>
<td>0.976</td>
</tr>
<tr>
<td>MIB</td>
<td>250</td>
<td>0.178</td>
<td>0.975</td>
</tr>
<tr>
<td>MIB</td>
<td>500</td>
<td>0.135</td>
<td>0.992</td>
</tr>
</tbody>
</table>
These values are comparable to those obtained for geosmin by Bellu (2007), which were from 0.18 to 0.35 min\(^{-1}\) at concentrations from 100 to 5,000 ng.L\(^{-1}\). Also the values of the rate constants evaluated in this study are comparable to those found by other authors for UV-based degradation processes (Ferguson et al., 1990; Eggins et al., 1997; Honglay and Jenq, 1998; Canela et al., 1999; Cole et al., 2003; Kim, 2008; Mascolo et al., 2008; Sanches et al., 2010).

For both initial concentrations of 250 and 500 ng.L\(^{-1}\), geosmin was found to be more easily degraded than MIB. Possible explanations include: (1) the lower solubility of geosmin (150.2 mg.L\(^{-1}\)) compared to MIB (194.5 mg.L\(^{-1}\)), thus making geosmin more easily transferred from the bulk liquid to near the TiO\(_2\) surface (Song and O’Shea, 2007) and (2) the more planer structure of geosmin compared to MIB (shown in Section 3.1.2) allows geosmin to be more amenable to oxidant attack (Ho et al., 2007).

The faster removal rates of geosmin than MIB have been observed using other AOP such as ozone/UV, hydrogen peroxide/UV and ultrasonic radiation (Lalezary et al., 1986; Glaze et al., 1990; Atasi et al., 1999; Song and O’Shea, 2007) and other treatment processes including activated carbon adsorption and ozonation (Atasi et al., 1999; Jung et al., 2004). However, our observations contrast with Lawton et al. (2003b) using UV/TiO\(_2\), who reported that MIB was easier to degrade than geosmin. This could be attributed to the different operation conditions used.

5.3.3.3 Influence of UV Intensity

The influence of the incident UV intensity (I) on the degradation of geosmin and MIB was investigated. Figure 5.7 shows the percentage of geosmin and MIB remaining as a function of degradation time at two incident UV intensities (7.41 and 14.82\(\times\)10\(^{-5}\) E.min\(^{-1}\)
1). Using the incident UV intensity of $14.82 \times 10^{-5}$ E.min$^{-1}$, geosmin and MIB were completely degraded within 10 and 20 minutes, respectively. Using the lower incident UV intensity of $7.41 \times 10^{-5}$ E.min$^{-1}$, geosmin and MIB were completely degraded within 20 and 30 minutes, respectively.

![Figure 5.7](image)

Figure 5.7 Influence of UV Intensity on the Degradation of Geosmin/MIB Using the Suspended TiO$_2$

[The insert shows the first-order degradation kinetics on $-\ln(C/C_0)$ versus time]

$[C_0 = 250 \text{ ng.L}^{-1}, [\text{TiO}_2] = 1 \text{ g.L}^{-1}, \text{UV intensity} = 7.41 \text{ and } 14.82 \times 10^{-5} \text{ E.min}^{-1}]$

Figure 5.7 (inset) shows that $\ln(C/C_0)$ vs time produced a straight line with $R^2 > 0.96$ (Table 5.6), indicating that the photocatalytic degradation of geosmin and MIB could be described by a first-order kinetic process in accordance with Equation 5.1. The rate constants, the coefficients of determination, the initial reaction rate and UV dose applied of geosmin and MIB degradation are listed in Table 5.6.
It can be seen from Table 5.6 that the rate constant increased when the incident UV intensity was raised. The rate constant of the degradation of geosmin increased from 0.222 to 0.342 min\(^{-1}\) when the incident UV intensity increased from 7.41×10\(^{-5}\) to 14.82×10\(^{-5}\) E.min\(^{-1}\). Similarly, the rate constant of MIB degradation increased from 0.145 to 0.178 min\(^{-1}\) when the incident UV intensity increased from 7.41×10\(^{-5}\) to 14.82×10\(^{-5}\) E.min\(^{-1}\).

**Table 5.6** Rate Constant (k), Initial Reaction Rate (r\(_0\)) and Coefficients of Determination (R\(^2\)) of Geosmin/MIB Degradation

<table>
<thead>
<tr>
<th>Compound</th>
<th>I (mW.cm(^{-2}))</th>
<th>k (min(^{-1}))</th>
<th>r(_0) (ng.min(^{-1}))</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geosmin</td>
<td>0.61</td>
<td>7.41×10(^{-5})</td>
<td>0.222</td>
<td>55.5</td>
</tr>
<tr>
<td>Geosmin</td>
<td>1.22</td>
<td>14.82×10(^{-5})</td>
<td>0.342</td>
<td>85.5</td>
</tr>
<tr>
<td>MIB</td>
<td>0.61</td>
<td>7.41×10(^{-5})</td>
<td>0.145</td>
<td>36.3</td>
</tr>
<tr>
<td>MIB</td>
<td>1.22</td>
<td>14.82×10(^{-5})</td>
<td>0.178</td>
<td>44.5</td>
</tr>
</tbody>
</table>

The initial reaction rate of both geosmin and MIB degradation was approximately proportional to the square root of the incident UV intensity. For example, the initial reaction rate of geosmin degradation was 85.5 ng.min\(^{-1}\) for the incident UV intensity of 14.82×10\(^{-5}\) E.min\(^{-1}\), approximately equaling the initial reaction rate of 55.5 ng.min\(^{-1}\) for the incident UV intensity of 7.41×10\(^{-5}\) E.min\(^{-1}\) multiplied by square root of 14.82×10\(^{-5}\) E.min\(^{-1}\)/7.41×10\(^{-5}\) E.min\(^{-1}\). Since the incident UV intensities used are in the intermediate range (7.41×10\(^{-5}\)-4.82×10\(^{-5}\) E.min\(^{-1}\)), the influence of light intensity is expected to be proportional to the square root of the incident UV intensity (Zhang *et al.*, 1996).
5.3.4 Immobilised TiO₂ System

5.3.4.1 Influence of TiO₂ Coating Density

The degradation of geosmin and MIB using different TiO₂ layer numbers (1, 3, 5 and 7 layers) with coating densities of 0.1, 0.3, 0.5 and 0.7 mg.cm⁻², respectively, in the immobilised form could be described by a first-order kinetic process. The first-order rate constants of the degradation of geosmin and MIB were calculated using the first 30 minutes of reaction time to avoid potential interferences from intermediate products.

Figure 5.8 shows the influence of TiO₂ coating density on the rate constants of geosmin and MIB degradation. It can be seen clearly that the lines for geosmin and MIB overlapped each other. The rate constant of either geosmin or MIB increased significantly from 0 to 0.026 min⁻¹ when the coating density increased from 0 to 0.3 mg.cm⁻². It then increased slightly to 0.027 min⁻¹ when the coating density increased from 0.3 to 0.5 mg.cm⁻². No further increase was observed with increasing coating density. Hence, five layers of the immobilised TiO₂ with a corresponding coating density of 0.5 mg.cm⁻² were considered as the optimum TiO₂ coating density in the immobilised form.

The above results agree with our UV absorption results for the immobilised TiO₂ shown in Chapter 3. The UV absorption efficiency of P25 increased significantly with increasing TiO₂ coating density. It increased from 55% for the coating density of 0.1 mg.cm⁻² to ~100% for a coating density of ≥0.3 mg.cm⁻².

A TiO₂ coating density of 0.5 mg cm⁻² was therefore considered as the optimum coating density and was used for further study in this thesis.
Figure 5.8  Influence of Coating Density on the Rate Constant of Geosmin/MIB Degradation Using the Immobilised TiO$_2$

$[C_0 = 250 \text{ ng.L}^{-1}, \text{ UV intensity} = 14.82 \times 10^{-5} \text{ E.min}^{-1}]$

5.3.4.2 Influence of Initial Concentration

The influence of the initial concentration of geosmin and MIB in the 0-500 ng.L$^{-1}$ range was investigated. Figure 5.9 shows the percentage of geosmin and MIB remaining as a function of degradation time and initial concentration (250 and 500 ng.L$^{-1}$). It can be seen that for all four curves the percentage remaining decreased slowly with time and for both initial concentrations the degradation rates of geosmin and MIB were similar. Only about 80% removal of geosmin and MIB was achieved within 60 minutes of oxidation at both initial concentrations of 250 ng.L$^{-1}$ and 500 ng.L$^{-1}$.

Figure 5.9 (inset) shows that ln($C/C_0$) vs time produced a straight line with $R^2>0.93$ (Table 5.7), again indicating that the photocatalytic degradation of geosmin and MIB could be described by a first-order kinetic process in accordance with Equation 5.1. The rate constants and the coefficients of determination of geosmin and MIB degradation are
listed in Table 5.7. The rate constant decreased slightly from 0.027 to 0.026 and from 0.027 to 0.024 min$^{-1}$ when the initial concentration of geosmin and MIB was increased from 250 to 500 ng$L^{-1}$, respectively.

![Figure 5.9](image)

**Figure 5.9** Photocatalytic Degradation of Geosmin/MIB Using the Immobilised TiO$_2$

[The insert shows the first-order degradation kinetics on $-\ln(C/C_0)$ versus time]

$[C_0 = 250$ and $500$ ng$L^{-1}$, Coating density = 0.5 mg$cm^{-2}$, UV intensity = $14.82 \times 10^{-5}$ E$min^{-1}]$

**Table 5.7** Rate Constant ($k$) and Coefficients of Determination ($R^2$) of Geosmin/MIB Degradation Using the Immobilised TiO$_2$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C_0$ (ng/L)</th>
<th>$k$ (min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geosmin</td>
<td>250</td>
<td>0.027</td>
<td>0.980</td>
</tr>
<tr>
<td>Geosmin</td>
<td>500</td>
<td>0.026</td>
<td>0.936</td>
</tr>
<tr>
<td>MIB</td>
<td>250</td>
<td>0.027</td>
<td>0.982</td>
</tr>
<tr>
<td>MIB</td>
<td>500</td>
<td>0.024</td>
<td>0.975</td>
</tr>
</tbody>
</table>
The degradation rate of geosmin and MIB using the immobilised TiO\textsubscript{2} was much slower compared to that using the suspended TiO\textsubscript{2}. The rate constants were 0.024-0.027 min\textsuperscript{-1} for the immobilised TiO\textsubscript{2} whereas they were 0.145-0.342 min\textsuperscript{-1} for the suspended TiO\textsubscript{2}. Moreover, the degradation rates of geosmin and MIB became similar using the immobilised TiO\textsubscript{2}. To explain this difference in behaviour between the suspended TiO\textsubscript{2} and the immobilised TiO\textsubscript{2} it is hypothesised that there are three different rate limiting steps involved between the two systems. They are the formation of HO\textsuperscript{•} radicals and the diffusion of geosmin and MIB to near the TiO\textsubscript{2} surface and subsequent reactions of geosmin and MIB with HO\textsuperscript{•} radicals (more discussions are presented in the mechanisms analysis in Chapter 6). In the immobilised TiO\textsubscript{2} the rate limiting steps could be either the formation of HO\textsuperscript{•} radicals or the diffusion of geosmin and MIB near the TiO\textsubscript{2} surface whereas in the suspended TiO\textsubscript{2} the rate limiting step could be the reactions between HO\textsuperscript{•} radicals and geosmin and MIB. Therefore, in the latter case differences in the reaction kinetics of the individual organic compounds were manifested.

5.3.4.3 Influence of Mixing Condition

The influence of mixing condition (0, 200, 400, 600 and 700 rpm) on the degradation of geosmin and MIB was studied. Mixing speeds of over 700 rpm were not considered due to excessive vortexes created by the high mixing energy. The degradation of geosmin and MIB under the different mixing conditions could be described by a first-order kinetic process. The first-order rate constants were calculated using the first 30 minutes of reaction time to avoid potential interference from intermediate products.
Figure 5.10 shows the rate constant of geosmin and MIB degradation as a function of mixing speed. It can be seen that the lines for geosmin and MIB almost overlapped. The rate constant increased from 0.024 to less than 0.027 min\(^{-1}\) when the mixing speed was increased from 0 to 400 rpm. The rate constant then increased slightly to 0.027 min\(^{-1}\) when the mixing speed was increased from 400 to 600 rpm. There was no difference in the rate constants between mixing speeds of 600 and 700 rpm.

![Figure 5.10 Influence of Mixing Speed on the Rate Constant of Geosmin/MIB Degradation Using the Immobilised TiO\(_2\)](image)

\[C_0 = 250 \text{ ng.L}^{-1}, \text{ Coating density} = 0.5 \text{ mg.cm}^{-2}, \text{ UV intensity} = 14.82 \times 10^{-5} \text{ E.min}^{-1}\]

It is expected that the mixing (hydrodynamic) conditions will play an important role in the degradation of geosmin and MIB. They influence the diffusion rates of geosmin and MIB near the TiO\(_2\) surface, making them available for reaction with HO\(^*\) radicals. For mixing speeds of less than 600 rpm the diffusion of geosmin and MIB near the TiO\(_2\) surface could be regarded as a limiting step. Increasing the mixing speed in the range of 0-600 rpm possibly leads to the increased diffusion of geosmin and MIB near the TiO\(_2\),
surface thus increasing the reaction rate. For mixing speeds of over 600 rpm the rate constant of geosmin and MIB remained the same, suggesting that under these mixing conditions the diffusion of geosmin and MIB near the TiO₂ surface is possibly not a limiting step. Instead, the limiting step is possibly the formation of HO• radicals.

A mixing speed of 600 rpm was therefore considered as the optimum mixing speed for the degradation of geosmin and MIB using the immobilised TiO₂ and it was chosen in all subsequent studies.

5.3.4.4 Influence of Solution pH

The influence of solution pH on the degradation of geosmin and MIB was studied. The degradation of geosmin and MIB at different solution pH values of 3.5, 4.1, 6.0, 7.7 and 9.1 could be described by a first-order kinetic process. The first-order rate constants of geosmin and MIB degradation were calculated using the first 30 minutes of reaction time to avoid potential interferences from intermediate products.

Figure 5.11 shows the rate constant of geosmin and MIB degradation as a function of solution pH. It can be seen that the lines for geosmin and MIB almost overlapped. The rate constants of both geosmin and MIB degradation remained at 0.027 min⁻¹ in the investigated pH range of 4.1-7.7. The rate constant, however, increased slightly in both highly acidic and alkaline environments (at pH of 3.5 and 9.1).

As mentioned in Chapter 2, the solution pH can influence the degradation of organic compounds by (1) changing the adsorption behaviour of the organic compounds, (2) changing the rate of forming hydroxyl radicals and (3) changing the flat band edge potentials of TiO₂. The degradation rate might be greatly different if the adsorption of
organic compounds strongly depended on solution pH. Otherwise, the degradation rate is expected to change only slightly. The slight influence of the solution pH on the degradation rate of geosmin and MIB is consistent with the unchanged adsorption behaviour of geosmin and MIB at different solution pH values (see Section 5.3.1).

![Graph illustrating the influence of solution pH on the rate constant of geosmin/MIB degradation using immobilised TiO2]

**Figure 5.11 Influence of Solution pH on the Rate Constant of Geosmin/MIB Degradation Using the Immobilised TiO2**

\[ C_0 = 250 \text{ ng.L}^{-1}, \text{ Coating density} = 0.5 \text{ mg.cm}^{-2}, \text{ UV intensity} = 14.82 \times 10^{-5} \text{ E.min}^{-1} \]

The slightly increasing the rate constant at low and high solution pH could be explained as follows. Firstly, compared to the neutral condition, under alkaline conditions more hydroxide ions (HO\(^-\)) might induce the generation of hydroxyl radicals, which is hypothesised to be the dominant oxidising species in the photocatalytic degradation of geosmin and MIB. More hydroxide ions might also increase the hydroxylation reaction rates of geosmin, MIB and their intermediates by reacting with hydroxide ions (refer to
the discussion provided in Chapter 6) (Litter, 1999). Secondly, under acidic conditions (low solution pH), the oxidation potential of valance band holes is slightly higher than that under neutral conditions, which might slightly increase the generation of hydroxyl radicals (Fox and Dulay, 1993).

5.3.5 Energy Efficiency

The energy requirement of the UV/TiO₂ process for geosmin and MIB degradation is of significant importance since it determines the operational viability of industrial-scale water treatment applications. The energy effectiveness of geosmin and MIB degradation by UV/TiO₂ was quantified in terms of the UV doses required. Table 5.8 shows the UV doses required for the degradation of geosmin and MIB using the suspended and immobilised TiO₂ systems as a function of light intensity (I) and removal percentage of geosmin and MIB.

<table>
<thead>
<tr>
<th>Compound</th>
<th>TiO₂ type</th>
<th>I (mW.cm⁻²)</th>
<th>(E.min⁻¹)</th>
<th>Removal (%)</th>
<th>UV dose (mJ.cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geosmin</td>
<td>Susp.*</td>
<td>0.61</td>
<td>7.41×10⁻⁵</td>
<td>100</td>
<td>6,230</td>
</tr>
<tr>
<td>Geosmin</td>
<td>Susp.</td>
<td>1.22</td>
<td>14.82×10⁻⁵</td>
<td>100</td>
<td>6,230</td>
</tr>
<tr>
<td>MIB</td>
<td>Susp.</td>
<td>0.61</td>
<td>7.41×10⁻⁵</td>
<td>100</td>
<td>12,460</td>
</tr>
<tr>
<td>MIB</td>
<td>Susp.</td>
<td>1.22</td>
<td>14.82×10⁻⁵</td>
<td>100</td>
<td>9,345</td>
</tr>
<tr>
<td>Geosmin</td>
<td>Immo.**</td>
<td>1.22</td>
<td>14.82×10⁻⁵</td>
<td>81</td>
<td>37,380</td>
</tr>
<tr>
<td>MIB</td>
<td>Immo.</td>
<td>1.22</td>
<td>14.82×10⁻⁵</td>
<td>82</td>
<td>37,380</td>
</tr>
</tbody>
</table>

* Susp. = Suspended TiO₂ and ** Immo. = Immobilised TiO₂

Table 5.8  UV Dose Required for Geosmin/MIB Degradation \( [C_0 = 250 \text{ ng.L}^{-1}] \)
It can be seen from Table 5.8 that the UV doses required for the complete degradation of 250 ng.L\(^{-1}\) each of geosmin and MIB using the suspended TiO\(_2\) system and the light intensity of \(14.82\times10^{-5}\) E.min\(^{-1}\) were estimated to be 6,230 mJ.cm\(^{-2}\) and 12,460 mJ.cm\(^{-2}\), respectively. Using the lower incident UV intensity of \(7.41\times10^{-5}\) E.min\(^{-1}\), the required UV dose remained the same for the complete degradation of geosmin but was lower (9,345 mJ.cm\(^{-2}\)) for MIB. The UV doses required for 81% removal of 250 ng.L\(^{-1}\) each of geosmin and MIB using the immobilised TiO\(_2\) system and the light intensity of \(14.82\times10^{-5}\) E.min\(^{-1}\) were estimated to be in the order of 37,380 mJ.cm\(^{-2}\), which were 4-6 times greater than that required for using the suspended TiO\(_2\) system.

Using the suspended TiO\(_2\) system, the required UV dose for the complete degradation of geosmin and MIB was an order of magnitude lower than that reported by Lawton et al. (2003b) of \(>15,000\) mJ.cm\(^{-2}\) for a geosmin and MIB initial concentration of 2000 ng.L\(^{-1}\). The UV doses required for the complete degradation of geosmin and MIB using UV/TiO\(_2\) were, however, relatively comparable to 460-10,000 mJ.cm\(^{-2}\) used for H\(_2\)O\(_2\)/UV and higher than 40-1,400 mJ.cm\(^{-2}\) used for O\(_3\)/UV (see Table 2.4 - Chapter 2). Unsurprisingly, for the immobilised TiO\(_2\) system, relatively much higher UV doses were required for the degradation of geosmin and MIB. The relatively high UV doses required for UV/TiO\(_2\) are to be expected due to the low photonic efficiencies of the UV/TiO\(_2\) process (Mills and Le Hunte, 1997). The photonic efficiencies of the UV/TiO\(_2\) process are discussed in following section.

**5.3.6 Photonic Efficiency**

The effectiveness of the degradation process can be quantified in terms of photonic quantum efficiency. For polychromatic light sources (blacklight bulbs), as used in this
study, it is appropriate (Mills and Le Hunte, 1997) to use the formal quantum efficiency, FQE, defined as:

\[
FQE = \frac{\text{Initial reaction rate}}{\text{Incident light intensity}}
\]

(5.2)

Generally, FQE is dependent on the initial concentrations of organic compounds since the initial rate of reaction decreases with decreasing initial concentrations of the organic compounds for photocatalytic processes (Hoffmann et al., 1995). Hence, the normalised formal quantum efficiency, NFQE, is used, i.e.:

\[
NFQE = \frac{FQE}{\text{Initial concentration}}
\]

(5.3)

The FQE and NFQE values for the degradation of geosmin and MIB using the suspended and the immobilised TiO\textsubscript{2} are reported in Table 5.9.

<table>
<thead>
<tr>
<th>Table 5.9</th>
<th>\textit{FQE and NFQE for Geosmin/MIB Degradation}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{Compound}</td>
<td>\textbf{TiO\textsubscript{2} type}</td>
</tr>
<tr>
<td>Geosmin Susp.*</td>
<td>250</td>
</tr>
<tr>
<td>Geosmin Susp.</td>
<td>500</td>
</tr>
<tr>
<td>MIB Susp.</td>
<td>250</td>
</tr>
<tr>
<td>MIB Susp.</td>
<td>500</td>
</tr>
<tr>
<td>Geosmin Immo.**</td>
<td>250</td>
</tr>
<tr>
<td>Geosmin Immo.</td>
<td>500</td>
</tr>
<tr>
<td>MIB Immo.</td>
<td>250</td>
</tr>
<tr>
<td>MIB Immo.</td>
<td>500</td>
</tr>
</tbody>
</table>

* Susp. = Suspended TiO\textsubscript{2} and ** Immo. = Immobilised TiO\textsubscript{2}
It can be seen that the FQE values for both the suspended and immobilised TiO₂ systems were low. The FQE values for the suspended TiO₂ were in the range of 1.8-5.0×10⁻⁶, that is about 10 times higher than that of using the immobilised TiO₂. The FQE values for the degradation of geosmin were nearly double that for MIB degradation using the suspended TiO₂. FQE values for geosmin degradation were, however, similar to that of MIB degradation using the immobilised TiO₂. In particular, the FQE values for the degradation of geosmin using the suspended and immobilised TiO₂ were in the range of 3.2-5.0×10⁻⁶ and 0.3-0.5×10⁻⁶, respectively whereas they were in the range of 1.8-2.7×10⁻⁶ and 0.3-0.5×10⁻⁶, respectively for the degradation of MIB. The FQE values obtained for the degradation of geosmin and MIB are much lower than the 10⁻²-10⁻⁴ range for the degradation of various other organic compounds reported in literature (Al-Sayyed et al., 1991; Mills and Morris, 1993; Coleman et al., 2000; Lawton et al., 2003b; Huang et al., 2008). The difference could be due to the extremely low initial concentrations of geosmin and MIB used.

As NFQE values are independent of the initial concentration, the NFQE values of various systems are shown in Table 5.9. It can be seen that the NFQE values for the suspended TiO₂ were in the range of 910-2,309 L.mol⁻¹, which were about 10 times higher than that for the immobilised TiO₂. Using the suspended TiO₂ the NFQE values for geosmin and MIB in this study were very high compared with 59.1-83.8 L.mol⁻¹ for 4-chloropenol (Al-Sayyed et al., 1991), 11 L.mol⁻¹ for 4-chloropenol (Mills and Morris, 1993), and 110-500 L.mol⁻¹ for monochlorobenzene (Huang et al., 2008), but they were smaller that 10,000+ L.mol⁻¹ for geosmin and MIB as reported by Lawton et al., 2003b. Using the immobilised TiO₂ the NFQE values for geosmin and MIB in this study were lower compared with 1,000+ L.mol⁻¹ for 17-β-oestradiol (Coleman et al., 2000).
The lower NFQE values obtained in this study for the immobilised TiO_2 compared to the suspended TiO_2 are most likely due to differences in the available active surface area. Quantitative analysis, factoring in the dispersion state of the TiO_2 particles, would be required to determine the available active surface area. These measurements were, however, not performed in this study.

5.4 CONCLUSIONS

The degradation of geosmin and MIB as a function of TiO_2 properties and reactor conditions has been investigated. The following observations and concluding remarks can be made:

1. Degussa P25 showed a higher photocatalytic activity compared to Millennium PCs for degradation of geosmin and MIB, most likely due to the difference in their compositions rather than the difference in their specific surface areas.

2. Among the PC photocatalysts the degradation performance for geosmin and MIB followed the order: PC50>PC105≈PC500. It is believed that surface area might not be an important factor. In fact, the decreased number of crystal defects due to the higher sintering temperatures used from PC500 to PC50 might greatly contribute to the obtained results. The results are consistent with the adsorption study and the zeta potential measurements, which showed that there were negligible amounts of geosmin and MIB adsorbed on the TiO_2 surface.

3. The degradation of geosmin and MIB for the suspended TiO_2 system could be modelled by first-order kinetic processes, having the first-order rate constants of
0.269 min\(^{-1}\) and 0.342 min\(^{-1}\) for geosmin and 0.135 min\(^{-1}\) and 0.178 min\(^{-1}\) for MIB at initial concentrations of 250 and 500 ng.L\(^{-1}\), respectively.

4. For the suspended TiO\(_2\) system, TiO\(_2\) loading of 1 g.L\(^{-1}\) was found optimum with the first-order rate constant of 0.35 min\(^{-1}\) and 0.18 min\(^{-1}\) for geosmin and MIB, respectively. The degradation rate of geosmin and MIB was found to be proportional to the square root of the incident UV intensity. The rate constant decreased with the increasing initial concentration. The suspended TiO\(_2\) system was effective in removing geosmin and MIB. Geosmin and MIB at the concentration range of 250-500 ng.L\(^{-1}\) were completely removed within 30 minutes. The key question with the suspended TiO\(_2\) system in terms of industrial-scale application for drinking water treatment may lie in the ability to recover of the photocatalyst after treatment.

5. The degradation of geosmin and MIB for the immobilised TiO\(_2\) system could also be modelled by first-order kinetic processes having similar the first-order rate constants of 0.024-0.027 min\(^{-1}\) for both geosmin and MIB. They were 5-13 times lower than that for the suspended TiO\(_2\) counterpart.

6. For the immobilised TiO\(_2\) system, TiO\(_2\) coating density of 0.5 mg.cm\(^{-2}\) was found optimum for the immobilised TiO\(_2\) system with the first-order rate constants of 0.027 min\(^{-1}\) for both geosmin and MIB. The rate constant increased slightly with increasing mixing speed. It reached 0.027 min\(^{-1}\) at a mixing speed of 600 rpm. The influence of solution pH on the rate constant was very small. The rate constant decreased with the increasing initial concentration. The immobilised TiO\(_2\) systems are much more appealing for industrial-scale
treatment applications because TiO$_2$ particle removal processes are not required after treatment. However, much higher UV doses than the suspended TiO$_2$ counterpart were needed. Therefore, the key to turn the immobilised system into practical applications would be to improve the photocatalytic efficiency.

7. Energy efficiencies of the suspended TiO$_2$ system for the degradation of geosmin and MIB at the concentration range of 250-500 ng.L$^{-1}$ were 6,000-12,000 mJ.cm$^{-2}$, which is comparable to those of H$_2$O$_2$/UV and higher than those of O$_3$/UV. Energy efficiencies of the immobilised TiO$_2$ system were, however, very low. A UV dose of 37,380 mJ.cm$^{-2}$ was required for ~81% degradation of 250-500 ng.L$^{-1}$ each of geosmin and MIB. The energy required was found to be in the order of 4-6 times higher than that of using the suspended TiO$_2$ system.

8. The photonic efficiencies of the degradation of geosmin and MIB were low. It could be due to the extremely low concentrations of geosmin and MIB investigated. NFQE being independent of initial concentration is therefore used. NFQE for the suspended TiO$_2$ were found in the range of 910-2,309 L.mol$^{-1}$, which is compatible with other studies using the suspended TiO$_2$. NFQE for the immobilised TiO$_2$ was, however, very low, which was about 10 times less than that for the suspended TiO$_2$.

To improve the degradation efficiency of geosmin and MIB by UV/TiO$_2$, especially for immobilised TiO$_2$ systems, it is important to understand the degradation mechanisms of geosmin and MIB, which are investigated and discussed in Chapter 6.
CHAPTER 6

MECHANISM OF GEOSMIN/MIB

DEGRADATION BY UV/TiO₂

A mechanistic analysis of the degradation of geosmin and MIB by UV/TiO₂ is presented in this chapter. Firstly, the influence of hydroxyl radical scavengers and radical promoters/scavengers on the degradation of geosmin and MIB is discussed. The negative effects of adding hydroxyl radical scavengers and the mixed effects of negativity and positivity of adding radical promoters/scavengers on the degradation of both geosmin and MIB are observed, which strengthens the HO• attack mechanism hypothesised previously in Chapter 5. Secondly, degradation mechanism models related to HO• attack are applied. The reaction intermediates of the photocatalytic degradation of geosmin and MIB are then identified and possible degradation pathways related to the HO• attack through H abstraction are proposed.
Mechanistic models describing the degradation of organic compounds by UV/TiO$_2$ are useful in (1) explaining kinetic results, (2) predicting how changes in an operation system might affect degradation performance and (3) improving degradation efficiency. Studying the mechanisms of geosmin and MIB degradation by UV/TiO$_2$ is crucial in order to understand the influence of reaction conditions on geosmin and MIB degradation and to optimise/improve the efficiency of the UV/TiO$_2$ process for the degradation of geosmin and MIB.

To the author knowledge there has been no study to date on the mechanisms of geosmin and MIB degradation by UV/TiO$_2$. However, there have been studies, which may prove useful on the mechanisms of geosmin and MIB degradation by other processes such as ozone (Morioka et al., 1993), UVC radiation (Kutschera et al., 2009), H$_2$O$_2$/UV (Rosenfeldt et al., 2005) and ultrasonic radiation (Song and O’Shea, 2007).

It was reported in most other treatment processes that hydroxyl radicals were the predominant species responsible for the degradation of geosmin and MIB. Morioka et al. (1993) has concluded that the degradation mechanisms of geosmin and MIB by ozone involve hydroxyl radical attack, by studying the influence of adding different hydroxyl radical scavengers such as bicarbonate ion and alcohols and hydroxyl radical promoters such as humic acid and fulvic acid. A similar conclusion was reported for the degradation of geosmin and MIB by UVC radiation by studying the influence of added hydroxyl radical scavengers such as bicarbonate and tert-butanol (Kutschera et al., 2009). Hydroxyl radicals were also found to be the predominant species responsible for the degradation of geosmin and MIB by H$_2$O$_2$/UV (Rosenfeldt et al., 2005).
There are, however, different proposed mechanisms for the degradation of geosmin and MIB. Song and O'Shea (2007) observed that some hydroxyl radical scavengers such as terephthalate and tert-butyl alcohol had a marked negative affect on the degradation of geosmin and MIB by ultrasonic radiation. They concluded that hydroxyl radicals might not be the primary oxidation species for the degradation of geosmin and MIB by ultrasonic radiation.

Based on the adsorption study and the kinetic study presented in Chapter 5, the degradation mechanisms of geosmin and MIB in UV/TiO₂ could possibly relate to an HO• attack. To elucidate the role of HO• in the degradation of geosmin and MIB by UV/TiO₂, the influence of hydroxyl radical scavengers (namely bicarbonate, methanol and ethanol) and radical promoters (namely humic acid and hydrogen peroxide) was investigated in this chapter. Degradation mechanism models were then developed. Reaction intermediates of the degradation of geosmin and MIB by UV/TiO₂ were identified and the degradation pathways were suggested to further support the proposed mechanism.

6.2 EXPERIMENTAL

Materials, apparatus and procedures of experiments were described in Chapter 3.

6.2.1 Hydroxyl Radical Scavengers and Radical Promoters

The immobilised TiO₂ system and the initial concentration of 250 ng.L⁻¹ each of geosmin and MIB were used to investigate the influence of added bicarbonate, methanol, ethanol, humic acid and hydrogen peroxide. As shown in Chapter 5, the rate
constants of both geosmin and MIB degradation using the immobilised TiO$_2$ system were independent of their initial concentration.

### 6.2.2 Intermediate Identification

#### 6.2.2.1 Sample Preparation

The identification of intermediates formed during geosmin or MIB degradation by UV/TiO$_2$ was carried out using the suspended TiO$_2$. Suspensions of 0.1 g.L$^{-1}$ TiO$_2$ with geosmin or MIB concentration of 30,000 ng.L$^{-1}$ were prepared in 500 mL volumetric flasks. The suspension was sonicated and mixed for 30 minutes prior to 60 mL being transferred to the reactor. The natural suspension pH (pH = 6.0) was used without further adjustment. After 0, 5, 10, 20, 30, 60 and 300 minutes of UV radiation, the entire 60 mL sample was filtered through 0.22 μm Millipore filters to recover the TiO$_2$ particles and the filtrate was used for identification analyses. A fresh sample was used for each oxidation time.

The filtrate was first pre-concentrated using the SPME technique prior to GC/MS analysis. The extraction procedure was largely similar to that used for geosmin and MIB quantification (see Section 4.4.4.1 - Chapter 4), with the difference being that in intermediate identification there was no addition of the internal standard and a mixture consisting of 25 mL of the filtrate (instead of 20 mL solution and 5 mL of internal standard) and 6 grams (24 wt%) of sodium chloride was added into a 40 mL capacity vial.
6.2.2.2 Detection by GC/MS

Detection of intermediate products of geosmin and MIB degradation after extraction was performed using GC/MS. A full scan mode was used at the m/z range of 30-180 u. This m/z range was chosen due to the fact that m/z values of intermediate products from the degradation of geosmin and MIB are expected to be smaller than 180 u. The desorption (injector) temperature was set at 270°C. The column temperature programme used was as follows: hold at 50°C for 2.5 minutes; raise to 120°C (20°C.min⁻¹) and hold for 4 minutes; raise to 150°C (20°C.min⁻¹) and hold for 4 minutes; finally raise to 250°C (50°C.min⁻¹) and hold for 2.5 minutes. The carrier gas was helium at a flow rate of 1 mL min⁻¹. The split mode was used for the full scan mode with the split ratio of 100. The electron impact (EI)-MS conditions were: transfer line temperature of 250°C, ion-trap temperature of 180°C and ionising voltages of 1,000 eV.

6.3.2.3 Borneol and Camphor

Borneol (97%) and camphor (natural) in powder form were used to help identify the intermediate products from the degradation of geosmin and MIB by UV/TiO₂. They were sourced from Sigma-Aldrich (Sydney, Australia). Borneol and camphor were detected by SPME and GC/MS using the same procedure used for the identification of geosmin and MIB described in Chapter 4. Standard solutions of borneol and camphor of 10,000 ng.L⁻¹ were used.
6.3 RESULTS AND DISCUSSION

6.3.1 Influence of Hydroxyl Radical Scavengers

6.3.1.1 Influence of Bicarbonate

The rate constant of geosmin and MIB degradation in the presence of sodium bicarbonate was calculated using the first 30 minutes of reaction time to avoid potential interferences from intermediate products. Quantitative comparison was made using the normalised first-order rate constant, \( K = k/k' \), where \( k' \) is the first-order rate constant in the absence of bicarbonate.

In Figure 6.1 \( K \) is plotted for both geosmin and MIB as a function of \( M \), which is the molar ratio of bicarbonate to geosmin or MIB, multiplied by \( 10^{-5} \). The molar ratio was used here in order to compare the effect of the bicarbonate with that of other hydroxyl radical scavengers on the degradation of geosmin and MIB. It can be seen that increasing the bicarbonate concentration resulted in increasing negative effects on the degradation of geosmin and MIB and the trends for both geosmin and MIB were similar. For \( M \) at about 0.7 (\( \text{NaHCO}_3 = 8 \text{ mg.L}^{-1} \) \( K \) decreased to 0.98. For higher \( M \) of 1.6 and 4.0 (\( \text{NaHCO}_3 = 20 \) and 50 \text{ mg.L}^{-1}, respectively) \( K \) decreased to 0.96 and 0.94, respectively. At very high sodium bicarbonate concentrations (\( M \) greater than 50) \( K \) decreased to 0.9 (results not shown).

Bicarbonate ion is widespread in natural surface water, which may play a role in the photocatalytic degradation of contaminants in drinking water. Since bicarbonate concentration in natural surface water is typically less than 50 \text{ mg.L}^{-1} sodium
bicarbonate (M = 4.0), its presence is thus expected to have only a slightly negative influence on the photocatalytic degradation of geosmin and MIB.

**Figure 6.1**  *Effect of Sodium Bicarbonate on the Degradation of Geosmin/MIB by UV/TiO₂*

\[
[C_0 = 250 \text{ ng L}^{-1}, \text{pH } = 6.6-7.5, [\text{NaHCO}_3] = 0-50 \text{ mg L}^{-1} \text{ or } 0-0.6 \text{ mM}]
\]

6.3.1.2 Influence of Alcohols

The rate constant of geosmin and MIB degradation in the presence of methanol or ethanol was calculated using the first 30 minutes of reaction time to avoid potential interferences from intermediate products. Quantitative comparison was also made using the normalised reaction rate constant, \( K = k/k' \), where \( k' \) is the degradation rate constant in the absence of added alcohol.

In Figure 6.2 \( K \) is plotted for both geosmin and MIB as a function of \( M \), which is the molar ratio of alcohol to geosmin or MIB, multiplied by \( 10^{-5} \). It can be seen that,
increasing the alcohol concentration showed increased negative effects on the degradation of geosmin and MIB and the trends for both geosmin and MIB were similar, this was consistent with the findings for the sodium bicarbonate additions. Comparing the influence of ethanol and methanol, it can be seen that ethanol had a greater negative influence than methanol for the same $M$. In the case of adding methanol, $K$ remained at unity for $M$ at about 0.8 (methanol = 3.5 mg.L$^{-1}$)$^3$ and decreased to 0.9 for $M$ at ten times higher (methanol = 35 mg.L$^{-1}$). In the case of adding ethanol, $K$ was 0.96 for $M$ at about 0.8 (ethanol = 5 mg.L$^{-1}$) and decreased to below 0.9 for $M$ at ten times higher (methanol = 35 mg.L$^{-1}$).

![Figure 6.2: Effect of Alcohols on the Degradation of Geosmin/MIB by UV/TiO$_2$
$[C_0 = 250$ ng.L$^{-1}$, pH = 6.6, [methanol] = 0-35$ mg.L$^{-1}$ or 0-1.1 mM, [ethanol] = 0-50$ mg.L$^{-1}$ or 0-1.1 mM]$]

$^3$It indicates that the methanol present in stock solutions, at concentrations of ≤2 mg.L$^{-1}$ should not have any noticeable effects on the degradation of either geosmin or MIB.
6.3.1.3 Discussion

It was found in Chapter 5 that negligible amounts of geosmin and MIB adsorbed onto the surface of the TiO$_2$ particles. On this basis it is more likely that the degradation mechanism is governed by HO$^\cdot$ radicals rather than positively charged hole attack. This notion is supported by the negative effect of adding bicarbonate and alcohols.

The bicarbonate ion is a known HO$^\cdot$ radical scavenger (Morioka et al., 1993). Bicarbonate ion can react with hydroxyl radicals to form CO$_3^{\cdot-}$ radicals according to Reaction 6.1:

$$\text{HCO}_3^- + \text{HO}^\cdot \rightarrow \text{CO}_3^{\cdot-} + \text{H}_2\text{O} \quad (6.1)$$

The CO$_3^{\cdot-}$ radicals are less reactive than HO$^\cdot$ radicals (Wiszniewski et al., 2004), thus reducing the degradation efficiency for geosmin and MIB.

Alcohols are known to be degraded by HO$^\cdot$ radicals in photocatalytic reaction systems (Chen et al., 1999a,b; Hatipoglu and Cinar, 2003). They are likely to compete directly with geosmin and MIB for reactions with HO$^\cdot$ radicals, thus reducing the degradation rate of geosmin and MIB. The rate constants for the reaction of geosmin and MIB with hydroxyl radicals were reported to be $1.400 \times 10^7$ and $820 \times 10^7$ M$^{-1}$.s$^{-1}$, respectively (Glaze et al., 1990) whereas the rate constants for the reaction of ethanol and methanol with hydroxyl radicals were reported to be $185 \times 10^7$ and $85 \times 10^7$ M$^{-1}$.s$^{-1}$, respectively (Anbar et al., 1966). The reported rate constants agree with the magnitude of the influence of ethanol and methanol on the degradation rate of geosmin and MIB.
Overall, the presence of either bicarbonate or alcohols was seen to have a negative influence on the degradation rate constant of geosmin and MIB. However, compared to sodium bicarbonate, the negative effects appeared to be more pronounced with methanol and ethanol. Overall, the trend observed in this study showed ethanol > methanol > bicarbonate reacting with HO• radicals corresponding to rate constants of $185 \times 10^7$, $85 \times 10^7$, and $1.5 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$, respectively (Anbar et al., 1966; Weeks and Rabani, 1966).

6.3.2 Influence of Radical Promoters/Scavengers

6.3.2.1 Influence of Humic Acid

The rate constant of geosmin and MIB degradation in the presence of humic acid was calculated using the first 30 minutes of reaction time to avoid potential interferences from intermediate products. Quantitative comparison was made using the normalised reaction rate constant, $K = k/k'$, where $k'$ is the degradation rate constant in the absence of added humic acid.

In Figure 6.3 $K$ is plotted for both geosmin and MIB as a function of humic acid concentration, which is in the range of 0-9.3 mg.L$^{-1}$. It can be seen that the degradation rates of both geosmin and MIB were negatively and positively influenced, depending on the added concentration of humic acid and the curves for both geosmin and MIB were similar. For the addition of up to 1.4 mg.L$^{-1}$ of humic acid $K$ increased slightly. However, increasing the humic acid concentration from 1.4 to 9.3 mg.L$^{-1}$ showed increasingly negative effects on geosmin and MIB degradation and a greater negative influence on MIB than on geosmin degradation. $K$ for geosmin degradation decreased from 1 to 0.9 whereas $K$ for MIB degradation decreased significantly from 1 to 0.6.
Humic acid is widespread in natural surface water. Typical levels of humic acid in natural surface water are 3-10 mg.L\(^{-1}\). Their presence is therefore expected to have a slight to strong negative effect on the photocatalytic degradation of geosmin and MIB.

6.3.2.2 Influence of Hydrogen Peroxide

The potential of using hydrogen peroxide to enhance the degradation rates of geosmin and MIB was investigated. The first-order rate constant of geosmin and MIB degradation in the presence of hydrogen peroxide was calculated using the first 30 minutes of reaction time to avoid potential interferences from intermediate products. Quantitative comparison was made using the normalised first-order rate constant, \( K = k/k' \), where \( k' \) is the first-order rate constant in the absence of added hydrogen peroxide.
In Figure 6.4 $K$ is plotted for both geosmin and MIB as a function of hydrogen peroxide concentration. Overall, hydrogen peroxide had a varying but very small influence on the degradation rates of both geosmin and MIB. There was a slightly negative effect which peaked at 30 mg.L$^{-1}$ of hydrogen peroxide. However, with further increases in hydrogen peroxide concentration $K$ started to increase gradually and at 300 mg.L$^{-1}$ the $K$ values for both geosmin and MIB degradation were at 1.02.

![Figure 6.4](image.png)

**Figure 6.4**  *Effect of Hydrogen Peroxide on the Degradation of Geosmin/MIB by UV/TiO$_2$*  

$[C_0 = 250$ ng.$L^{-1}$, $pH = 4.8-6.6$, $[H_2O_2] = 0-300$ mg.$L^{-1}$]

Individual contributions of UV, TiO$_2$ and hydrogen peroxide as well as their combined effects on geosmin and MIB degradation were also investigated to decipher the effects of hydrogen peroxide addition on the photocatalytic process since H$_2$O$_2$/UV itself is one of AOP. It was found that in the absence of UV radiation or TiO$_2$ photocatalyst there was almost no degradation of either geosmin or MIB by 300 mg.L$^{-1}$ hydrogen peroxide.
UV alone also showed an insignificant degradation of geosmin and MIB. However, geosmin and MIB could be actually degraded by H$_2$O$_2$/UV, notwithstanding the fact that the UV wavelength of 365 nm used is not the ideal wavelength that would be used in a typical H$_2$O$_2$/UV process. The percentage of geosmin and MIB remaining as a function of hydrogen peroxide dose under UV illumination is shown in Figure 6.5. It can be seen that the percentages remaining decreased gradually from 100% to about 60% in the case of geosmin and from 100% to 50% in the case of MIB with increasing concentration of hydrogen peroxide from 0 to 300 mg.L$^{-1}$. The low degradation efficiency of H$_2$O$_2$/UV observed in this study could possibly due to the use of UVA compared to UVC typically employed in other studies (Romain et al., 2003; Rosenfeldt et al., 2005).

![Figure 6.5](image-url)  

**Figure 6.5** Degradation of Geosmin/MIB by H$_2$O$_2$/UVA  

$[C_0 = 250$ mg.L$^{-1}$, $pH = 6.2$, $[H_2O_2] = 0-300$ mg.L$^{-1}]$
The degradation rates of geosmin and MIB by H$_2$O$_2$/UV/TiO$_2$ were found to be much slower than the combined performance of the two separate UV/TiO$_2$ and H$_2$O$_2$/UV processes. Assuming that the degradation of geosmin and MIB by H$_2$O$_2$/UV/TiO$_2$ has a synergetic effect of UV/TiO$_2$ (under the influence of added H$_2$O$_2$) and H$_2$O$_2$/UV processes, the actual effect of adding H$_2$O$_2$ on the degradation rate of geosmin and MIB by UV/TiO$_2$ would become negative, as shown in Figure 6.6.

**Figure 6.6  Actual Effect of Hydrogen Peroxide on the Degradation of Geosmin/MIB**

\[ C_0 = 250 \text{ ng.L}^{-1}, [H_2O_2] = 0-300 \text{ mg.L}^{-1} \]

Quantitative comparison was made using the normalised reaction rate constant, $K = k/k'$, where $k'$ is the degradation rate constant in the absence of hydrogen peroxide. In Figure 6.6 $K$ is plotted for the actual effect of adding H$_2$O$_2$ on the degradation rate of geosmin and MIB by UV/TiO$_2$ as a function of hydrogen peroxide concentration. It can be seen that increasing the hydrogen peroxide concentration from 0 to 300 mg.L$^{-1}$ showed increasingly negative effects on the degradation rate of geosmin and MIB and a
greater negative influence on geosmin degradation than on MIB degradation. $K$ values for geosmin degradation decreased from 1 to $\sim0.4$ whereas $K$ values for MIB degradation decreased from 1 to 0.6 when the hydrogen peroxide concentration was increased from 0 to 300 mg.L$^{-1}$. The results are discussed in the next section.

6.3.2.3 Discussion

The slightly positive influence of humic acid (up to 1.4 mg.L$^{-1}$) on the degradation rate of geosmin and MIB may be attributed to the sensitisation effects of humic acid. Humic acid are electron-rich compounds, capable of absorbing visible and UV lights, and producing electrons from their excited state. Under visible and UV lights, electrons are produced via photoionisation processes (Aguer and Richard, 1999):

\[ \text{HA} \xrightarrow{hv} \text{HA}^{+}\text{e}^{-} \]  \hspace{1cm} (6.2)

In oxygenated solutions, these electrons are found to be transformed into hydroxyl radicals:

\[ \text{e}^{-} \xrightarrow{O_{2}} \text{O}_{2}^{=} \xrightarrow{\text{HO}_{2}^{\cdot}} \text{H}_{2}\text{O}_{2} \]  \hspace{1cm} (6.3)

\[ \text{H}_{2}\text{O}_{2} \xrightarrow{hv} 2\text{HO}^{\cdot} \]  \hspace{1cm} (6.4)

\[ \text{e}^{-}+\text{H}_{2}\text{O}_{2} \rightarrow \text{HO}^{\cdot}+\text{HO}^{-} \]  \hspace{1cm} (6.5)

The additional radicals would lower the radical induction period in UV/TiO$_{2}$ processes and increase the radical reaction rate, thus increasing the overall degradation rate. The negative effects of humic acid at high concentrations (>1.4 mg.L$^{-1}$) on the degradation of geosmin and MIB may be explained by the hole scavenger role of humic acid, thus reducing the number of hydroxyl radicals generated. It has been reported that humic
acid adsorbs on TiO$_2$ surfaces at a pH 5-7 (Liu et al., 2008; Li and Li, 2002; Selli et al., 1999). The electrons produced via photoionisation processes of humic acid behave as scavengers of valance band holes. Addition of high concentrations of humic acid may significantly decrease the number of holes available for generating hydroxyl radicals, thus reducing the degradation rate of geosmin and MIB (Fox and Dulay, 1993).

Similar effects of humic acid on the degradation of geosmin and MIB by an ozonation process have been reported (Morioka et al., 1993). Small amounts of reagent humic acid (up to 1.0 mg.L$^{-1}$) enhanced the degradation rate of geosmin and MIB (initial concentration of 300 ng.L$^{-1}$ each). The degradation rate then, decreased with increasing humic acid concentrations.

Mixed effects of humic acid on the photocatalytic degradation of organic compounds have been widely reported. The positive effects of humic acid on the photocatalytic degradation have been found in the case of phenanthrene, pyrene, benzo[a]pyrene (Zhang et al., 2008), estrone and 17β-estradiol (Zhang et al., 2007). On the other hand, the negative effects of humic acid have been reported as in the case of 4-chlorophenol, 1,2,3-trochlorobenzene (Lin and Lin, 2007) and formetanate (Marinas et al., 2001).

The negative effects of adding hydrogen peroxide on the photocatalytic degradation of geosmin and MIB can be explained by hole and hydroxyl radical scavenger roles of hydrogen peroxide (Yu et al., 2006), as described in Reactions 6.6-6.8:

$$
\text{H}_2\text{O}_2 + h_{vb}^+ + 2\text{HO}^- \rightarrow \text{O}_2^{\cdot -} + 2\text{H}_2\text{O} \quad (6.6)
$$

$$
\text{H}_2\text{O}_2 + \text{HO}^\cdot \rightarrow \text{H}_2\text{O} + \text{HO}_2^\cdot \quad (6.7)
$$

$$
\text{HO}_2^\cdot + \text{HO}^\cdot \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (6.8)
$$
Since hydrogen peroxides have a greater affinity for TiO₂ than water, they form layers on the TiO₂ surface (Kartal et al., 2001). Holes and hydroxyl radicals formed on the TiO₂ surface would react with hydrogen peroxide, thus reducing the number of hydroxyl radicals available for the degradation of geosmin and MIB (Wang and Hong, 1999; Malato et al., 2000; Dionysiou et al., 2004). Hence, it follows that the degradation rate of geosmin and MIB is markedly decreased.

6.3.3 Mechanistic Model

The Langmuir-Hinshewood mechanistic model has been popular to describe the photocatalytic degradation of many organic compounds. However, the model is based on the adsorption of organic compounds on the catalyst surface and hence may not be suitable to describe the degradation of geosmin and MIB due to their negligible amount of adsorption on the surface of TiO₂. Alternatively, the Eley-Rideal mechanistic model implies that the residence time of organic compounds at the TiO₂ surface would be short enough for the adsorbed amount to remain extremely low. Another mechanistic model developed by Turchi and Ollis (1990) proposes that the organic compounds can react not only in the monolayer, but also in the multi-layers of water in the neighbourhood of the TiO₂ surface. The model suggests that HO• radicals can migrate from the surface into the aqueous solution. The distance over which HO• radicals migrate from the surface into the aqueous solution could be up to 1 μm depending on the organic concentration.

In the mechanistic model developed by Turchi and Ollis (1990) four highly plausible mechanisms involving HO• attack have been proposed:

1. An adsorbed hydroxyl radical reacts with an adsorbed organic compound.
2. A free hydroxyl radical reacts with the adsorbed organic compound.

3. Adsorbed hydroxyl radical reacts with a free organic compound passing the catalyst surface.

4. A free hydroxyl radical reacts with a free organic compound.

The kinetic rate expression for all four cases is:

$$rate(r) = -\frac{dC}{dt} = \frac{k_{obs}K_{obs}C}{1 + K_{obs}C},$$

where $k_{obs}$ is the observed (apparent) reaction rate constant and $K_{obs}$ is the observed (apparent) adsorption equilibrium constant.

$k_{obs}$, representing the reaction rate, which is proportional to UV intensity ($I$) and illuminated photocatalyst surface area at low $I$ or to square root of UV intensity ($I^{1/2}$) and photocatalyst surface area at high $I$. Hence, $k_{obs}$ is a function of only catalyst properties and reaction conditions. Therefore, $k_{obs}$ is independent of the organic compound being degraded, i.e., $k_{obs}$ should be the same for the degradation of organic compounds using the same reactor and operating under the same conditions. $K_{obs}$ represents the adsorptivity of organic compounds on the surface of TiO$_2$.

The linear transform of Equation 6.9 (plot of (1/r) versus (1/C) with slope and y interception being $(1/k_{obs}K_{obs})$ and $(1/k_{obs})$, respectively) and $k_{obs}$, $K_{obs}$ values usually provide information on the validity of the model.

The mechanistic model developed by Turchi and Ollis was applied for the degradation of geosmin and MIB. Table 6.1 shows the initial concentrations of geosmin and MIB,
the rate constants, the initial reaction rates, the reciprocal initial concentrations and the reciprocal initial reaction rates for both the suspended and the immobilised TiO₂ system.

**Table 6.1** *Comparison of Initial Concentration (C₀), Rate Constant (k), Initial Reaction Rate (r₀), Reciprocal Initial Concentration (1/C₀) and Reciprocal Initial Reaction Rate (1/r₀) of Geosmin/MIB Degradation*

<table>
<thead>
<tr>
<th>Comp.</th>
<th>TiO₂ Type</th>
<th>C₀ (ng.L⁻¹)</th>
<th>k (min⁻¹)</th>
<th>r₀ (nM.min⁻¹)</th>
<th>1/C₀ (nM⁻¹)</th>
<th>1/r₀ (nM.min⁻¹⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geosmin Susp.*</td>
<td>62.5</td>
<td>0.343</td>
<td>0.525</td>
<td>0.180</td>
<td>2.915</td>
<td>5.553</td>
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<tr>
<td></td>
<td>125</td>
<td>0.686</td>
<td>0.384</td>
<td>0.263</td>
<td>1.458</td>
<td>3.796</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1.371</td>
<td>0.342</td>
<td>0.469</td>
<td>0.729</td>
<td>2.133</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>2.742</td>
<td>0.269</td>
<td>0.738</td>
<td>0.365</td>
<td>1.356</td>
</tr>
<tr>
<td>MIB Susp.</td>
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<td>0.258</td>
<td>0.096</td>
<td>2.688</td>
<td>10.419</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>0.743</td>
<td>0.250</td>
<td>0.186</td>
<td>1.346</td>
<td>5.384</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1.486</td>
<td>0.178</td>
<td>0.265</td>
<td>0.673</td>
<td>3.781</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>2.972</td>
<td>0.135</td>
<td>0.401</td>
<td>0.336</td>
<td>2.492</td>
</tr>
<tr>
<td>Geosmin Immo.**</td>
<td>62.5</td>
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<td>0.035</td>
<td>0.012</td>
<td>2.915</td>
<td>83.299</td>
</tr>
<tr>
<td></td>
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<td>0.029</td>
<td>0.020</td>
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</tr>
<tr>
<td></td>
<td>250</td>
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<td>0.027</td>
<td>0.037</td>
<td>0.729</td>
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</tr>
<tr>
<td></td>
<td>500</td>
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<td>0.026</td>
<td>0.071</td>
<td>0.365</td>
<td>14.027</td>
</tr>
<tr>
<td>MIB Immo.</td>
<td>62.5</td>
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<td>0.034</td>
<td>0.013</td>
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</tr>
<tr>
<td></td>
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<tr>
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<td>0.024</td>
<td>0.071</td>
<td>0.336</td>
<td>14.020</td>
</tr>
</tbody>
</table>

Figure 6.7 shows plots of reciprocal initial rate (1/r₀) versus reciprocal initial concentration (1/C₀) of geosmin and MIB degradation using the suspended TiO₂ system.
Figure 6.7  Plot of Reciprocal Initial Rate ($1/r_0$) versus Reciprocal Initial Concentration ($1/C_0$) of Geosmin/MIB Degradation Using the Suspended TiO$_2$

Figure 6.8 shows plots of reciprocal initial rate ($1/r_0$) versus reciprocal initial concentration ($1/C_0$) of geosmin and MIB degradation using the immobilised TiO$_2$ system.
It can be seen that linear graphs were obtained in both cases with $R^2 > 0.97$ (Table 6.2). The values of $k_{obs}$ and $K_{obs}$ were determined from linear lines in Figures 6.7 and 6.8 with the intercept of the lines being equal to $1/k_{obs}$ whereas the slopes of the lines are equal to $(1/k_{obs}K_{obs})$. The values of $k_{obs}$ and $K_{obs}$ are given in Table 6.2. The $k_{obs}$ values of the degradation of geosmin and MIB for the suspended TiO$_2$ were 1.02 and 0.77 nM.min$^{-1}$, respectively and the $k_{obs}$ values were the same at 0.14 nM.min$^{-1}$ for the immobilised TiO$_2$. The degradation rates for the suspended TiO$_2$ were 5.5-7.3 times greater than that for the immobilised TiO$_2$. These values are similar to those found by Bellu (2007).
Table 6.2  
Comparison of Observed Reaction Rate Constant and Adsorption Constant of Geosmin/MIB Degradation for the Suspended and Immobilised TiO$_2$ Systems

<table>
<thead>
<tr>
<th>TiO$_2$ Type</th>
<th>Compound</th>
<th>$k_{obs}$ (nM.min$^{-1}$)</th>
<th>$K_{obs}$ (nM$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended</td>
<td>Geosmin</td>
<td>1.02</td>
<td>0.60</td>
<td>0.974</td>
</tr>
<tr>
<td>Suspended</td>
<td>MIB</td>
<td>0.76</td>
<td>0.40</td>
<td>0.993</td>
</tr>
<tr>
<td>Immobilised</td>
<td>Geosmin</td>
<td>0.14</td>
<td>0.26</td>
<td>0.990</td>
</tr>
<tr>
<td>Immobilised</td>
<td>MIB</td>
<td>0.14</td>
<td>0.27</td>
<td>0.990</td>
</tr>
</tbody>
</table>

The similarity of the $k_{obs}$ values for the immobilised TiO$_2$ system is consistent with the independence of $k_{obs}$ to the organic compound being degraded, as suggested by Turchi and Ollis (1990). However, the $k_{obs}$ values for the suspended TiO$_2$ system were higher for the degradation of geosmin. The low $K_{obs}$ values of 0.2-0.6 nM$^{-1}$ obtained in all cases agree with the results presented in Chapter 5 showing negligible adsorption amounts of geosmin and MIB on the TiO$_2$ surface. In addition, the plots of reciprocal initial rate (1/$r_0$) versus reciprocal initial concentration (1/$C_0$) of geosmin and MIB degradation using the suspended and immobilised TiO$_2$ systems show linear trends. In general, the degradation of geosmin and MIB by UV/TiO$_2$ fitted well with Turchi and Ollis’s mechanistic model.

In the next section the identification of intermediates of the degradation of geosmin and MIB by UV/TiO$_2$ and degradation pathways are presented.
6.3.4 Identification of Intermediate Products and Degradation Pathways

6.3.4.1 Geosmin Degradation

The GC/MS chromatograms of irradiated geosmin solutions as a function of degradation time are shown in Figure 6.9. There were two peaks (P1 and P2) clearly present in the GC/MS chromatographs after 5, 10, 20 and 60 minutes of UV radiation. Since these peaks were not found at the start (T = 0), their appearance suggests that they possibly represent two intermediates formed during the degradation of geosmin. The complete disappearance of these two peaks (P1 and P2) after 300 minutes of reaction with the disappearance of geosmin further confirms that P1 and P2 would be due to intermediates from geosmin degradation.

Figure 6.9 Total Ion Chromatograms of Geosmin Degradation
The interpretation of GC/MS chromatograms can be a difficult and complex task because of the absence of commercially available standards for the reaction intermediates. The mass spectra are therefore used to assist in comparing suspected intermediate products with tentative compounds recorded in the Varian Spectra Library.

P1 and P2 were tentatively identified as 1-propanol, 2-(2-hydroxypropoxy)- and 2-butanol, 3,3’-oxybis-, respectively. They were identified by comparing the mass spectra of P1 and P2 with the mass spectra of 1-propanol, 2-(2-hydroxypropoxy)- and 2-butanol, 3,3’- taken from the Varian Spectra Library as shown in Figure 6.10.

**Figure 6.10** Comparison of Mass Spectra, (A) 1-Propanol, 2-(2-hydroxypropoxy)- from Varian Library, (B) P1 in Sample Solution, (C) 2-Butanol, 3,3’-oxybis- from Varian Library, (D) P2 in Sample Solution
The mass spectra of 1-propanol, 2-(2-hydroxypropoxy)-(Figure 6.10-A) and P1 (Figure 6.10-B) having the same m/z of 103, 59 and 41 are 35% similarity whereas the mass spectra of 2-butanol, 3,3’-oxybis- (Figure 6.10-C) and P2 (Figure 6.10-D) having the same m/z of 103, 59 and 45 are 41% similar.

The retention time, m/z, and suggested molecular structure of P1 (now called 1-propanol, 2-(2-hydroxypropoxy)-) and P2 (now called 2-butanol, 3,3’-oxybis-) are given in Table 6.3. It can be seen that the molecular structures of 1-propanol, 2-(2-hydroxypropoxy)- and 2-butanol, 3,3’-oxybis- are similar, but they greatly differ from the molecular structure of geosmin. While 1-propanol, 2-(2-hydroxypropoxy)- has 6 carbons in its chain, 2-butanol, 3,3’-oxybis- has 8. 1-Propanol, 2-(2-hydroxypropoxy)- has double hydroxyl groups in its molecular structure but it has no -CH$_3$ with H in the $\beta$ position compared to the 2-butanol, 3,3’-oxybis- molecular structure. 2-Butanol, 3,3’-oxybis- has double hydroxyl groups in its molecular structure and it has two -CH$_3$ with 6 H in the $\beta$ position.
Table 6.3  Retention Time, m/z and Suggested Intermediate Products of Geosmin Degradation

<table>
<thead>
<tr>
<th>Intermediate Product</th>
<th>Retention Time (min)</th>
<th>Peak Area During 60 min. Reaction Time</th>
<th>m/z</th>
<th>Suggested Compound</th>
<th>Molecular Formula</th>
<th>Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>9.4</td>
<td>Constant</td>
<td>103/59/41</td>
<td>1-Propanol, 2-(2-hydroxypropoxy)-</td>
<td>C₆H₁₄O₃</td>
<td>![Molecule P1 Image]</td>
</tr>
<tr>
<td>P2</td>
<td>9.6</td>
<td>Constant</td>
<td>103/59/45</td>
<td>2-Butanol, 3,3’-oxybis-</td>
<td>C₈H₁₈O₃</td>
<td>![Molecule P2 Image]</td>
</tr>
</tbody>
</table>
The retention times of 2-butanol, 3,3’-oxybis- and 1-propanol, 2-(2-hydroxypropoxy)- are 9.4 and 9.6 minutes, which are much shorter than that of geosmin (13.8 minutes), suggesting they are not direct reaction intermediates of geosmin degradation and they are probably the result of several successive reactions. It matches with the fact that 2-butanol, 3,3’-oxybis- and 1-propanol, 2-(2-hydroxypropoxy)- have a much different molecular structure compared to that of geosmin.

The peak areas of both 2-butanol, 3,3’-oxybis- and 1-propanol, 2-(2-hydroxypropoxy)- were rather stable during 60 minutes of reaction (see Figure 6.9). It is possible that the formation rates and the degradation rates of both 2-butanol, 3,3’-oxybis- and 1-propanol, 2-(2-hydroxypropoxy)- are similar, thus making their peak areas constant during 60 minutes of radiation.

From the structures of the intermediates identified by GC/MS, the tentative degradation pathways of geosmin are proposed which accounts for the main processes originated. The pathways presented in Figure 6.11 do not include every possible reaction pathway or potential intermediates. They only focus on those reaction pathways that are consistent with the experimental data obtained.
Figure 6.11  Proposed Degradation Pathway of Geosmin by UV/TiO₂
It is not clear what mechanisms are involved at the first stage of geosmin degradation when geosmin is degraded to form 2-butanol, 3,3’-oxybis- (stage I – Figure 6.11) due to the lack of intermediates detected. The lack of intermediates detected could be due to the short lives of intermediates (if any) or their high reactivity, making them easily degraded further.

The pathways for the degradation of 2-butanol, 3,3’-oxybis- to form 2-butanol, 3,3’-oxybis- may relate to HO• attack through H-abstraction (stage II – Figure 6.11). 2-butanol, 3,3’-oxybis- has 6 Hβ in 2 CH3 bondings, which are related to two possible routes involving the H abstraction at the β position by HO• attack. Both routes are shown in stage II – Figure 6.11. In both routes, the first three Hβ in one -CH3 were attacked to form hydrocarbon radicals. These radicals would quickly react with HO− to form alcohols. Subsequently, other hydroxylation reactions with corresponding Hβ abstraction by HO• attack and by HO− to form aldehydes and then carboxylic acids before decarboxylation reactions. The whole reaction chain would occur for the second three Hβ in the other -CH3 before 1-propanol, 2-(2-hydroxypropoxy)- was formed. Alternatively, the hydroxyl radical reaction through H abstraction could simultaneously occur for Hβ in both –CH3 groups.

The hydroxyl radical attack reactions through Hβ abstraction of alcohols to form aldehydes, carboxylic acid before decarbocylation have been reported in literature (Blake and Griffin, 1988; Chen et al., 1999a,b,c; Pichat, 2007). For example, Blake and Griffin (1988) have determined that the intermediates of the photocatalytic degradation of 1-butanol are 1-butanal and 1-buten, indicating that the hydroxyl radical attack reactions through Hβ abstraction could be a major step. Similarly, Chen et al.
(1999a,b,c) have studied the photocatalytic degradation of methanol and ethanol in aqueous TiO$_2$ suspensions finding that formaldehyde and acetaldehyde were the intermediates, respectively.

The consistence of peak areas of the two peaks representing the two intermediates during a long reaction time suggests that the degradation rate in stage I could be similar to the degradation rate in stage II. Since the formation of two intermediates of geosmin degradation in stage II could possibly involve reaction routes related to HO$^\bullet$ reactions, it is possible that the degradation of geosmin in stage I could also involve HO$^\bullet$ attack. This is supported by the negative effects of adding hydroxyl radical scavengers on the degradation of geosmin described in Section 6.3.1.

It has been widely reported that the photocatalytic degradation of organic compounds would lead to the formation of short chain aliphatic alcohols, aldehydes and carboxylic acids before being completely mineralised to carbon dioxide and water (Han et al., 2009; Yang et al., 2009). It is possible that the complete degradation of geosmin would undergo those steps. 1-Propanol, 2-(2-hydroxypropoxy)- could possibly react further to form short chain aliphatic alcohols, aldehydes and carboxylic acids (stage III – Figure 6.11) before being completely degraded to carbon dioxide and water (stage IV – Figure 6.11).

6.3.4.2 MIB Degradation

The GC/MS chromatograms of irradiated MIB solutions as a function of degradation time are shown in Figure 6.12. There were three clear peaks (P3, P3’ and P4) shown in GC/MS chromatograms after 10, 30 and 60 minutes of UV radiation. Since these peaks were not found at the beginning (reaction time = 0), their presence suggests that they
possibly represent three reaction intermediates formed during the degradation of MIB. The complete disappearance of these three peaks (P3, P₃’ and P4) after 300 minutes of reaction with the disappearance of MIB further confirms that they would be among the intermediates of the degradation of MIB.

![Figure 6.12 Total Ion Chromatograms of MIB Degradation](image)

Figure 6.12  Total Ion Chromatograms of MIB Degradation

The mass spectra are used to assist in comparing suspected intermediate products with tentative compounds recorded in the Varian Spectra Library. There was no compound in Varian Spectrum Library matching the mass spectrum of P₃’. On the other hand, reaction intermediates corresponding to P3 and P4 were tentatively identified as camphor and borneol, respectively.

To confirm that P3 and P4 are likely to be camphor and borneol, respectively, their retention times and mass spectra were compared with that of standard solutions of...
camphor and borneol. Figure 6.13 clearly shows that the retention times of standards of camphor and borneol are 7.9 and 8.3 minutes, respectively, which matched those of P3 and P4, respectively.

**Figure 6.13  Total Ion Chromatogram of Standards of Camphor and Borneol**

\[
[C_{\text{Camphor}} = C_{\text{Borneol}} = 10,000 \text{ ng.L}^{-1}] 
\]

The mass spectra of camphor (Figure 6.14-A) and P3 (Figure 6.14-B) having the same m/z of 152, 108, 95, 82, 69, 55 and 41 are 34% similar whereas the mass spectra of borneol (Figure 6.14-C) and P4 (Figure 6.14-D) having the same m/z of 110, 95, 82, 67, 55 and 41 are 45% similar.
Figure 6.14  Comparison of Mass Spectra, (A) Camphor in Standard Solution, (B) P3 in Sample Solution, (C) Borneol in Standard Solution, (D) P4 in Sample Solution

The retention time, m/z, and suggested molecular structure of P3 (now called camphor) and P4 (now called borneol) are given in Table 6.4. It can be seen that the molecular structures of both borneol and camphor are very similar to that of MIB. Borneol is 1 - CH₃ shorter than MIB and camphor is 2 hydrogen atoms less than borneol. Both borneol and camphor have 10 carbons in their chain, which is 1 carbon shorter than that of MIB.
Table 6.4  Retention Time, m/z and Suggested Intermediate Products of MIB Degradation

<table>
<thead>
<tr>
<th>Intermediate Product</th>
<th>Retention Time (min)</th>
<th>Peak Area During 60 min. Reaction Time</th>
<th>m/z</th>
<th>Suggested Compound</th>
<th>Molecular Formula</th>
<th>Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3</td>
<td>7.9</td>
<td>Increased</td>
<td>152/108/95/82/69/55/41</td>
<td>Camphor</td>
<td>C_{10}H_{16}O</td>
<td><img src="image" alt="Camphor Structure" /></td>
</tr>
<tr>
<td>P4</td>
<td>8.3</td>
<td>Constant</td>
<td>110/95/82/67/55/41</td>
<td>Borneol</td>
<td>C_{10}H_{18}O</td>
<td><img src="image" alt="Borneol Structure" /></td>
</tr>
</tbody>
</table>
The retention times of camphor and borneol were 7.9 and 8.3 minutes, which are slightly shorter than that of MIB (8.9 minutes), suggesting that they could be among the direct reaction intermediates from the degradation of MIB. It matches with the similarity of molecular structures of camphor and borneol.

From the structures of the intermediates, identified by GC/MS, tentative degradation pathways of MIB are proposed which accounts for the main processes originated. The pathways described in Figure 6.15 do not include every possible reaction pathway or potential intermediates. They only focus on those reaction pathways that are consistent with the experimental data obtained.

The pathways for the degradation of MIB to form borneol possibly relate to HO\(^{•}\) attack through H-abstraction (stage I – Figure 6.15). MIB has three H\(_{\beta}\) in its molecular structure. The H\(_{\beta}\) of the MIB was first attacked by HO\(^{•}\) to form MIB radicals, which react quickly with HO\(^{-}\) to form an alcohol. Subsequently, other hydroxylation reactions take place with corresponding H\(_{\beta}\) abstraction by HO\(^{•}\) attack and HO\(^{-}\) to form aldehydes. Aldehydes are then oxidised to carboxylic acids before the decarboxylation reaction to produce borneol. Borneol was possibly attacked by HO\(^{•}\) to H\(_{\alpha}\) to produce borneol radicals, which then react quickly with HO\(^{-}\) before dehydration to yield camphor (Stage II – Figure 6.15).
Figure 6.15 Proposed Degradation Pathway of MIB by UV/TiO$_2$

**I**

MIB $\rightarrow$ Camphor $\rightarrow$ Borneol

**II**

Camphor $\rightarrow$ Borneol

**III**

$\text{R-OH} + h^+, e^-, \text{HO}^-, \text{O}_2, \text{HO}^-$

**IV**

$\text{R-OH} + h^+, e^-, \text{HO}^-, \text{O}_2, \text{HO}^- \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
The peak area of borneol increased slightly during 60 minutes of radiation (see Figure 6.12). It is possible that the formation rate of borneol is slightly higher than its degradation rate, i.e., the reaction rate of $\text{HO}^\cdot$ with MIB could be faster than that of $\text{HO}^\cdot$ with borneol (if borneol is a direct intermediate of MIB degradation). This is reasonable due to the position of H being attacked in the two reactions. While $H_\beta$ was attacked in the former reaction, $H_\alpha$ was attacked in the latter. The hydroxylation reaction rates with $H_\beta$ abstraction by $\text{HO}^\cdot$ attack have been reported to be faster than that with $H_\alpha$ in many cases (Hatipoglu and Cinar, 2003).

The peak area of camphor increased significantly with increasing radiation time from 10 to 60 minutes (see Figure 6.12). It is possible that the formation rate of camphor is significantly higher than its degradation rate, i.e., the reaction rate of $\text{HO}^\cdot$ with borneol is much faster than that of $\text{HO}^\cdot$ with camphor (if camphor is a direct intermediate of borneol degradation). This is reasonable due to the molecular structure difference of borneol and camphor. Borneol has 1 $H_\alpha$ whereas camphor only has $H_\gamma$ and $H_\delta$ in its molecular structure. The higher rate constants of $H_\alpha$ compared to $H_\gamma$ and $H_\delta$ in aliphatic alcohols for $\text{HO}^\cdot$ attack by H abstraction have been reported elsewhere (Hatipoglu and Cinar, 2003).

The detection of two intermediates of MIB degradation in stages I and II with possible reaction routes related to $\text{HO}^\cdot$ attack suggests that the involvement of $\text{HO}^\cdot$ in stages I and II could be a major reaction step in the degradation of MIB. This was supported by the negative effects of adding hydroxyl radical scavengers on the degradation of MIB described in Section 6.3.1.
Similarly to the case of geosmin, the intermediate of MIB degradation (camphor) would be degraded to form short chain aliphatic alcohols, aldehydes and carboxylic acids (stage III – Figure 6.15) before being completely degraded to CO₂ and H₂O (stage IV – Figure 6.15).

6.4 CONCLUSIONS

The mechanism analysis of the photocatalytic degradation of geosmin and MIB has been investigated. The following observations and concluding remarks are given:

1. The degradation rates of both geosmin and MIB decreased with increasing concentration of sodium bicarbonate, methanol and ethanol. The negative effects observed (ethanol>methanol>bicarbonate) is consistent with their decreasing magnitudes of the corresponding rate constant of reaction with HO• radicals. This behaviour agreed with the notion that the degradation mechanism of geosmin and MIB involved hydroxyl radical attack.

2. The positive effects and negative effects of respectively adding small and large amounts of humic acid could be explained by the radical promoter and radical scavenger roles of humic acid on the degradation of geosmin and MIB. These findings again support the involvement of hydroxyl radicals in the degradation of geosmin and MIB. The findings also show a potential method to improve the photocatalytic degradation rate of geosmin and MIB.

3. Despite the fact that the corresponding hydrogen peroxide/UV process alone exhibited significant degradation of geosmin and MIB, the addition of hydrogen peroxide did not lead to a significant increase in the overall degradation rate of
geosmin and MIB. In fact, the increasing negative effects of adding hydrogen peroxide concentration on the photocatalytic degradation of geosmin and MIB were observed and the effects could be possibly due to the hole and hydroxyl radical scavenger roles of hydrogen peroxide.

4. The degradation mechanisms of geosmin and MIB could be well described by hydroxyl radical attack mechanisms developed by Turchi and Ollis. The plots of reciprocal initial rate (1/r₀) versus reciprocal initial concentration (1/C₀) of geosmin and MIB degradation using the suspended and immobilised TiO₂ systems showed linear trends and behaviours. The observed reaction rate constants (kₘₐₓ) for both the suspended and immobilised TiO₂ systems were relatively similar for the degradation of geosmin and MIB.

5. Using GC/MS chromatogram analysis the two main intermediate products of the geosmin degradation were tentatively identified as 1-propanol, 2-(2-hydroxypropoxy)- and 2-butanol, 3,3'-oxybis- whereas camphor and borneol were confirmed as the intermediate products of the degradation of MIB. From the molecular structures of the intermediates detected, their retentions times and peak areas during reaction, it was concluded that the photocatalytic degradation mechanism of geosmin and MIB is mainly related to hydroxyl radical attack through H abstraction.

Identification of the mechanism for geosmin and MIB degradation is believed to be beneficial in predicting and modifying the reaction kinetics and more importantly in developing effective and economical processes for the removal of geosmin and MIB in drinking water treatment applications.
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

General conclusions of this study are presented in this chapter. Recommendations for future work are also included.
7.1 CONCLUSIONS

The study has led to a number of research findings. Firstly, it was found that geosmin and MIB could be quantitatively measured down to the nano-gram-per litre level for both components using SPME in conjunction with GC/MS. Accurate and reproducible measurements were achieved with biphenyl-d$_{10}$ as the internal standard and preconditioning the fibre prior to the adsorption stage. Optimum extraction temperature and duration were found to be 270°C and 30 minutes, respectively. It was also found that correct quantification of both geosmin and MIB required the calibration curves needed to be at the same pH as that of the sample water, especially when it was outside of the pH range of 4-8.

Following the development of the methodology for the quantification of geosmin and MIB, degradation experiments were carried out using various commercial TiO$_2$ photocatalysts, including Degussa P25 and Millennium PCs with different specific surface areas. These types of photocatalyst were found to be effective, with Degussa P25 giving the best performance. Interestingly, there was no apparent correlation between the specific surface area of the photocatalyst powder and the degradation rate. A reason for this is possibly related to the agglomeration occurring when the material is suspended in water.

The experiments examining the degradation rate of geosmin and MIB involved both suspended and immobilised photocatalysts systems. Dark adsorption studies showed that there was negligible adsorption of either geosmin or MIB onto the TiO$_2$ surface. This observation was supported by zeta potential measurements which identified repulsion between the different surfaces. The degradation rate of both geosmin and MIB
involving the activation of TiO$_2$ photocatalyst with UV light followed a first-order kinetic processes with respect to TiO$_2$ loading, geosmin and MIB concentration, pH, UV intensity and mixing condition. The degradation rates for the suspended Degussa P25 photocatalyst exhibited energy efficiencies comparable to those of existing treatment processes such as H$_2$O$_2$/UV. However, the energy efficiencies were for the immobilised system was 4-6 times lower than that of the suspended system. To find out why this was the case, mechanistic studies were undertaken.

The mechanistic studies focused on understanding the generation process for hydroxyl radicals. It was found that the presence of bicarbonate and alcohols, that are known hydroxyl radical scavengers, resulted in a decrease in the degradation rates for both geosmin and MIB. The increased negative effect bicarbonate< methanol< ethanol was consistent with corresponding reduction in the amount of available HO$^\cdot$ radicals. Humic acid, commonly present in raw water, exhibited both positive and negative influences on the degradation rate. This was because humic acid can act as both promoter and scavenger of hydroxyl radicals depending on the conditions. At low concentrations, humic acid slightly increased the degradation rate for both geosmin and MIB. However, this effect was quickly reversed as the concentration of humic acid was increased. Again, this effect was thought to be related to the availability of hole and hydroxyl radicals in the degradation process. The negative effects of adding hydrogen peroxide could be attributed to the hole and hydroxyl radical scavenger roles of hydrogen peroxide.

The GC/MS analyses identified the presence of 1-propanol, 2-(2-hydroxypropoxy)- and 2-butanol, 3,3’-oxybis- as the intermediates of geosmin degradation, and the presence of camphor and borneol as the intermediates of MIB degradation. From the experimental
investigation using known hydroxyl radical scavengers/promoters and the GC/MS analysis the degradation pathways, based on the involvement of hydroxyl radicals, have been proposed. Successful application of the Turchi and Ollis kinetic model based on hydroxyl radical attack, has further reinforced the likelihood hydroxyl radicals are the major contributor to geosmin and MIB degradation resulting from UV/TiO₂ process.

7.2 RECOMMENDATIONS

The outcomes of this work have provided an improved understanding of the fundamentals underlying the kinetics and mechanisms of the process, which can be useful for the application of the process in water treatment. Careful and appropriate selection of reaction conditions, such as catalyst loading, UV intensity, mixing condition and pH can lead to the best removal efficiency for the degradation of geosmin and MIB. Areas of the research that warrant further consideration include:

1. There are two main photocatalytic reactor configurations, depending on the state of the photocatalysts: (1) reactors with suspended photocatalyst particles and (2) reactors with photocatalyst immobilised. Suspended-type photocatalytic reactors usually perform high total surface areas of photocatalyst per unit volume, while the immobilised-type photocatalytic reactors are often associated with mass transfer limitation. The suspended photocatalytic reactor has been still preferred configuration due to its high total surface area per unit volume. In addition, the photocatalyst particles can be separated by settling tanks or external cross-flow filtration system to enable continuous operation of the suspended photocatalyst reactor. A technically promising solution for solving the downstream separation of photocatalyst particles after treatment is via the application of hybrid
photocatalysis-membrane processes, which has been discussed elsewhere (Chong et al., 2010). The development of this type of reactor for the degradation of geosmin and MIB would be recommended.

2. The photonic efficiencies of the current TiO\textsubscript{2} photocatalysts were very low. The reasons for this need to be determined so that either improvement to the existing photocatalysts can be made or new ones developed.

3. To improve the degradation efficiency of the investigated TiO\textsubscript{2} photocatalysts, one possible option is to modify the TiO\textsubscript{2} by doping it with ions. The positive effects of doped TiO\textsubscript{2} photocatalysts on the degradation of various compounds have been reported (Kabra et al., 2004; Chong et al., 2010; Mazill et al., 2010).

4. The identification and quantification of intermediates need to be investigated further. While this study was successful in the identifying some of the intermediates of the degradation process of geosmin and MIB, their quantification would greatly enhance the understanding of what is taking place. Possibly, high performance liquid chromatography, high performance ionic chromatography, infrared spectroscopy and gas chromatography/mass spectrometry can be used to do this.

5. Finally, the quantification of hydroxyl radicals by using the method proposed by Westerhoff et al. (2006) based on R\textsubscript{CT}, which is the ratio of hydroxyl radical and ozone concentrations or by using the electron spin resonance would be highly desirable.
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