THE EVALUATION OF METAL ION COMPETITION ON THE FLUORIDE REMOVAL FROM SOLUTIONS USING NATURAL MOLECULAR SIEVE AND CALCITE

by

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DECLARATION

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.

I hereby certify that the work embodied in this thesis contains published paper of which I am a joint author.

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Abstract

Industrial wastewaters often consist of a complex chemical cocktail with treatment of target contaminants complicated by adverse chemical reactions. The impact of metal ions on the removal of fluoride by natural zeolite and calcite was investigated in the present study via laboratory batch reactor kinetics and column tests.

In order to better understand the kinetics, the intra-particle diffusion (IPD), pseudo-second order (PSO) and Hill (Hill 4 and Hill 5) models were applied on the basis of kinetics test results. As these models have different numbers of parameters, model fitting was compared using the Akaike Information Criterion (AIC) and the Schwarz Bayseian Information Criterion (BIC) methods capable of comparing models having different numbers of parameters. The Hill models (Hill 4 and Hill 5) were found to be superior in describing the fluoride removal processes which reflects the process of chemisorption during fluoride removal. Results indicate that the presence of Mn (100 $mg.L^{-1}$) and Cd (100 $mg.L^{-1}$) respectively increase the rate of fluoride sorption by zeolite by a factor of ~28.3 and ~10.9, with the maximum sorption capacity increased by a factor ~2.2 and ~1.7. The presence of Ba (100 $mg.L^{-1}$) in the zeolite sample initially inhibited fluoride removal and very poor fits were obtained for all models. Fitting was best described with a biphasic sigmoidal model with the degree of inhibition decreasing with increasing temperature suggesting at least two processes are involved with fluoride sorption onto natural zeolite in the presence of Ba.

With calcite, results reveal that the presence of Co^{2+} adversely affects the process of defluoridation resulting in a lowest amount of fluoride removal in the order Co^{2+} < stonedust (a 99% pure natural calcite) ≈ Cd^{2+} < Mn^{2+} < Ba^{2+}. Calculation of reaction half-lives ($t_{0.5}$), a measure of the length of time required to remove 50% of the initial fluoride mass, showed that $t_{0.5}$ increased in the order Ba^{2+} ≈ stonedust < Cd^{2+} < Co^{2+} < Mn^{2+}, with Mn^{2+} and Co^{2+} requiring ~95 and ~140 minutes more to achieve half their respective predicted fluoride removal.

Column tests studying the effect of metal ions on fluoride transport in the presence of calcite or zeolite showed that the defluoridation efficiencies of zeolite and calcite are much lower than those in the batch tests, being only ~49% and ~20% respectively. This is attributed to the fact that the contact between sorbent and sorbate are temporal and spatial in column tests with the residence time much less than experienced during kinetics tests. The addition of Ba^{2+} and Cd^{2+} in the zeolite column sample respectively decreases the fluoride removal by ~13% and ~10% after four pore volumes had passed through the column while in the calcite sample, Cd^{2+} has similar defluoridation amount with the blank (no metals) and the presence of Ba^{2+} lowered the amount by ~8% at 4.5 PV. CXTFIT a program to model 1D transport processes was used to fit the tracer (Br^-) data from each column test. This allows the column characteristics such as the effective porosity, Darcy velocity, and dispersity to be calculated and used to assess the retardation of fluoride. PHREEQC geochemical modelling was also applied to both the kinetics data and the column experimental results. Modelling of the column tests using calcite required the addition of a hypothetical phase with a different solubility than calcite. By varying log k, calcite solubility can be changed with an

increasing log k indicating an enhanced calcite dissolution. It is found that the best match achieved between the observed and modelled calcite column data when log k is 1.1, 0.75, 1.2 for the blank, Ba^{2+} and Cd^{2+} samples respectively. This implies that calcite dissolution is suppressed by the presence of Ba^{2+}, which is inconsistent with the findings in the batch reactor kinetics tests. As for the zeolite columns, the log k of LinearF^- which defines the phases and the associated hypothetical reactions with F^- is altered by trial and error until the best fit is obtained. The log k of LinearF^- used in the zeolite blank column is -100.05, while it changes to -100.22 in the presence of Ba^{2+} and Cd^{2+}. Results show good fits with the observed data. Geochemical modelling of the kinetics data however was more problematic with the initial instantaneous sorption part of the model curves closely matching the observed data, however the final part of the model curves over predicted fluoride removal. The initial development of the PHREEQ geochemical model presented here shows potential in being able to be used as a predictive tool for the design of fluoride remediation strategies such as permeable reactive barriers.