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SORPTION OF SELECTED RADIONUCLIDES TO CLAY IN THE PRESENCE OF HUMIC ACID

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Abstract

Within the framework of the FUNMIG programme, Loughborough University is performing work to increase understanding of the sorption behaviour of selected radionuclides with various minerals in the absence and presence of competing complexing ligands, such as humic acid (HA).

The determination of the distribution ratios ($R_d$) of binary (metal- and humic-solid), and ternary (metal-solid-humic) systems using a batch adsorption technique is reported. Four radionuclides have been used; $^{137}$Cs, $^{63}$Ni, $^{152}$Eu and $^{109}$Cd, to facilitate modelling. Montmorillonite, kaolinite and $\alpha$-goethite have been used as solids.

Humic acid concentrations (2 - 300 ppm (w/v)) were determined using UV spectrophotometry. Radiometric analysis was used for radionuclide measurement.

Construction of sorption isotherms using the Langmuir and Freundlich Equations has allowed characterisation of sorption types, and has provided maximum sorption capacities of the solid surfaces for each of the metals in the binary systems. Distribution relationships between metal and humic acid for each ternary system have been established and correlated.

Introduction

Several attempts have been made to predict the speciation of radionuclides in the presence of humic substances. Reliable predictions are dependent on accurate models. It is well documented that humic substances can significantly affect the sorption of radionuclides on natural solids. Murphy et al. postulated that mineral bound humic substances modify inorganic surfaces, changing the nature and number of complexation sites for contaminants [1], therefore providing a natural sink for the removal of contaminants from aquifers. In general, the suppression of radionuclide and heavy metal sorption by humic and fulvic substances at low pH and enhancement of sorption at high pH has been observed.

It has been proposed that the formation of a surface mineral-humate complex with a high affinity for metals occurs [2]. The work reported here examines the effect of increasing humic acid concentration on the distribution of four metals on three mineral surfaces.
Objectives

To measure the distribution ratios of metal-ligand, metal-solid, ligand-solid and metal-ligand-solid interactions using the batch experiment method.

To fit the distribution data of binary and ternary systems to a sorption model.

Experimental

Materials

Unless otherwise stated, all chemicals used were reagent grade. Water was supplied from a Barnstead/Nanopure system. Kaolin (~Al₂Si₂O₆(OH)₄, Aldrich), Montmorillonite (K-10 Grade, Aldrich) and α-Goethite (Fe(OH)O, Fluka) were all used as supplied. 4-Morpholineethanesulfonic acid (MES, Fisher, 0.1 mol dm⁻³) was used to stabilise the pH at 6 and control ionic strength. Unless otherwise stated, all experiments were conducted on the bench at ambient temperature. During equilibration, samples were shaken on a rotary shaker at 300 rpm.

Solutions

All HA solution dilutions were typically made by weight from a 1000 ppm (weight volume) stock solution containing purified Aldrich humic acid. Metal stock solutions were prepared from analytical grade chloride and nitrate salts.

Ternary Batch Experiments

HA / MES buffer 0.1 mol dm⁻³ solutions (2, 5, 10, 15, 20, 25, 35, 50, 60, 75, 90, 100, 115, 130, 150, 200, 250 and 300 mg dm⁻³ HA; 20 cm³) were contacted with 0.1 g of either montmorillonite, kaolin or goethite (solid:solution ratio 1:20). Control HA samples were prepared containing no solid. The samples were prepared in quadruplicate, mixed and equilibrated for 7 days. After the first equilibration period, two samples were removed, filtered and the absorbance measured at 254 nm. The pH was also measured. A radioactive spike (≈1600 Bq; 0.1 cm³) was added to the two remaining samples. These were then re-mixed and equilibrated for a further 7 days. After the second equilibration period, the samples were filtered, absorbance and pH measured and the activity of a 1 cm³ aliquot measured by gamma or liquid scintillation counting.

Metal Solid Binary Batch Experiments

Metal salt / MES buffer 0.1 mol dm⁻³ solutions (1.0 x 10⁻⁴, 5.0 x 10⁻⁴, 1.0 x 10⁻³, 5.0 x 10⁻³, 1.0 x 10⁻², 5.0 x 10⁻², 0.1, and 0.2 mol dm⁻³ metal salt; 20 cm³) were contacted with 0.1 g of either montmorillonite, kaolin or goethite (solid:solution ratio 1:20). An active metal spike (≈1600 Bq; 0.1 cm³) was added to each sample. The samples were prepared in duplicate and mixed and equilibrated for 7 days. After equilibration, the pH was measured and a radiometric measurement taken as described above.

Stability Constant Determination Experiments

The Schubert ion exchange method was used to determine the conditional stability constant for each metal humate system using the procedure as described by Warwick and Evans [3]. The stoichiometry of the metal humate complex was assumed to be 1:1.

UV Spectrophotometry

The buffer solution (MES) was used as a baseline for all absorbance measurements. The UV peak absorbance at 254 nm was measured for all the humic acid solutions. Using the absorbance values at 254 nm, calibration
graphs were used for determining the amount of bound and solution phase humic acid for all the binary and ternary experiments using a Varian Cary Series 50 Bio Model UV/Vis Scanning Spectrophotometer.

**Activity Measurements.** Where the metal was a beta emitter liquid scintillation counting was used on a Canberra Packard TRI-Carb 2750TR/LL and where the metal is a gamma emitter, gamma counting was used on a Packard Cobra II Auto Gamma Counter. For liquid scintillation counting quench correction curves were determined for both the humic acid solutes and coloured chloride solutions.

**Results & Discussion**

**Metal-Solid Binary System** Data from these experiments were fitted to sorption isotherms. All systems demonstrated Langmuir type relationships. From these the maximum adsorption capacity of each solid for each metal was found to be:

\[
[M^{+}]_{\text{saturation of solid}} = \text{montmorillonite} > \text{goethite} > \text{kaolinite}
\]

and

\[
[M^{+}]_{\text{saturation of solid}} = \text{cadmium} > \text{caesium} > \text{nickel} > \text{europium}
\]

The mineral’s capacity to be saturated with metal is in general in agreement with their respective cation exchange capacities of 80-150, 4 and 2-15 for montmorillonite, goethite and kaolinite respectively [4], and the affinity of most cations for an adsorbing surface is greater (i) for divalent rather than monovalent ions, and (ii) for large rather than small cations of equivalent charge.

**Humic-Solid Binary System** The humic acid showed greater sorption to goethite, probably due to its slight negative charge and relatively large available surface area (BET surface area of 58 m\(^2\) g\(^{-1}\), 267 m\(^2\) g\(^{-1}\), and 12.6 m\(^2\) g\(^{-1}\) for goethite, montmorillonite and kaolinite respectively) [5] compared with montmorillonite and kaolinite. The isotherms for humic acid in the absence of metal are shown in figure 1, and are in line with the results reported by other research groups. Table 1 provides \(R_d\) values for each humic concentration from 2 mg dm\(^{-3}\) to 300 mg dm\(^{-3}\) (units of mol/mol).

**Metal-Humic Binary System** The conditional stability constants are shown in table 2 below.

**Metal-Humic-Solid Ternary System** The humic acid distributions in the presence of metal can be seen in figure 1. The humic acid distribution in all ternary systems was comparable to its respective 7 day binary distribution with no metal present, excluding goethite whose humic acid sorption generally increased with the presence of trace metal. A plateau region was observed in all the Cd and Cs systems suggesting single layer sorption, however for Ni and Eu many of the systems did not reach a plateau or the plateau was hard to define, which indicated multilayer sorption.

The metal distribution in the presence of HA gave a maximum metal sorption trend of goethite>montmorillonite>kaolinite. For each system the amount
of metal in solution increased as the concentration of humic acid in solution increased, as shown in figure 2.

Table 1- Average Humic-Solid Distribution Ratio’s ($R_{d2}$)

<table>
<thead>
<tr>
<th>Humic Acid - Mineral $R_{d2}$</th>
<th>Montmorillonite $R_{d2}$</th>
<th>Kaolinite $R_{d2}$</th>
<th>Goethite $R_{d2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humic acid Concentration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1.06 \times 10^{-6}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.318</td>
<td>0.256</td>
<td>3.783</td>
</tr>
<tr>
<td>$2.65 \times 10^{-5}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.780</td>
<td>0.554</td>
<td>7.789</td>
</tr>
<tr>
<td>$5.90 \times 10^{-5}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>1.913</td>
<td>0.543</td>
<td>26.756</td>
</tr>
<tr>
<td>$7.95 \times 10^{-4}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.323</td>
<td>0.628</td>
<td>40.685</td>
</tr>
<tr>
<td>$1.06 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.768</td>
<td>0.499</td>
<td>12.133</td>
</tr>
<tr>
<td>$1.33 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.575</td>
<td>0.453</td>
<td>7.600</td>
</tr>
<tr>
<td>$1.86 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.493</td>
<td>0.368</td>
<td>3.024</td>
</tr>
<tr>
<td>$2.65 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.469</td>
<td>0.304</td>
<td>1.719</td>
</tr>
<tr>
<td>$3.18 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.754</td>
<td>0.384</td>
<td>0.574</td>
</tr>
<tr>
<td>$3.90 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.422</td>
<td>0.266</td>
<td>0.693</td>
</tr>
<tr>
<td>$4.77 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.311</td>
<td>0.275</td>
<td>0.496</td>
</tr>
<tr>
<td>$5.30 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.327</td>
<td>0.240</td>
<td>0.658</td>
</tr>
<tr>
<td>$6.10 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.365</td>
<td>0.223</td>
<td>0.455</td>
</tr>
<tr>
<td>$6.89 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.317</td>
<td>0.200</td>
<td>0.415</td>
</tr>
<tr>
<td>$7.95 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.314</td>
<td>0.212</td>
<td>0.357</td>
</tr>
<tr>
<td>$8.75 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.372</td>
<td>0.173</td>
<td>0.407</td>
</tr>
<tr>
<td>$1.06 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.733</td>
<td>0.146</td>
<td>0.381</td>
</tr>
<tr>
<td>$1.33 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.852</td>
<td>0.158</td>
<td>0.338</td>
</tr>
<tr>
<td>$1.59 \times 10^{-3}$ mol dm$^{-3}$ Humic Acid, 0.1 mol dm$^{-3}$ MES</td>
<td>0.129</td>
<td>0.026</td>
<td>0.325</td>
</tr>
</tbody>
</table>

Table 2- Metal-Humic Stability Constants ($R_{d3}$)

<table>
<thead>
<tr>
<th>Metal - Humic Acid $R_{d3}$</th>
<th>Log $R_{d3}$</th>
<th>$R_{d3}$</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caesium $^{137}$</td>
<td>2.57</td>
<td>9.33E+02</td>
<td>±0.74</td>
</tr>
<tr>
<td>Nickel $^{57}$</td>
<td>5.77</td>
<td>5.89E+05</td>
<td>±0.21</td>
</tr>
<tr>
<td>Cadmium $^{115}$</td>
<td>4.28</td>
<td>1.91E+04</td>
<td>Not Reported</td>
</tr>
<tr>
<td>Europium $^{153}$</td>
<td>8.25</td>
<td>1.78E+08</td>
<td>Not Reported</td>
</tr>
</tbody>
</table>

Figure 1- Sorption isotherms of humic acid to the minerals montmorillonite, kaolinite, and goethite in the absence and presence of trace metal
Solid squares symbols indicate $^{152}$Eu; open squares indicate $^{63}$Ni; solid circles indicate $^{109}$Cd; open circles indicate $^{137}$Cs; and crossed vertical bars indicate the absence of trace metal.

To examine the distribution of the metal relative to the HA concentration, graphs of HA bound to free ratio against the metal bound to free ratio were plotted to fully understand the extent of HA influence over metal sorption. For all the systems a line of best fit through the data yielded slopes close or equal to 1, suggesting the metal distribution follows that of the humic acid.

Figure 2 – Percentage Metal Sorption Isotherms for Ternary Systems

Performance Assessment

Humic substances are the largest fraction of natural organic matter in ground waters and are known to sorb at mineral surface sites to form organic coatings that may significantly alter the sorptive capacity at the mineral phase. The importance of this work is to better understand the effect of humic acid on the sorption of radionuclides on mineral surfaces, organic coated mineral surfaces and the formation of ternary metal-humic-surface complexes in a far field environment so as
to be considered as part of radionuclide migration modelling for performance assessment of an intermediate to low level waste repository.

Conclusions

Increased metal sorption in the presence of humic acid has been observed in this study. There is a significant increase in percentage sorption for the same level of trace metal added to each of the ternary systems compared to the appropriate binary systems.

From data provided by the investigations it is clear that the metal distribution is correlated with the distribution of the humic acid, i.e. lower metal sorption onto the solid when there is higher humic concentration in solution. This is attributed to simple mass action and diffusion laws, whereby in a steady state system the metal distribution follows distribution of the bulk solutes. It is also clear that this relationship is somewhat different for each metal studied due to the different affinity of each metal for the humic acid and different minerals.

The extent of correlation between the metal and humic in solution is considerable for all metals studied. The correlation is observed to a lesser degree for cadmium and caesium when compared with europium and nickel. This difference can be explained by the influence of electrostatics interactions of the relative surface and metal charges.

References


