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KINETIC STUDIES OF THE QUARTZ/SAND, EU$^{3+}$ AND HUMIC ACID TERNARY SYSTEM

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[Abstract]

The interactions of Eu$^{3+}$ ions, humic acid and quartz in ternary system experiments have been studied. The variations in the amount of humic acid and Eu$^{3+}$ with time have been determined as a function of humic acid concentration. The desorption of both humic acid and europium have also been measured. A simple mathematical model has been developed that is able to predict the behaviour of both metal ion and humic acid. There is multi-component behaviour in the experiments, and the modelling suggests that for the sorption step at least, heterogeneity of the surface binding sites dominates. However, there is hysteresis in the desorption behaviour of the humic, which could be due to chemical and/or size fractionation on the quartz surface.
Humic substances and mineral surfaces bind most cationic radionuclides very strongly. Therefore, under certain conditions, humic substances can increase the solution phase concentration of radionuclides by direct competition with mineral surfaces. Such behaviour could increase mobility. However, at other times, the formation of surface ternary complexes (metal bound to humic bound to surface) can increase the sorbed radionuclide fraction, decreasing mobility. It is essential to be able to predict these interactions if reliable predictions of radionuclide mobility are to be possible. Unfortunately, these ternary systems are complex and poorly understood. They are also dominated by kinetics, although only equilibrium behaviour is usually studied.

Initial studies of the Eu$^{3+}$/quartz sand/humic acid ternary system have been reported previously (Abrahamsen et al 2005). This work has been expanded to include desorption data and more complex experiments. The aim is to develop and test a mathematical model that can predict the reaction kinetics of the ternary system, which could be used in the calculation of radionuclide migration, for example in the post-closure radiological performance assessment (RPA) of radioactive waste repositories.

The batch experiments (polysulphone tubes) contained quartz sand and humic acid solutions (0 – 500 ppm; pH = 6.0 ± 0.1, adjusted with HCl/NaOH; I = 0.1, NaClO$_4$). The solid:solution ratio was 1 g: 2 ml. In addition, some experiments contained Eu: $^{152}$Eu radiotracer (0.13 kBq ml$^{-1}$) and stable Eu to give total metal concentrations in the range $7.91 \times 10^{-10}$ – $1 \times 10^{-5}$ mol dm$^{-3}$. For some experiments, humic and Eu$^{3+}$ were equilibrated prior to contact with the solid, whilst in others the metal and solid were equilibrated prior to the addition of the humic. The tubes were shaken lengthways at 100 rpm on an automatic shaker. At regular intervals, the tubes were allowed to settle for five minutes before aliquots were removed and filtered using Millex Millipore syringe driven filter units (PVDF, 0.1$\mu$m pore size, 33mm diameter). Humic substance concentrations were determined spectrophotometrically and Eu concentrations with a semi-conductor HPGe gamma-ray spectrometer. In some experiments, after a period of time, the solution and solid phases were separated, and either the solid or solution phase exchanged for a ‘clean’ sample. This technique allowed desorption behaviour to be studied.

A selection of the experimental results from these systems are presented in the figures (1 – 4): not all data can be reported here due to the constraints of space. Some of the results (Figures 1, 4) are presented as $C/C_o$ versus contact time, where $C$ is the concentration of humic acid or Eu in solution at any given time, and $C_o$ is the total concentration in the system.

Figure 1 shows that the initial rapid stage of adsorption of humic onto quartz sand occurs within hours of contact. The fraction of Eu removed from solution (as either direct binary or ternary complex) decreases with increasing [HA]. For the 50 and 100 ppm systems, a rapid initial fall in [Eu] over the first 24 hours is followed
by a slower decrease. In the absence of humic, the system achieves equilibrium within minutes. The kinetic behaviour of the Eu$^{3+}$ matches that of the humic, and is due to the formation of ternary complexes (Abrahamsen et al. 2005), i.e., the slow sorption of Eu$^{3+}$/humic complexes. There are at least two first order processes involved in the adsorption of humic to sand: fast (several hours) and slow (days/weeks).

**Figure 1:** (A) humic (left) and (B) Eu$^{3+}$ (right) sorption to quartz sand, experiment and model fits: left, Models 1 and 2; right, Model 1 only.

Certain binary components of the system have been studied before, and there are existing, tested mathematical models, in particular the separate binary interactions of metal ion with the humic and mineral surface have already been addressed. The interaction of Eu$^{3+}$ with the humic is described using two components, with initial uptake to an exchangeable fraction, Eu$_{\text{exch}}$, which is assumed to be instantaneous,

$$\text{Eu}^{3+}_{(aq)} + \text{HA}_{\text{exch}} \leftrightarrow \text{Eu}^{3+}_{\text{exch}} \quad \text{K}_{\text{exch}} = \frac{[\text{Eu}^{3+}_{\text{exch}}]}{[\text{Eu}^{3+}_{(aq)}][\text{HA}_{\text{exch}}]} \quad (1),$$

where HA$_{\text{exch}}$ is the humic exchangeable binding site, and K$_{\text{exch}}$ an equilibrium constant for the process. Subsequent transfer to and from the non-exchangeable fraction, Eu$_{\text{non-exch}}$, is a first-order kinetic (slow) process.

$$\text{Eu}^{3+}_{\text{exch}} \rightarrow \text{Eu}^{3+}_{\text{non-exch}} \quad \frac{d[\text{Eu}^{3+}_{\text{non-exch}}]}{dt} = k_f[\text{Eu}^{3+}_{\text{exch}}] - k_b[\text{Eu}^{3+}_{\text{non-exch}}] \quad (2)$$

where $k_f$ and $k_b$ are the forward and backward rate constants, respectively. The interaction of Eu$^{3+}$ with the quartz surface is described with a single reaction,

$$\text{Eu}^{3+}_{(aq)} + S_M \rightarrow \text{Eu}^3_{S} \quad \frac{d[\text{Eu}^3_{S}]}{dt} = k_{MS}[\text{Eu}^{3+}_{(aq)}][S_M] - k_{MBS}[\text{Eu}^3_{S}] \quad (3)$$
where $S_M$ is a metal binding site on the quartz sand surface, $E_{uS}$ is Eu sorbed to the surface and $k_{MSf}$ and $k_{MSb}$ are the forward and backward rate constants, respectively.

The interaction of humics and humic/metal complexes with mineral surfaces is less well understood than the other interactions. The humic sorption data in Figure 1 show two clear classes of behaviour (fast and slow), and there is clearly more than one chemical reaction. Therefore, the modelling has used two equations. The heterogeneity could be the result of heterogeneous humic binding sites on the surface, or due to the heterogeneity of the humic material in solution, or of course, both. Van de Weerd et al (1999) have modelled humic uptake to iron oxide phases with a model that contains a single surface site and multiple (3 – 6) humic fractions. However, the surface is different here, and so the two distinct approaches have been tested: Model 1 assumes a single humic species in solution and two surface sites:

\[
\text{HA}_\text{free} + S_{HA1} \rightleftharpoons HA_{SI} \quad \frac{d[HA_{SI}]}{dt} = k_{HAS1f}[HA_{free}][S_{HA1}] - k_{HAS1b}[HA_{SI}] \quad (4)
\]

\[
\text{HA}_\text{free} + S_{HA2} \rightleftharpoons HA_{S2} \quad \frac{d[HA_{S2}]}{dt} = k_{HAS2f}[HA_{free}][S_{HA2}] - k_{HAS2b}[HA_{S2}] \quad (5)
\]

where: $S_{HA1}$ and $S_{HA2}$ are surface binding sites, type 1 and 2, respectively; $HA_{SI}$ and $HA_{S2}$ are humic bound to surface sites, type 1 and 2, respectively; and $k_{HAS1f}$, $k_{HAS1b}$, $k_{HAS2f}$ and $k_{HAS2b}$ are rate constants. Model 2 has one surface site and two humic fractions in solution:

\[
HA_{free} + S_{HA} \rightleftharpoons HA_{S} \quad \frac{d[HA_{S}]}{dt} = k_{HASf}[HA_{free}][S_{HA}] - k_{HASb}[HA_{S}] \quad (6)
\]

\[
HA_{free} + S_{HA} \rightleftharpoons HA_{S} \quad \frac{d[HA_{S}]}{dt} = k_{HASf}[HA_{free}][S_{HA}] - k_{HASb}[HA_{S}] \quad (7)
\]

Figure 1A shows the fit obtained to the humic sorption using the two models. Although both models are able to simulate the general behaviour, Model 1 is better on balance. However, the fit from Model 2 is sufficiently close that it cannot be eliminated with these data alone. Hence, a number of other experiments were used to test the models further: Figure 2 shows an example. In this experiment, the solution was separated from the solid after 20 days, and a new sample of sand introduced. The fit for Model 1 is clearly superior. In all of these more advanced tests, although Model 2 could be made to fit the data for a single system, by a suitable choice of parameters: it could not fit the data for more than one experiment simultaneously with a single parameter set, whereas Model 1 is able to fit all behaviour for a single sand sample with one set of parameters, even though it has the same number of adjustable parameters as Model 2. Therefore, Model 1 is the best description of kinetic behaviour for these systems. Even though different samples of sand required slightly different parameters for the best fit, the variation is small, considering that the samples have different origins, for example: Figure 2 - $k_{HAS1f}=1.4\times10^{-6}$, $k_{HAS1b}=1.5\times10^{-5}$, $k_{HAS2f}=2.0\times10^{-8}$, $k_{HAS2b}=6.0\times10^{-7}$, [S1]=0.04 mg/g, [S2]=0.06 mg/g; Figure 1A - $k_{HAS1f}=1.4\times10^{-6}$, $k_{HAS1b}=7.0\times10^{-6}$, $k_{HAS2f}=1.0\times10^{-8}$, $k_{HAS2b}=1.0\times10^{-7}$, [S1]=0.030 mg/g, [S2]=0.050 mg/g. Therefore, Model 1 has been adopted for the quartz system. Calculations have also been performed to simulate the behaviour of Eu$^{3+}$. All of these calculations assume that humic/metal complexes
will sorb to the mineral surface in the same way as unbound humic, i.e., equations (4) and (5) with the same parameters are used to describe ternary complex formation.

Figure 1B shows the fit to the uptake of Eu³⁺ in the ternary experiments as a function of humic concentration: the fit is reasonable, particularly given the complexity of the system. Figure 4A shows the variation in [Eu] with time, as a function of total [HA], for systems where Eu was pre-equilibrated with the solid phase for 24 hours prior to the addition of humic. Eu desorption increases with [HA]. After the addition of humic, [Eu] increases over several days up to a maximum. Following this, there is a subsequent decrease. This behaviour can be attributed to two simultaneous reactions. The humic in solution and the surface compete for Eu, and so there is an initial increase in [Eu]. However, the sorption of humic begins to return Eu to the surface, via ternary complexes, but this process is in part slow. In a separate experiment, this procedure was repeated, but using a ‘pure quartz’ sample, rather than sand: the results are shown in Figure 4B. The same mathematical equations and rate constants were able to simulate the behaviour in this experiment. The only change that was required was in the surface site specific concentrations, which is not surprising, given that the two solids are from different samples. For all of the Eu data, it is not possible to simulate the results without including ternary complexes. For the data in Figures 1 – 4 the fits (with Model 1) are quite good, especially given that the model is very simple. However, the fit is not
perfect: for example, although it captures the general behaviour in Figure 4A, the model fit is not exact, especially for the 10 ppm system.

Figure 4: desorption of sorbed Eu\(^{3+}\) from A – quartz sand, B pure quartz;

Quartz is often considered to be a simple surface, and indeed we have found that these experiments have been largely predictable. However, even for this surface some complex behaviour has been observed. For example, Figure 3 shows the results of an experiment where humic acid was allowed to sorb to a sample of quartz sand, and after 24 days, the solution containing the humic was replaced with clean, humic free electrolyte (pH = 6, I = 0.1), and the desorption of the humic measured. The figure also shows the fits obtained with the model (eqns 4, 5). Although the fit to the sorption step is good, the fit is less good for the desorption: the model has overestimated the amount of humic re-entering the solution, which is evidence of hysteresis. The modelling has suggested that the majority of the heterogeneity during the uptake phase is due to surface binding site variability. However, these desorption results suggest that intrinsic heterogeneity in the humic itself may also be important.

[Conclusions]

A model has been developed to predict the kinetic behaviour of Eu\(^{3+}\) and humic in quartz ternary systems. It performs reasonably well, although there are certain aspects that need improvement, in particular, the desorption behaviour of the humic.

[References]