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Competitive effect of iron(III) on metal complexation by humic substances: characterisation of ageing processes

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Abstract

Aiming at an assessment of counteractive effects on colloid-borne migration of actinides in the event of release from an underground repository, competition by Fe(III) in respect of metal complexation by dissolved organic matter was investigated for the example of Eu(III) as an analogue of trivalent actinides. Complexation with different humic materials was examined in cation exchange experiments, using ⁵⁹Fe and ¹⁵²Eu as radioactive tracers for measurements in dilute systems as encountered in nature. Competitive effects proved to be significant when Fe is present at micromolar concentrations. Flocculation as a limiting process was attributed to charge compensation of humic colloids. Fe fractions bound to humic acids (HA) were higher than 90%, exceeding the capacity of binding sites at high Fe concentrations. It is thus concluded that the polynuclear structure of hydrolysed Fe(III) is maintained when bound to HA, which is also inferred from UV-Vis spectrometry. The competitive effect was found to be enhanced if Fe and HA were contacted before Eu was added. Depending on the time of Fe/HA pre-equilibration, Eu complexation decreased asymptotically over a time period of several weeks, the amount of bound Fe being unchanged. Time-dependent observations of UV-Vis spectra and pH values revealed that the ageing effect was due to a decline in Fe hydrolysis rather than structural changes within HA molecules. Fe polycations are slowly degraded in contact with humic colloids, and more binding sites are occupied as a consequence of dispersion. The extent of degradation as derived from pH shifts depended on the Fe/HA ratio.

Keywords: Humic substances; Iron (Fe); Europium (Eu); Complexation; Competition; Ageing

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1. Introduction

Assessments of the transport behaviour of actinides in case of release from subterranean radwaste repositories are an essential part of long-term safety analyses (performance assessment?). The mobility of metals and radionuclides in geochemical systems is substantially determined by interaction with organic and inorganic colloids as part of the aqueous phase (Lieser *et al.*, 1990; Dearlove *et al.*, 1991; Kim *et al.*, 1992) (we would normally put the “*et al*” in italics but it’s up to you). In particular, the complexing ability of humic and fulvic acids (HA, FA) as major constituents of the dissolved organic carbon (DOC) can dominate the speciation of multivalent metals (Buffle, 1988; Choppin, 1992). In a competitive situation, binding of actinides can be counteracted by other higher-valent metals which are present in natural waters, and a mitigating effect on mobilisation is possible. For the development of transport models, the influence of competing electrolyte constituents on actinide-humate complexation needs to be quantified.

Pertinent studies hitherto published were mostly concerned with the displacement of divalent trace metals (Ni, Cu, Zn, Cd, Pb) by calcium or magnesium (e.g., Buffle *et al.*, 1980; Hering and Morel, 1988; Cabaniss and Shuman, 1988; Cao *et al.*, 1995; Van den Hoop *et al.*, 1995; Mandal *et al.*, 2000), several papers dealt with the competitive effect of aluminium (e. g., Susetyo *et al.*, 1990; Pinheiro *et al.*, 2000; Lippold *et al.*, 2005). There are only few investigations on the influence of iron(III), although it is the most abundant trivalent electrolyte in terrestrial waters, and expected to be very effective in out competing other metals. Kerndorff and Schnitzer (1980) reported that adsorption of Fe onto flocculated HA dominated the adsorption of other metals when added simultaneously at increasing concentrations. Adsorption of Hg/Fe and Cu/Fe onto suspended HA was examined by Huljev (1986) and Tipping *et al.* (2002), respectively. Alberts and Filip (1998) reported on the effect

of Fe on Cu binding capacities of dissolved HA and FA. Teterin et al. (2001) investigated competitive humate complexation of iron and uranyl.

In order to evaluate the counteractive effect of Fe on humic-bound actinide migration in natural systems, competition must be investigated at adequate concentration levels. This requirement arises from the fact that interaction of metals with humic substances has been found to be dependent on the concentration ratio (of what to what?) (Bidoglio et al., 1991; Seibert et al., 2001). In the present study, we have examined the influence of Fe(III) on the humic complexation of Eu(III) as an analogue for trivalent actinides (Am, Cm), employing ^{59}Fe and ^{152}Eu as radioactive tracers to enable precise measurements in very dilute systems to be made. Various humic and fulvic acids were chosen for comparative investigations. The competitive reactions of Fe are limited by the stability of colloidal Fe/HA systems. Generally, the influence of multivalent electrolyte constituents on humic colloid-borne transport of contaminant metals is not confined to displacement effects but is also characterised by flocculation processes, leading to complete immobilisation (Lippold et al., 2005). For this reason, experiments on the dependence of colloidal stability on concentration and pH were included in this study.

Binding of higher-valent metals to humic substances has been reported to be accompanied by time-dependent transformations that entail a decreasing availability to competing ligands in dissociation experiments (Van den Bergh et al., 2001; Geckeis et al., 2002). Such findings are of some importance in view of current modelling strategies, which are based on thermodynamic equilibrium constants. Similar kinetic effects may also be expected in respect of competitive metal complexation if both metals seek the same binding sites. Complexation of Eu was therefore investigated for pre-equilibrated Fe/HA systems at high Fe loads depending on ageing time. Results are discussed with regard to the polynuclear characteristics of aqueous Fe(III) species interacting with HA.

2. Experimental

2.1. Materials

Aquatic humic and fulvic acids isolated from an aquifer in the area of Gorleben (Lower Saxony, Germany), designated as GoHy-573 HA / FA, were supplied by Forschungszentrum Karlsruhe, Germany. Humic acid purchased from Sigma-Aldrich (Taufkirchen, Germany), herein referred to as AHA, was purified by repeated precipitation and redissolution with 0.1 M HCl and 0.1 M NaOH / 0.01 M NaF, respectively. A further humic acid was extracted from soil collected from the raised bog “Kleiner Kranichsee” (Saxony, Germany). Isolation was performed in accordance with the procedures adopted by the International Humic Substances Society (Swift, 1996). Table 1 shows the elemental compositions of the purified materials, determined with a Vario EL III elemental analyser (Elementar, Hanau, Germany).

[¹⁵²Eu]EuCl₃ ($T_{1/2} = 13.3$ a) was purchased from Isotope Products Laboratories (USA), [⁵⁹Fe]FeCl₃ ($T_{1/2} = 44.5$ d) was provided by Amersham Biosciences (UK). After transformation into perchlorate systems, stock solutions in 0.1 M NaClO₄ were prepared. Experimental concentrations were adjusted by adding Eu(NO₃)₃ or Fe(NO₃)₃ (analytical grade, Sigma-Aldrich) in 0.1 M NaClO₄ solution.

2.2. Methods

Humic-bound metal fractions were determined by the cation exchange method (Schubert, 1948), using Bio-Rad AG 50W-X2 exchange resin which was converted into the Na⁺ form by treatment with 1 M NaOH. Solutions of HA / FA, Eu and Fe in 0.1 M NaClO₄ (pH 4) were prepared with pH-adjusted stock solutions and spiked with tracer amounts of ¹⁵²Eu or ⁵⁹Fe. Equilibration with the cation exchange resin was performed in PE vials at a solid-liquid ratio

of 10 mg / 10 mL. After shaking for 48 h, 2 mL aliquots of the supernatant were taken for measurement of activity, using a Packard Cobra II Auto Gamma Counter (GMI, USA). The concentration of bound metal $[M_{\text{bound}}]$ was calculated from the relationship

$$[M_{\text{bound}}] = [M_{\text{total}}] \left(1 - \frac{D}{D_0} \right) \quad (1)$$

with D and D_0 denoting the solid-liquid distribution ratios of the radiotracer in the presence and in the absence of humic material, respectively. To account for wall adsorption, analogous test series were performed without exchange resin.

For long-term observations of UV-Vis spectra and pH values of Fe/HA systems depending on ageing time, solutions were dispensed into separate vials and kept therein until use. UV-Vis spectrometry was conducted by means of a spectrophotometer Cadas 100 (Lange, Germany), pH measurements were carried out with a SenTix 41 combination electrode (WTW, Germany).

Flocculation of Fe/HA systems was investigated in jar tests using 20 mL clear glass vials. A total of ~ 300 pH-adjusted solutions with varying concentrations were allowed to stand undisturbed over a period of 2 weeks. Sedimentation of flocculated HA was then examined by measuring the UV absorbance at 254 nm.

3. Results and discussion

3.1. *Competitive effect of Fe - dependence on concentration*

Complexation of Eu in the presence of Fe was investigated for 3 humic acids and 1 fulvic acid. Figure 1 shows how the concentration of organically bound Eu depends on the total concentration of Fe. The bound fractions of Fe are shown in Fig. 2. Throughout the

nanomolar range, a competitive influence is not discernible, but significant effects are observed at micromolar Fe concentrations. About one third of originally bound Eu is excluded from humate complexation in the presence of 10^{-4} M Fe. For the fulvic acid, however, no displacement was detected in the concentration range studied. As can be seen in Fig. 2, Fe is bound to a lesser degree in this case, but the different behaviour is primarily explained by the higher content of acidic groups in FA compared to HA, providing more binding sites per unit mass. Accordingly, competition will gain in importance at higher Fe concentrations. Reduction of Fe(III) to Fe(II) by quinoidal or phenolic groups within the humic materials is unlikely at moderate pH values, as has been shown in several studies (Kallianou and Yassoglou, 1985; Goodman and Cheshire, 1987; Deiana *et al.*, 1995; Davies *et al.*, 1997; Pullin and Cabaniss, 2003).

3.2. *Flocculation of humic acid on addition of Fe*

The experiments on competitive complexation were limited to Fe concentrations up to 10^{-4} M. If this value is exceeded, flocs of Fe/HA agglomerates are precipitated. This process may be even more important than displacement reactions since outcompeted actinide species are not necessarily immobilised subsequent to detachment. For the example of AHA, flocculation on metal addition was systematically investigated at different HA concentrations and pH values (Fig. 3). As the colloids differ in size and chemical composition, precipitation proceeds gradually within a certain range of metal concentration, indicated by the bars.

The concentration of Fe required for flocculation depends linearly on the concentration of HA, i. e., the colloidal stability is determined by the Fe/HA ratio. It may be concluded that flocculation is induced by charge compensation. At pH 6, more Fe is needed than at pH 4 because deprotonation of acidic groups results in a higher colloid charge to be compensated. Furthermore, the effective charge of the Fe species is reduced due to hydrolysis. (In the

attached document is some speciation I've done for you on Fe³⁺ which I think could be included here)

The process is also of importance in drinking water treatment where removal of DOC is accomplished by addition of Fe or Al salts. Concerning the mechanism of flocculation, there is some controversy about whether organic compounds are scavenged by adsorption onto precipitated iron hydroxide colloids (Ying *et al.*, 1988; Tseng *et al.*, 1989) or the organic colloids are precipitated as a consequence of charge compensation by dissolved Fe (Schmitt *et al.*, 1996; Vilg -Ritter *et al.*, 1999; Cheng, 2002; Jung *et al.*, 2005). In fact, precipitates of humic acid and colloidal iron hydroxide look very similar. It is, however, obvious from Fig. 3 that the iron colloids are not destabilised by interaction with HA since they are stable when HA is present in excess. Instead, precipitation is clearly attributable to the humic colloids, even at pH 6 where the Fe colloids are very susceptible to flocculation in the absence of HA (dotted line). Here, stability against precipitation is even enhanced by the presence of HA.

3.3. *Characteristics of Fe-HA interaction*

In Figs. 2 and 3, data for Al have been included for comparison. Interaction with HA is much weaker for Al than for Fe, but on the other hand, less Al is required to initiate flocculation. In a previous paper, we have demonstrated that the flocculation efficiencies of the trivalent metals Al, Ga, In, Sc, Y and La are directly related to the stabilities of their humate complexes, supporting the proposition that precipitation is determined by charge compensation at humic colloids (Lippold *et al.*, 2005). The deviating findings for Fe suggest that the mode of interaction with HA is likely to be different from normal, i. e. mononuclear, metal-humate complexation. In weakly acidic solutions, Fe is present in the form of polynuclear species as a consequence of hydrolysis, with an effective charge considerably lower than 3. Apparently, this oligomeric structure is not eliminated when Fe is bound to HA.

This would explain the large amount necessary for flocculation in spite of the high degree of binding.

In most studies on Fe-HA interaction, a regular complexation of mononuclear Fe is assumed. Several authors arrived at the conclusion that bidentate complexes (1 iron atom coordinated by 2 organic ligands) are formed (Elgala *et al.*, 1976; Takahashi *et al.*, 1997; Ghatak *et al.*, 2004). At the highest Fe concentrations in Fig. 2, however, the number of bound Fe atoms is close to the total number of acidic groups (carboxyl and phenolic hydroxyl) for AHA and bog soil HA (about 5 mmoles per gram HA), i. e., the maximum possible colloid charge would be overcompensated by far if Fe was complexed in the form of ferric ions. (is this evidence for mixed complexes, i.e. it is actually FeOH or Fe(OH)₂ that is complexing?) Similar “overloads” were found by Van den Bergh *et al.* (2001) and Kislenco and Oliynyk (2004).

The structure of Fe/HA complexes was the subject of investigations by Mössbauer spectroscopy (Hansen and Mosbaek, 1970; Dickson *et al.*, 1979; Senesi, 1981; Solomonov *et al.*, 1991) as well as EPR spectroscopy (Senesi *et al.*, 1977; Senesi *et al.*, 1986; Senesi and Calderoni, 1988; Goodman and Cheshire, 1987; Davies *et al.*, 1997), yielding evidence of strong and weak binding sites where Fe is octahedrally and/or tetrahedrally coordinated. In respect of polynuclear species, results were interpreted differently. Goodman and Cheshire (1987) suggested that some of the Fe is present in the form of clusters involving oxide or hydroxide bridges. Based on the extractability by Na₄P₂O₇, Hermann and Gerke (1992) differentiated between organically bound and inorganic precipitated Fe in humic substances. In flocculated Fe/HA precipitates, the presence of iron oligomers could be detected by X-ray spectroscopy (Vilgé-Ritter *et al.*, 1999; Jung *et al.*, 2005).

The UV/Vis spectra shown in Fig. 4 corroborate the supposition that the polynuclear nature of hydrolysed Fe is maintained when bound to HA. Visible absorption of an Fe(III) solution at pH 4 is solely due to the formation of Fe polycations. In the presence of HA, the spectral

enhancement is nearly additive, although most Fe is bound to the organic colloids.

Consequently, it appears that the aqueous Fe species are not decomposed in the interaction.

3.4. *Time-dependent effects*

In the experiments shown in Fig. 1, Fe and Eu were simultaneously contacted with the humic materials, which does not actually correspond to real situations to be considered, since the contact with the competing ion will occur prior or subsequent to actinide-humate complexation. Figure 5 shows a time-dependent study where the metals were introduced in two steps. Solutions of HA and Fe had been pre-equilibrated for different periods of time before Eu was added (simultaneously to all systems within a test series), covering a time frame of 1 week and 4 months, respectively. It turned out that the degree of Eu-humate complexation is markedly influenced by the time of Fe/HA pre-equilibration; Eu binding decreases asymptotically over a period of several weeks. During that time, the amount of bound Fe proved to be unchanged (data not shown). Consequently, the effect must be caused by structural alterations, impeding Eu/HA interaction. The possibility that these changes are due to ageing of HA or Fe as single components can be discounted since the same stock solutions were used throughout a test series, and data of short-term and long-term tests (conducted with different stock solutions) match each other.

In some respect, these results are in accordance with time-dependent studies on dissociation of metal-humate complexes, showing that a detachment by competing ligands or cation exchangers becomes more difficult with increasing contact time. This was also observed for iron (Van den Bergh *et al.*, 2001). Such kinetic effects are often interpreted as slow diffusion processes within the humic colloids. Following a fast equilibration with weak binding sites on the surface, the metals are assumed to move to stronger sites inside, which are not directly accessible (e. g., Cacheris and Choppin, 1987; Rao *et al.*, 1994; King *et al.*, 2001). However, this reasoning implies that the initial sites are vacated and should thus be available for competing metal ions. Consequently, the transfer model fails to explain the time-dependent effects observed in this study. Other kinetic approaches are based on different binding modes

which do not necessarily refer to separate sites (e. g., Schüßler *et al.*, 2000). Instead, dissociation may be complicated by slow structural changes which are induced by the metal, for instance, intra- or intermolecular bridging.

Considering the fact that Fe(III) is not bound as a single ion but as an oligomeric species, an alternative explanation is conceivable, namely that the Fe polycations undergo a slow degradation process when associated with HA, and more binding sites are occupied due to dispersion of Fe species. Figure 6 shows the results of a long-term observation of the pH value for an Fe/HA system which had initially been adjusted to pH 4.0. Normally, the pH of a HA solution decreases when metal salts are added since protons from the acidic binding sites are released in exchange for metal ions. In the present case, however, there is an increase in pH. This anomalous effect can only be attributed to the Fe component. For adjusting an Fe(III) salt solution to pH 4, large amounts of NaOH must be added because the formation of polynuclear hydrolysis species is associated with a release of protons which has to be compensated for. Apparently, this process is inverted in the presence of HA. Protons are consumed to degrade the oligomeric structure of hydrolysed Fe. Interestingly, the time profile corresponds to the temporal change in the competitive effect (Fig. 5). As depicted in Fig. 7, the process is also accompanied by changes in the UV/Vis spectrum. These findings strongly suggest that the time dependence in Fe competition is due to the fact that polynuclear Fe is metastable when bound to HA. Decomposition into smaller units reduces the number of available binding sites, and complexation of Eu is counteracted more effectively.

Whether Fe oligomers are completely degraded to monomers is a question that cannot be answered definitely. In Fig. 8, the rise in pH is shown for systems with varying HA concentrations, measured after 3 weeks of standing. Up to a concentration of $\sim 100 \text{ mg L}^{-1}$ HA, the effect increases, i. e., the more binding sites are provided, the more Fe is degraded. At higher concentrations, however, this trend levels off. Obviously, further decomposition is not possible at this stage. One may assume that bound Fe is then present in a monomeric

form. The total concentration of potential ligands would in fact be sufficient in this range; 100 mg L⁻¹ of HA correspond to 0.5 mM of acidic groups, which is the fivefold amount compared to Fe.

4. Conclusions

Due to its valency and abundance, Fe(III) has a unique potential to counteract humic colloid-borne transport of contaminant metals in aquifer systems. At micromolar concentrations, competitive effects proved to be significant. Displacement is limited by flocculation, which was shown to be induced by charge compensation at HA colloids on metal loading.

Precipitation of colloidal Fe(III) is not promoted by the presence of HA.

The competitive influence of Fe was found to be kinetically controlled. Accordingly, the applicability of equilibrium models must be considered carefully. Unlike dissociation kinetics, the observed time dependence can hardly be explained on the basis of transfer processes between different binding sites. Instead, the present results indicate that the effect arises from the polynuclear nature of hydrolysed Fe(III). When interacting with humic colloids, its oligomeric structure is not disrupted immediately. Strictly, this first-stage association cannot be termed as humate complexation. In the bound state, however, the polycations are slowly decomposed, possibly into monomeric Fe(III), and more binding sites are occupied at equal Fe load. Thus, regular complexation is merely preceded by a metastable state. The ageing process is not assigned to structural changes within humic molecules.

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FIGURE CAPTIONS

- Fig. 1.** Competitive effect of Fe(III) on complexation of Eu(III) with different humic materials (10^{-8} M Eu, 5 mg L^{-1} HA/FA, 0.1 M NaClO₄, pH 4.0, simultaneous addition of Fe and Eu).
- Fig. 2.** Complexation of Fe(III) and Al(III) with humic materials (experimental conditions as in Fig. 1).
- Fig. 3.** Flocculation of AHA on addition of Fe(III) and Al(III) at pH 4 and pH 6. The bars indicate the concentration ranges in which precipitation proceeds. The dotted line shows the stability limit of a Fe(III) solution at pH 6.
- Fig. 4.** UV/Vis spectra of AHA (20 mg L^{-1}) and Fe(III) (10^{-4} M) in single and mixed systems (0.1 M NaClO₄, pH 4.0).
- Fig. 5.** Complexation of Eu(III) with AHA after pre-equilibration of AHA and Fe(III) (10^{-8} M Eu, 5×10^{-5} M Fe, 5 mg L^{-1} HA, 0.1 M NaClO₄, pH 4.0). Full and open symbols refer to different test series.
- Fig. 6.** Changes in pH of a mixed AHA/Fe(III) system depending on time (20 mg L^{-1} HA, 10^{-4} M Fe, 0.1 M NaClO₄).
- Fig. 7.** Changes in UV/Vis absorption of a mixed AHA/Fe(III) system depending on time (20 mg L^{-1} HA, 10^{-4} M Fe, 0.1 M NaClO₄).
- Fig. 8.** pH of mixed AHA/Fe(III) systems, initially adjusted to pH 4.0, after 21 days of standing (10^{-4} M Fe, 0.1 M NaClO₄).

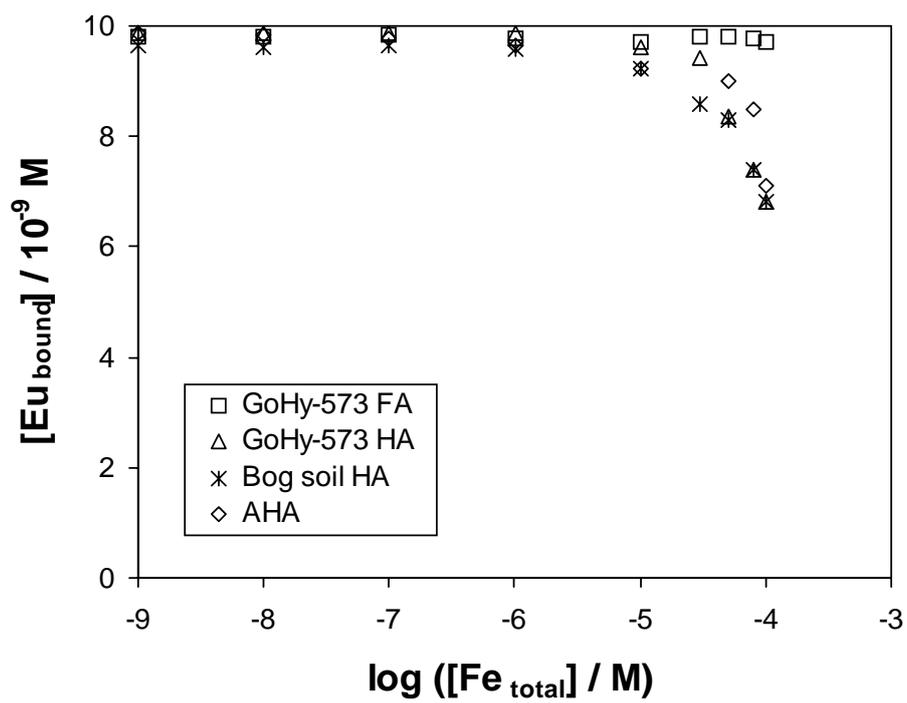


Figure 1

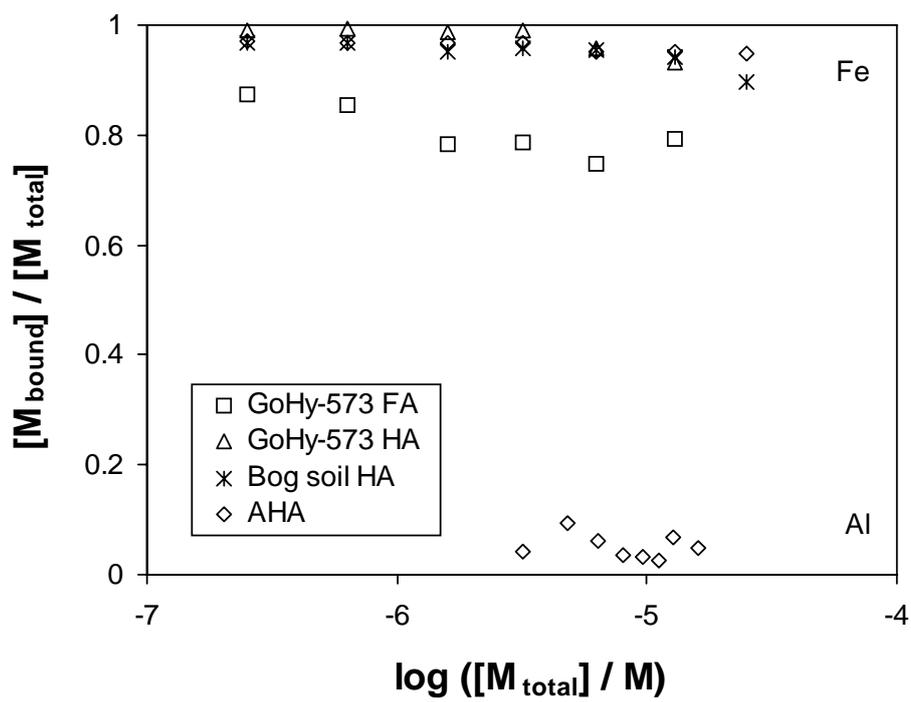


Figure 2

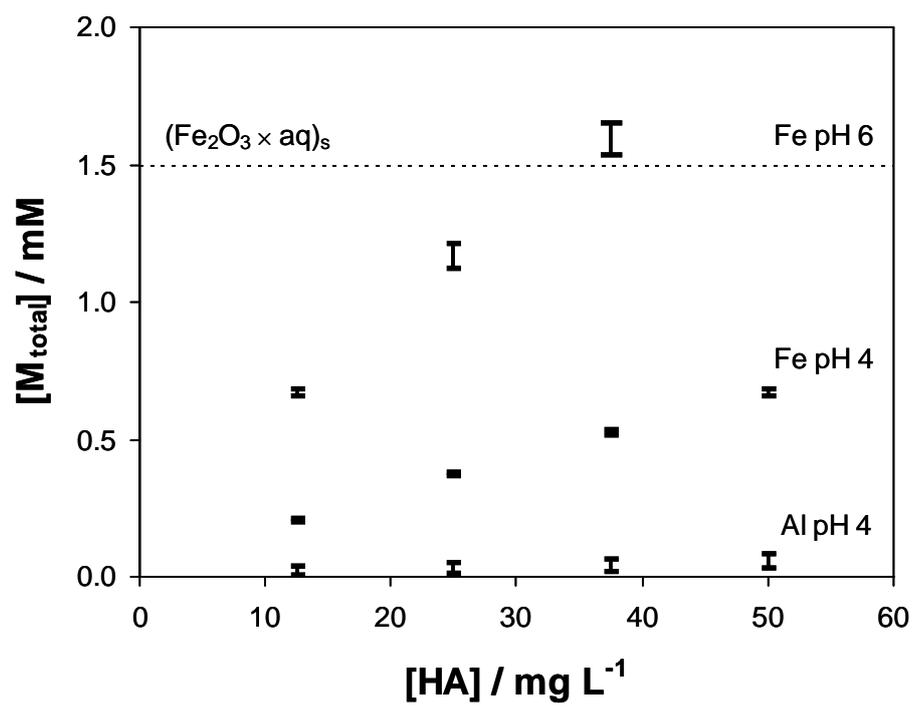


Figure 3

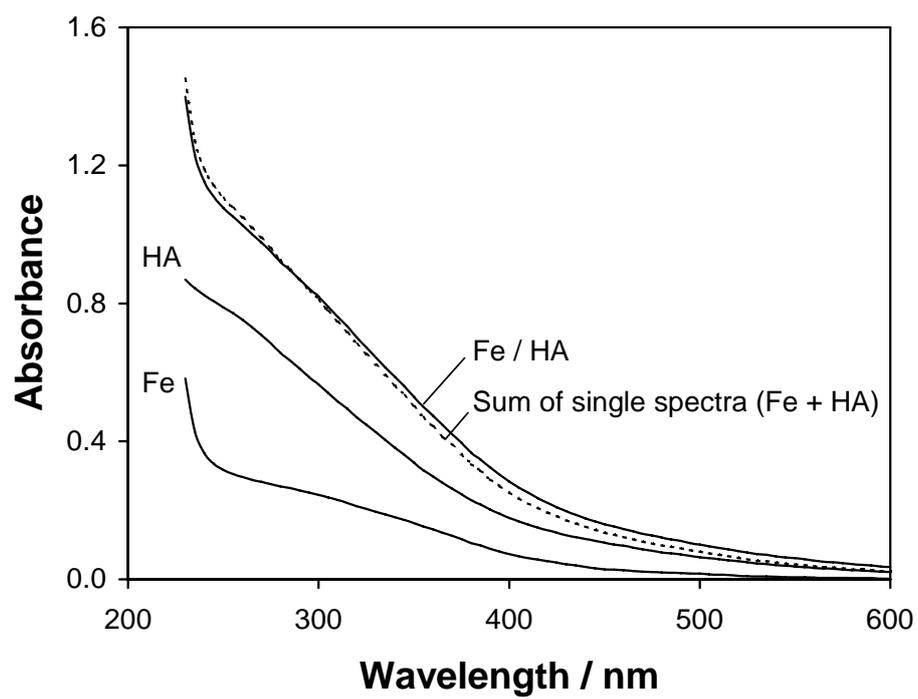


Figure 4

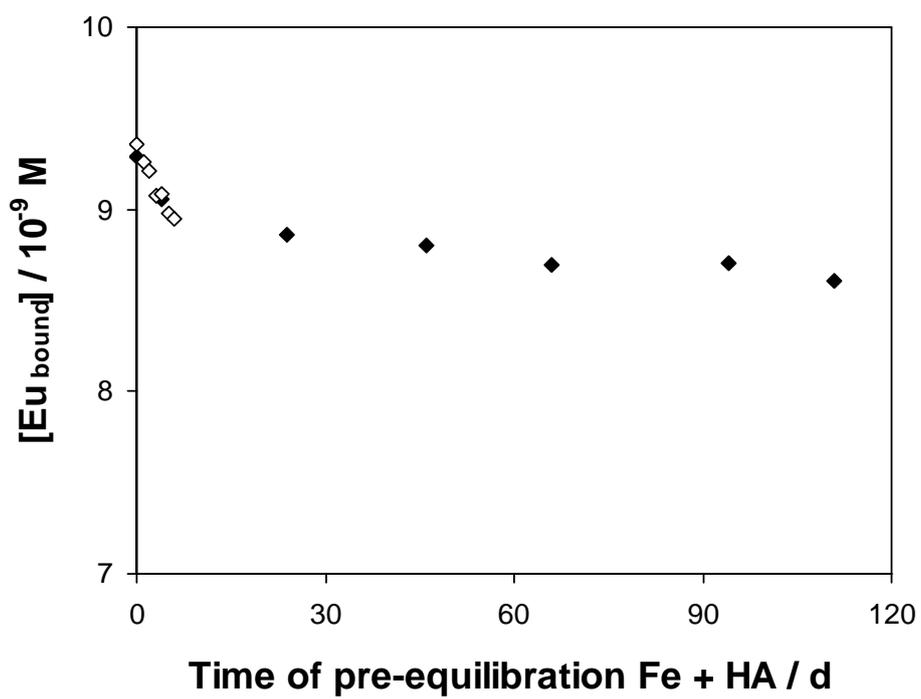


Figure 5

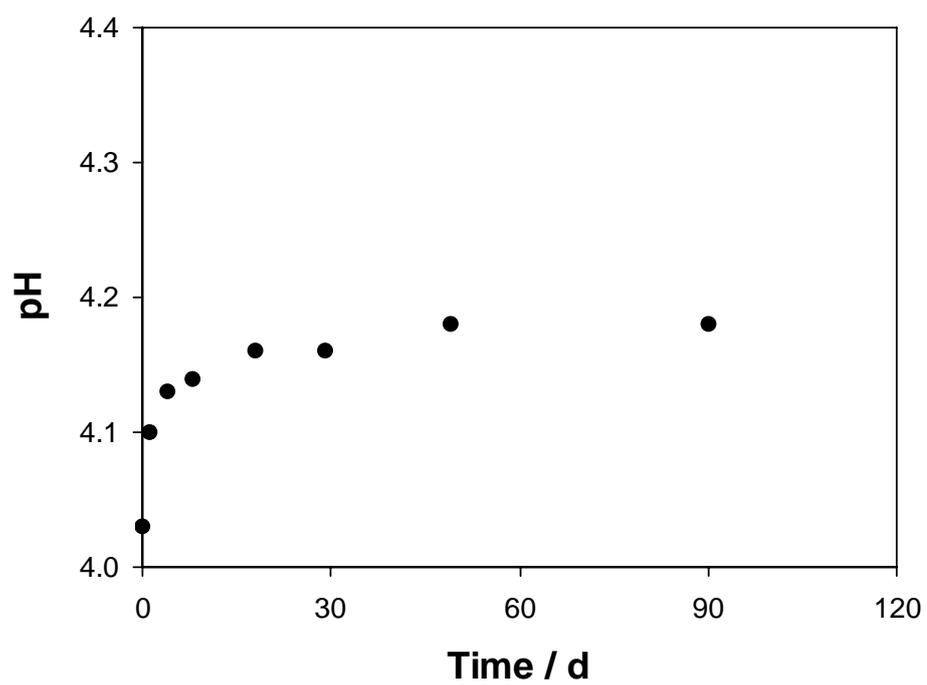


Figure 6

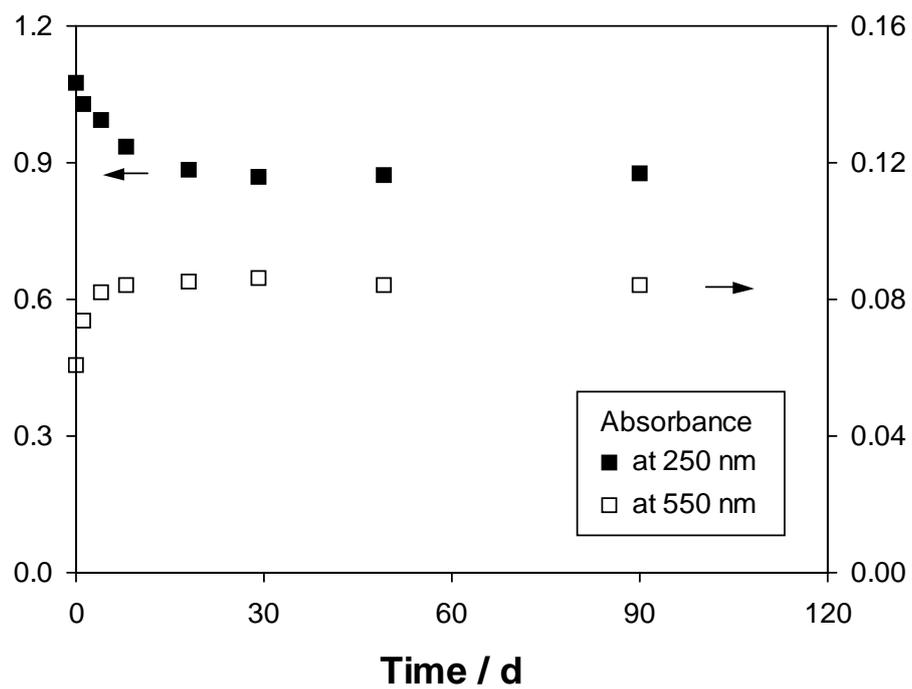


Figure 7

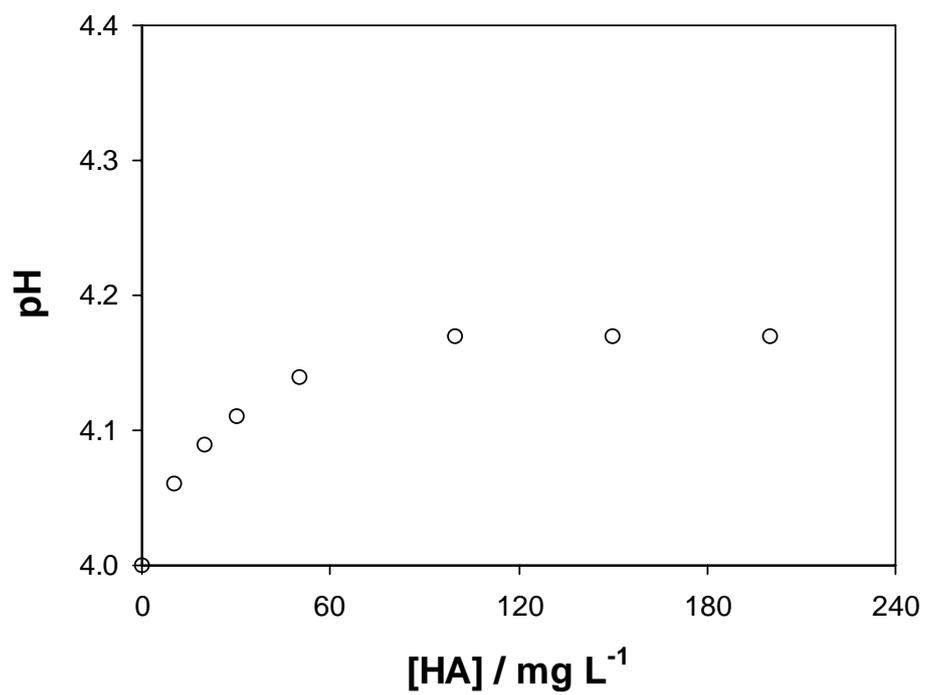


Figure 8

Table 1. Elemental compositions of HA and FA in wt% (normalised to dry weight, values of H and O corrected for H₂O content).

	AHA	Bog soil HA	GoHy-573 HA	GoHy-573 FA
C	53.2	53.2	58.3	51.7
H	4.2	4.4	4.3	4.2
O	38.0	34.1	33.4	41.6
N	0.8	2.4	1.9	1.1
S	3.7	0.5	2.0	1.3