A Study of the Kinetic Interactions of Complex Metal Ion - Humic and Magnetite Ternary Systems

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A Study of the Kinetic Interactions of Complex Metal Ion - Humic and Magnetite Ternary Systems

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Science and Engineering

2011

Nigel Chun Yip Li

School of Chemistry
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Abstract

The University of Manchester
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Doctor of Philosophy

Development of Kinetic Speciation Models for Complex Metal Ion-Humic and Magnetite Ternary Systems

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The sorption of humic acid (HA) and HA size fractions onto magnetite has been studied. There is considerable irreversibility in the interaction of the humic with the magnetite surface, but the presence of Eu$^{3+}$ ions has no effect on the sorption of humic onto magnetite. The magnitude of the sorption to magnetite increases with HA fraction size for all ionic strengths between 0.01 and 3 mol dm$^{-3}$. Increasing ionic strength also increases sorption. Asymmetric Flow Field Flow Fractionation analysis of HA sorption to magnetite after 1 day revealed preferential sorption of lower molecular weight material. Eu$^{3+}$ sorption onto magnetite was studied as a function of Eu concentration, which showed an increase in relative sorption as Eu concentration decreased. The behaviour of Eu$^{3+}$ in ternary (HA/Eu$^{3+}$/magnetite) systems is heavily influenced by HA, and from the data there is direct evidence for ternary complex formation. Larger HA size fractions retain more Eu$^{3+}$ in solution than the smaller fractions. The binding strengths of HA size fractions were determined through ion exchange resin experiments: generally the larger fractions (> 10 kDa) showed stronger binding than the smaller components, but the unfractionated sample showed the strongest binding.

First order dissociation rate constants have been determined for the whole HA and HA size fractions. The dissociation rate constants are independent of HA fraction size, but the larger species bind more Eu non-exchangeably. Time series ultrafiltration of Eu$^{3+}$/whole humic mixtures has shown a shift in the distribution of metal ions to larger size fractions after a few days.

Two ternary system kinetic speciation models have been developed to predict the behaviour of HA and Eu$^{3+}$ in ternary systems. The two differ in their description of the multi-component behaviour of the binary HA-mineral interaction. The first assumes a single HA species and two surface binding sites and was found to perform better overall than the second, which has a single surface sorption site and two HA species in solution. The exchangeable binding strengths for the different HA samples calculated from both models showed similarities to those measured experimentally.
Declaration

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Dedication

For my family, Rebecca, Colin, Jonathan and Anderson.
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Chapter 1

Introduction
1.1 Humic Substances

1.1.1 What are Humic Substances?

Organic matter in the environment (soils, sediments and natural waters) can be divided into two classes of compounds, non humic material (e.g proteins, polysaccharides, nucleic acids and small molecules such as sugars and amino acids) and humic substances (Jones and Bryan, 1998). Humic substances (HS) are polydisperse, organic, polyelectrolyte molecules. Hayes et al (1989) found that HS are universal and will be found wherever organic matter is being decomposed, and so HS make up approximately 60-70% of soil organic matter (Jones and Bryan, 1998) and 30-50% of surface organic matter (Thurman and Malcolm, 1981). It is believed that HS are the most abundant naturally occurring organic macromolecules (2-3 x 10¹⁰ tons worldwide) (Bazilevich, 1974). HS have important roles in the carbon cycle & the biogeochemistry of all metallic elements (Livens, 1991).

Humic materials are the principal organic compounds of soils and waters throughout the world, but their composition may vary depending on the geographical location, origin and history (Kononova, 1966; Stevenson, 1982). They possess characteristics that make them different from the materials from which they were formed (Wood, 1995). For example, HS can be dissolved in alkali and certain components can dissolve in acid. They also have the capacity to absorb heavy metals, as well as pesticides and other organic chemicals. They are in general dark brown/black in colour and have an effect on the physical and chemical properties of soil (e.g colour, texture, moisture holding). They also have a high capacity for proton exchange (Wood, 1995).

Humic substances are by-products of microbial activity, and will be formed wherever organic matter is decaying (Stevenson, 1982; Hayes et al., 1989). Plant residues are organic polyelectrolyte macromolecules derived from a combination of
the molecules making up a variety of organisms (Jones and Bryan, 1998; Stevenson, 1982).

HS are structurally complex, large to macro-molecules and consist of carbon, oxygen, hydrogen, small amounts of nitrogen and occasionally phosphorus and sulphur (Jones and Bryan, 1998). The structures of HS are ill-defined, despite many decades of research, although many tentative structures have been proposed (Kononova, 1966; Langford et al., 1983; Schnitzer et al., 1983; Averett et al. 1989, Swain et al., 1970; Frummel and Christman, 1988; Schulten and Schnitzer, 1993; Schulten and Schnitzer, 1995). In the broadest of terms, the structures can be described as assemblies of covalently linked aromatic and aliphatic residues carrying carboxyl, phenolic and alkoxy groups, although sulphate esters, alanine moieties, semi-quinone, phosphate ester (Averett et al., 1989) and hydroquinone (Frummel and Christman, 1988) groups have been proposed to exist in some humic isolates. Fig. 1.1 shows one proposed structure based on pyrolysis studies (Schulten and Schnitzer, 1993), which has a molecular mass of 5539.7 and an empirical formula of $C_{308}H_{328}O_{90}N_5$. As well as benzene moieties, it has pyridine, pyrrole and furan residues.
1.1.2 The Humification Process

The formation of HS occurs through humification, which is important in the carbon cycle, and is thought to be mediated by microbes (Swift et al., 1987). The formation of HS in soils and aquatic environments can occur through one of many pathways, such as directly from the lignified tissues of plant material, or through polymerization of simple products generated in the degradation of plant material (McKnight and Aiken, 1998). The actual formation of HS, from plant and animal remains has four possible mechanisms which are:

- The plant residues undergo microbial transformation to form reducing sugars and amino acids. These undergo non-enzymic polymerisation to form HS.
• The non-lignin (cellulose) sources of plant residue form polyphenols as a result of microbial metabolism. The polyphenols form quinones via enzymatic oxidation which, in the presence or absence of amino compounds, polymerise to form HS.

• Plant residues yield phenolic aldehydes and acids as these are released from lignin during microbial decomposition. Via an enzymic conversion, the phenolic aldehydes and acids form quinones, which then polymerise to form HS.

• Incomplete utilisation of lignin by microorganisms yields modified ligins, which undergo demethylation, oxidation and condensation with nitrogen containing compounds, such as proteins, to form HS.

The three widely accepted mechanisms are the lignin, sugar-amine condensation and polyphenol mechanisms. Stevenson (1982) suggested that a combination of these mechanisms is most likely to be the overall mechanism for the formation of HS in soils.

1.1.3 Classification

There are three classes of HS, which are defined by their solubilities: Humin (insoluble in aqueous systems at all pH values); Humic Acid (HA) (soluble at pH>2); and Fulvic Acid (FA) (soluble in water at any pH). This classification is preferred to one based on chemical & structural criteria, because all HS are heterogeneous mixtures exhibiting similar macroscopic properties, but of different microscopic chemical structures (Livens, 1991; Buffle et al., 1990). This method of defining HS is not entirely satisfactory, since it can include organic compounds that are not HS (Swift, 1999).
Choppin (1988) showed that HA has greater molecular weight than FA & has a
greater aromatic composition compared to FA (40-60% & 20-50%, respectively).
Both acid types contain roughly the same amount of phenolic, carbonyl and
methoxy groups per unit weight (Schnitzer, 1978). Carbon and oxygen are the
most abundant elements in HS by weight. HA contains 10% more C and 10% less
O than FA, while both have similar S, N and H contents. The total acidity of FA is
higher than that of HA (Schnitzer and Kahn, 1972).

1.1.4 Characteristics of Humic Materials
HS have increasing solubility with increasing pH (Hayes et al., 1989) which is due
to increasing ionisation of carboxylic acid groups and phenolic groups, causing the
molecules to repel and separate. In addition, the molecular arrangements become
smaller and better orientated with decreasing pH (Swift, 1989a, b). At low pH or
high metal ion concentration, macromolecular molecules tend to aggregate,
forming bundles of elongated fibres as a direct result of interactions such as
hydrogen bonding; Van der Waal’s forces; interactions between electrons of
adjacent ring structures; and homolytic reactions of free radicals (Swift, 1989a, b;
Wershaw, 1986; 1993). The most important property of HS is their heterogeneous
nature, both in terms of molecular structure & weight (Livens, 1991; Jones and
Bryan, 1998). HS are complex mixtures, which do not exhibit specific physical &
chemical characteristics (McBride, 1989). Livens (1991) suggests that no two
humic molecules are the same, and so the observed characteristics are only
averaged properties.

1.1.5 Colloidal Properties
HS are a major class of naturally occurring organic molecules, which not only
demonstrate colloidal phenomena by themselves, but display a range of important
colloidal interactions in the presence of other substances (Bryan et al., 1998).
In general, the colloidal state represents an intermediate phase between the dissolved phase and suspended molecules, where the species are sufficiently large to settle under the influence of gravity. The colloidal nature of HS means that they show the attributes of both a bulk material and a dissolved species. A major characteristic of humic species is the large surface area-to-mass ratio compared to a solid phase, which enhances their chemical and physical reactions. The dominating surface chemistry of the system becomes more significant as particle size decreases. This also results in a greater mobility in surface or ground waters in the environment, approaching that of a simple solute (Gaffney et al., 1996).

1.1.6 Weight Determination of Humic Substances

The different studies of the molecular weights (M\text{w}) of HS have shown that they can differ by many orders of magnitude. The reason for this is due to either the heterogeneity or polydispersity of the humics or the limitations of the techniques used to analyse them. The methods used so far in determining the M\text{w} have been viscosity, vapour pressure osmometry, centrifugation, gel filtration, laser light scattering, mass spectrometry, flow field flow fractionation and electrospray ionisation mass spectrometry (Gaffney et al., 1996; Schimpf and Petteys, 1997; Pitois et al., 2008; Plancque et al., 2001).

Gel (size exclusion) chromatography study of HS has shown that the most highly oxidized materials have M\text{w} values of the order of 2000 Da and less (Swift, 1996). However, the bulk of the material isolated from soil in sodium hydroxide solution under ambient temperature conditions was in the 20,000 to 50,000 Da range.

Osmometry, viscometry and diffusion of the HS have suggested that the molecular weight is of the order of 2000 Da (Scheffer and Ulrich, 1960; Schnitzer and Khan, 1972), but Flaig and Beutelspacher (1958) showed, using ultracentrifugation that the M\text{w} values were in the range of 30,000 - 50,000 Da for HA and about 10,000 Da for FA. Much confusion with regard to M\text{w} determinations of HS has arisen as a
result of the use of ultracentrifugation sedimentation-velocity and diffusion methods, because they are not suitable for polydisperse systems due to the multiple diffusion coefficients and sedimentation constants for the different size fractions (Wershaw and Aiken, 1985). Studies of HA extracts have produced $M_w$ values ranging from 25,000 to more than 200,000 Da (Stevenson et al., 1953; Piret et al., 1960). Flaig and Beutelspacher (1968), when working with polydisperse humic solutions, found that $M_w$ values varied from 77,000 Da, when 0.2 M NaCl was added to depress the repulsive electrostatic interactions, to only 2050 Da in the absence of the background electrolyte. This is evidence that the technique will see aggregates as single species, and so will overestimate the sample $M_w$.

In an attempt to decrease the polydispersity of HS, Cameron et al. (1972) fractionated soil-extracted HA by ultrafiltration and gel permeation chromatography (GPC) extensively. They subjected the fractions to sedimentation-velocity ultracentrifugation. The fractions obtained were more homogeneous than the unfractionated solution, but these could still not be considered to be monodisperse. They reported $M_w$ values for the fractions that ranged from 2600 to a large 1,360,000 Da. The reason for this large $M_w$ value could be that the measurement of sedimentation coefficients of polydisperse materials that include subunits such as HS leads to $M_w$ values with large errors. Other studies using sedimentation-velocity ultracentrifugation (Geraldine et al., 1982; Posner and Creeth, 1972; Reid et al., 1991) also showed polydispersity in HS and confirmed the unreliability of the $M_w$ values obtained from sedimentation velocity methods. There is no such problem with “equilibrium” or “approach to equilibrium” methods which gives a mass distribution ranging from 1927 to 4750 Da and a weight-average molecular mass of $3282 \pm 23$ Da for HS (Wilkinson et al., 1993).

Schimpf et al. (1997) found that flow field-flow fractionation (FFFF) can be a useful technique for studying the hydrodynamic behaviour of humic materials. They found
that the hydrodynamic size increases with pH in each of the humic materials, but HA aggregates with increasing severity as the pH is reduced.

Electrospray ionisation mass spectrometry (ESI-MS) has been used to characterise the molecular structure of FA from different sources (Plancque et al., 2001). It was found that the typical molecular mass of the molecules was approximately 450 Da. Further, the patterns in the mass spectra of the molecules and their fragments (losses of 18 Da (H$_2$O) and 44 Da (CO$_2$)) indicated the presence of carboxylic acid functional groups. There was sufficient information for a hypothetical structure for FA based on experimental evidence to be proposed for the first time. The predicted structure was found to be consistent with the elemental analysis of FA.

It is difficult to determine the real $M_w$ of HS as different techniques measure different things, e.g. Ultrafiltration will measure aggregates, but ESI-MS will measure only individual molecules. There is more consensus in the $M_w$ values obtained for FA. There is a general agreement that the $M_w$ of fulvic molecules is in the 400 - 1500 Da range. This has been determined by a variety of methods (Aiken and Gillam, 1989; Wershaw, 1989; Stevenson, 1994).

1.2 Models of Humic Structure

1.2.1 The Random Coil Model
The random coil model treats the humic as a single molecular strand, which coils randomly with respect to time and space. This strand carries, along its length, charged and hydrated functional groups. It assumes a conformation that is roughly spherical in shape and in which the distribution of mass is Gaussian about its centre. That is, the mass density is greatest at the centre and decreases to zero at the edge (Keepax et al., 2002). The solvent penetrates throughout the structure and that at the periphery exchanges freely with the bulk solvent. As density increases, towards the centre of the colloid, the solvent may become trapped
Hayes and Swift (1978; 1990) suggested that the colloid may become tightly or loosely coiled, depending on certain factors: the nature of the solvent; the extent of the solvent penetration; the charge of the colloid; the concentration of counterions; the surrounding pH. It has been suggested that the carboxylate groups of HS, which will be deprotonated at ambient pH, account for the relatively high charge of humic colloids, and the associated inter- and intra-molecular forces (Swift, 1999). Swift (1996) showed that a soil humic substance will contain four to eight carboxylate groups per 1000 Daltons. In the solid state, short-range, non-electrostatic forces are dominant and only very tightly bound water is retained. Solid state HS may retain a certain amount of flexibility and solvent accessibility due to the presence of some entrapped water. It could be this that gives rise to rapid ion exchange reactions and other interactions at the humic surface (Swift, 1999). The intermolecular interactions are controlled by very similar factors. Two highly charged colloids in solution will repel each other, and thus they will be kept apart (Swift, 1989a, b). High ionic strengths or charge neutralisation suppress the electrostatic repulsive forces, which are then superseded by short range attractive forces. Such attractive interactions include Van der Waals forces, dipolar interactions and hydrogen bonds. At the point where the molecules are so poorly solvated and/or charged, that they can no longer remain in solution, they aggregate, and eventually precipitate (Swift, 1989a).

Information about molecular size and shape can be determined with ultracentrifugation: the shape of the molecule can be determined from the frictional ratio, \( \frac{f}{f_0} \) which is the ratio of frictional coefficient of the real sample (f) divided by the frictional coefficient of a hypothetical molecule of the same volume, but having a condensed spherical conformation \( f_0 \) (Swift, 1989a, b). The values for humic substances range from 1.14, for lower molecular weights to 2.14 for higher weight fractions (Cameron et al., 1972; Swift, 1989b). These values provide evidence for a random coil model of humic, since they agree with the derived theoretical relationship \( \frac{f}{f_0} = 0.3M^{0.167} \) (Swift, 1989a, b). Further evidence for a random
coiled structure, and which contradicts a hard, rigid sphere model, includes their random ternary structure, high charge density, rapid ion exchange and high water uptake (Swift, 1999). Schulten and Schnitzer (1993) have shown experimental evidence for significant cross-linking, so a more realistic description of the humic is a sponge like structure, which is cross-linked, but is still able to expand and contract to allow penetration by the solvent and small ions. The net effect is a penetrable gel like structure (Benedetti et al 1996), as shown in Figure 1.2.

Figure 1.2: penetrable gel like structure of humic acid. Also shows penetration of structure by small ions and the diffuse part of the double layer.

1.2.2 The Self-Association Model

The self-association model describes the larger humic species observed in solution as weakly bound aggregates of smaller moieties (Wershaw, 1986; Wershaw, 1993; Piccolo et al., 1996; Piccolo, 1997; Conte and Piccolo, 1999). Piccolo et al. (1996) and Conte and Piccolo (1999) have shown evidence that the systems are complex, and that the same concentrations of hydrochloric acid have had no effects in some cases, but substantial effects in others. One study has exposed humics to treatments such as acid precipitation, washing, redissolution and dialysis (De Nobili and Chen, 1999) which showed no effect upon the weight distribution of the
samples. If the large humic species in solution were fairly weakly bound agglomerates, then one might have expected these experiments to have an effect (Swift, 1989a, b). The mechanism by which the smaller molecules in solution might be held together is uncertain. Hydrogen bonding, π bonds, charge transfer complexes and bridging metal ions have been proposed (Wershaw, 1986, 1993) along with hydrophobic interactions (Piccolo et al., 1996, Piccolo 1997). Piccolo et al. (1996) found that multivalent cations are capable of bridging between charged carboxylate groups in the same or different molecules, and their addition in large quantities is known to cause precipitation of HS. However, it has been suggested that for any molecular aggregation to occur, it would have to be held together by something stronger than hydrophobic interactions, meaning that the aggregates would have to be linked by interactions similar to a covalent bond (Swift, 1999).

### 1.2.3 Micelle Model

The micelle model describes the humic species as micelle-like structures. In the micelle concept, the hydrophilic parts are considered to be orientated towards the exterior, whilst the interiors consist of associations of the hydrophobic parts. This requires the HS to have amphiphilic properties in which the molecules have hydrophobic (non-polar) and hydrophilic (polar) parts (Wershaw, 1999). In humic micelle structures, the polar or charged groups would face in the same direction, and so the hydrophilic functionalities would face outwards. This arrangement would be thermodynamically less favourable should the acidic groups dissociate, because the molecules would favour conformations in which charge interactions are the least (Clapp and Hayes, 1999).

Undissociated acidic species would allow hydrogen bonding, and this bonding can be intermolecular and/or intramolecular (Clapp and Hayes, 1999). For intermolecular bonding it is not necessary to alter the configurations of the interacting species from their preferred orientations, but for intramolecular hydrogen bonding, the interacting species must have the correct orientation, which
results in the configurations/conformations of the molecules being more rigid. This can lead to strain which could inhibit interactions. Von Wandruszka, (1998) suggested that cation-bridging to bring two charged species into proximity could produce pseudo-micellar structures of HS.

1.2.4 The Correct Model?
There is evidence for the random coil, the self-association models and the micelle model for humic structure, but none have been proven to be conclusive. It is likely that the most accurate representation of humic structure in solution will incorporate aspects from all the models. Some evidence for this has been provided by Pédrot et al. (2010) who studied: (i) the size of humic molecules as a function of ionic strength and pH by combined ultrafiltration and aromaticity data and rare earth element (REE) fingerprinting, and (ii) the pH and ionic strength effect on the distribution of associated rare earth elements in soil solution. They suggested that the dissolved humics were only slightly sensitive to ionic strength, probably because of the trace elements carried by humic substances. By contrast, pH seems to play a key role in the size distribution of humic substances. A pH increase destabilized the humic association and led to an increase in small molecules, which was interpreted as the disruption of the supramolecular assemblies. Therefore, they conclude that both supramolecular associations of small molecules and macromolecules are present in the dissolved organic matter.

1.3 Interaction of Humic Substances with Metal Ions

1.3.1 Properties that Govern Metal-Humic Binding
Humics will bind virtually all metal ions, and interact most strongly with the transition metals, the lanthanides and the actinides (Jones and Bryan, 1998; Illés and Tombácz, 2006). The humic-metal ion interaction is pH and ionic strength dependent; the interaction is stronger with increasing pH and decreasing ionic strength (Livens, 1991).
1.3.2 Environmental Implications of Metal-Humic Interaction

HS interact very strongly with virtually all metal cations (Tipping and Hurley, 1992). This results in an impact upon the environmental behaviour of both naturally occurring and anthropogenic metals (Bryan et al., 2000).

It is important to study metal-humate interactions, because metal ions bound to humics show very different behaviour compared to the free metal ions or simple inorganic complexes (Saar and Weber, 1982). Humics are suspected of enhancing the environmental mobility of metals (McCarthy et al., 1998; Bowell et al., 1993; Khan et al., 1985). It is thought that HS could interact with radionuclides in radioactive waste repositories, and thereby mobilise species, which would otherwise be contained due to their low solubilities in inorganic, non-colloidal systems (Choppin, 1988; Ramsay, 1988).

Bowell et al. (1993) have shown that FA mediates the environmental mobility of the heavy metal Au. Another study has shown that HS have led to the migration of radionuclides away from a radioactive waste repository (McCarthy et al., 1998). Many other studies have also demonstrated the importance of humics to the environmental chemistry of radionuclides, such as Pu. For example, the Pu specific activity of a soil from Cumbria, UK was 2860 Bq kg\(^{-1}\), but that of the humic fraction was 27400 Bq kg\(^{-1}\). For Am, the whole sample activity was 2650 Bq kg\(^{-1}\), and for the humic fraction it was 18600 Bq kg\(^{-1}\) (Livens and Singleton, 1991).

In the case of heavy metals, the toxicity is primarily associated with the free metal, and not with the total solution phase concentration (Buffle et al., 1990; Livens 1991). Hence we would expect that humics and fulvics, which complex heavy metals and reduce the free concentration, would reduce toxicity (Petersen 1982; Gjessing et al., 1989). However, in some cases, because humics can significantly increase solubility, inhibit precipitation and retain metals in the solution phase, their
net overall effect may increase toxicity (Buchwalter et al., 1996). In addition to this, humics will affect the bioavailability of metals (Livens, 1991). For example, Sedlaceck et al. (1989) have shown that HS, especially the smaller fractions, increase the uptake of Cd$^{2+}$ by plants.

Humics have a crucial role in the behaviour of radionuclides in the environment (Livens, 1991). However, because of their heterogeneous and complex nature, the understanding of metal-humate interactions is still uncertain, and there are still many areas that are poorly understood.

### 1.3.3 The Double Layer

HS in solution will have a large negative charge due to the ionisation of their functional groups, particularly carboxylates (Jones and Bryan, 1998). Along with the charge, the humic will generate an associated potential, which attracts positive ions in the solution, and repels anions (Bartschat et al., 1992). The result is that the HA is surrounded by an atmosphere of cations, called a double layer. The double layer has a large impact on the interaction of humics with radionuclides, which largely exist in solution as cationic species (Jones and Bryan, 1998). The potential and double layer induced by a colloid depends on the colloidal charge, ionic strength and the physical state of the colloid itself. Colloids are often thought of as impenetrable, with their charges distributed over the surface. A number of studies have treated humics in this way, either as impenetrable spheres (Nederlof et al., 1993) or cylinders (De Wit et al., 1993; Milne et al., 1995a, b). But there is some conflicting evidence that humics are not impenetrable, and that solvent and small ions can gain access to the interior. A penetrable approach provides a better description of the system (Van Riemsdijk et al., 1996; Kinniburgh et al., 1996).

### 1.3.4 Binding of Metal Ions

The binding of metal ions by humics has been studied extensively (Warwick et al., 2000; Bryan et al., 2000; Schüßler et al., 2000). Warwick et al. (2000) have proved
that metal ions bind in an ‘exchangeable’ mode, and as such are bound very strongly, but they may still be removed instantly by a ligand or surface with a higher affinity. The initial exchangeable binding is followed by some degree of rearrangement, which makes the metal ion resistant to removal (Choppin, 1988). The ‘non-exchangeable’ bound metal ion may dissociate, but the process is slow, and the rate is independent of the strength or concentration of the competing sink (Warwick et al., 2000; Cacheris and Choppin, 1987; Choppin and Clark, 1991; King et al., 2001).

There have been a number of studies that have examined this kinetic effect (Choppin, 1988, Choppin and Clark, 1991; Chakrabarti et al., 1994; Cacheris and Choppin, 1987; Schussler et al 1998; King et al., 2001; Schussler et al., 1999; Warwick et al., 2000; Monsallier et al., 2003). There are a number of non-exchangeable components, and a number of first order rate constants are required to describe the data completely. Choppin et al. (Choppin, 1988; Choppin and Clark, 1991, Cacheris and Choppin, 1987; King et al., 2001) have used a ‘kinetic spectrum’ approach, which defines a number of these components.

1.3.5 Mechanisms of ‘non-Exchangeable’ Metal Ion Binding
HS are known to bind metal ions non-exchangeably, but the mechanism by which it happens is uncertain. Von Wandruszka et al. (1997) showed that, although solution phase humic species are broadly hydrophilic, the addition of metal ions resulted in the formation of hydrophobic zones, with metals of high charge density being the most efficient. In addition, structural changes have been observed that take place on the time-scale of days after initial binding, which is similar to that observed for the development of non-exchangeable binding (Engebretson and Von Wandruszka, 1998). Choppin (1988) introduced the idea of the metal ion moving from exchangeable (weaker) to non-exchangeable (stronger) sites. Warwick et al. (2000) have suggested a system as shown in Figure 1.3, where the metal ions move from an exchangeable site on the surface to a non-exchangeable one inside
the humic. In both of these cases, the metal ion is required to move from one place on the humic to another.

Conte and Piccolo, (1999) have suggested that the large humic species that exist in solution are actually aggregates of much smaller species. For such aggregates, if aggregation is dynamic, a metal ion may become trapped within an association of small molecules and isolated. Other authors, such as Geckeis et al. (2002), have suggested that the metal ion might bind to a humic molecule and then itself act as a bridge to a second humic species, rendering it non-exchangeable. Associations of inorganic and humic material could also play a role (Artinger et al., 2002). Alternatively, a metal ion might bind to a humic species, and initially be available for exchange, but rearrangement of the humic structure around the metal ion could lead to a more complete coordination, which could render it non-exchangeable. There have been observations of the formation of hydrophobic zones with time following initial complexation, with metal ions of the highest charge density producing the greatest effect (Von Wandruszka et al., 1997; Engebretson and Von Wandruszka, 1998).

Figure 1.3: Binding of metal ions in ‘exchangeable’ and ‘non-exchangeable’ sites. Adapted from Warwick et al (2000). M_S: metal ion bound to surface, M_aq: metal ion in aqueous phase, M_Eq: metal bound to exchangeable site of HA, M_Fix: metal ion bound to the non-exchangeable site of HA.
1.3.6 Evidence for ‘Exchangeable’ and ‘non-Exchangeable’ Interactions

Artinger et al. (1998) found that increasing the humic substance concentration reduced Am sorption onto sand and enhanced its transport and solubility as colloid-borne Am species in column and batch experiments. Am becomes less available for the surface complexation onto sand during the migration period in the column. The phenomenon of a time-dependent strong binding of a trivalent metal ion with humic colloids was also found by Rao et al. (1994), who studied the interaction of Eu (III) with HA using cation exchange columns. The column experiments indicate some reversible binding of Am onto mobile humic species, i.e., an increased Am sorption onto sand with an advancing migration front of humic-bound Am in an uncontaminated aquifer is expected (Artinger et al., 1998). However, there was also evidence for non-exchangeably bound Eu that was able to transport rapidly through the columns, and this fraction did not appear to be retarded by sorption to the mineral surface. More importantly, Artinger et al. (1998) found that the amount of Am that reaches the end of the column increases as the time that the HA and Am are equilibrated prior to injection in the column is increased. The amount of Am that reaches the end of the column increases with increasing flow rate. Both of these results gave evidence for the nature of non-exchangeable binding as a separate fraction to the exchangeable.

Other column experiments have also shown that non-exchangeable binding is responsible for rapid, humic mediated metal ion transport (Artinger et al., 2002, Bryan et al., 2005, Schuessler et al., 2000, Schussler et al., 2001, Warwick et al., 2000). Modelling of these results has shown that the amount of metal that transports rapidly is sensitive to only two parameters, the first order dissociation rate constant for the slowest dissociating non-exchangeable fraction and the amount of metal bound in that fraction. The exchangeable interaction makes little difference to the amount of metal that transports (Bryan et al., 2007).
The rate of dissociation of metal ions from the non-exchangeable fraction is very important to their humic mediated transport. Bryan et al. (2007) found that metal bound exchangeably is not expected to transport rapidly in the environment. Although metal bound in the exchangeable fraction is relatively strongly bound, the vast excess of mineral surface binding sites means that metal bound exchangeably is quickly transferred to the mineral surface during transport. For the non-exchangeable, the rate of removal, and the effectiveness of the humic as a transport vector for the metal do not depend upon the relative metal ion binding strengths of the humic and the mineral surfaces, but rather the first order dissociation rate constant.

1.3.7 Measuring Metal Ion-Humic Kinetics

Monsallier et al. (2003) investigated the kinetics of Eu (III) - humate interaction by ion exchange resins using the resins Dowex 50Wx4 and Cellphos (cellulose phosphate). Exchange resins can be very useful for chemical speciation and determination of metal humate complexation, since they have comparable reactivity to humic materials for trivalent f-elements and an ability to repel humics due to their negative charge. Therefore, these resins are suitable for the rapid separation of free metal ions from humic associated metal species. King et al. (2001) found that the higher the mass of resin used, the smaller the influence of resin mass becomes when using Dowex 50Wx4, which agreed with the results of Monsallier et al. (2003). The mass of resin should be sufficiently high that all free and exchangeably bound metal ion is instantaneously removed from solution. In this case, the dissociation rate of the non-exchangeable fraction becomes the rate limiting step, allowing the first order dissociation rate to be determined. Equation 1.1 shows the interactions of the metal ion between humic and exchange resins.

\[
M_{\text{resin}} \leftrightarrow M_{\text{(aq)}}^{n+} \leftrightarrow M_{\text{exch}} \xleftarrow{k_f} \xrightarrow{k_b} M_{\text{non-exch}}
\]  

Equation 1.1
where $M_{resin}$ is the metal ion bound to resin, $M^{n+}_{aq}$: metal ion in aqueous phase, $M_{exch}$: metal bound exchangeably, $M_{non-exch}$: metal ion bound non-exchangeably, $k_f$: the forward rate constant between $M_{exch}$ and $M_{non-exch}$, $k_b$: the backward rate constant between $M_{exch}$ and $M_{non-exch}$.

Some transport studies (Schussler et al., 1998; Schussler et al., 1999; Warwick et al., 2000; Bryan et al., 2005) have considered the existence of the faster dissociating fractions, but have concentrated on the longest lived fraction, since this is expected to be the most significant for transport in the environment (Bryan et al., 2007). The results show a continuum of dissociation rates, ranging from virtually instantaneous to a slowest fraction, and that this slow fraction is found for all humic samples. Outside of some small variation, the rate constant for this fraction is the same for most metal ions, regardless of metal ion chemistry (Bryan et al., 2007). This behaviour is in contrast to that for exchangeable binding, where the binding strength depends very much on the identity of the metal ion (Tipping and Hurley, 1992; Read and Falck, 1996).

Monsallier et al. (2003) showed that the humic concentration affects the Eu removal from solution; an increase in the humic concentration slows down the Eu uptake by the exchange resin. As the total initial Eu concentration increases, the absolute amount of Eu sorbed non-exchangeably to humic increases for all reaction times. In contrast, the relative amount of metal bound is lower.

### 1.3.8 Natural and Synthetic Metal-Humate Complexes

Most kinetic studies to date have involved ‘synthetic’ metal-humate complexes. That is, metal ions and humics are mixed in the laboratory, and allowed to equilibrate, before the dissociation kinetics are measured. However, Geckeis et al. (2002) have found that metal ions introduced to the humic via natural processes, show different dissociation kinetics. They found that metals naturally present in humic samples dissociated with rates significantly slower than for the same
elements added in the lab. In fact, they have found some evidence for 'pseudo-
irreversible' binding, i.e. some fraction of the natural loading would not desorb even
after long times (months). Artinger et al. (2002) also found this effect for Am added
to humic in the lab. If these observations are true, then such metal fractions would
migrate very effectively, particularly if they are associated with weakly sorbing
humic fractions. For the synthetic process (Eu$^{3+}$ added to purified HS in the
laboratory) the kinetic data were fitted with 2 humic non-exchangeable
components: one relatively quickly dissociating and a slower one. With time, there
was a movement of material from the faster to the slower component, which was
accompanied by a shift of the bound Eu$^{3+}$ to larger humic species (Geckeis et al.,
2002).

1.3.9 Dissociation Rate Constants

Table 1.1 shows a selection of dissociation rate constants from the literature. There
is only a small variation in the dissociation rate constant for the most slowly
dissociating fraction, even when different metal ions are studied. King et al. (2001)
determined first-order dissociation rates in the range 1.5 - 3.3 x 10^{-7} s^{-1} for Eu$^{3+}$ (pH
6.5, 10 ppm (w.v) HS), while Davis et al. (2000) observed 1.6 - 2.8 x 10^{-7} s^{-1} for
Th$^{4+}$ (pH 6.4 - 7.8, 30 ppm (w.v) HS). For ‘synthetic’ metal–humate complexes, the
amount of metal in the non-exchangeable fraction increases with increasing metal
ion – humic pre-equilibration time, with the rate of increase falling after 14 days
(King et al., 2001; Geckeis et al., 2002; Artinger et al., 1998; Schuessler et al.,
2000). However, the dissociation rate constant is not affected by the metal-humic
pre-equilibration time (King et al., 2001; Monsallier et al., 2003).

For the exchangeable component, the binding strength does depend upon the
chemistry of the metal ion, and the values of the equilibrium constants vary greatly
from one metal ion to another (Bryan et al., 2000). However, for the kinetics, there
is no such effect, and all metal ions show the same dissociation rate constant for a
given humic sample and conditions. In general, the variation in rate constant is
relatively small from system to system, and all of the values in Table 1.1 cover only 2 orders of magnitude, and most are within a factor of 10 of each other. The rate constants are also independent of the pH and the presence of competing cations (King et al., 2001).

Table 1.1: Kinetic data for humic-metal complexes: Natural = data for metal ions already present (complexed) in the humic sample; Synthetic = data for metal ions introduced (complexed) to the humic in the lab. Data taken from the following references, A = Bryan et al., (2008); B = King et al., (2001); C = Geckeis et al., (2002); D = Davis et al., (2000).

<table>
<thead>
<tr>
<th>Ref</th>
<th>Metal Used</th>
<th>Synthetic Or Aldrich</th>
<th>Humic Concentration [HA] ppm (w.v)</th>
<th>Equilibration Time in Synthetic Systems</th>
<th>Amount of metal in non-exchangeable fraction (C/C₀)t=0 (%)</th>
<th>First Order Dissociation Rate Constant kᵣ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Am Natural</td>
<td>-</td>
<td>600</td>
<td>31 ± 2</td>
<td>7.3 ± 2 x 10⁸</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Am Natural</td>
<td>-</td>
<td>600</td>
<td>28 ± 1</td>
<td>5.9 ± 1 x 10⁸</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Np Natural</td>
<td>-</td>
<td>540</td>
<td>53 ± 8</td>
<td>2.4 ± 2 x 10⁴</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Am Natural</td>
<td>-</td>
<td>140</td>
<td>17 ± 8</td>
<td>4.9 ± 2.7 x 10⁴</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Am Synthetic</td>
<td>600</td>
<td>7 days</td>
<td>14 ± 1</td>
<td>4.5 ± 0.5 x 10⁴</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Eu Synthetic</td>
<td>600</td>
<td>7 days</td>
<td>6.5 ± 1</td>
<td>4.3 ± 0.7 x 10⁴</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Am Synthetic</td>
<td>140</td>
<td>7 days</td>
<td>29 ± 7</td>
<td>4.5 ± 3 x 10⁴</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Eu Synthetic</td>
<td>10</td>
<td>1 day</td>
<td>68 ± 12</td>
<td>4.7 ± 0.5 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Eu Synthetic</td>
<td>10</td>
<td>7 days</td>
<td>38 ± 5</td>
<td>2.5 ± 0.5 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Eu Aldrich</td>
<td>100</td>
<td>7 days</td>
<td>5.4 ± 2.1</td>
<td>3.0 ± 2.7 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Eu Aldrich</td>
<td>100</td>
<td>7 days</td>
<td>5.4 ± 1.5</td>
<td>1.5 ± 1.5 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Eu Aldrich</td>
<td>100</td>
<td>7 days</td>
<td>3.6 ± 2.5</td>
<td>4.6 ± 3.9 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Am Aldrich</td>
<td>100</td>
<td>7 days</td>
<td>13.8 ± 4.7</td>
<td>3.3 ± 2.3 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Eu Aldrich</td>
<td>100</td>
<td>7 days</td>
<td>4.9 ± 2.5</td>
<td>5.6 ± 3.9 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Eu Aldrich</td>
<td>100</td>
<td>7 days</td>
<td>7.5 ± 1.2</td>
<td>2.6 ± 1.1 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Eu Aldrich</td>
<td>200</td>
<td>7 days</td>
<td>9.7 ± 0.9</td>
<td>2.6 ± 0.6 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>Eu Aldrich</td>
<td>500</td>
<td>7 days</td>
<td>16.6 ± 1.0</td>
<td>9.7 ± 4.1 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>Eu Synthetic</td>
<td>10</td>
<td>9 days</td>
<td>-</td>
<td>2.2 ± 0.5 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>Eu Synthetic</td>
<td>10</td>
<td>131 days</td>
<td>-</td>
<td>1.5 ± 0.2 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>Eu Synthetic</td>
<td>60</td>
<td>9 days</td>
<td>-</td>
<td>8.3 ± 2.8 x 10⁸</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>Eu Synthetic</td>
<td>10</td>
<td>9 days</td>
<td>-</td>
<td>2.3 ± 0.3 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>Eu Synthetic</td>
<td>10</td>
<td>9 days</td>
<td>-</td>
<td>3.3 ± 0.3 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>Eu Synthetic</td>
<td>30</td>
<td>Aprox 1 hr 42</td>
<td>-</td>
<td>2.1 ± 0.3 x 10⁸</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>Th Synthetic</td>
<td>30</td>
<td>Aprox 1 - 4</td>
<td>-</td>
<td>1.6 ± 0.6 x 10⁷</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>Th Synthetic</td>
<td>30</td>
<td>Aprox 1 - 4</td>
<td>-</td>
<td>2.8 ± 1.3 x 10⁷</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1.1: Kinetic data for humic-metal complexes: Natural = data for metal ions already present (complexed) in the humic sample; Synthetic = data for metal ions introduced (complexed) to the humic in the lab. Data taken from the following references, A = Bryan et al., (2008); B = King et al., (2001); C = Geckeis et al., (2002); D = Davis et al., (2000).
The dissociation of metal-fulvate complexes has not been studied as much as humic acid systems; however King et al. (2001) found that the fulvic and humic dissociation rates are quite similar but the amount of metal bound non-exchangeably is lower for fulvics than for humics. Keepax et al. (2002) suggested this difference may be due to the lower concentration of larger species in a fulvic acid, compared to a humic acid.

1.4 Mineral Properties

Natural aqueous systems not only contain dissolved organic matter (e.g., humic and FAs) but also contain dispersed mineral (e.g., clay and metal oxide) particles (Buffle, 1990; Deng et al., 2002; Johnston and Tombácz, 2002; Aiken et al., 1985; Sposito, 1984). Iron is the third most abundant element in the lithosphere, and so iron oxides are widespread in environmental systems (Bigham et al., 2002; Cornell and Schwertmann, 1996). Iron oxides occur in several forms (e.g., hematite, goethite, etc., among them the ferromagnetic magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃)). Such materials often affect the distribution of natural organic matter and free metal concentrations, due to interfacial processes in aqueous dispersions (Tombácz, 2002). In aqueous systems, iron oxide particles are hydrated, and Fe-OH groups completely cover their surface. Hydrous iron oxides have amphoteric character (Sposito, 1984; Cornell and Schwertmann, 1996; Sposito, 1992; Sun et al., 1998; Tombácz and Csanaky, 2001), i.e. the Fe-OH sites on the surface can react with H⁺ or OH⁻ ions, and positive (Fe-OH₂⁺) or negative (Fe-O⁻) charges develop on the surface in protolytic reactions, depending on the pH of the electrolyte solution:

\[
\begin{align*}
\text{Fe–OH} + \text{H}^+ & \leftrightarrow \text{Fe–OH}_2^+ & \text{Equation 1.2} \\
\text{Fe–OH} + \text{OH}^- & \leftrightarrow \text{Fe–O}^- + \text{H}_2\text{O} & \text{Equation 1.3} \\
\text{Fe–OH} & \leftrightarrow \text{Fe–O}^- + \text{H}^+ & \text{Equation 1.4}
\end{align*}
\]
In the absence of specifically adsorbing ions, amphoteric metal oxides have a characteristic pH, the pH of the point of zero charge (PZC), where the net surface charge is zero, i.e., the positive and the negative sites have equal concentration. At pH lower than the PZC, the pure oxide surface is positively charged, while it has a negative charge above it (Bigham et al., 2002; Cornell and Schwertmann, 1996; Tombácz, 2002; Sposito, 1992). In oxide suspensions, aggregation occurs at pH around the PZC, even at low ionic strength, because the charge density is very low in this pH range. Colloidal dispersions are stable far from the PZC, but an increase in electrolyte concentration can still induce coagulation of the particles at any pH (Bigham et al., 2002; Cornell and Schwertmann, 1996; Tombácz, 2003; Elimelech et al., 1995; Lyklema, 1995; Tombácz et al., 1999).

1.5 HS Interactions with Mineral Surfaces

1.5.1 Processes and Mechanisms
The sorption of HS onto mineral surfaces has been studied previously, mostly via batch experiments. A number of studies (e.g. Tipping, 1984; Schlautman and Morgan, 1994; Tessier et al., 1996) have found that the adsorption step may be simulated with Langmuir or modified Langmuir isotherms, although the derived parameters may be conditional. A variety of processes/mechanisms have been proposed to explain the sorption of natural organic matter by mineral surfaces, including: ligand exchange; cation bridging; entropy-driven physical sorption; cation exchange; proton exchange; anion exchange; water bridging; hydrogen bonding and van der Waals interactions (McCarthy et al., 1989; Sposito, 1989; Schlautman and Morgan, 1994). However, the major mechanisms for sorption are probably anion exchange (electrostatic interactions); ligand exchange; surface complexation; hydrophobic interactions; entropic effects; hydrogen bonding and cation bridging (Sposito, 1984). Although the interaction mechanisms are uncertain, some authors (Lenhart and Honeyman, 1999) agree that it is not possible to treat HS as simple ligands.
Van der Waals interactions between HS and mineral surfaces can be strong and long range (e.g. greater than atomic distances), and are effective when the solution ionic strength is high enough to screen negatively-charged functional groups on the large HS molecules or when the pH neutralises the net charge (Sposito, 1984). The adsorption of a mixture of HA and FA, on nonporous hematite showed that, in time the larger HA molecules replace the readily sorbed, small FA molecules that are able to coat the surface first (Vermeer and Koopal, 1998).

McCarthy et al. (1994) found that the adsorption of HS on iron oxide was strongly pH dependent. This result is commonly observed for HS adsorption on oxide surfaces (Murphy et al., 1990; Murphy et al., 1992; Tipping, 1981; Davis, 1982). The adsorption pattern seemed consistent with an anion exchange (or electrostatic interaction) mechanism, since the surface of the iron oxide becomes more positively charged as pH decreases, whereas HS become less negatively charged (Davis et al., 1981, Liang et al., 1993; Sposito, 1984). Van de Weerd et al. (1999) modelled humic acid uptake to iron oxide phases with a single surface site and multiple humic acid fractions, and found evidence for at least six humic acid fractions with distinct kinetic properties.

1.5.2 Magnetite

Magnetite is a ferromagnetic black mineral with chemical formula Fe₃O₄, one of several iron oxides and a member of the spinel group. The formula for magnetite may also be written as FeO·Fe₂O₃, which is one part wüstite (FeO) and one part hematite (Fe₂O₃). The mixed valence nature of this compound was confirmed by X-ray Absorption Near Edge Structure spectroscopy by Sasaki (1995), and is what makes magnetite special. Magnetite is the most magnetic of all the naturally occurring minerals on Earth (Harrison et al., 2002). Small grains of magnetite occur in almost all igneous and metamorphic rocks. Magnetite also occurs in many sedimentary rocks, including banded iron formations. In many igneous rocks, magnetite-rich and ilmenite-rich grains occur that precipitated together from
magma. Many magnetite particles are largely produced as a result of microbial iron metabolism (Stolz et al., 1986a; Stolz et al., 1986b; Vali et al., 2004).

Under anaerobic conditions, the ferrous hydroxide (Fe(OH)$_2$) can be oxidized by the protons of water to form magnetite and molecular hydrogen (Schikorr 1933). This process is described by the Schikorr reaction and is given below:

$$3 \text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 2 \text{H}_2\text{O} \quad \text{Equation 1.5}$$

The well-crystallized magnetite (Fe$_3$O$_4$) is thermodynamically more stable than the ferrous hydroxide. This process also occurs during the anaerobic corrosion of iron and steel in oxygen-free groundwater and in reducing soils below the water table. Lovley et al. (1987) also suggested that bacteria can also generate magnetite from iron reduction under anaerobic conditions. For these reasons, magnetite is expected to be common around a deep underground radioactive waste repository.

The structure of magnetite is a cubic inverse spinel structure with Fe$^{2+}$ cations in octahedral sites and Fe$^{3+}$ cations in both octahedral and tetrahedral sites, surrounded by oxygen anions (Fleet 1986; Barbieri et al., 1993; Gossuin et al., 2009). The structure of magnetite is presented in Figure 1.4.
Magnetite is ferrimagnetic; because of super-exchange oxygen-mediated coupling, all the magnetic moments of the tetrahedral iron ions are aligned in a specific direction, while all the octahedral iron magnetic moments are aligned in the opposite direction (Néel 1948).

As magnetite is quite abundant in the environment, it may play a vital role in the transport of radionuclides, and therefore it would be quite beneficial to study the interactions of magnetite with HS and metal ions.

1.5.3 Previous work with Magnetite
Illés and Tombácz (2004) found that magnetite is a particularly good adsorbent for HA in the study of ionic strength dependence of HA adsorption on magnetite at pH 5, 8 and 9. The amount of HA adsorbed is influenced by the pH and also by the ionic strength. The dominant interaction is a ligand-exchange reaction between the functional groups of HA and the active sites on the magnetite surface. Surface complexation takes place at an electrical interface, and the local electrostatic field
influences the distribution of humic species between the surface and solution. This Coulombic contribution to the interaction becomes significant with decreasing pH below the PZC. Illés and Tombácz (2006) found that the PZC of magnetite seems to be at pH 7.9 ± 0.1. This means that below this pH, HA removal by adsorption is effective, the aqueous phase contains only very small concentrations of dissolved organic matter, and the equilibrium concentration of HA approaches zero. Based on their experimental results, Illés and Tombácz (2004) stated that the smaller humic size-fractions are adsorbed preferentially on the surface of magnetite particles, probably due to their enhanced affinity for ligand-exchange reactions.

Illés and Tombácz (2006) have revealed that HA can modify the surface charge properties of magnetite, the extent depending on the amount adsorbed. HA partially neutralizes the positively charged Fe-OH$_2^+$ sites below the PZC of the oxide and oppositely charged patches form on the surface of particles. Therefore, the aggregation of magnetite particles is enhanced at low HA loading. However, in the presence of larger amounts of HA, the particle surface is covered completely by an adsorbed layer of humic molecules, and the magnetite particles become highly negatively charged, even under acidic conditions. These humate-coated magnetite nanoparticles form a stable colloidal dispersion, and particle aggregation and sedimentation do not occur in these systems over a wide range of pH and increasing ionic strength. The combined steric and electrostatic stabilization hinders the separation of magnetite particles in a magnetic field (Illés and Tombácz 2006).

Sorption of $^{137}$Cs, $^{90}$Sr, $^{154}$Eu and $^{141}$Ce by magnetite has been studied at varying pH (4 to 11) and ionic strength (0.01 - 0.2 mol dm$^{-3}$ NaClO$_4$) in the presence and absence of humic acid (0 - 20 ppm (w.v)) (Singh et al., 2009). The sorption of $^{137}$Cs and $^{90}$Sr was found to be pH dependent, with the sorption increasing with increasing pH of the suspension. At any pH, the percentage of $^{90}$Sr sorbed was higher than that of $^{137}$Cs. The results have been explained in terms of the
electrostatic interaction between the positively charged metal ions and the surface charge of the magnetite which becomes increasingly negative with increasing pH. On the other hand, $^{154}$Eu and $^{141}$Ce were found to be strongly sorbed by the magnetite at all pH values, with the sorption being independent of pH. The strong sorption of trivalent and tetravalent metal ions suggests the role of complexation reactions during sorption, in addition to electrostatic interactions. However, in the case of $^{141}$Ce, surface precipitation of Ce (III) formed by reduction of Ce (IV) in the presence of magnetite cannot be ruled out. The presence of humic acid (2 mg/L) was found to have a negligible effect on sorption of all metal ions. Singh et al. (2009) suggested that it could be due to strong sorption of HA by magnetite. They suggested that magnetite colloids may greatly influence the migration of long lived radionuclides in aquatic environments in the presence or absence of humic acid.

Hu et al. (2010) studied the effect of humic acid (HA) on surface charge and aggregation potential of magnetite ($\text{Fe}_3\text{O}_4$) nanoparticles (NPs), over a wide range of solution pH and ionic strength. Through zeta potential (ZP) measurements, they found that HA can adsorb to magnetite particles hence modifying their surface charge status. At low loadings, the presence of HA can induce a shift in the PZC due to partial neutralization of the positive charges on magnetite NPs. At high loadings, however, HA is capable of completely covering magnetite particles, giving rise to a suspension ZP profile similar to its own (observed in presence of 20 mg L$^{-1}$ HA). The changes of the surface charge correspond well with the observed aggregation behaviours. From dynamic light scattering measurements, fast aggregation, which was independent of solution chemistry, occurred when the pH is close to the PZC and the ionic strength was above the critical coagulation concentration. At high ionic strength, a small dose (2 mg L$^{-1}$) of HA stabilized the NP suspension significantly. This stabilization effect is substantially enhanced with increasing HA concentration (Hu et al., 2010). The calculated DLVO (Derjaguin-Landau-Verwey-Overbeek) interaction energy profiles, using experimentally determined values of the Hamaker constant reveals the possible presence of
secondary energy minima and the possibility of dis-aggregation of magnetite agglomerates. Hu et al. (2010) confirmed the interaction of HA–NPs and the HA effects on NP aggregation by using atomic force microscope observations.

1.6 Ternary Systems
There has not been much study of 'ternary' systems (metal ions, humic substances and mineral phases together) even though they are quite common in the environment. It is crucial to understand these systems, and to be able to predict their behaviour. The current studies in this area have focussed upon the behaviour of metal ions in ternary systems. In these systems, there are a number of interactions that need to be considered: the metal ion with the humic; the metal ion with the mineral and the humic with the mineral. The binary interactions must be studied and modelled first before the full ternary system can be studied. There are only a few models that model ternary system data, and all those consider the behaviour at equilibrium.

1.7 Fractionation of HS on Exposure to Mineral Surfaces
In the study of humic acid sorption onto a quartz sand surface, Pitois et al. (2008) discovered that the sorption of humic acid occurs at every initial humic acid concentration (20 ppm (w.v) to 500 ppm (w.v)). There is an initial rapid uptake of the humic acid during the first few days, followed by a much slower uptake over the next few weeks, i.e. there is multicomponent behaviour. They suggest that the heterogeneity in kinetic behaviour could be the result of heterogeneous humic binding sites on the surface, or due to the heterogeneity of the humic material in solution, or, more probably, both.

Pitois et al. (2008) found that the preferential adsorption of humic acid fractions onto mineral surfaces is significant, since it modifies the composition of the humic acid remaining in equilibrium in the aqueous phase. There is an initial, rapid uptake of humic acid molecules onto quartz sand, followed by a much slower uptake. The
molecular weight distribution of residual humic acid in solution after adsorption deviates from the original molecular weight distribution, showing preferential adsorption of certain molecular weight components. Weight-average molecular weights ($M_w$) of Aldrich humic acid originally, after the initial, rapid uptake (3 days), and after the slower uptake (45 days) were found to be 3900, 4750, and 3800 Da, respectively. Fractionation changes with time from 3 to 45 days. Humic acid molecules of molecular weight below 4800 Da and of $M_w$ 1450 Da were adsorbed after the fast kinetic step, whereas humic acid molecules in the molecular weight range 1400-2900 Da and of $M_w$ 3700 Da were adsorbed after the slower uptake. Pitois et al. (2008) suggest that these results combined with absorbance ratio data suggest that the adsorption of low molecular weight aromatic humic components takes place initially, followed by the adsorption of higher molecular weight, more aliphatic humic components. No displacement of low molecular weight fractions by higher molecular weight fractions has been observed over time. In the ternary Eu$^{3+}$/HA/quartz sand system, the sorption behaviour of the Eu$^{3+}$ is closely related to that of the humic acid, because of the formation of ternary complexes, i.e. the slow sorption of Eu$^{3+}$/humic acid complexes.

1.8 Modelling

1.8.1 Modelling Binary Systems

In order to predict metal ion behaviour in the environment, it is important to develop models of metal ion/HS speciation. A majority of previous studies have focussed on the behaviour of stable element systems, such as the heavy metals. Although a number of models have been proposed over the years to describe the interaction of stable element metal ions, two models have worked better and have been applied more widely than the others. These models are Model VI (Tipping, 1998) that simulates the chemical heterogeneity with a finite number of discrete binding sites and the NICA model (Kinniburgh et al., 1999) that uses a continuous
distribution approach. Despite their heterogeneity, it has been found that metal ion binding to HA and FA is independent of the source, and for both models generic parameters have been determined that work well for all HA/FA samples (Milne et al., 2003; Tipping, 1998). The advantage of these models is that both have been included in general speciation codes, WHAM-VI (MODEL VI) and ECOSAT (NICA), which allow inorganic processes such as hydrolysis and complexation by simple ligands to be simulated. These codes have been used to simulate metal ion speciation in complex systems containing HA/FA such as ECOSAT/NICA, which has been used to calculate the speciation of metals in groundwaters, soils and soil solutions (Fest et al., 2007; Lumsdon, 2004; Weng et al., 2002). WHAM/MODEL VI has been applied to lake and river waters and soils (Cory et al., 2007; Guthrie et al., 2005; Almas et al., 2007). Although they were developed for stable elements, they can be applied to radionuclide systems.

In a study of the heavy metal ion Am, Mills et al. (1991) showed that the equilibrium binding of metal ions to colloids enhanced the transport of metals. A one-dimensional model for simulating transport of contaminants and colloids in porous media (COLTRAP) was used to compare the simulation results with experimental data. The work showed that COLTRAP can successfully describe some of the important characteristics of colloid facilitated transport of radionuclides under certain conditions (Van de Weerd, 1997). The dissociation of Am from the humic colloids was a slow process, and without treating the interaction between Am and humic colloid with kinetics, the experimental data were impossible to simulate.

NOMADS is a relatively simple mechanistic model that describes the competitive kinetic adsorption behaviour of a heterogeneous mixture of natural organic molecules. Van de Weerd et al (1999) showed that the adsorption and desorption data on to iron and aluminium hydroxides, including hysteresis, can be described well with a relatively simple kinetic model. The model describes all the data without changing the model parameters.
Sasaki et al. (2008) developed a discrete fragment model for complex formation of Eu$^{3+}$ with humic acid. The model decomposes the humic into discrete fragments of functional groups (carboxyl and phenolic groups) and chelating bridges connecting the functional groups. The model requires the thermodynamic parameters corresponding to all the fragments. The acid dissociation and metal complexation constants of all the sites and pairs were taken from the literature and experimental values in order to calculate the overall values for the humic acid system. The simulated curves of the overall formation constant depending on the concentration of Eu were consistent with the experimental data and the model was found to be useful for metal complexation reactions of polyvalent metal ions with strong but less abundant binding sites.

The effect of metal loading on the binding of all of the rare earth elements (REE) to humic acid (HA) was studied by combining ultrafiltration and Inductively Coupled Plasma Mass Spectrometry techniques (Marsac et al., 2010). REE–HA binding experiments were performed at pH 3 for REE/C (molar ratio ranging from $10^{-3}$ to $1.5 \times 10^{-2}$, with C corresponding to the amount of organic carbon). The relative amount of REE bound to HA strongly increases with decreasing REE/C. Binding strengths at low metal loading exhibit a regular increase from La$^{3+}$ to Lu$^{3+}$. The authors propose that the variability of REE–HA binding patterns studied so far (Yamamoto et al., 2005, 2006; Sonke and Salters, 2006; Pourret et al., 2007; Stern et al., 2007) is not an artefact resulting from the use of different analytical procedures. Further, this effect is the result of the presence of two types of humic binding site, which occur in distinct proportions and have different binding affinities for the REE.

Calculations performed using Tipping's (1998) Model VI show that the two types of sites involved in the binding of REE with HA can be defined by the Model VI intrinsic $\log K_{MA}$ and $\Delta LK_2$ parameters, the $\Delta LK_2$ parameter being free to vary along the REE series. High-density, but weak sites determine the distribution of
REE to HA at high REE/C, favouring the complexation of the middle REE (Nd³⁺ to Ho³⁺). By contrast, the few strong sites determine the distribution of REE to HA at low REE/C, favouring the heavier REE (Ho³⁺ to Lu³⁺) complexation. Some studies suggest that the few strong sites activated at low REE/C could be multi-dentate carboxylic sites, or perhaps N-, or P-functional groups, whereas the weak sites involved at high metal loading are likely to be monodentate carboxylic sites (Sonke and Salters 2006; Pourret et al., 2007; Yamamoto et al., 2010). Model VI closely reproduces the observed variations. Hence, this model is a very powerful tool for studying REE binding by HA within the humic mixture. Overall, the results suggest that further factors, such as competition from other cations and/or colloidal nano-oxides within the humic mixture could be responsible for the differences between model predictions and reality. They suggest that including these factors could improve the understanding and prediction of cycling and transport in natural systems (Marsac et al., 2010).

1.8.2 Modelling Ternary Systems

Bryan et al. (2005) used the k1-D transport code to model the effect of humic substances on the transport of Co²⁺ through columns packed with sand, and Eu³⁺ through intact sandstone blocks. In both cases, two humic bound metal fractions were required, exchangeable and non-exchangeable. No significant elution of metal ions occurred when humic was absent for either study. The humic/Co²⁺ complex was retarded when compared to a conservative tracer by formation of ternary complexes. The interaction did however seem to be reversible and could be modelled using a single equilibrium constant. The humic/Eu³⁺ complexes in the sandstone experiments also showed retardation, but it was more complex, requiring two kinetic equations and associated rate constants. Warwick et al. (2000) were successful in modelling Eu³⁺ transport in humic equilibrated columns using the k1-D code without considering humic/metal complex sorption, but these experiments were carried out using sand, rather than sandstone.
In the Linear Additive approach, the behaviour of the full ternary system is simulated with just the separate binary models: this is not always successful (Lippold and Lippmann-Pipke, 2009), since the presence of humic may affect the behaviour of the metal ion and vice versa (Evans et al., 2007). The formation of ternary complexes is crucial to understanding these systems. There are two general types: in the first, type (I), the humic acts as a bridge between the mineral and the metal ion, whilst in the second, type (II), it is the metal ion that bridges. In the ternary systems, there are two general limiting behaviours for the metal. If the metal-mineral interaction dominates, then the metal sorption will not be affected by the presence of the humic (provided that the humic does not prevent sorption by coating the surface), but if the humic-metal interaction dominates, then the metal sorption will follow the behaviour of the host humic (which may be different to that of the bulk). The importance of ternary complexes depends upon the metal ion. Warwick et al. (2005) studied ternary systems of Cs⁺, Cd²⁺, Ni²⁺ and Eu³⁺ with goethite, montmorillonite and kaolinite. They found that the importance of ternary complexes increased in the order: Cs⁺ ≈ Cd²⁺ < Ni²⁺ ≈ Eu³⁺. It has been shown that the success of the linear additive approach is a function of the metal ion/humic stability constant. As it increases, the humic dominates the chemistry, and the performance of the linear additive approach improves (Evans et al., 2007), which makes this a very significant development. Lippold and Lippmann-Pipke (2009) showed that metal adsorption onto clay materials increased in the presence of humic matter throughout the acidic pH range (pH 2 - 5). Although the general trends of this effect can be explained by the pH dependences of metal–humate complexation and humic acid adsorption, quantitative estimates by means of the linear additive approach did not reproduce the experimental data. Lenhart and Honeyman (1999) modelled uranium (VI) sorption to hematite in the presence of HA using a multi-ligand, equilibrium approach, with 5 distinct components, each with a distinct interaction.
In the ternary systems, the metal ions may behave like the humic itself, which has important implications for predicting radionuclide transport. Therefore, a number of groups have studied the behaviour of the humic itself. Using C(1s)-NEXAFS and UV spectroscopy, Claret et al. (2007, 2008) found that at high humic to solid phase ratios, fractionation of humic substances takes place as certain parts of the humic distribution are preferentially sorbed. For Al$_2$O$_3$ and fulvic acid, fractionation is significant for ratios larger than 20 mg FA per g of solid, and for humic acid, the limiting ratio is 25 mg HA per g of solid. Importantly, they see differences in the luminescence spectra of the Eu$^{3+}$ complexes as fractionation proceeds. Hence, fractionation like this may be partly responsible for the failure of the linear additive approach since the humics on the surface and in solution appear to have different coordination. Support comes from another study that found that the various fractions of humic acid can show different complexation properties (Brevet et al., 2007).

Kaplan et al. (2009) studied the sorption of Eu to two sediments (clayey sediment and sandy sediment from Savannah River Site) in the presence of natural organic matter (NOM). Europium sorption to sediments systematically increased as pH increased from 3.9 to 6.7. Europium sorption increased to a maximum and then decreased with increasing additions of NOM (Kaplan et al., 2009). The initial increase of sorption with increasing NOM additions was presumed to be attributed to NOM sorbing to the sediment and creating more surface sorption sites, NOM$_{sed}$, and/or increasing the association constant (log K) for the Eu-sediment surface reaction, which is clear evidence for a ternary complex. Decreased Eu sorption at higher NOM levels was attributed to Eu partitioning to NOM$_{aq}$, rather than to the NOM$_{sed}$ or directly to the sediment. Kaplan et al. (2009) developed a multiple sorption model to describe the Eu–NOM-sediment system by combining models developed to describe three binary systems: Eu–NOM$_{aq}$, Eu-sediment and NOM$_{aq}$-sediment. The model simulations predict that at all levels of added NOM, Eu speciation was dominated by interaction with NOM$_{aq}$ or NOM$_{sed}$. Conditional
stability constants for the complexation of Eu to \( \text{NOM}_{\text{sed}} \) were as much as four orders of magnitude greater than that for \( \text{NOM}_{\text{aq}} \), the authors suggested that this was the result of the \( \text{NOM}_{\text{sed}} \) becoming more negative due to charge associated with sediment surfaces, but the actual mechanism requires further elucidation. At high \( \text{NOM}_{\text{aq}} \) levels, >99 mg/L C, the model captured the trend of reduced Eu sorption but tended to over-estimate Eu sorption. The additivity approach (combining binary models to form a ternary model but allowing the sediment phase humic to have a different affinity for the metal ion) was generally successful and shows an advance over the simplification of treating the chemistry of \( \text{NOM}_{\text{sed}} \) as identical to that of \( \text{NOM}_{\text{aq}} \). The model has been used in a risk assessment for Eu transport at a low level waste disposal facility, where the NOM concentrations were projected to range from <1 to 200 mg/L C.

1.9 Aims and Objectives

A major aim of this work is to gain further understanding of the mechanisms involved in the binding of metal ions by HS, in both binary and ternary systems. The work will attempt to further understand the kinetics of the metal humic interaction.

The range of experiments was selected to investigate the interactions in metal ion/magnetite/humic ternary systems, which can determine the solid/solution partitioning of metal ions in the environment, and hence has consequences for radionuclide transport. The reason for choosing magnetite is that not much work has been done with magnetite, but it could play a vital part in the transport of radioactive materials away from a waste repository in the environment, because it is predicted to form in the environment of a radioactive waste repository.

The overall aim of this type of work is to develop mathematical descriptions of the processes so that predictions of radionuclide mobility may be made in support of safety cases in the radiological performance assessment (RPA) of radioactive
waste repositories or for the general prediction of radionuclide transport in the environment.

Little previous work has investigated the simultaneous interaction of humic acid and metal ions with magnetite. The adsorption/desorption interactions of binary systems (HA/magnetite) and ternary systems (HA/Eu³⁺/magnetite) under a range of conditions will be studied. Batch experiments studying the sorption behaviour of HA and Eu encountering multiple ‘fresh’ samples of magnetite surface in binary systems and ternary systems will be studied. This successive sorption type experiment will simulate humics and humic-metal complexes encountering fresh magnetite surfaces as they transport.

Previous work has shown that fractionation of humic occurs on contact with mineral surfaces (Pitois et al. 2008; Claret et al. 2007, 2008), therefore whole humic acid will be ultrafiltrated and split into four size fractions (HA<3 kDa; 3<HA<10 kDa; 10<HA<100 kDa and HA>100 kDa) in order to investigate the separate behaviour of the fractions and to compare that with the behaviour of the whole humic. For the first time, these humic acid fractions will be investigated in the adsorption/desorption interactions of binary systems (HA fractions/magnetite) and ternary systems (HA fractions/Eu³⁺/magnetite). The successive sorption of HA fractions and their complexes in binary and ternary systems will also be studied. For the first time, the Aysmmetric Flow Field Fractionation technique will be used to study the size fractionation of humic acid upon sorption to magnetite surface.

The dissociation rate constants for non-exchangeably bound Eu³⁺ and the amounts of Eu³⁺ in whole unfractionated HA and the HA size fractions for different equilibration times (the time that the humic acid and metal ions are left to equilibrate) will be measured. The Eu³⁺ binding strength of the whole HA and the HA size fractions will be studied using an ion exchange technique.
A mathematical model will be developed that will attempt to predict the binary interactions (whole HA and HA size fractions with magnetite) and ternary interactions (whole HA/HA fractions/Eu$^{3+}$/ magnetite). The k1-D modelling of Bryan et al. (2005) that includes the exchangeable and non-exchangeable binding modes will form the basis of the modelling of the ternary system data. The dissociation rate constants for non-exchangeably bound Eu$^{3+}$ from the resin experiments will be used to calculate the rate constant parameters and these parameters will be applied to the model to help reduce the number of undefined parameters. It is hoped that the model developed here will contribute to the prediction of radionuclide migration in the environment.
Chapter 2

Experimental
2.1 Experimental Techniques

2.1.1 UV/Vis Spectroscopy

UV/Vis spectroscopy was used to determine the concentration of humic acid solutions by using a single wavelength each time to determine the concentrations. Some initial spectra of various Aldrich humic acid solutions were taken in the wavelength range 200 – 700 nm. Humic acid solutions absorb most strongly in the UV region and weakly in the longer wavelength, visible region. To minimise the error associated with absorbance measurements, the absorbance values must be sufficiently high so that they can be accurately measured by the spectrometer. Very low absorbance values (A < 0.05) will have a relatively large error associated with them. Absorbances that are very high (A > 1) are subject to a large error due to > 90 % of the incoming radiation being absorbed by the sample. Tests showed that humic acid concentrations above 200 ppm (w.v) had very high absorbances with inherent noise at wavelengths below 400 nm. For the concentrations being analysed in this study, 400 nm was chosen as the ideal wavelength for determining the concentrations.

For all experiments involving just humic acid in the presence of the mineral, magnetite, UV/vis spectra were recorded in a 1 cm quartz cuvette on a PG instruments T-60 UV-visible spectrometer.

2.1.2 Gamma Spectroscopy

The $^{152}$Eu analytical concentration was determined by gamma spectrometry. Aliquots (1.5 ml) were counted on either a high purity germanium semi-conductor gamma-detector (Canberra Ltd.) or a Lo-ax low energy gamma photon semiconductor detector (EG&G), both attached to a signal treatment analyser EG&G Model 919 ADC (analogue-to digital converter) and MCA (multi channel analyser).
2.2 Experimental Methods

A major aim of this work was to investigate the processes and reactions that are involved in the transport of metal ions in the environment.

The range of experiments performed were selected in order to investigate the interactions in metal ion / mineral / humic ternary systems, which can determine the solid / solution partitioning of metal ions, and hence the consequences for metal radionuclide transport.

Previous studies have shown that metal ions bound to HA ‘non-exchangeably’ take on the properties of the humic molecule itself. As such, the first stage of this work was to focus on the sorption and desorption behaviour of HA under a wide range of experimental conditions. Simple sorption batch experiments were performed at a wide range of initial humic concentrations. For the humic-magnetite binary experiments the lowest initial concentration was 10 ppm (w.v), as concentrations below this approach the instrument’s limit of detection. The highest initial humic concentration studied was 200 ppm (w.v).

In each experiment, a range of reactant concentrations was studied. In most cases, it was humic concentration that varied, but in some cases it was the size of humic fraction. The wide range of concentrations chosen was to enable rigorous testing of the mathematical models. A good test for a model is its ability to predict behaviour over a wide range of concentrations.

Experiments were generally performed at pH 6, which is a realistic value for typical environmental conditions.

The kinetics of reactions in these systems were studied, as this may have important consequences for transport.
A migrating humic molecule or humic / metal ion complex is likely to encounter new, ‘fresh’ mineral surface during transport. Batch experiments were carried out to investigate the sorption behaviour of a humic solution exposed to multiple, successive samples of mineral surface. After a period of sorption the humic solution was separated from the mineral phase and introduced to a fresh mineral sample and the subsequent sorption measured.

Experiments carried out using gamma-ray spectrometry had a total Eu concentration of $7.9 \times 10^{-10}$ mol dm$^{-3}$. This trace concentration was selected as it represents the concentrations of radionuclides that may be found some distance from a waste repository (far-field).

All the volumes of solutions in the following experiments were measured using Finn-pipettes and all chemicals were at analytical grade. All solid chemicals were measured out in a weighing boat on a 6 figure balance. When adjusting the pH, HCl (0.01 mol dm$^{-3}$) and NaOH (0.01 mol dm$^{-3}$) were used. All water used in the experiments was 18 MΩ deionised water (Millipore). The humic acid used in the experiment was obtained from the Aldrich Company and is a sodium salt. Samples were left to stand for 5 minutes after being removed from shaker and were centrifuged at 3500 rpm for 5 minutes on a MSE 3000i centrifuge prior to analysis (UV/vis spectrometry or γ spectrometry).

### 2.2.1 Humic Stock Solution

A 1000 ppm (w.v) stock solution was made by dissolving humic acid (0.1 g) in water (100 ml) made up to volume in a 100 ml volumetric flask. The solution was transferred to a 125 ml polypropylene container and screw cap, which was sealed with parafilm.
2.2.2 Conditioning of Cellphos

Cellulose phosphate sodium salt (Cellphos) resin (10 g) was conditioned by stirring it for 24 hours in an electrolyte solution of NaClO₄ (0.1 mol dm⁻³, 10 ml) and water (90 ml), in a 100 ml polypropylene container with screw cap with the ratio of 1 g resin to 10 ml electrolyte. The pH was maintained at pH = 6.0 ± 0.1. After 24 hours, the resin was allowed to settle, and the supernatant was removed. The resin was air-dried and stored in a 100 ml polypropylene container with screw cap.

2.2.3 Conditioning of Dowex

Dowex 50WX4-200 (20 g) was added to a column and washed with the following solutions in order: Deionised water (150 ml), HCl (2 mol dm⁻³, 500 ml), Deionised water (500 ml), NaCl (3 mol dm⁻³, 500 ml), NaOH (0.1 mol dm⁻³, 500 ml) and deionised water (500 ml). The Dowex was then transferred to a 250 ml beaker with NaClO₄ (1 mol dm⁻³, 10 ml) and water (90 ml) at pH = 6.0 ± 0.1 and left to stir for 4 - 6 hours. After stirring, the Dowex was filtered using filter paper and a glass funnel, and then transferred to a large watch glass, where it was left to dry overnight and then stored in a 100 ml polypropylene container with screw cap.

2.2.4 Ultrafiltration

Humic stock (200 ml) was ultrafiltrated through a Millipore ultrafiltration 100 kDa membrane (regenerated cellulose) using a Millipore Amicon 8200 stirred ultrafiltration cell connected to a regulator on a pressurised nitrogen gas cylinder at 75 psi. After the solution was fully filtered, the remaining solution was a concentrated HA>100 kDa fraction. The filtered solution was then filtered through a 10 kDa membrane using the same method which gave a remaining concentrated fraction of 10<HA<100 kDa. The filtered fraction from the 10kDa was then filtered one last time through a 3 kDa membrane using same method which yielded two concentrated fractions of 3<HA<10 kDa and HA<3 kDa. The following 4 concentrated fractions: HA>100 kDa, 10<HA<100 kDa, 3<HA<10 kDa and HA<3
kDa were then diluted to 20, 50 and 100 ppm (w.v) humic concentrations by water using the PG instruments T-60 UV-visible spectrometer and a 1 cm quartz cuvette.

2.3 Experimental Summary

The Figure below shows the various interactions of HA / HA fractions / Metal Ion / Mineral in the experiments.

![Figure 2.1: Summary of interactions in the experimental.](image)

2.4 General Description for UV/Vis Analysis

In order to compare the results directly, all samples were (unless stated otherwise) prepared and analysed as described below.

For all experiments with the magnetite as a constant mineral: a solid solution ratio of 0.05 g to 10 ml was used. Prior to the addition of the mineral, the humic acid solutions were made up in 10 ml polysulphone tubes with screw caps, and sealed using Parafilm. The pH was adjusted to 6.0 ± 0.1 using an Orion model 720 pH meter with a BDH glass combination electrode using HCl and NaOH. Ionic strength was fixed at 0.1 mol dm⁻³ using NaClO₄. Aliquots were removed for analysis at intervals and then returned to the experiment, so that the total volume was
constant. Between analyses, the sample tubes were shaken lengthways at 100 rpm on an automatic shaker. Prior to analysis, the samples were removed from the shaker and allowed to settle for five minutes after which centrifugation was performed. The aliquots were returned to the sample tubes following analysis.

2.4.1 Sorption of Humic Acid for 1 Month
Solutions were prepared as described in the general description with humic acid present in the following concentrations: 10, 50, 100 and 200 ppm (w.v) with a solid solution ratio of 0.05 g to 10 ml. Analysis was performed on the solutions prior to the addition of mineral, and at regular intervals afterwards over a period of 30 days.

2.4.2 Humic Acid Desorption
The reversibility of HA sorption was tested in desorption experiments. Humic acid solutions were prepared with concentrations of 10, 50 and 100 ppm (w.v). UV/Vis spectra were recorded before the addition of magnetite, and at regular intervals afterwards. After 4 days the solution was separated from the mineral and a fresh solution (with the same ionic strength and pH, but without any humic acid) was added to the mineral. UV/Vis spectra were taken at regular intervals for a further 8 days to observe if any humic acid desorbed and re-entered solution.

2.4.3 Humic Sorption in the Presence of Europium
UV/Vis absorption spectroscopy was used to study the interaction of humic acid with magnetite in the presence of europium at regular intervals for 31 days. The effect of europium solution concentration on the sorption behaviour of humic acid was investigated. Samples were prepared as described in the general description, except that the solutions also contained additional varying amounts of non-radioactive isotopes of europium, in the form of Eu(NO₃)₃. Solutions of 10⁻⁵, 10⁻⁶, 10⁻⁷ and 10⁻⁸ mol dm⁻³ Eu were each equilibrated with 50 and 100 ppm (w.v) humic acid. The humic acid and europium were allowed to equilibrate in the sample tubes for 24 hours before the mineral was added.
2.4.4 Humic Acid Successive Sorption

The behaviour of multiple, successive humic sorption steps was investigated and prepared in the general description, with HA concentrations of 50, 100 and 200 ppm (w.v). After 9 days (216 hours) of contact time with the magnetite (in which regular analysis was performed), the humic acid solutions were separated from the magnetite. Another amount of fresh magnetite was then added to each solution maintaining the solid solution ratio of 0.05 g to 10 ml. The sorption behaviour was analysed for a further 6 days (144 hours) and then the magnetite was replaced again with fresh sample with further analysis for 6 more hours giving three sorption steps.

2.4.5 Sorption of Humic Fractions for 1 Month

Solutions were prepared as described in the general description except with humic fractions (HA<3 kDa, 3<HA<10 kDa, 10<HA<100 kDa and HA>100 kDa) in the following concentrations: 20, 50 and 100 ppm (w.v) for the magnetite with a solid solution ratio of 0.05 g to 10 ml. Analysis was performed on the solutions prior to the addition of mineral, and at regular intervals afterwards over a period of 31 days. Prior to analysis, the samples were removed from the shaker and allowed to settle for five minutes after which centrifugation was performed. The aliquots were returned to the sample tubes following analysis.

2.4.6 Humic Fractions Desorption

The reversibility of HA size fraction sorption was studied. Humic fraction (<3 kDa, 3<HA<10 kDa, 10<HA<100 kDa and HA>100 kDa) solutions were prepared with concentrations of 100 ppm (w.v). UV/Vis spectra were recorded before the addition of magnetite, and at regular intervals afterwards. After 14 days the fractions were separated from the mineral and a fresh solution (with the same ionic strength and pH, but without any humic acid) was added to the mineral. UV/Vis spectra were
taken at regular intervals for a further 16 days to observe if any humic acid desorbed and re-entered solution.

2.4.7 Humic Fractions Sorption in the Presence of Europium

The behaviour of humic fractions (<3 kDa, 3<HA<10 kDa, 10<HA<100 kDa and HA>100 kDa) in presence of higher concentration of europium was studied. Samples were prepared as described in the general description, except that the solutions also contained additional varying amounts of stable isotopes of europium, in the form of Eu(NO$_3$)$_3$. Solutions of 10$^{-5}$, 10$^{-6}$, 10$^{-7}$ and 10$^{-8}$ mol dm$^{-3}$ Eu were each equilibrated with 20, 50 and 100 ppm (w.v) humic acid. The humic acid and europium were allowed to equilibrate in the sample tubes for 24 hours before the mineral was added. UV/vis spectra were taken at regular intervals for 31 days.

2.4.8 Humic Fractions Successive Sorption

This experiment was quite similar to the humic successive sorption experiment, except that humic fractions (<3 kDa, 3<HA<10 kDa, 10<HA<100 kDa and HA>100 kDa) were used, at concentrations of 50 ppm (w.v), and 100 ppm (w.v). After 14 days of contact time with magnetite (with UV/vis spectra taken at regular intervals), the humic fraction solutions were separated from the magnetite. Another amount of fresh magnetite was then added to each solution, keeping the solid: solution ratio of 0.05 g to 10 ml. The sorption behaviour was analysed for a further 14 days, and then the magnetite was replaced again with fresh sample and UV/vis spectra taken regularly for 4 more days, giving a third sorption step.

2.4.9 Humic Fractions sorption at Varying Ionic Strengths

Solutions were prepared as described in the general description with humic fractions (<3 kDa, 3<HA<10 kDa, 10<HA<100 kDa and HA>100 kDa) except the ionic strengths were varied between 0.01, 0.1, 1 and 3 mol dm$^{-3}$, with the humic concentration being constant at 100 ppm (w.v). Once magnetite was added, UV/vis spectra of the samples were taken regularly for 31 days.
2.4.10 Humic Fraction Combination Sorption

Solutions were prepared as described in the general description except with humic fractions combined (HA<3 kDa and 3<HA<10 kDa, HA<3 kDa and HA>100 kDa) in the following concentrations: 20 and 100 ppm (w.v) with a solid: solution ratio of 0.05 g to 10 ml. Analysis was performed on the solutions prior to the addition of mineral, and at regular intervals afterwards over a period of 30 days.

2.5 General Description for γ - Spectrometry Analysis

The techniques for preparing samples for analysis by gamma spectroscopy were the same as those for UV-Vis analysis, but with the following exceptions: unless otherwise stated, the total Eu concentration (active plus non-active isotopes) was $7.91 \times 10^{-10}$ mol dm$^{-3}$ and $^{152}$Eu activity was 0.13 kBq ml$^{-1}$; analysis was performed on 1.5 ml aliquots from each sample. The europium solution concentration was determined by observing the net area of the characteristic $^{152}$Eu gamma peak at 121.8 keV. Prior to analysis, the samples were removed from the shaker and allowed to settle for five minutes after which centrifugation was performed (3500 rpm, 5 minutes). The aliquots were returned to the sample tubes following analysis.

2.5.1 Europium Sorption in the Presence of Humic Acid

Gamma ray spectrometry was used to study the interaction of $^{152}$Eu with magnetite in the presence of HA. The HA concentrations studied were 0 (no HA present), 20, 50 and 100 ppm (w.v). The 0 ppm (w.v) HA systems were used to determine the strength of the interaction between europium and the mineral in the absence of humic acid. Gamma ray spectra of the samples were recorded before the mineral was added. The humic acid and europium were allowed to equilibrate in the sample tubes for 24 hours before the mineral was added. After the addition of mineral, the solution concentration of $^{152}$Eu was monitored for 30 days.
2.5.2 Europium 24 hours / 7 days Adsorption / Desorption in the Presence of Humic Acid

The reversibility of europium sorption to magnetite in the presence of humic acid was investigated. Two batches of humic acid with concentrations of 50, 100 and 200 ppm (w.v) were used. The humic acid solutions were equilibrated with europium for 24 hours, their gamma ray spectra were recorded, and then magnetite was added. After 1 day, one batch had the solutions removed and fresh solutions of the same ionic strength and pH were added that had the same humic acid concentrations before the addition of magnetite (50, 100 and 200 ppm (w.v)). The gamma ray spectra of the samples were recorded at regular intervals for a further 16 days. For the other batch the same process was repeated except the samples were left for 7 days once magnetite was added with gamma ray spectra taken at regular intervals before the samples had the solutions removed and replaced. The gamma ray spectra of the samples were recorded at regular intervals for a further 10 days.

2.5.3 Europium 14 days Adsorption / Desorption

The reversibility of europium sorption to magnetite was studied at an Eu concentration of $10^{-5}$ mol dm$^{-3}$. The sample was prepared as described in the general description, except that the solution contained amounts of non-radioactive isotopes of europium, in the form of Eu(NO$_3$)$_3$. The magnetite and europium were left for 14 days in electrolyte solution (Gamma ray spectra taken at regular intervals) before the solution was removed and replaced with the same fresh solution of the same ionic strength and pH. Gamma ray spectra were then taken at regular intervals for 24 days.

2.5.4 Europium Sorption in the Presence of Humic Acid

The study of europium sorption in presence of humic acid was studied as a function of Eu concentration. Samples were prepared as described in the general description, except that the solutions also contained additional varying amounts of
non-radioactive isotopes of europium, in the form of Eu(NO$_3$)$_3$. Solutions of 10$^{-5}$, 10$^{-6}$, 10$^{-7}$ and 10$^{-8}$ mol dm$^{-3}$ Eu were each equilibrated with 10, 50 and 100 ppm (w.v) humic acid. The humic acid and europium were allowed to equilibrate in the sample tubes for 24 hours before the mineral was added. Gamma ray spectra were taken at regular intervals for 31 days.

2.5.5 Europium Successive Sorption in Presence of Humic Acid

The behaviour of multiple, successive europium sorption steps was investigated. The systems were prepared in the general description, with HA concentrations of 10, 50, 100 and 200 ppm (w.v). After 13 days of contact time with the magnetite (during which regular gamma ray spectra was taken), the europium / humic acid solutions were separated from the magnetite. Another amount of fresh magnetite was then added to each solution maintaining the solid solution ratio of 0.05 g to 10 ml. The sorption behaviour was analysed for a further 13 days and then the magnetite was replaced again with fresh mineral with further gamma ray spectra taken at regular intervals for 7 more days giving three sorption steps.

2.5.6 Europium Sorption in the Presence of Humic Fractions

Solutions were prepared as described in the general description except with humic fractions (HA<3 kDa, 3<HA<10 kDa, 10<HA<100 kDa and HA>100 kDa) in the following concentrations: 20, 50 and 100 ppm (w.v) with a solid: solution ratio of 0.05 g to 10 ml. Gamma Ray Spectra were taken of the solutions prior to the addition of mineral, the europium and humic fractions was given 24 hours to equilibrate before the addition of magnetite. The samples were analysed at regular intervals afterwards over a period of 30 days. This procedure was repeated but the europium and humic fractions were given 7 days to equilibrate.

2.5.7 Europium Adsorption / Desorption in Presence of Humic Fractions

The reversibility of europium sorption to magnetite in the presence of humic fractions (HA<3 kDa and HA>100 kDa) was investigated. Humic fraction solutions
were equilibrated with europium for 24 hours, their gamma ray spectra were recorded, and then magnetite was added. After 13 days the solutions were removed and fresh solutions of the same ionic strength and pH were added that had the same humic fractions concentrations before the addition of magnetite. The gamma ray spectra of the samples were recorded at regular intervals for a further 3 days.

2.5.8 Varying Order of Preparation and Equilibration Time for Europium Sorption in the Presence of Humic Fractions

The order in which the systems were prepared (humic fractions, europium and magnetite) along with equilibration times were investigated. Preparation of the solutions followed the general description except with humic fractions (HA<3 kDa, 3<HA<10 kDa, 10<HA<100 kDa and HA>100 kDa) in the following concentrations: 20, 50 and 100 ppm (w.v). In one batch the europium and magnetite were left to equilibrate for 7 days before humic fractions were added, and then gamma ray spectra were taken regularly for 28 days. In another batch, the humic fraction and magnetite was left to equilibrate for 24 hours and 7 days in another batch. After the equilibration time, europium was added to both batches and the gamma ray spectra were taken at regular intervals for 31 days.

2.5.9 Europium Successive Sorption in Presence of Humic Fractions

The behaviour of multiple, successive europium sorption steps was investigated and prepared in the general description except with humic fractions (HA<3 kDa, 3<HA<10 kDa, 10<HA<100 kDa and HA>100 kDa) with concentrations of 20, 50, and 100 ppm (w.v). After 13 days of contact time with the magnetite (in which regular gamma ray spectra were taken), the europium / humic acid solutions were separated from the magnetite. Another amount of fresh magnetite was then added to each solution maintaining the solid solution ratio of 0.05 g to 10 ml. The sorption behaviour was analysed for a further 13 days and then the magnetite was replaced.
again with fresh mineral with further gamma ray spectra taken at regular intervals for 7 more days giving three sorption steps.

2.5.10 Europium Sorption in the Presence of Combined Humic Fractions
Solutions were prepared as described in the general description except with humic fractions combined (HA<3 kDa and 3<HA<10 kDa, HA<3 kDa and HA>100 kDa) in the following concentrations: 20 and 100 ppm (w.v) with a solid: solution ratio of 0.05 g to 10 ml. Gamma ray spectra were recorded on the solutions prior to the addition of mineral, and at regular intervals afterwards over a period of 31 days.

2.5.11 Europium Equilibration Ultrafiltration
100 ppm (w.v) humic acid europium mixtures were prepared as followed: Eight lots of NaClO₄ (0.1 mol dm⁻³, 10 ml), water (76.667 ml), humic stock (10 ml) and ¹⁵²Eu (1kBqml⁻¹, 13.333 ml) were added to a 100 ml polypropylene tub with screw caps. The samples were adjusted to pH = 6.0 ± 0.1 and were left for 24 hours, 2, 3, 4, 5, 6, 7 and 14 days to equilibrate before being filtered using a Millipore Amicon 8200 stirred ultrafiltration cell connected to a regulator on a pressurised Nitrogen gas cylinder at 75 psi. Gamma ray spectra were taken of each sample after it had gone through 100 kDa, 10 kDa and 3 kDa membranes.

2.5.12 Eu Dissociation using Cellphos
Two lots of solutions were prepared as described in the general description with 20 ppm (w.v) humic concentrations. In one solution the humic and europium were left to equilibrate for 24 hours, while the other solution was left to equilibrate for 7 days. After these times the conditioned cellphos was added (1 g: 10 ml). Gamma ray spectra were taken prior to addition of the cellphos and at regular intervals afterwards over a period of 39 days.
2.5.13 Eu Dissociation from Size Fractions

The procedure in 2.5.13 was repeated using humic size fractions and concentrations of 20 and 100 ppm (w.v).

2.5.14 Europium Sorption / Desorption in the Presence of Dowex and Humic Fractions

The partition of Eu\(^{3+}\) between solution and Dowex resin was investigated. Dowex (1 g: 10 ml) was left to equilibrate with europium for 48 hours (gamma ray spectra were taken at regular intervals). Solutions were prepared as described in the general description using unfractionated HA, HA<3 kDa, 3<HA<10 kDa, 10<HA<100 kDa and HA>100 kDa at 10 ppm (w.v) concentrations. The humic solutions were added to the Dowex/Eu mixture. Gamma ray spectra were recorded for a further 96 hours.

2.6 Calibration of AF4 Technique.

When using the AF4 technique to analyse samples, calibration was needed at the start of each day. Postnova Polystyrenesulfonate standards (1 kDa, 0.002 g, 10 kDa, 0.002 g and 30 kDa, 0.004 g) were added to water (1000 ml) and mixed well using a 1 litre volumetric flask. An aliquot (0.2 ml) of the PSS standards mixture was removed using a 1 ml syringe and analysed using the AF4 technique to obtain the calibration of the machine for that day. This technique was repeated at the start of the day whenever the AF4 technique was used.

The parameters used in the AF4 analysis are detailed in Table 2.1. The AF4 channel was flushed for 15 min at the start of each day. Flushing was achieved using flow rates of 1 ml min\(^{-1}\), 0.5 ml min\(^{-1}\) and 0.5 ml min\(^{-1}\) for tip flow, focus flow and cross flow, respectively. Flushing was also performed for 15 min between runs. Overnight, flushing occurred at a very low rate (0.1 ml min\(^{-1}\) for both tip and focus flows, with no cross flow).
<table>
<thead>
<tr>
<th>Asymmetric Flow-Field Flow Fractionation</th>
<th>Postnova Analytics AF 2000 Focus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Regenerated cellulose with a cut-off of 5 kDa</td>
</tr>
<tr>
<td>Channel thickness</td>
<td>250 μm</td>
</tr>
<tr>
<td>Injection volume</td>
<td>19.6 μL</td>
</tr>
<tr>
<td>Detector flow rate</td>
<td>1 mL/min</td>
</tr>
<tr>
<td>Focus step</td>
<td></td>
</tr>
<tr>
<td>Injection flow</td>
<td>0.20 mL/min</td>
</tr>
<tr>
<td>Injection time</td>
<td>2 min</td>
</tr>
<tr>
<td>Cross-flow rate</td>
<td>4 mL/min</td>
</tr>
<tr>
<td>Transition time</td>
<td>1 min</td>
</tr>
<tr>
<td>Elution step</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>15 min</td>
</tr>
<tr>
<td>Cross-flow rate</td>
<td>4 mL/min constant</td>
</tr>
<tr>
<td>Carrier solution</td>
<td>0.005 M TRIS solution at pH 9.1</td>
</tr>
<tr>
<td>UV/Visible absorption spectrophotometer</td>
<td>Postnova Analytics SPD-20A</td>
</tr>
<tr>
<td>Wavelength</td>
<td>225 nm</td>
</tr>
</tbody>
</table>

Table 2.1: Experimental conditions for the Asymmetric Flow-Field Flow Fractionation apparatus and the UV/Visible absorption spectrophotometer (AAF4-UV)

### 2.6.1 AF4 Analysis of Humic Sorption

The AF4 technique was used to compare the molecular weight distributions of solution phase HA before and after sorption to magnetite over a period of a month. Water (8.8 ml), NaClO₄ (1 mol dm⁻³, 1 ml), and humic stock (0.2 ml) were added to a 10 ml polypropylene tube and mixed well. The solution was adjusted to pH 6.0 ± 0.1 and then an aliquot (0.2 ml) of solution was removed from the sample tube using a 1 ml syringe and was analysed using AF4 technique on a Postnova Analytics AF2000 Focus Asymmetric Flow-Field Flow Fractionation apparatus...
coupled with a Postnova Analytics SPD-20A Prominence UV/Visible absorption spectrophotometer detector. Due to the destructive nature of the AF4 technique, it was not possible to return the aliquot to the sample tube after analysis. Magnetite (0.05 g) was added to the solution (with readjustment to pH = 6.0 ± 0.1) and the tube was placed in an automatic shaker at 60 rpm for 2 hours. Afterwards, the solution was centrifuged at 3500 rpm for 5 minutes on a MSE 3000i centrifuge, and an aliquot (0.2 ml) of solution was removed from the sample tube using a 1 ml syringe and was analysed using the AF4 technique. This procedure was repeated weekly for a period of a month.
Chapter 3

Results and Discussion
Throughout this chapter, the concentration of HA is expressed in ppm (w.v) and unfractionated humic acid is referred to as HA unless stated otherwise. Eu concentration is expressed as C/C₀, where C is concentration remaining in solution at time = t, and C₀ is the concentration at time = 0. In some figures concentration is expressed as ln(C/C₀) where this gives improved separation of the results. The amount of Eu sorbed, expressed as a percentage of Eu in the system is calculated using (1 - C/C₀) multiplied by 100, and the amount of Eu in the solution, expressed again as a percentage, is calculated using C/C₀ multiplied by 100.

3.1 Kinetics

3.1.1 Europium Dissociation from Humic Acid / Humic Fractions

A series of experiments were used to measure the dissociation kinetics of Eu³⁺-humic complexes and to determine the amount of metal in the non-exchangeable fraction. The resin competition method was used, which has been described earlier.

![Graph](image)

Figure 3.1 (a): The dissociation of Eu³⁺ from humic acid after equilibration times of 1 and 7 days ([HA] = 20 ppm (w.v), pH = 6, I = 0.1 mol dm⁻³, cellphos concentration = 1000 g dm⁻³).
The dissociation of europium from unfractionated humic acid (20 ppm (w.v)) after 1 and 7 days equilibration using cellphos strong exchange resin is shown in Figure 3.1 (a). In both experiments there is a rapid initial removal of Eu$^{3+}$ corresponding to removal of free and exchangeable Eu$^{3+}$. Thereafter, the concentration of Eu$^{3+}$ corresponds to the non-exchangeable fraction. Linear regression was used on the dissociation data to determine the first order dissociation rate constants and the amounts in the non-exchangeable fraction. Table 3.1 shows the first order dissociation rate constants that were calculated from the 1 and 7 days data in Figure 3.1. The first order dissociation rate constant is determined from the gradient of the plots. Because of the low concentrations and the size of the experimental errors, sometimes it is not possible to define an accurate rate constant and instead the data only provide an upper limit (recorded in tables as $<$). Even in experiments where the rate constant could not be defined, it was still possible to estimate the amount bound non-exchangeably.

<table>
<thead>
<tr>
<th>Equilibration Time (Days)</th>
<th>Rate Constant (s$^{-1}$)</th>
<th>Amount in non-exch. (% of total Eu$^{3+}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$&lt; 1.5 \times 10^{-7}$</td>
<td>2.1 (+0.5 / -0.3)</td>
</tr>
<tr>
<td>7</td>
<td>$1.3 (+/- 0.9) \times 10^{-7}$</td>
<td>2.8 (+0.7 / -0.5)</td>
</tr>
</tbody>
</table>

Table 3.1: Humic dissociation kinetics of 1 day and 7 days equilibration between HA and Eu$^{3+}$ along with amounts in non-exchangeable errors = 1σ.

The amount of metal ions in the non-exchangeable is similar for the 1 day and 7 day systems. The rate constants for the 7 day system compares well with those in the literature, where King et al. (2001) found the first-order dissociation rates to be in the range $1.5 - 3.3 \times 10^{-7}$ s$^{-1}$ for Eu$^{3+}$ (pH 6.5, 10 ppm (w.v) HS), while Davis et al. (2000) observed $1.6 - 2.8 \times 10^{-7}$ s$^{-1}$ for Th$^{4+}$ (pH 6.4 - 7.8, 30 ppm (w.v) HS) and Bryan et al. (2008) observed $2.5 - 5.6 \times 10^{-7}$ s$^{-1}$ for Eu$^{3+}$ (pH 6.0, 10 ppm (w.v) HA). The amount of Eu in the non-exchangeable that they observed for a 7 day
equilibration time system (4.9 ± 2.5 %) also matches well with the result in Table 3.1.

Figure 3.1 (b): The dissociation of Eu\(^{3+}\) from humic fractions after equilibration time of 1 day ([HA] = 20 ppm (w.v), pH = 6, I = 0.1 mol dm\(^{-3}\), cellphos concentration = 1000 g dm\(^{-3}\)).

Figure 3.1 (b) shows the dissociation data (cellphos) for different HA size fractions (20 ppm (w.v)) after the Eu\(^{3+}\) and humics were allowed to equilibrate for 24 hours. Table 3.2 gives the kinetic parameters associated with the data in Figure 3.1 (b).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Rate Constant (s(^{-1}))</th>
<th>Amount in non-exch. (% of total Eu(^{3+}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA&lt;3 kDa</td>
<td>&lt; 0.5 x10(^{-7})</td>
<td>1.3 (+0.4 / -0.3)</td>
</tr>
<tr>
<td>3&lt;HA&lt;10 kDa</td>
<td>&lt; 1.8 x10(^{-7})</td>
<td>1.0 (+ 0.4 / -0.2)</td>
</tr>
<tr>
<td>10&lt;HA&lt;100 kDa</td>
<td>1.8 (+/- 0.8) x10(^{-7})</td>
<td>3.0 (+0.4 / -0.3)</td>
</tr>
<tr>
<td>HA&gt;100 kDa</td>
<td>3.3 (+/- 1.9) x10(^{-7})</td>
<td>4.1 (+0.5 / -0.4)</td>
</tr>
</tbody>
</table>

Table 3.2: Humic dissociation kinetics: separate humic fractions rate constants and amounts in non-exchangeable for 1 day equilibration between HA fractions and Eu\(^{3+}\) errors = 1\(\sigma\).

From the data in Table 3.2 as the HA fraction size increases, the amount of europium in the non-exchangeable does increase significantly. Although the rate
constants appear to show an increase, taking into account the scatter in the experimental data, it seems likely that this is an artefact that results from the fact that many of the concentrations are near the limit of detection in these systems.

Figure 3.1 (c): The dissociation of Eu\(^{3+}\) from humic fractions after equilibration time of 7 days ([HA] = 20 ppm (w.v), pH = 6, I = 0.1 mold dm\(^{-3}\), cellphos concentration = 1000 g dm\(^{-3}\)).

The dissociation of europium from different HA size fractions (20 ppm (w.v)) after 7 days equilibration is shown in Figure 3.1 (c). The kinetic parameters are given in Table 3.3.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Rate Constant (s(^{-1}))</th>
<th>Amount in non exch. (% of total Eu(^{3+}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA&lt;3 kDa</td>
<td>3.8 (+/- 0.5) x10(^{-7})</td>
<td>5.1 (+0.5 / -0.4)</td>
</tr>
<tr>
<td>3&lt;HA&lt;10 kDa</td>
<td>2.2 (+/- 0.9) x10(^{-7})</td>
<td>4.0 (+0.8 / -0.6)</td>
</tr>
<tr>
<td>10&lt;HA&lt;100 kDa</td>
<td>2.0 (+/- 0.9) x10(^{-7})</td>
<td>4.5 (+0.9 / -0.6)</td>
</tr>
<tr>
<td>HA&gt;100 kDa</td>
<td>3.3 (+/- 0.4) x10(^{-7})</td>
<td>8.1 (+0.7 / -0.6)</td>
</tr>
</tbody>
</table>

Table 3.3: Humic dissociation kinetics: separate humic fractions rate constants and amounts in non-exchangeable for 7 days equilibration between HA fractions and Eu\(^{3+}\) errors = 1σ.
Taking into account the magnitude of the errors (those in the table are ‘1σ’) there seems to be no significant difference between the rate constants. The most significant result is that the HA>100 kDa fraction has the highest amount of Eu\(^{3+}\) (8.1 %) in the non-exchangeable. Taking into account the errors, similar amounts of metal ion in the non-exchangeable are seen for the other fractions. Comparing the data in Tables 3.2 (1 day) and 3.3 (7 days) given the large uncertainties, particularly for the data in Table 3.2, it is probably impossible to tell if the rate constant changes with the equilibration time, and although the values produced by the regression appear larger in Table 3.3, these data provide no strong evidence for a significant change in rate constant. Further, King et al. (2001) and Monsallier et al. (2003) found that the dissociation rate constant for whole unfractionated humic samples is not affected by the metal-humic pre-equilibration time.

The 7 day data do show higher amounts of Eu\(^{3+}\) in the non-exchangeable across the HA fractions compared to the 1 day data (on average, a 3.1 % increase in absolute terms). For unfractionated humic data, this is expected as a longer equilibration time has been shown to result in transfer from the exchangeable to the non-exchangeable (e.g. Warwick et al., 2000; Bryan et al., 2007).

King et al. (2001) found that the fulvic and humic dissociation rates are quite similar but that the amount of metal bound non-exchangeably is lower for fulvics than for humics. Keepax et al. (2002) suggested this difference may be due to the higher concentration of larger species in humic acid, compared to a fulvic acid. The data in Tables 3.2 and 3.3 support this suggestion as the largest size fractions contain the highest amount of Eu bound non-exchangeably.
Figure 3.1 (d): The dissociation of Eu$^{3+}$ from humic fractions after equilibration times of 24 hours ([HA] = 100 ppm (w.v), pH = 6, I = 0.1 mol dm$^{-3}$, cellphos concentration = 1000 g dm$^{-3}$).

Figure 3.1 (d) shows the dissociation data for different HA size fractions and whole unfractionated humic (100 ppm (w.v)).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Rate Constant (s$^{-1}$)</th>
<th>Amount in non-exch. (% of total Eu$^{3+}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA&lt;3 kDa</td>
<td>&lt; 6.8 x10$^{-6}$</td>
<td>1.0 (+0.2 / -0.1)</td>
</tr>
<tr>
<td>3&lt;HA&lt;10 kDa</td>
<td>&lt; 1.3 x10$^{-7}$</td>
<td>1.1 (+0.2 / -0.1)</td>
</tr>
<tr>
<td>10&lt;HA&lt;100 kDa</td>
<td>&lt; 8.3 x10$^{-8}$</td>
<td>1.1 (+0.2 / -0.1)</td>
</tr>
<tr>
<td>HA&gt;100 kDa</td>
<td>&lt; 6.1 x10$^{-8}$</td>
<td>1.1 (+0.1 / -0.1)</td>
</tr>
<tr>
<td>Whole HA</td>
<td>1.1 (+/- 0.4) x10$^{-7}$</td>
<td>3.5 (+0.2 / -0.2)</td>
</tr>
</tbody>
</table>

Table 3.4: Humic dissociation kinetics: separate humic fractions and whole humic rate constants and amounts in non-exchangeable for the 24 hrs equilibration time. 100 ppm (w.v) data. errors = 1σ.
The dissociation rate constants and amounts of metal ions in the non-exchangeable calculated from the data in Figure 3.1 (d) are shown in Table 3.4. As for the 20 ppm (w.v) 24 hour data, the magnitude of scatter makes it impossible to define values for the rate constants and so it is hard to draw firm conclusion on whether an increase in humic concentration really affects the rate constants.

The most significant result is that the amounts of Eu in the non-exchangeable fraction are not significantly different compared to the amounts for the 20 ppm (w.v) 1 day systems (Figure 3.1 (b)). Therefore, there is no evidence here that humic concentration has an effect on the amount in the non-exchangeable fraction, at least in the concentration range 20-100 ppm (w.v).

### 3.3.2 Equilibration of Europium and Humic Followed by Ultrafiltration

Figure 3.2 below shows the amounts of Eu$^{3+}$ that were measured in each HA size fraction after HA and Eu$^{3+}$ were left for different equilibration times. After 24 hours equilibration the 3<HA<10 kDa fraction has bound the most metal ions. After 2 days the 10<HA<100 kDa fraction has bound more metal ions and the amount in the 3<HA<10 kDa fraction has reduced. The smallest size fraction is responsible for a minority of the Eu binding over the first week of contact but thereafter, it plays no role. The most striking result is that the HA>100 kDa fraction dominates the distribution beyond 3 days. This shows that the largest HA fractions are mainly responsible for binding the metal ion once the equilibration time passes a few days.

Therefore, the results show a distinct shift from the <10 kDa size range to the >10 kDa size range (largely) over a period of a few days. It has been observed that the transfer from exchangeable to non-exchangeable takes place over a time period of a few days to a week (King et al. 2001; Schuessler et al. 2000; Bryan et al. 2007). It is tempting to associate the transfer of metal from exchangeable to non-exchangeable with the shift in distribution.
Figure 3.2: Varying the equilibration times of HA / Eu$^{3+}$ followed by ultrafiltration. (pH 6, I = 0.1 M).
3.2 Humic Interactions in the Magnetite / Eu$^{3+}$ / Humic Ternary System

3.2.1 Simple Humic Acid Sorption on Magnetite

Figure 3.3: Humic sorption in binary HA – magnetite system. (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.3 shows the sorption of HA onto the magnetite surface as a function of humic concentration (pH = 6.0, I = 0.1). Figure 3.3 shows that there is rapid sorption of HA at the start of the experiment when the magnetite is added (10.2, 17.1, 30.2 and 72 % of HA sorbed onto magnetite after 1 day for 200, 100, 50 and 10 ppm (w.v), respectively). The data suggest there is further, slower uptake with time, but the magnitude of the sorption is certainly very low compared to the rapid uptake (16, 28.5, 47 and 89 % of HA sorbed in total after 31 days contact with magnetite for 200, 100, 50 and 10 ppm (w.v)). The relative uptake associated with both the fast and slow sorption of the plots decrease as humic acid concentration increases.
3.2.2 Humic Acid Desorption from Magnetite

Figure 3.4: Replacement of solution in binary HA - magnetite system. (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.4 shows the desorption of HA after 4 days of sorption. In this experiment after 4 days of sorption, the solution was removed and replaced with humic free electrolyte. For systems with total humic concentrations of 100, 50 and 10 ppm (w.v), the concentrations left in solution after sorption were 77.1, 27 and 2.3 ppm (w.v), respectively. There is little desorption of HA from the magnetite back into the fresh electrolyte solution. If the HA interaction with magnetite were reversible, then we would expect 17.7, 12.4 and 1.8 ppm (w.v) observations for the 100, 50 and 10 ppm (w.v) samples, respectively, whereas the actual humic concentrations at the end of the experiment are 0, 1 and 3.3 ppm (w.v), respectively. The 3.3 ppm (w.v) result seems too high and maybe an artefact caused by experimental error due to the very low HA concentration. Therefore, the results show that there is considerable irreversibility in these systems for the 100 and 50 ppm (w.v) systems at least. The system with the lowest humic concentration does appear to give an amount desorbed of the same order as that predicted assuming reversibility, but at such low humic concentrations, the uncertainty is significant.
3.2.3 Humic Sorption in the Presence of Europium

Figure 3.5 (a): The effect of Eu concentration on the sorption of HA onto magnetite ([HA] = 50 ppm (w.v), pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figures 3.5 (a) and (b) shows the effect of europium concentration on the sorption of HA onto magnetite in systems with total concentrations of 50 ppm (w.v) and 100 ppm (w.v), respectively. Eu concentration, even up to relatively high concentrations, appears to have no effect on the sorption of humic onto magnetite at 50 and 100 ppm (w.v). This result is significant, because it means that model parameters for predicting humic behaviour derived from binary humic and magnetite experiments should be valid in the full ternary system too.
Figure 3.5 (b): The effect of Eu concentration on the sorption of HA onto magnetite ([HA] = 100 ppm (w.v), pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

3.2.4 Successive Humic Sorption onto Magnetite

Figure 3.6: Successive adsorption steps of HA onto magnetite (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).
Figure 3.6 shows three successive HA sorption steps onto the magnetite surface as a function of HA concentration. In these experiments, the magnetite was replaced with fresh magnetite after sorption slowed. At each step, there is a rapid uptake of HA when the magnetite is added, followed by slow uptake that appears to approach equilibrium over time. In the first adsorption step, the rapid uptake accounts for 19, 12 and 7.1 % of HA adsorbed after 5 hours for the 50, 100 and 200 ppm (w.v) systems, followed by a more gradual increase in sorption to 32.4, 19.2 and 10.6 % at 216 hours. The amounts sorbed in the 2nd rapid step are 24.7, 13.5 and 8.7 % with respect to the concentration remaining in solution immediately prior to the replacement. There is some evidence for a slower uptake of HA again following the initial drop. In the third and final sorption step 30.4, 16 and 6.3 % of HA is sorbed rapidly to magnetite. Qualitatively at least, the same behaviour (rapid then slow sorption) is observed at all steps and for all concentrations. Table 3.5 shows the summary of the relative humic sorbed at each ‘sorption step’.

<table>
<thead>
<tr>
<th>Sorption step</th>
<th>Time (hours)</th>
<th>50 ppm (w.v) sorbed (%)</th>
<th>100 ppm (w.v) sorbed (%)</th>
<th>200 ppm (w.v) sorbed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st rapid sorption</td>
<td>5</td>
<td>19.0 (± 1.6)</td>
<td>12.0 (± 1.1)</td>
<td>7.1 (± 0.7)</td>
</tr>
<tr>
<td>1st slower sorption</td>
<td>216</td>
<td>13.4 (± 1.2)</td>
<td>7.2 (± 0.7)</td>
<td>14.2 (± 1.3)</td>
</tr>
<tr>
<td>2nd rapid sorption</td>
<td>220</td>
<td>24.8 (± 2.0)</td>
<td>13.5 (± 1.2)</td>
<td>8.7 (± 0.8)</td>
</tr>
<tr>
<td>2nd slower sorption</td>
<td>336</td>
<td>14.1 (± 1.3)</td>
<td>7.1 (± 0.7)</td>
<td>3.3 (± 0.3)</td>
</tr>
<tr>
<td>3rd rapid sorption</td>
<td>340</td>
<td>30.4 (± 2.3)</td>
<td>16.0 (± 1.4)</td>
<td>6.3 (± 0.6)</td>
</tr>
<tr>
<td>3rd slower sorption</td>
<td>672</td>
<td>42.2 (± 2.8)</td>
<td>10.2 (± 0.9)</td>
<td>6.3 (± 0.6)</td>
</tr>
</tbody>
</table>

Table 3.5: Summary of relative HA adsorbed (% of total HA) to magnetite at 50, 100 and 200 ppm (w.v) from the successive adsorption data in Figures 3.6 errors = 1σ.

The rapid uptake increases with each sorption step for the 50 and 100 ppm (w.v) systems. For the slow uptake, there is a significant increase between the steps with the 50 ppm (w.v) system. Table 3.5 shows that the relative rapid and slow sorption of humic changes from step to step.
3.2.5 Humic Fractions Sorption on Magnetite

Figure 3.7 (a): Humic sorption in binary humic fractions – magnetite system. ([HA] = 20 ppm (w.v), pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.7 (b): Humic sorption in binary humic fractions – magnetite system. ([HA] = 50 ppm (w.v), pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).
Figures 3.7 (a), (b) and (c) show the sorption of humic onto the magnetite surface as a function of HA fraction size over 30 days at concentrations of 20, 50 and 100 ppm (w.v), respectively. The whole HA data from Figure 3.3 are reproduced for comparison. Figure 3.7 (a) shows that, as for the whole humic, there is rapid initial sorption of the HA fractions when magnetite is added, followed by a slower uptake for certain fractions. For the lowest concentration of humic (20 ppm (w.v)), the different HA fractions exhibit significantly different levels of sorption in the order of (HA>100 kDa) > (10<HA<100 kDa) > (3<HA<10 kDa) > (HA<3 kDa) > whole HA. This is different to the work of Illés and Tombácz (2004), who measured the size distribution of HA solutions before and after adsorption on magnetite using size exclusion chromatography. They suggested that the smaller humic size-fractions are adsorbed preferentially on the surface of magnetite. Instead, this work suggests that the larger HA sorb most strongly to mineral surfaces, as suggested in previous studies (Pitois et al., 2008; Chorover and Amistadi, 2001; Vermeer and Koopal, 1998; Schmitt et al., 1996; Gu et al., 1995).
Generally, the amount of sorption increases with HA fraction size, but the degree of separation decreases with increasing concentrations (compare Figures 3.7 (a) and (c)).

The results show that binding strengths increase with humic fraction size. Previously, Van de Weerd et al. (1999) have suggested that larger humic fractions should show stronger binding than the smaller fractions, if only because less entropy is lost when covering a surface with a smaller number of large species, compared to a large number of smaller species. Van Riemsdijk et al. (1996) have also suggested that large humic species can sorb more strongly, because they are less prone to electrostatic repulsion from the mineral surface. These experimental results provide evidence to back up these approaches.

The difference in binding strength is significant for radionuclide behaviour, because it suggests that a radionuclide attached to a larger humic species is more likely to be retarded. The reduction in separation with increasing humic concentration may be explained in terms of surface sorption capacity since in the 3 experiments the number of surface binding sites is constant. At low humic concentrations, there are many available sites and hence the capacity to remove large amounts of strongly sorbing species, whilst at higher concentrations the available sites become filled, and so a lower fraction of even strongly sorbing fractions can be removed from solution. The behaviour of the whole humic is interesting, since it most closely resembles the lower size fractions at low concentrations, but becomes more like the larger fractions at higher concentrations.
3.2.6 Humic Fractions Desorption from Magnetite

Figure 3.8: Replacement of solution in binary humic fractions - magnetite system. ([HA] = 100 ppm (w.v), pH 6, I = 0.1 mol dm\(^{-3}\), magnetite concentration = 50 g dm\(^{-3}\)).

Figure 3.8 shows the results of an experiment to test the desorption of the humic size fractions with fresh electrolyte solution after 14 days of sorption in systems with initial concentrations of 100 ppm (w.v). Very small amounts of desorption (3.85 % on average between the different HA fractions) from magnetite are seen. These results are quite similar to the behaviour of the whole humic shown in Figure 3.4. If the sorption were fully reversible, then concentrations of 15.1, 17.5, 18.2 and 18.75 ppm (w.v) would be expected for the HA<3, 3<HA<10, 10<HA<100 and HA>100 kDa systems, respectively. However, the amounts that have actually desorbed are far lower.

Therefore, as for the whole humic experiment, there is considerable irreversibility in these systems. Combined with the results in Figure 3.4, there are implications for radionuclide mobility, since the results suggest that any radionuclide associated with a sorbed humic may be prevented from re-entering solution, and that the retardation due to ternary complex formation will be greater than might be
suggested by a simple $K_d$ determined from batch uptake data. Conversely, given that the humic sorption seems to be irreversible to some extent, once the surface is coated, it might prevent further sorption of humic associated radionuclides.

### 3.2.7 Humic Fractions Sorption in the Presence of Europium

![Graph](image)

**Figure 3.9 (a):** The effect of the sorption of humic fractions onto magnetite in presence of europium $1 \times 10^{-5}$ dm$^{-3}$ ($[HA] = 20$ ppm (w.v), pH 6, $I = 0.1$ mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).
Figure 3.9 (b): The effect of the sorption of humic fractions onto magnetite in presence of europium 1x10^{-6} \text{ dm}^{-3} ([HA] = 20 \text{ ppm (w.v)}, pH 6, I = 0.1 \text{ mol dm}^{-3}, magnetite concentration = 50 \text{ g dm}^{-3}).

Figure 3.9 (c): The effect of the sorption of humic fractions onto magnetite in presence of europium 1x10^{-7} \text{ dm}^{-3} ([HA] = 20 \text{ ppm (w.v)}, pH 6, I = 0.1 \text{ mol dm}^{-3}, magnetite concentration = 50 \text{ g dm}^{-3}).
Figure 3.9 (d): The effect of the sorption of humic fractions onto magnetite in the presence of europium $1 \times 10^{-8} \text{ mol dm}^{-3}$ ($[HA] = 20 \text{ ppm}$, $pH = 6$, $I = 0.1 \text{ mol dm}^{-3}$, magnetite concentration = $50 \text{ g dm}^{-3}$).

Figures 3.9 (a), (b), (c) and (d) show the sorption of HA fractions onto magnetite in the presence of Eu$^{3+}$ at concentrations of $1 \times 10^{-5}$, $1 \times 10^{-6}$, $1 \times 10^{-7}$ and $1 \times 10^{-8} \text{ mol dm}^{-3}$, respectively. There is the same general trend that sorption increases with increasing fraction size for each different Eu concentration (as for the experiments with no Eu). The whole HA system in the presence of Eu shows greater sorption than the smaller individual HA fractions (HA$<3$ kDa and $3<HA<10$ kDa). This suggests that the large fractions ($10<HA<100$ and HA$>100$ kDa) dominate the humic behaviour in the whole unfractionated HA and are mainly responsible for the sorption behaviour in these ternary systems at low HA concentrations.
Figure 3.9 (e): The effect of Eu concentration on the sorption of humic fraction onto magnetite (HA<3 kDa, [HA] = 20 ppm (w.v), pH 6, I = 0.1 mol dm\(^{-3}\), magnetite concentration = 50 g dm\(^{-3}\)).

Figure 3.9 (f): The effect of Eu concentration on the sorption of humic fraction onto magnetite (3<HA<10 kDa, [HA] = 20 ppm (w.v), pH 6, I = 0.1 mol dm\(^{-3}\), magnetite concentration = 50 g dm\(^{-3}\)).
Figure 3.9 (g): The effect of Eu concentration on the sorption of humic fraction onto magnetite (10<HA<100 kDa, [HA] = 20 ppm (w.v), pH 6, I = 0.1 mol dm\(^{-3}\), magnetite concentration = 50 g dm\(^{-3}\)).

Figure 3.9 (h): The effect of Eu concentration on the sorption of humic fraction onto magnetite (HA>100 kDa, [HA] = 20 ppm (w.v), pH 6, I = 0.1 mol dm\(^{-3}\), magnetite concentration = 50 g dm\(^{-3}\)).

Figures 3.9 (e), (f), (g) and (h) show the sorption of the HA fractions (HA<3, 3<HA<10, 10<HA<100 and HA>100 kDa, respectively) onto magnetite in the
presence of different Eu concentrations. For the smaller size fractions (HA<3 kDa; 
3<HA<10 kDa) there is a very slight increase in sorption for the highest Eu concentration (10^{-5} \text{ mol dm}^{-3}). There is little significant difference between the systems at lower Eu concentrations. For the larger HA fractions, there is no significant difference between any of the plots. This suggests that for all the HA fractions, sorption onto a mineral surface is independent of the interaction of Eu with humic species, except for the smallest fractions at the highest concentrations. This result is important because it suggests that in magnetite/HA/Eu ternary systems, the behaviour of the humic may be predicted using model fits from the humic/magnetite binary systems.

### 3.2.8 Successive Humic Fractions Sorption onto Magnetite

![Successive adsorption steps of humic fractions onto magnetite](image)

**Figure 3.10 (a):** Successive adsorption steps of humic fractions onto magnetite ([HA] = 50 ppm (w.v), pH 6, I = 0.1 \text{ mol dm}^{-3}, magnetite concentration = 50 g dm^{-3}).
Figures 3.10 (a) and (b) show the successive sorption of HA size fractions onto the magnetite surface at two different humic concentrations (50 and 100 ppm (w.v)). In these experiments, the magnetite was replaced with fresh magnetite twice to give three ‘sorption steps’. Tables 3.6 and 3.7 show the summary of the relative amounts of HA adsorbed onto the magnetite surface for each HA fraction for the data in Figures 3.10 (a) and (b). In both figures and at both steps, the sorption onto magnetite increases with increasing HA fraction size (see Tables 3.6 and 3.7). At the lower concentration, there is a greater degree of separation between the smallest HA<3 kDa fraction and the other HA fractions. The data points at day 14 and 28 for the HA<3 kDa in Figure 3.10 (a) seem to be irregular as they do not match the general trend for the HA<3 kDa data: this is probably due to experimental error incurred when replacing the magnetite.
### Table 3.6: Summary of relative HA fractions adsorbed (% of total HA) to magnetite at 50 ppm (w.v) from the successive adsorption data in Figures 3.10 (a) errors = 1σ.

<table>
<thead>
<tr>
<th>Sorption step</th>
<th>Time (Days)</th>
<th>HA&lt;3 kDa sorbed (%)</th>
<th>3&lt;HA&lt;10 kDa sorbed (%)</th>
<th>10&lt;HA&lt;100 kDa sorbed (%)</th>
<th>HA&gt;100 kDa sorbed (%)</th>
<th>HA sorbed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; rapid sorption</td>
<td>1</td>
<td>27.5 (± 2.5)</td>
<td>32.8 (± 3)</td>
<td>30.8 (± 2.8)</td>
<td>35.3 (± 3.2)</td>
<td>20.8 (± 2.0)</td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; slower sorption</td>
<td>14</td>
<td>6.5 (± 0.7)</td>
<td>8.8 (± 0.9)</td>
<td>13.6 (± 1.3)</td>
<td>8.3 (± 0.9)</td>
<td>11.6 (± 1.2)</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; rapid sorption</td>
<td>15</td>
<td>28.8 (± 2.6)</td>
<td>50.0 (± 4.4)</td>
<td>50.4 (± 4.4)</td>
<td>58 (± 5.0)</td>
<td>28.9 (± 2.7)</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; slower sorption</td>
<td>28</td>
<td>10.6 (± 1.1)</td>
<td>19.4 (± 1.8)</td>
<td>25.2 (± 2.3)</td>
<td>22.5 (± 2.1)</td>
<td>9.9 (± 1.0)</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; rapid sorption</td>
<td>29</td>
<td>30.0 (± 2.8)</td>
<td>81.6 (± 6.7)</td>
<td>85.3 (± 7.0)</td>
<td>66.7 (± 5.6)</td>
<td>30.4 (± 2.8)</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; slower sorption</td>
<td>30</td>
<td>25.0 (± 2.3)</td>
<td>18.4 (± 1.8)</td>
<td>14.7 (± 1.4)</td>
<td>33.3 (± 3.0)</td>
<td>32.3 (± 2.9)</td>
</tr>
</tbody>
</table>

### Table 3.7: Summary of HA fractions adsorbed (% of total HA) to magnetite at 100 ppm (w.v) from the successive adsorption data in Figures 3.10 (b) errors = 1σ.

<table>
<thead>
<tr>
<th>Sorption step</th>
<th>Time (Days)</th>
<th>HA&lt;3 kDa sorbed (%)</th>
<th>3&lt;HA&lt;10 kDa sorbed (%)</th>
<th>10&lt;HA&lt;100 kDa sorbed (%)</th>
<th>HA&gt;100 kDa sorbed (%)</th>
<th>HA sorbed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; rapid sorption</td>
<td>1</td>
<td>15.0 (± 1.3)</td>
<td>14.1 (± 1.3)</td>
<td>15.3 (± 1.4)</td>
<td>16.5 (± 1.4)</td>
<td>14.8 (± 1.3)</td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; slower sorption</td>
<td>14</td>
<td>3.6 (± 0.4)</td>
<td>8.5 (± 0.8)</td>
<td>8.6 (± 0.8)</td>
<td>8.5 (± 0.8)</td>
<td>4.4 (± 0.4)</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; rapid sorption</td>
<td>15</td>
<td>13.6 (± 1.2)</td>
<td>17.8 (± 1.5)</td>
<td>25.2 (± 2.0)</td>
<td>30.2 (± 2.3)</td>
<td>17.1 (± 1.5)</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; slower sorption</td>
<td>28</td>
<td>6.8 (± 0.6)</td>
<td>6.4 (± 0.6)</td>
<td>5.6 (± 0.5)</td>
<td>8.6 (± 0.8)</td>
<td>3.5 (± 0.3)</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; rapid sorption</td>
<td>29</td>
<td>19.1 (± 1.6)</td>
<td>7.3 (± 0.7)</td>
<td>38.8 (± 2.7)</td>
<td>51.1 (± 3.0)</td>
<td>21.8 (± 1.8)</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; slower sorption</td>
<td>38</td>
<td>3.5 (± 0.3)</td>
<td>8.4 (± 0.8)</td>
<td>3.9 (± 0.4)</td>
<td>6 (± 0.6)</td>
<td>4.6 (± 0.4)</td>
</tr>
</tbody>
</table>
For the 50 ppm (w.v) system, the relative uptakes for the rapid and slow parts increase for all the humic samples with each ‘sorption step’, most significantly for the HA size fractions (3<HA<10 kDa; 10<HA<100 kDa and HA>100 kDa). However, for the 100 ppm (w.v) system, the increase in the relative rapid uptake is much less than for the 50 ppm (w.v) system, and in some fractions (HA<3 kDa; 10<HA<100 kDa and whole HA) the relative slow uptake actually decreases between the 1st and 2nd ‘sorption step’. Overall, the results show that the relative sorption for the rapid and slow parts for each ‘sorption step’ will not be the same. This suggests that the sorption here is complex.

3.2.9 Effect of Ionic Strengths on Humic Fraction Sorption to Magnetite

Figure 3.11 (a): The sorption of humic fractions onto magnetite ([HA] = 100 ppm (w.v), pH 6, I = 0.01 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).
Figure 3.11 (b): The sorption of humic fractions onto magnetite ([HA] = 100 ppm (w.v.), pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.11 (c): The sorption of humic fractions onto magnetite ([HA] = 100 ppm (w.v.), pH 6, I = 1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).
Figures 3.11 (a), (b), (c), and (d) show the sorption of the humic size fractions at different ionic strengths. There is an increase in sorption onto the magnetite surface as HA fraction size increases across all four ionic strengths with unfractionated HA sorbing the most in the 0.01 and 0.1 mol dm$^{-3}$ systems, and the HA>100 kDa fraction sorbing the most in the 1 and 3 mol dm$^{-3}$ systems. Therefore whatever the reason for the stronger sorption of larger fractions, it is the case at all ionic strengths from 0.01 to 3 mol dm$^{-3}$. 

Figure 3.11 (d): The sorption of humic fractions onto magnetite ([HA] = 100 ppm (w.v), pH 6, $I = 3$ mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).
Figure 3.11 (e): The effect of ionic strength on the sorption of humic acid onto magnetite (whole HA, [HA] = 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.11 (f): The effect of ionic strength on the sorption of humic acid onto magnetite (HA<3 kDa, [HA] = 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).
Figure 3.11 (g): The effect of ionic strength on the sorption of humic acid onto magnetite (3<HA<10 kDa, [HA] = 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.11 (h): The effect of ionic strength on the sorption of humic acid onto magnetite (10<HA<100 kDa, [HA] = 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).
Figure 3.11 (i): The effect of ionic strength on the sorption of humic acid onto magnetite (HA>100 kDa, [HA] = 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).

Figures 3.11 (e), (f), (g), (h) and (i) show the sorption of individual humic size fractions at different ionic strengths. The same trend is seen for all of the fractions: the systems with an ionic strength of 3 mol dm$^{-3}$ have the highest sorption of humic onto magnetite, and the 0.01 mol dm$^{-3}$ sorb the least. It is interesting to note that the highest ionic strength greatly enhances sorption for three of the samples (e, h and i).

The unfractionated humic data matches well with the work of Illés and Tombácz (2004) who studied the adsorption of HA onto magnetite and found that increasing ionic strength enhances HA adsorption at each pH due to charge screening. They suggested the dominant interaction is probably a ligand-exchange reaction. Given that the point of zero charge of magnetite is 7.9, these ionic strength effects might seem strange, since the mineral surface will carry a positive charge under the conditions used here, and so the humic will experience an electrostatic attraction towards the mineral surface, which for a simple species would be reduced as ionic strength increases, and the surface and humic charges are shielded. However, an
increase in humic sorption, regardless of surface charge polarity has been observed previously for other surfaces (e.g. Liang et al. 2011; Weng et al. 2007; Tombácz et al., 2000; Kretzschmar et al., 1997; Schlautman and Morgan 1994). The explanation that has been proposed is that the humic substances contract with increasing ionic strength, which reduces the space that each requires on the surface. Further, when the surface is positively charged, because the humic has contracted in size, it is able to get its centre of mass closer to the surface, which increases the attraction and helps to offset any reduction in sorption affinity due to an increase in shielding (Weng et al 2007).

Whatever the mechanism, it is important to be able to predict the effect of ionic strength on humic sorption, because it will indirectly affect the behaviour of any humic bound radionuclides.

3.2.10 Humic Fraction Combinations Sorption to Magnetite

![Graph showing sorption of humic fraction combinations onto magnetite compared with single size fractions HA<3 kDa and 3<HA<10 kDa (HA<3 kDa & 3<HA<10 kDa, [HA] = 20 ppm (w.v), pH 6, magnetite concentration = 50 g dm⁻³).]

Figure 3.12 (a): The sorption of humic fraction combinations onto magnetite compared with single size fractions HA<3 kDa and 3<HA<10 kDa (HA<3 kDa & 3<HA<10 kDa, [HA] = 20 ppm (w.v), pH 6, magnetite concentration = 50 g dm⁻³).
Figure 3.12 (b): The sorption of humic fraction combinations onto magnetite compared with single size fractions HA<3 kDa and 3<HA<10 kDa (HA<3 kDa & 3<HA<10 kDa, [HA] = 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm⁻³).

Figure 3.12 (c): The sorption of humic fraction combinations onto magnetite compared with single size fractions HA<3 kDa and HA>100 kDa (HA<3 kDa & HA>100 kDa, [HA] = 20 ppm (w.v), pH 6, magnetite concentration = 50 g dm⁻³).
Figure 3.12 (d): The sorption of humic fraction combinations onto magnetite compared with single size fractions HA<3 kDa and HA>100 kDa (HA<3 kDa & HA>100 kDa, [HA] = 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm⁻³).

The sorption of HA fraction combinations (HA<3 & 3<HA<10 kDa, HA<3 & HA>100 kDa) onto magnetite at 20 and 100 ppm (w.v) compared with the single size fractions is shown in Figures 3.12 (a), (b), (c) and (d). In these experiments, the total humic concentration is made up of a 50:50 mixture of the two fractions. The combination of HA<3 & HA>100 kDa fractions has higher sorption (79.8 % in (c) and 29.3 % in (d)) onto the magnetite surface than the HA<3 & 3<HA<10 kDa combination (64.5 % in (a) and 23.2 % in (b)). This is not surprising since the HA>100 kDa fraction shows the strongest sorption of the humic size fractions (see Fig. 3.7 (a), (b) and (c)). The aim of the experiment was to test whether the sorption behaviour of the combinations could be predicted from the averaged behaviour of the separate fractions, i.e., to determine whether the combinations behaved like simple binary mixtures, or whether the combination would lead to interactions that would cause the behaviour to differ. In Figure 3.12 (a) the predicted average fits some parts of the fraction combination (particularly the rapid uptake), but not all of the data points. The sorption characteristics of this
combination most closely resemble that of the of HA<3 kDa single fraction more
than that of the 10<HA<100 kDa sample. For the higher humic concentration
(Figure 3.12(b)), it is difficult to distinguish between the single fractions and the
fraction combination as they have similar levels of sorption. In (c) the average
sorption behaviour of the separate size fractions (HA<3 kDa and HA>100 kDa)
predicts the sorption of the combined fractions very well. At a higher humic
centration the fraction combination can be predicted by the average up to day
11, but afterwards the combination resembles the HA>100 kDa sorption more than
the average. Overall, these results show that it the sorption behaviour of fraction
combinations is close to that of the individual fraction averages, although there can
be some small deviations.

3.2.11 AF4 Analysis

AF4 calibration was achieved using polystyrene sulphonate (PS) standard colloids
of masses 1, 10 and 30 kDa. PS colloids were used, as opposed to globular
proteins, because they more closely resemble HA colloids in terms of density and
shape (Baalousha et al. 2011).

Each day, a dilute solution containing a selection of the PS colloids was analysed
using the conditions in Table 2.1. The detector wavelength of 225 nm corresponds
to the maximum absorption wavelength of PS colloids. A distribution of detector
signal (mV) vs. elution time (s) was obtained. A typical distribution for PS colloids is
presented in Figure 3.13. The three peaks correspond to PS colloids of masses 1,
10 and 30 kDa. Each peak is distinct and well-resolved. A linear relationship exists
between the logs of the elution time and molecular weight, as shown in Figure
3.14, allowing the conversion of elution time to molecular weight in the analysis of
HA samples. It was found that the elution times for a given set of PS standard
colloids varied slowly with time (by several tens of seconds over 24 hours).
Therefore, calibration was performed at the start of each day.
Figure 3.13: AF4 elution profile of PS standards (1, 10 and 30 kDa)

Figure 3.14: Calibration plot using PS standards (1, 10 and 30 kDa)
3.2.12 AF4 Analysis of Humic Acid Sorption

Figure 3.15: FFF analysis of humic acid sorption onto magnetite ([HA] = 20 ppm (w.v), pH = 6.0, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.15 shows the AF4 data for the 20 ppm (w.v) humic system before and after addition of magnetite over a period of one month. There is an single peak for the HA before the addition of magnetite, and once magnetite is introduced the size of the peak is reduced, but the position does not change. After this initial sorption, over time there is a redistribution in the mass peak, as it shifts to the right and becomes relatively stable after 1 week with a peak position of 4243 Da and an average weight of 6444 (See Table 3.8). The weight average molecular weight (MW) of the whole HA is 4480 Da which is within the range previously reported: 3300 Da (Manh Thang et al., 2001), 4100 Da (Chin et al., 1994), 4300 Da (Chin et al., 1991) and 4890 Da (Hur et al., 2003). The most probable masses and weight average MW of the data in Figure 3.15 are presented in Table 3.8.
Table 3.8: Probable mass and weight average MW of experimental data for AF4 technique unfractionated 20 ppm (w.v) HA sorption to magnetite.

The HA remaining in solution after 1 day contact with magnetite exhibits a weight average MW shift of 1469 Da, compared to the original HA. This shift to higher mass indicates the preferential sorption of lower molecular weight fractions to the magnetite surface. The HA distribution following 29 days contact has a weight average MW shift of 2119 Da, compared to the original HA. This higher shift in mass compared to 1 day contact with magnetite indicates that preferential sorption of lower molecular weight HA fractions is still observed after 29 days, but the effect is more pronounced than the 1 day contact with magnetite. It is interesting to note that the observed behaviour seen here is the opposite of the trend seen in section 3.2.5 Figure 3.7 (a) where the larger HA fractions (highest molecular weight) were adsorbed the more strongly than the smaller HA fractions, even though the conditions (pH = 6, 20 ppm (w.v), I = 0.1 mol dm$^{-3}$) are exactly the same. Figures 3.15 and Table 3.8 show that fractionation does occur. The weight average MW increases as the contact time with magnetite increases.

It is known that the measured mass distributions for humics depends strongly on the technique (Jones and Bryan 1998), and that techniques like AF4 give lower average and most probable masses than techniques such as analytical ultracentrifugation. In particular, the AF4 technique is poor at detecting larger
humic species. This is why the distribution tails off by 20 kDa, although it is clear from the ultrafiltration that there are much larger species present. In fact, the values in Table 3.8 are all small compared to the sizes separated by ultrafiltration. Hence, it is hard to compare the AF4 results with the data in Fig 3.7 (a). However, the AF4 data do show that fractionation is occurring, and that certain humic species sorb more than others, and that the fractionation changes with time.

Pitois et al. (2008) found that fractionation and preferential adsorption occurs in the sorption of humic acid onto a quartz sand surface, with the adsorption of low molecular weight humic components taking place initially, followed by adsorption of higher weight components. Other studies have also observed fractionation during adsorption onto mineral surfaces, with preferential adsorption of higher molecular weight fractions observed for the adsorption of aquatic humic substances onto goethite surface at apparent steady state (Wang et al. 1997). For other mineral surfaces, preferential adsorption of intermediate molecular weight fractions has been observed (Zhou et al. 2001; Davis and Gloor 1981). Van de Weerd et al. (1999) suggested that at high humic concentrations, lower molecular weight components are expected to be adsorbed initially and then displaced by higher molecular weight components, which were more thermodynamically favoured. Higher molecular weight fractions of an aquatic humic acid were preferentially sorbed onto kaolinite and hematite, whereas different fractionation trends were observed for a terrestrial peat humic acid, i.e., preferential adsorption of higher molecular weight fractions onto kaolinite and lower molecular weight fractions onto hematite. (Hur and Schlautman 2003). The AF4 data support these findings, and matches with the behaviour of the hematite system of Hur and Schlautman (2003) which might be expected as magnetite has some chemical similarities with hematite.
3.3 Europium / Magnetite / Humic Ternary Systems

3.3.1 Eu Sorption onto Magnetite as a Function of Eu Concentration

Figure 3.16 (a): Eu$^{3+}$ sorption onto magnetite in the presence of inactive Eu (pH 6, I = 0.01 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.16 (b): Adsorption isotherm of Eu$^{3+}$ sorbing to magnetite. Data derived from Figure 3.14 (a). (pH 6, I = 0.01 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).
Figure 3.16 (c): Eu$^{3+}$ sorption onto magnetite in the presence of inactive Eu (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.16 (d): Adsorption isotherm of Eu$^{3+}$ sorbing to magnetite. Data derived from Figure 3.14 (c). (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

The sorption of Eu$^{3+}$ onto magnetite at different total Eu concentrations at (I = 0.01 and 0.1 mol dm$^{-3}$) is shown in Figures 3.16 (a) and (c). There is slightly higher
sorption of Eu$^{3+}$ generally across the different Eu concentrations at $I = 0.1$. Figures 3.16 (b) and (d) show the adsorption isotherms derived from the data in Figures (a) and (c) at selected times. As the equilibration time increases, the isotherms in both figures shift to the left which indicates an increase in sorption strength as time increases.

Although the sorption strength is only slightly higher at $I = 0.1$ mol dm$^{-3}$, this does make sense because the magnetite point of zero charge is 7.9. This means that the surface will carry a net positive charge at $pH = 6$, and so higher ionic strengths will reduce the electrostatic repulsion between the Eu$^{3+}$ and the surface charge.

### 3.3.2 Europium 14 days Adsorption / Desorption

![Graph of Eu$^{3+}$ desorption](image)

Figure 3.17: Desorption of Eu$^{3+}$ from magnetite after 14 days adsorption ([Eu] = $10^{-5}$ mol dm$^{-3}$, pH 6, $I = 0.1$ mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.17 shows desorption of Eu$^{3+}$ from magnetite after the electrolyte solution is replaced with fresh electrolyte solution after 14 days adsorption (30.6 % of the total metal ion concentration has sorbed after 14 days). Taking into account the Eu removed after the electrolyte solution is replaced, the point at day 15 represents a desorption of 23 % of the Eu. The amount released in to solution appears to
increase until day 25, before decreasing again to the same level as after 14 days, but this may largely be due to experimental error (see error bars in Fig 3.17).

The most significant result here is that the position between solid and solution after the solution change is in the range that would be predicted for a system with this total Eu concentration (3x10^{-6} mol dm^{-3}) from the data in Figure 3.16 (c). Therefore, under these conditions at least, it seems that the Eu/magnetite interactions may be reversible, unlike that of the humic with surface.

### 3.3.3 Europium Sorption onto Magnetite in Presence of Humic

![Figure 3.18: Effect of humic concentration on Eu^{3+} sorption onto magnetite (pH 6, I = 0.1 mol dm^{-3}, magnetite concentration = 50 g dm^{-3}).](image)

Figure 3.18 shows the effect of whole HA concentration on Eu^{3+} sorption onto magnetite. There is rapid sorption of Eu^{3+} at the start of the experiment when the magnetite is added. There is a further uptake of Eu^{3+} with time, but the magnitude of the sorption is small compared to the initial rapid uptake. There is greater sorption of Eu^{3+} onto the magnetite with decreasing HA concentration (after 30 days 22.5, 36.4 and 71.7 % of Eu^{3+} adsorbed for the 100, 50 and 20 ppm (w.v) systems, respectively). In the absence of humic, sorption of Eu^{3+} is much higher.
(96.4 % at 28 days). In these systems, the results show ‘typical ternary’ behaviour in that the humic is acting as a competing ligand that competes with the magnetite surface. Figure 3.3 shows that the concentration of humic remaining in solution increases with increasing total humic concentration in the system. This causes the amount of Eu held in solution to increase. However, it is likely that the distribution of Eu in the system is complicated by formation of the ternary complexes, since if the solution phase humic can compete with the pure magnetite surface, then it seems likely that humic sorbed on the surface will also be a significant sink, as suggested by Evans et al. (2007).

3.3.4 Humic-induced Desorption of Europium from Magnetite

![Graph showing desorption of Eu from magnetite](image)

Figure 3.19 (a): HA-induced desorption of Eu from magnetite after 24 hours adsorption (pH 6, \( I = 0.1 \text{ mol dm}^{-3} \), magnetite concentration = 50 g dm\(^{-3} \)).
Figure 3.19 (b): HA-induced desorption of Eu from magnetite after 7 days adsorption (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

The desorption of Eu$^{3+}$ from magnetite when the HA electrolyte solution was replaced with fresh HA electrolyte solution with the same humic concentration in solution (so that the total amount of humic in the system remained constant) after 24 hours and 7 days is shown in Figures 3.19 (a) and (b). When the solution was replaced with fresh HA electrolyte solution after 1 day of pre-equilibration, desorption of 7.7, 57.8, and 65.2 % of Eu$^{3+}$ was seen for the 50, 100 and 200 ppm (w.v) systems, respectively. After the replacement of the HA electrolyte solution with fresh HA solution in the system that had been pre-equilibrated for 7 days, desorption of 15.5, 52.6 and 26.1 % of Eu$^{3+}$ was observed for the 50, 100 and 200 ppm (w.v) systems, respectively. There is not much change in the amount of desorption between the 24 hours and the 7 days data for the 100 ppm (w.v) system. For the 50 ppm (w.v) system, the amount desorbed after 7 days equilibration is double that in the 24 hour system. It is also interesting to note that the desorption of metal ions was greatest for the 200 ppm (w.v) systems, after 24 hours equilibration, but after 7 days there was a significant (39.1 %) decrease in the amount of metal ions desorbed.
In these systems, Eu can be removed back into solution by two mechanisms:

- Initially, the Eu could bond directly to the magnetite surface or be in a magnetite-humic-Eu ternary complex. When the humic solution is replaced, the fresh humic in solution could compete for the sorbed Eu and ‘pull’ it from the surface.
- The Eu could be involved in a magnetite-humic-Eu ternary complex, and the humic to which the Eu is bound could be displaced by a different humic species.

Both of these mechanisms could produce the observed desorption. However, the data in Figure 3.4 have shown that there is considerable irreversibility in the humic-magnetite interaction, and so that might suggest that the observed desorption is the result of direct transfer of Eu from binary or ternary surface complexes to solution phase humic complexes. Whatever the mechanism, the behaviour is complex, because one would expect that a direct transfer would give the greatest desorption for the 200 ppm (w.v) system, but this is not the case for the 7 days data. Also, it is not clear why longer pre-equilibration times result in more desorption.

Comparing the amounts sorbed for the 1 and 7 day experiments with those at the end of the simple uptake experiments (Table 3.9), it is clear that the system is not in equilibrium and that a higher relative concentration of Eu remains sorbed in the desorption experiments. In the absence of humic, the system was reversible, but the introduction of the humic has changed that, which is probably due to the irreversibility of the humic/magnetite interaction seen in Figure 3.4. Humic sorption irreversibility has been observed previously (Gu et al., 1994; Avena and Koopal 1999; Vermeer and Koopal 1998) and Bryan et al. (2007) have shown in theoretical calculations that these interactions could affect the behaviour of radionuclides in ternary systems.
<table>
<thead>
<tr>
<th>HA concentration (w.v)</th>
<th>batch uptake (%)</th>
<th>1 day desorption (%)</th>
<th>7 day desorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ppm</td>
<td>36.4 (± 2.7)</td>
<td>92.3 (± 2.9)</td>
<td>84.5 (± 3.0)</td>
</tr>
<tr>
<td>100 ppm</td>
<td>22.5 (± 2.2)</td>
<td>42.2 (± 2.8)</td>
<td>47.4 (± 2.9)</td>
</tr>
</tbody>
</table>

Table 3.9: Comparison of simple sorbed amounts of Eu in Fig. 3.18 after desorption step with amounts of Eu sorbed from data in Fig. 3.19 (a) and (b) errors = 1σ.

3.3.5 Effect of Eu concentration on Eu Sorption onto Magnetite in the Presence of Humic

Figure 3.20 (a): Eu\(^{3+}\) sorption onto magnetite in the presence HA and inactive Eu ([HA] = 10 ppm (w.v), I = 0.1 mol dm\(^{-3}\), pH 6, magnetite concentration = 50 g dm\(^{-3}\)).
Figures 3.20 (a) and (b) show the sorption of Eu$^{3+}$ onto magnetite in the presence of different Eu$^{3+}$ concentrations for whole humic concentrations of 10 and 100 ppm (w.v). In Figure 3.20 (a), the removal of Eu from solution is in the order of $1 \times 10^{-5} < 1 \times 10^{-6} < 1 \times 10^{-8} \approx 1 \times 10^{-7}$ mol dm$^{-3}$.

To understand the data in Figure 3.20 (a), we have to appreciate that the amount of humic remaining in solution will be very low, because humic sorption is high at this low concentration (Fig. 3.3). Therefore, whether the Eu$^{3+}$ favours binding to the humic or magnetite in this system, we would expect most of it to be sorbed. This explains why the observed sorption for Eu concentrations of $10^{-8}$ and $10^{-7}$ mol dm$^{-3}$ in Fig. 3.20 (a) is similar to the amount of sorption for an experiment without humic (Fig. 3.18). The $10^{-6}$ mol dm$^{-3}$ data show that the behaviour here though is more complex than just direct sorption to the magnetite, because the sorption of the Eu in the $10^{-6}$ mol dm$^{-3}$ experiment in Fig 3.20 (a) is very different to that in an experiment with the same Eu concentration, but no humic (Fig 3.16 (c)), with much more sorption in the presence of the humic. This is strong evidence for the
importance of ternary complexes in this system. In the $10^{-5}$ mol dm$^{-3}$ system, the behaviour more closely resembles that of the humic free system and it seems that the capacity of the surface may have been exceeded (humic coated or not).

For the 100 ppm (w.v) systems, the humic is clearly able to compete, and more than that, it is clear that the behaviour of the ternary system is independent of Eu concentration until it is greater than $10^{-6}$ mol dm$^{-3}$. The reduction in solution phase concentration for the $10^{-5}$ mol dm$^{-3}$ is clearly not due to sorption, because that does not happen in Figure 3.20 (a). It seems likely that this effect is due to the precipitation of Eu$^{3+}$/HA complexes, which has been observed previously (Bryan et al. 2001). The very different effect of the humic in the 10 and 100 ppm (w.v) systems may be explained by the fact that most of the already low humic concentration in the 10 ppm (w.v) system will be sorbed to the magnetite (Fig 3.3), whilst a significant fraction of the humic remains in solution at 100 ppm (w.v).

The results in Figure 3.20 (b) are significant because they suggest that the same parameters maybe used to describe humic-Eu interactions up to high radionuclide concentrations (higher than one would expect in the far-field of a radioactive waste repository).
3.3.6 Successive Europium Sorption onto Magnetite in Presence of Humic

![Figure 3.21: Successive adsorption steps of Eu$^{3+}$ onto magnetite in presence of varying humic concentration (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).](image)

The successive sorption of Eu$^{3+}$ to magnetite in the presence of different concentrations of whole humic is shown in Figure 3.21. In this experiment, the magnetite was replaced at 13 and 26 days. There is an increase in adsorption of europium as the HA concentration decreases (see Table 3.10), and this trend is also seen in Figure 3.18. For the 10 ppm (w.v) system at day 9, most of the europium (99.3 %) in the solution has been adsorbed onto the magnetite and further measurements could no longer detect Eu$^{3+}$ in the solution. The 50 ppm (w.v) HA data show larger relative sorption in the second and third steps than the higher HA concentrations.
Table 3.10: Summary of relative sorptions of Eu\(^{3+}\) (% of total Eu\(^{3+}\)) to magnetite at 10, 50, 100 and 200 ppm (w.v) from the successive adsorption data in Figure 3.21 errors = 1\(\sigma\).

<table>
<thead>
<tr>
<th>Adsorption step</th>
<th>Time (Days)</th>
<th>10 ppm (w.v)</th>
<th>50 ppm (w.v)</th>
<th>100 ppm (w.v)</th>
<th>200 ppm (w.v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st rapid sorption</td>
<td>1</td>
<td>66.1 (± 3.1)</td>
<td>23.2 (± 2.2)</td>
<td>16.6 (± 1.8)</td>
<td>10.9 (± 1.4)</td>
</tr>
<tr>
<td>1st slower sorption</td>
<td>13</td>
<td>-</td>
<td>18.3 (± 1.9)</td>
<td>9.5 (± 1.3)</td>
<td>8.7 (± 1.2)</td>
</tr>
<tr>
<td>2nd rapid sorption</td>
<td>14</td>
<td>-</td>
<td>17.7 (± 1.9)</td>
<td>10.6 (± 1.4)</td>
<td>4.0 (± 0.7)</td>
</tr>
<tr>
<td>2nd slower sorption</td>
<td>26</td>
<td>-</td>
<td>12.9 (± 1.6)</td>
<td>8.3 (± 1.2)</td>
<td>4.1 (± 0.7)</td>
</tr>
<tr>
<td>3rd rapid sorption</td>
<td>27</td>
<td>-</td>
<td>9.8 (± 1.3)</td>
<td>7.9 (± 1.1)</td>
<td>6.0 (± 0.9)</td>
</tr>
<tr>
<td>3rd slower sorption</td>
<td>33</td>
<td>-</td>
<td>12.7 (± 1.6)</td>
<td>6.6 (± 1.0)</td>
<td>1.6 (± 0.3)</td>
</tr>
</tbody>
</table>

The relative sorption of Eu in the rapid and slow parts generally decreases with each ‘sorption step’ for all the humic concentrations.

These successive sorption experiments are useful, because they mimic the behaviour in the subsurface, where the groundwater solution (and any radionuclides in that phase) will encounter successive fresh regions of mineral surface as it migrates. With this in mind, the data suggest that an extremely high humic concentration (>100 ppm (w.v)), the humic will be effective at retaining most of the metal ion in solution. However, for humic concentrations less than 50 ppm (w.v), the metal ion will be sorbed to the surface easily. Generally, humic concentrations in the environment are much less than 50 ppm (w.v). This could be important in radiological performance assessment or the general prediction of radionuclide transport in the environment.
3.3.7 Sorption of Europium onto Magnetite in presence of Humic Fractions

Figure 3.22 (a): Sorption of Eu$^{3+}$ onto magnetite in presence of humic fractions (Humic and Eu$^{3+}$ equilibrated for 24 hours, [HA] = 20 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.22 (b): Sorption of Eu$^{3+}$ onto magnetite in presence of humic fractions (Humic and Eu$^{3+}$ equilibrated for 24 hours, [HA] = 50 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).
Figure 3.22 (c): Sorption of Eu$^{3+}$ onto magnetite in presence of humic fractions (Humic and Eu$^{3+}$ equilibrated for 24 hours, [HA] = 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).

The sorption of Eu$^{3+}$ onto magnetite in the presence of different HA size fractions at humic concentrations of 20, 50 and 100 ppm (w.v) are shown in Figures 3.22 (a), (b) and (c), respectively. Table 3.11 gives a summary of the amounts sorbed after 1 and 30 days. As would be expected, the extent of sorption decreases with increasing humic concentration, as observed for the data in Figure 3.18. The same sorption patterns of europium for each HA fraction can be seen for the 20 and 100 ppm (w.v) concentrations with the order of highest Eu$^{3+}$ sorption being 3<HA<10 > HA<3 > 10<HA<100 > HA>100 kDa. Intriguingly the same sorption behaviour is not present in (b) for the 50 ppm (w.v) concentration, where the HA<3 kDa is the highest sorbing system.

It is interesting to note that the whole (unfractionated) HA system has the lowest sorption of Eu$^{3+}$ for all three concentrations. Therefore, the general trend is that as humic fraction size increases, the humic becomes more effective at retaining the Eu in solution. However, the interactions in this system are complex, because the humic species are themselves partitioned between the solid and solution phase,
and so we cannot interpret the amount of Eu remaining in solution in these experiments as directly proportional to the binding strength of the size fraction. For example, the results in Figure 3.7 (a) and (b) show that for the 20 and 50 ppm (w.v) systems, the amount of the HA>100 kDa fraction sorbed to the surface is large, and so a strong interaction of the Eu with the HA>100 kDa species could result in a low amount of Eu remaining in solution. In this respect, the data in Figure 3.22 (c) are the easiest to interpret, because the majority of all of the humic fractions remain in solution. Here, there is a clear trend for the larger fractions (10<HA<100 kDa; HA>100 kDa) to be more effective at retaining the Eu than the smaller fractions, and given the distribution of the humic in these systems, that strongly suggests that the larger fractions show stronger binding. The most interesting result here is that it seems that separating the humic population into sub-fractions reduces the overall binding strength.

These results show that studies of metal behaviour in whole HA in ternary systems do not fully explain the interactions of the individual components in the humic population, and that further studies are required in order to gain this understanding. This is important, as the results above have shown that fractionation of the whole humic is likely during transport.

<table>
<thead>
<tr>
<th>HA ppm (w.v)</th>
<th>Time (Days)</th>
<th>HA&lt;3 kDa Eu³⁺ (%)</th>
<th>3&lt;HA&lt;10 kDa Eu³⁺ (%)</th>
<th>10&lt;HA&lt;100 kDa Eu³⁺ (%)</th>
<th>HA&gt;100 kDa Eu³⁺ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1</td>
<td>48.9 (± 2.9)</td>
<td>73.0 (± 3.0)</td>
<td>92.0 (± 2.9)</td>
<td>66.4 (± 3.1)</td>
</tr>
<tr>
<td>30</td>
<td>71.7 (± 3.1)</td>
<td>97.6 (± 2.8)</td>
<td>98.6 (± 2.8)</td>
<td>90.3 (± 2.9)</td>
<td>86.9 (± 2.9)</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>21.1 (± 2.1)</td>
<td>59.6 (± 3.0)</td>
<td>21.1 (± 2.1)</td>
<td>47.0 (± 2.9)</td>
</tr>
<tr>
<td>30</td>
<td>36.4 (± 2.7)</td>
<td>97.0 (± 2.8)</td>
<td>67.6 (± 3.1)</td>
<td>69.8 (± 3.1)</td>
<td>75.7 (± 3.0)</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>14.8 (± 1.7)</td>
<td>24.5 (± 2.3)</td>
<td>41.8 (± 2.8)</td>
<td>20.5 (± 2.1)</td>
</tr>
<tr>
<td></td>
<td>22.5 (± 2.2)</td>
<td>69.0 (± 3.1)</td>
<td>84.0 (± 3.0)</td>
<td>47.9 (± 2.9)</td>
<td>40.5 (± 2.8)</td>
</tr>
</tbody>
</table>

Table 3.11: Summary of Eu³⁺ adsorbed (% of total Eu³⁺) to magnetite in presence of different HA fraction sizes at 20, 50, and 100 ppm (w.v) from the 1 month adsorption data in Figures 3.22 (a), (b) and (c) errors = 1σ.
3.3.8 Humic Fractions Induced Desorption of Europium from Magnetite

Experiments were conducted to measure the desorption of Eu from the magnetite in systems where the humic solution was replaced with a fresh humic solution of the same concentration, but containing no Eu. Experiments were performed with total humic concentrations of 100 ppm (w.v) for the HA<3 kDa and HA>100 kDa size fractions. In the case of the 3 kDa system, no significant desorption of Eu was observed whilst in the HA>100 kDa system very low concentrations of Eu were observed in solution for a few days after the exchange of the solution (~1 %), but after 3 days, the Eu concentration fell below the limit of detection. It is clear that the fractions are much less effective at removing Eu from the surface than the whole humic.

3.3.9 Effect of Pre-equilibration Time on Eu\(^{3+}\) Sorption to Magnetite in the Presence of Humic Fractions

![Figure 3.23 (a): The sorption of Eu\(^{3+}\) onto magnetite in presence of humic fractions (Humic and Eu\(^{3+}\) equilibrated for 7 days, [HA] = 20 ppm (w.v), pH 6, magnetite concentration = 50 g dm\(^{-3}\)).](image)

Figure 3.23 (a): The sorption of Eu\(^{3+}\) onto magnetite in presence of humic fractions (Humic and Eu\(^{3+}\) equilibrated for 7 days, [HA] = 20 ppm (w.v), pH 6, magnetite concentration = 50 g dm\(^{-3}\)).
Figure 3.23 (b): The sorption of Eu$^{3+}$ onto magnetite in presence of humic fractions (Humic and Eu$^{3+}$ equilibrated for 7 days, [HA] = 50 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.23 (c): The sorption of Eu$^{3+}$ onto magnetite in presence of humic fractions (Humic and Eu$^{3+}$ equilibrated for 7 days, [HA] = 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).
The sorption of Eu\textsuperscript{3+} onto magnetite in the presence of humic size fractions at 20, 50 and 100 ppm (w.v) for a pre-equilibration time between the HA fractions and the Eu\textsuperscript{3+} of 24 hours is shown in Figures 3.22 ((a), (b) and (c)) and the data for a pre-equilibration time of 7 days in Figures 3.23 ((a), (b) and (c)). In general, as the concentration of the HA size fractions decreases, the sorption of Eu\textsuperscript{3+} increases, this behaviour was also present in Figures 3.18 and 3.22 (a), (b) and (c). A summary of the sorption data for the 24 hours and 7 days equilibration times can be seen in Table 3.12.

<table>
<thead>
<tr>
<th>HA Conc ppm (w.v)</th>
<th>Time (Days)</th>
<th>HA\textsuperscript{3+} (%)</th>
<th>HA&lt;3 kDa Eu\textsuperscript{3+} (%)</th>
<th>3&lt;HA&lt;10 kDa Eu\textsuperscript{3+} (%)</th>
<th>10&lt;HA&lt;100 kDa Eu\textsuperscript{3+} (%)</th>
<th>HA&gt;100 kDa Eu\textsuperscript{3+} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 (24 hours)</td>
<td>3</td>
<td>55.0 (± 3.0)</td>
<td>95.9 (± 2.8)</td>
<td>96.8 (± 2.8)</td>
<td>86.5 (± 2.9)</td>
<td>76.3 (± 3.0)</td>
</tr>
<tr>
<td>50 (24 Hours)</td>
<td>3</td>
<td>69.2 (± 3.1)</td>
<td>97.8 (± 2.8)</td>
<td>98.4 (± 2.8)</td>
<td>91.2 (± 2.9)</td>
<td>86.2 (± 2.9)</td>
</tr>
<tr>
<td>100 (24 Hours)</td>
<td>3</td>
<td>27.0 (± 2.4)</td>
<td>90.1 (± 2.9)</td>
<td>48.9 (± 2.9)</td>
<td>48.9 (± 2.9)</td>
<td>64.5 (± 3.0)</td>
</tr>
<tr>
<td>20 (7 Days)</td>
<td>28</td>
<td>33.6 (± 2.6)</td>
<td>97.0 (± 2.8)</td>
<td>68.4 (± 3.1)</td>
<td>68.4 (± 3.1)</td>
<td>75.5 (± 3.0)</td>
</tr>
<tr>
<td>50 (7 Days)</td>
<td>3</td>
<td>35.5 (± 2.7)</td>
<td>96.5 (± 2.8)</td>
<td>64.3 (± 3.1)</td>
<td>72.0 (± 3.1)</td>
<td>74.1 (± 3.0)</td>
</tr>
<tr>
<td>100 (7 Days)</td>
<td>3</td>
<td>19.9 (± 2.0)</td>
<td>46.0 (± 2.9)</td>
<td>70.7 (± 3.1)</td>
<td>32.8 (± 2.6)</td>
<td>30.4 (± 2.5)</td>
</tr>
</tbody>
</table>

Table 3.12: Comparison of Eu\textsuperscript{3+} adsorbed (% of total Eu\textsuperscript{3+}) to magnetite in presence of different HA fraction sizes (Humic and Europium equilibrated for 24 hours and 7 days) at 20, 50, and 100 ppm (w.v) from the adsorption data in Figures 3.22 (a), (b), (c) and 3.23 (a), (b) and (c) errors = 1σ.

From the table, there are no significant differences between the 24 hours and 7 days equilibration experiments except for the 100 ppm (w.v) data where there is slightly higher sorption for the 24 hour system for the whole humic and the 3<HA<10 kDa fraction. This suggests that for lower HA concentrations (i.e. those
that would be expected in the environment) the metal ion interactions are independent of the equilibration time between the humic and the metal ions in HA / metal ion / magnetite ternary systems for times up to 1 week. Bryan et al. (2007) have suggested that solid/solution partition should be largely independent of slow humic/metal ion kinetics because the non-exchangeable does not represent a more stable state (in terms of free energy). These results agree with that suggestion.

**Figure 3.24 (a):** The sorption of Eu$^{3+}$ onto magnetite in presence of humic fractions (Humic and magnetite equilibrated for 24 hours, [HA] = 50 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).
Figure 3.24 (b): The sorption of Eu\(^{3+}\) onto magnetite in presence of humic fractions (Humic and magnetite equilibrated for 24 hours, [HA] = 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm\(^{-3}\)).

Figure 3.24 (c): The sorption of Eu\(^{3+}\) onto magnetite in presence of humic fractions (Humic and magnetite equilibrated for 7 days, [HA] = 50 ppm (w.v), pH 6, magnetite concentration = 50 g dm\(^{-3}\)).
Figures 3.24 (a) and (b) show the results of experiments where the humic and magnetite were equilibrated for 24 hours before europium was introduced into the system using the humic size fractions at 50 and 100 ppm (w.v), respectively. Figures 3.24 (c) and (d) show equivalent experiments with equilibration times of 7 days. For the 24 hour equilibration data at 50 ppm (w.v), there is lower level of sorption of europium than for the 7 day experiment (Table 3.13). For the 100 ppm (w.v) data, there is generally only a small difference between the 24 hour and 7 day experiments, but there is a difference towards the start of the experiments, so that although the equilibrium position is not affected, the reaction kinetics are. As for the previous results, the order of sorption strength is generally (HA<3 kDa) > (3<HA<10 kDa) > (10<HA<100 kDa) > (HA>100 kDa) > whole HA.
<table>
<thead>
<tr>
<th>HA Conc (ppm)</th>
<th>Time (Days)</th>
<th>HA&lt;3 kDa Eu³⁺ (%)</th>
<th>HA&lt;3 kDa Eu³⁺ (%)</th>
<th>3&lt;HA&lt;10 kDa Eu³⁺ (%)</th>
<th>10&lt;HA&lt;100 kDa Eu³⁺ (%)</th>
<th>HA&gt;100 kDa Eu³⁺ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2</td>
<td>11.3 (± 1.4)</td>
<td>43.3 (± 2.9)</td>
<td>33.7 (± 2.6)</td>
<td>14.0 (± 1.7)</td>
<td>15.5 (± 1.8)</td>
</tr>
<tr>
<td>(24 Hours)</td>
<td>29</td>
<td>29.5 (± 2.5)</td>
<td>96.7 (± 2.8)</td>
<td>75.2 (± 3.0)</td>
<td>57.9 (± 3.0)</td>
<td>57.9 (± 3.0)</td>
</tr>
<tr>
<td>100</td>
<td>2</td>
<td>12.6 (± 1.5)</td>
<td>28.9 (± 2.4)</td>
<td>27.6 (± 2.4)</td>
<td>5.3 (± 0.9)</td>
<td>12.2 (± 1.5)</td>
</tr>
<tr>
<td>(24 Hours)</td>
<td>29</td>
<td>35.8 (± 2.7)</td>
<td>89.0 (± 2.9)</td>
<td>74.2 (± 3.0)</td>
<td>40.2 (± 2.8)</td>
<td>38.9 (± 2.8)</td>
</tr>
<tr>
<td>50</td>
<td>2</td>
<td>34.1 (± 2.6)</td>
<td>67.2 (± 3.1)</td>
<td>19.3 (± 2.0)</td>
<td>25.3 (± 2.3)</td>
<td>18.3 (± 1.9)</td>
</tr>
<tr>
<td>(7 Days)</td>
<td>28</td>
<td>60.0 (± 3.0)</td>
<td>97.0 (± 2.8)</td>
<td>58.3 (± 3.0)</td>
<td>58.5 (± 3.0)</td>
<td>61.1 (± 3.1)</td>
</tr>
<tr>
<td>100</td>
<td>2</td>
<td>9.9 (± 1.3)</td>
<td>39.7 (± 2.8)</td>
<td>45.7 (± 2.9)</td>
<td>10.0 (± 1.3)</td>
<td>13.9 (± 1.6)</td>
</tr>
<tr>
<td>(7 Days)</td>
<td>28</td>
<td>33.4 (± 2.6)</td>
<td>87.3 (± 2.9)</td>
<td>69.9 (± 3.1)</td>
<td>30.8 (± 2.5)</td>
<td>36.2 (± 2.7)</td>
</tr>
</tbody>
</table>

Table 3.13: Comparison of Eu³⁺ adsorbed (% of total Eu³⁺) to magnetite in presence of different HA fraction sizes (Humic and magnetite equilibrated at 24 hours and 7 days) at 50 and 100 ppm (w.v) from the adsorption data in Figures 3.24 (a), (b), (c) and (d) errors = 1σ.

In Table 3.13, there are no significant differences between the 24 hour system and the 7 day system in regards to the amounts of Eu adsorbed after day 29; however there are differences in the rapid sorption amounts at day 2, with the 7 day experiments generally having higher sorption than those with 24 hour pre-equilibration times. This suggests that equilibration time between humic and magnetite does affect the rapid initial uptake of Eu onto HA/magnetite initially, but after time (a few days) the result is insensitive to the humic and magnetite pre-equilibration time.

There does seem to be an effect on the sorption of Eu to magnetite with the order of addition (compare Tables 3.12 and 3.13). The systems where HA and Eu³⁺ were pre-equilibrated before addition to the magnetite generally have higher amounts of Eu adsorbed than the experiments where the humic and magnetite were pre-equilibrated first before addition of Eu. This is particularly true for the 3<HA<10, 10<HA<100 and HA>100 kDa fractions. The pre-equilibration between HA and magnetite may hinder the sorption of Eu as some of the HA could sorb onto the magnetite surface (as seen in Figure 3.7), reducing the amount of metal ion
binding sites on the magnetite surface. However, it is impossible to deduce the mechanism from the batch data alone.

3.3.10 Successive Europium Sorption onto Magnetite in Presence of Humic Fractions

Figure 3.25 (a): Successive adsorption steps of Eu$^{3+}$ onto magnetite in presence of humic fractions ([HA] = 50 ppm (w.v), pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

The successive adsorption of europium onto magnetite in the presence of different HA fractions at a total concentration of 50 ppm (w.v), where the magnetite was replaced with fresh magnetite at days 13 and 26, is shown in Figure 3.25 (a). The relative amounts of europium sorbed onto the magnetite surface at each step can be seen in Table 3.14. 23 days after introducing the metal ions into the system most of the europium, except for the unfractionated humic system, had been adsorbed onto the magnetite, and no Eu$^{3+}$ could be detected in solution. The 10<HA<100 kDa fraction system was the first to fall below the limit of detection, after 16 days, followed by the HA<3 kDa system after 19 days and then by both the 3<HA<10 and HA>100 kDa systems together after 23 days. The 50 ppm (w.v) unfractionated humic system shows much less sorption of Eu$^{3+}$ than the other HA
fractions, requiring the magnetite to be replaced twice and 33 days to get to a similar level of sorption that the other size fractions reached in 14 days.

<table>
<thead>
<tr>
<th>Sorption step</th>
<th>Time (Days)</th>
<th>HA&lt;3 kDa sorbed (%)</th>
<th>3&lt;HA&lt;10 kDa sorbed (%)</th>
<th>10&lt;HA&lt;100 kDa sorbed (%)</th>
<th>HA&gt;100 kDa sorbed (%)</th>
<th>HA sorbed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st rapid sorption</td>
<td>1</td>
<td>66.3 (± 3.1)</td>
<td>34.7 (± 2.6)</td>
<td>33.2 (± 2.6)</td>
<td>35.5 (± 2.7)</td>
<td>23.2 (± 2.2)</td>
</tr>
<tr>
<td>1st slower sorption</td>
<td>13</td>
<td>29.9 (± 2.5)</td>
<td>26.7 (± 2.4)</td>
<td>32.8 (± 2.6)</td>
<td>37.2 (± 2.7)</td>
<td>18.3 (± 1.9)</td>
</tr>
<tr>
<td>2nd rapid sorption</td>
<td>14</td>
<td>2.6 (± 0.5)</td>
<td>33.3 (± 2.6)</td>
<td>31.0 (± 2.5)</td>
<td>18.9 (± 2.0)</td>
<td>17.7 (± 1.9)</td>
</tr>
<tr>
<td>2nd slower sorption</td>
<td>26</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.9 (± 1.6)</td>
</tr>
<tr>
<td>3rd rapid sorption</td>
<td>27</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.8 (± 1.3)</td>
</tr>
<tr>
<td>3rd slower sorption</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.7 (± 1.6)</td>
</tr>
</tbody>
</table>

Table 3.14: Summary of total Eu$^{3+}$ adsorbed to magnetite in presence of different HA fractions at 50 ppm (w.v) from the successive adsorption data in Figures 3.25 (a) errors = 1σ.

As the Eu can no longer be detected in solution during the 2nd sorption step, it is hard to tell how the relative rapid and slow sorption differ between the different HA size fractions. The results do show that the HA size fraction systems do have a high level of sorption of Eu when the magnetite is replaced in these experiments, and once again, the whole humic is much more effective at retaining the Eu in solution.
Figure 3.25 (b): Successive adsorption steps of Eu$^{3+}$ onto magnetite in presence of humic fractions ([HA] = 100 ppm (w.v), pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.25 (b) shows data similar to that in Figure 3.23 (a), except with total humic concentrations of 100 ppm (w.v). As the humic concentration is higher, there is less sorption of Eu$^{3+}$ at each step, meaning that the replacement of magnetite could be repeated twice for all samples. Table 3.15 shows a summary of the relative amount of europium adsorbed onto the magnetite at each step. This time, the 3<HA<10 kDa system is the fastest sorbing, having the highest percentage of sorption at day 27 of 97.9 %, after which the concentration of Eu fell below the limit of detection. The sorption of Eu$^{3+}$ follows the order (3<HA<10 kDa) > (HA>3 kDa) > (10<HA<100 kDa) > (HA>100 kDa) > whole HA.
<table>
<thead>
<tr>
<th>Sorption step</th>
<th>Time (Days)</th>
<th>HA&lt;3 kDa sorbed (%)</th>
<th>3&lt;HA&lt;10 kDa sorbed (%)</th>
<th>10&lt;HA&lt;100 kDa sorbed (%)</th>
<th>HA&gt;100 kDa sorbed (%)</th>
<th>HA sorbed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st rapid sorption</td>
<td>1</td>
<td>29.4 (± 2.5)</td>
<td>39.9 (± 2.8)</td>
<td>26.8 (± 2.4)</td>
<td>24.8 (± 2.3)</td>
<td>16.4 (± 1.8)</td>
</tr>
<tr>
<td>1st slower sorption</td>
<td>13</td>
<td>38.1 (± 2.7)</td>
<td>41.4 (± 2.8)</td>
<td>15.1 (± 1.7)</td>
<td>16.4 (± 1.8)</td>
<td>9.7 (± 1.3)</td>
</tr>
<tr>
<td>2nd rapid sorption</td>
<td>14</td>
<td>15.6 (± 1.8)</td>
<td>11.8 (± 1.5)</td>
<td>20.6 (± 2.1)</td>
<td>21.5 (± 2.1)</td>
<td>10.6 (± 0.5)</td>
</tr>
<tr>
<td>2nd slower sorption</td>
<td>26</td>
<td>7.2 (± 1.1)</td>
<td>3.7 (± 0.7)</td>
<td>12.8 (± 1.6)</td>
<td>7.3 (± 1.1)</td>
<td>8.3 (± 1.4)</td>
</tr>
<tr>
<td>3rd rapid sorption</td>
<td>27</td>
<td>4.6 (± 0.8)</td>
<td>1.1 (± 0.3)</td>
<td>13.5 (± 1.6)</td>
<td>17.1 (± 1.9)</td>
<td>7.9 (± 1.1)</td>
</tr>
<tr>
<td>3rd slower sorption</td>
<td>33</td>
<td>2.2 (± 0.4)</td>
<td>-</td>
<td>5.1 (± 0.8)</td>
<td>5.1 (± 0.8)</td>
<td>6.6 (± 1.0)</td>
</tr>
</tbody>
</table>

Table 3.15: Summary of total Eu\(^{3+}\) adsorbed to magnetite in presence of different HA fractions at 100 ppm (w.v) from the successive adsorption data in Figures 3.25 (b) errors = 1σ.

In Figure 3.25 (b), the relative sizes of the rapid and slow sorption for all the HA size fractions decrease with each ‘sorption step’, which is a similar trend to that observed with the whole HA in Figure 3.22.

### 3.3.11 Sorption of Europium onto Magnetite in Presence of Humic Fraction Combinations

The sorption of europium onto magnetite surface in the presence of HA combinations of humic size fractions at 20 and 100 ppm (w.v) are shown in Figures 3.26 (a), (b), (c) and (d).
Figure 3.26 (a): The sorption of Eu$^{3+}$ onto magnetite in presence of humic fraction combination compared with single size fractions HA<3 kDa and 3<HA<10 kDa (HA<3 kDa & 3<HA<10 kDa, 20 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.26 (b): The sorption of Eu$^{3+}$ onto magnetite in presence of humic fraction combination compared with single size fractions HA<3 kDa and HA>100 kDa (HA<3 kDa & HA>100 kDa, 20 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).
Figure 3.26 (c): The sorption of Eu$^{3+}$ onto magnetite in presence of humic fraction combination compared with single size fractions HA<3 kDa and 3<HA<10 kDa (HA<3 kDa & 3<HA<10 kDa, 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).

Figure 3.26 (d): The sorption of Eu$^{3+}$ onto magnetite in presence of humic fraction combination compared with single size fractions HA<3 kDa and HA>100 kDa (HA<3 kDa & HA>100 kDa, 100 ppm (w.v), pH 6, magnetite concentration = 50 g dm$^{-3}$).
For the 20 ppm (w.v) systems, both combinations (HA<3 kDa + 3<HA<10 kDa and HA<3 kDa + HA>100 kDa) adsorb strongly, particularly the smaller fraction combination, and after 2 days, no more europium could be detected (97.5 % of total Eu\(^{3+}\) adsorbed for the HA<3 kDa + 3<HA<10 kDa at day 2 and 91.9 % total Eu\(^{3+}\) adsorbed for the HA<3 kDa + HA>100 kDa at day 2). As in Figure 3.10, the average Eu sorption observed for the two separate fractions was used to predict the sorption behaviour of the fraction combination. The average of the single size fractions cannot predict the fraction combination sorption behaviour at 20 ppm (w.v), because the Eu\(^{3+}\) could no longer be detected beyond 3 days.

For the 100 ppm (w.v) data, the same trend is present, with the HA<3 kDa + 3<HA<10 kDa combination showing 84.1 % of Eu\(^{3+}\) sorbed at day 31, whilst the HA<3 kDa + HA>100 kDa combination has only 53.5 % sorption of the same time. This time the average behaviour of the two separate HA size fractions gives a reasonably good fit to the combined fraction data in both Figures 3.26 (c) and (d). The reason for the very different behaviours at 20 and 100 ppm (w.v) is unclear.

### 3.3.12 Sorption / Desorption of Europium from Dowex in the Presence of Humic Acid / Humic Fractions.

In order to test the relative binding strengths of the unfractionated humic and the humic size fractions, competition experiments were used, where the humic samples were made to compete with a sample of DOWEX exchange resin.
The Eu$^{3+}$ was added to the resin first so that there would be no time for metal to enter the humic non-exchangeable fraction before the humic had to compete with the resin. Figure 3.27 shows the uptake of Eu$^{3+}$ onto Dowex resin for 48 hours, followed by the introduction of unfractionated HA / HA size fractions. Once the HA is added, the Eu$^{3+}$ desorbs from the Dowex and re-enters the solution. A more strongly binding sample will result in a higher solution phase concentration. The different HA samples do show different binding strengths, because they remove different amounts of Eu$^{3+}$ from the resin. At 68 hours, the unfractionated HA removes the metal ions the most, followed by the HA>100 kDa, 10<HA<100 kDa, HA<3 kDa, with the 3<HA<10 kDa fraction removing the least. Table 3.16 shows a summary of the amount of Eu$^{3+}$ left in solution for the experiment.

There is some evidence of a change in the amount of Eu in solution for some of the systems at longer times (144 hours). It is known that metal/humic interactions are prone to complex kinetics, and so the data immediately after addition of the humic
(68-72 hours) probably give the best indication of the intrinsic binding strength of the sample.

<table>
<thead>
<tr>
<th>Time (Hours)</th>
<th>HA&lt;3 kDa sorbed (%)</th>
<th>3&lt;HA&lt;10 kDa sorbed (%)</th>
<th>10&lt;HA&lt;100 kDa sorbed (%)</th>
<th>HA&gt;100 kDa sorbed (%)</th>
<th>HA sorbed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>2.2 (± 0.4)</td>
<td>2.3 (± 0.5)</td>
<td>2.1 (± 0.4)</td>
<td>2.5 (± 0.5)</td>
<td>2.1 (± 0.4)</td>
</tr>
<tr>
<td>48</td>
<td>1.7 (± 0.4)</td>
<td>1.7 (± 0.4)</td>
<td>2.1 (± 0.4)</td>
<td>2.0 (± 0.4)</td>
<td>1.3 (± 0.3)</td>
</tr>
<tr>
<td>68</td>
<td>23.6 (± 2.2)</td>
<td>14.2 (± 1.7)</td>
<td>47.7 (± 2.9)</td>
<td>49.2 (± 3.0)</td>
<td>75.4 (± 3.0)</td>
</tr>
<tr>
<td>72</td>
<td>23.9 (± 2.2)</td>
<td>14.1 (± 1.7)</td>
<td>47.4 (± 2.9)</td>
<td>48.7 (± 2.9)</td>
<td>73.9 (± 3.0)</td>
</tr>
<tr>
<td>144</td>
<td>22.1 (± 2.1)</td>
<td>13.4 (± 1.6)</td>
<td>43.7 (± 2.9)</td>
<td>36.4 (± 2.7)</td>
<td>57.7 (± 3.0)</td>
</tr>
</tbody>
</table>

Table 3.16: Summary of total Eu³⁺ remaining in solution after 48 hours equilibration with Dowex followed introduction of HA fractions at 10 ppm (w.v) data taken from Figure 3.27 errors = 1σ.

When the resin exchange technique is being used to measure dissociation kinetics, the mass of resin and the resin binding strength should be sufficiently high that all exchangeable bound metal ion is instantaneously removed from solution, so that the dissociation rate of the non-exchangeable fraction becomes the rate limiting step, allowing the first order dissociation rate to be determined (Monsallier et al. 2003). The Dowex resin used in the experiment is a weak ion exchange resin, so that the humic samples can remove some of the bound metal ion from the resin instantly. The concentration of the humic (10 ppm (w.v)) was chosen so that not all of the metal ions were removed. Further, the total metal concentration is such that neither the resin nor the humic approach their capacity to bind Eu³⁺ in any of the experiments. Therefore, the number of available humic and resin binding sites will be independent of the portion of Eu³⁺ that have bound to them (to a first approximation). Therefore, the binding power of the humic sample, \( P_{\text{humic}} \), will be given by,

\[
P_{\text{humic}} = [HA]K_{\text{humic}} \quad \text{Equation 3.1}
\]

while binding power of the resin, \( P_{\text{resin}} \), is given by,

\[
P_{\text{resin}} = [\text{Resin}]K_{\text{resin}} \quad \text{Equation 3.2}
\]
where \([HA]\) and \([\text{Resin}]\) are the humic and resin binding site concentrations respectively, and \(K_{\text{humic}}\) and \(K_{\text{resin}}\) are the humic and resin intrinsic equilibrium constants, respectively. The amounts bound to the two sinks will be determined by the relative sizes of \(P_{\text{humic}}\) and \(P_{\text{resin}}\),

\[
\frac{\text{amount bound to humic}}{\text{amount bound to resin}} = \frac{P_{\text{humic}}}{P_{\text{resin}}} \tag{Equation 3.3}
\]

Since the amount of resin is the same in each experiment, the relative binding strengths of the different fractions will be given by the ratio of the amounts bound to the humic in the different experiments,

\[
\frac{\text{amount bound to humic \#1}}{\text{amount bound to humic \#2}} = \frac{P_{\text{humic} \ (#1)}}{P_{\text{humic} \ (#2)}} \tag{Equation 3.4}
\]

From the table (3.16), it is apparent that the \(3<HA<10\) kDa fraction is the weakest binding, but by comparing the amounts bound we can express the relative binding powers of the different fractions (see Table 3.17).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>HA&lt;3 kDa</th>
<th>3&lt;HA&lt;10 kDa</th>
<th>10&lt;HA&lt;100 kDa</th>
<th>HA&gt;100 kDa</th>
<th>Whole HA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative binding power w.r.t. 3&lt;HA&lt;10 kDa fraction</td>
<td>1.8 (± 0.2)</td>
<td>1.0 (± 0.1)</td>
<td>3.6 (± 0.2)</td>
<td>3.8 (± 0.2)</td>
<td>5.9 (± 0.2)</td>
</tr>
</tbody>
</table>

Table 3.17: Relative binding powers of the unfractionated HA and HA size fractions w.r.t. to 3<HA<10 kDa fraction errors = 1\(\sigma\).

The most striking result in Table 3.17 is that the whole humic value is much higher than any of the component fractions. This does help explain some of the ternary system data. For example, Figure 3.22, 3.23 and 3.25, where the unfractionated sample was able to retain more metal ion in solution.

The observations for Figure 3.22 (section 3.3.7) are consistent with the relative binding power of the whole HA and HA size fractions. The order of binding strength
is as follows: whole HA > (HA>100 kDa) > (10<HA<100 kDa) > (HA<3 kDa) > (3<HA<10 kDa). This order is reflected in (a) and (c), where the whole HA retains the most europium, followed by the HA>100 kDa and 10<HA<100 kDa fraction, with the 3<HA<10 kDa retaining the least Eu as it has the weakest binding strength of the samples.

It was found in section 3.3.9 that HA size fractions are much less effective at removing Eu from the surface than the whole humic. This matches well with the higher binding strength observed for the whole humic. In Figure 3.25, for all sorption steps, the order of effectiveness at retaining Eu in solution is: whole HA > (HA>100 kDa) > (10<HA<100 kDa) > (HA<3 kDa) > (3<HA<10 kDa). This is consistent with the relative binding powers, shown in Table 3.17.
Chapter 4

Modelling
4.1 Modelling Interactions

The interactions of HA and radionuclides have been studied previously (Bryan et al., 2005, 2007; King et al., 2001). This work has shown that the initial interaction is a rapid uptake of aqueous metal ion, $M^{n+}_{(aq)}$ ($Eu^{3+}_{(aq)}$ in the experiments reported here), by HA to an ‘exchangeable fraction’, which is assumed to be an instantaneously reversible process,

$$M^{n+}_{(aq)} + HA_{exch} \leftrightarrow M_{exch}$$  \hspace{1cm} \text{Equation 4.1}

$$K_{exch} = \frac{[M_{exch}]}{[M^{n+}_{(aq)}][HA_{exch}]}$$  \hspace{1cm} \text{Equation 4.2}

where $HA_{exch}$ is the HA exchangeable binding site, $M_{exch}$ is the metal ion bound to HA in the exchangeable fraction and $K_{exch}$ is the equilibrium constant for the process. The second, subsequent component is a first-order kinetic (slow) transfer of $M_{exch}$ to a ‘non-exchangeable fraction’, $M_{non-exch}$,

$$M_{exch} \xleftrightarrow{k_{HAf} k_{HAb}} M_{non-exch}$$  \hspace{1cm} \text{Equation 4.3}

$$\frac{d[M_{non-exch}]}{dt} = k_{HAf}[M_{exch}] - k_{HAb}[M_{non-exch}]$$  \hspace{1cm} \text{Equation 4.4}

where $k_{HAf}$ and $k_{HAb}$ are the forward and backward rate constants, respectively.

In all of the modelling data below, the total europium concentration in the system is very low ($7.91 \times 10^{-10} \text{ mol dm}^{-3}$). Therefore, the data do not define the total concentration of humic exchangeable binding sites ($[HA_{exch}]$). In fact, because of the low concentration of Eu, the experimental data define only the product of the equilibrium constant and the binding site concentration, $K_{exch} \times [HA_{exch}]$. Therefore, an arbitrary value of 1 was selected for the humic binding site concentration in a solution of [HA] = 100 ppm (w.v). The value was reduced in proportion to the
concentration of the humic sample. For example, for the 50 ppm (w.v) systems, the concentration is reduced to 0.5. Therefore, although the true values of $K_{exch}$ and $[HA_{exch}]$ will be different to those discussed below, their product will be the same. Therefore, the $K_{exch}$ parameters given below for the different samples give a measure of the relative binding power of the sample.

In all of the modelling described here, the interaction of the metal ion with the surface is described with a kinetic $K_d/R_d$ approach, i.e.,

$$M_{(aq)}^{n+} \xrightleftharpoons[k_{sb}][k_{sf}] M_S$$  \hspace{1cm} \text{Equation 4.5}

$$\frac{d[M_S]}{dt} = k_{sf}[M_{(aq)}^{n+}] - k_{sb}[M_S]$$  \hspace{1cm} \text{Equation 4.6}

where $k_{sf}$ and $k_{sb}$ are the forward and backward rate constants, respectively and $M_S$ represents metal ion complexed directly to the surface.

Two simple mathematical models were developed to predict the behaviour of metal ions and humics in the experiments. The treatment of the binary interaction between humic acid and metal ion is common to both models: initial rapid uptake to an exchangeable fraction, followed by slower transfer to the non-exchangeable fraction. Both models assume that the interaction of the humic with the mineral surface is unaffected by the complexation of metal ions. The difference between the models is that Model 1 (Figure 4.1) assumes that the observed heterogeneity derives from multiple binding sites on the surface of the iron oxide, whilst the second, Model 2 (Figure 4.2) assumes that it is the result of chemical or size heterogeneity of the humic itself. The interaction of HA and mineral is complex and involves multiple (at least four) kinetic components (Van de Weerd et al 1999; Bryan et al 2007). However, there are two clear classes of behaviour in the data, one showing fast sorption and another slower. Hence, initial modelling has used two fractions, and each kinetic component was assigned a pair of forward and backward rate constants. Initially, the behaviour was modelled on the assumption that the two kinetic components are due to the presence of two different HA
binding sites on the surface. This is referred to as ‘Model 1’. The equations for Model 1 are given by,

\[ HA_{\text{free}} + S_{HA1} \xrightleftharpoons[] {k_{HAS1f}/k_{HAS1b}} HA_{S1} \]  
Equation 4.7

\[ \frac{d[HA_{S1}]}{dt} = k_{HAS1f}[HA_{\text{free}}][S_{HA1}] - k_{HAS1b}[HA_{S1}] \]  
Equation 4.8

\[ HA_{\text{free}} + S_{HA2} \xrightleftharpoons[] {k_{HAS2f}/k_{HAS2b}} HA_{S2} \]  
Equation 4.9

\[ \frac{d[HA_{S2}]}{dt} = k_{HAS2f}[HA_{\text{free}}][S_{HA2}] - k_{HAS2b}[HA_{S2}] \]  
Equation 4.10

where \( S_{HA1} \) and \( S_{HA2} \) are surface binding sites, type 1 and 2, respectively; \( HA_{S1} \) and \( HA_{S2} \) are HA bound to surface binding sites, type 1 and 2, respectively; and \( k_{HAS1f}, k_{HAS1b}, k_{HAS2f} \) and \( k_{HAS2b} \) are rate constants for the forward and backward steps for HA sorption to type 1 and type 2 sites, respectively. These interactions are represented in Figure 4.1.
HA and iron oxide (not magnetite) surface interactions have been successfully modelled assuming multiple fractions of HA binding to a homogeneous surface with a single surface binding site (e.g., Van de Weerd et al., 1999). Therefore to test this hypothesis, a second model (Model 2) was developed, which had 2 HA fractions and 1 surface binding site. The equations for Model 2 are given by,

\[
HA_{1\,\text{free}} + S_{HA} \xleftrightarrow{k_{HA1S}} HA_{1S} \tag{4.11}
\]

\[
\frac{d[HA_{1S}]}{dt} = k_{HA1S}[HA_{1\,\text{free}}][S_{HA}] - k_{HA1S}[HA_{1S}] \tag{4.12}
\]

\[
HA_{2\,\text{free}} + S_{HA} \xleftrightarrow{k_{HA2S}} HA_{2S} \tag{4.13}
\]

\[
\frac{d[HA_{2S}]}{dt} = k_{HA2S}[HA_{2\,\text{free}}][S_{HA}] - k_{HA2S}[HA_{2S}] \tag{4.14}
\]
where $\text{HA}_{1}\text{free}$ and $\text{HA}_{1S}$ are HA species (fraction 1) that are in the solution phase and sorbed, respectively; $S_{HA}$ is the surface binding site; and $k_{HA1Sf}$ and $k_{HA1Sb}$ are the forward and backward rate constants for HA fraction 1 binding to the surface, respectively. The equations for HA fraction 2 are analogous to those for HA fraction 1. All of the interactions in Model 2 are shown in Figure 4.2.

![Figure 4.2: Ternary System Model 2: terms defined in the text.](image)

The two models were tested with the experimental data to see how well they could fit the sorption behaviours of the various HA / magnetite binary systems and HA / Eu$^{3+}$ / magnetite ternary systems, including the successive HA and Eu sorption data. There was particular interest to see how the 2 models would cope in modelling the experiments using humic size fractions, as the behaviours there differed significantly compared to unfractionated HA.
4.2 Development of the Models

The usual approach in kinetic modelling is to use a batch computer program, in which the model is provided with a series of input parameters that are used to produce an output file containing the model data. The contents of the output file are then compared to the experimental data. This process is repeated with different parameters until the best fit is obtained. This method is time-consuming and inefficient.

In the development of the models, the author of the thesis worked with the project supervisor to develop a kinetic model within a Microsoft Excel workbook. The main advantage of this process is that ‘live fitting’ is possible, which is quicker than batch processing. In this type of fitting, model output data are instantly plotted on the same axes as the experimental data being modelled, allowing for immediate comparison.

Fitting was done by manually adjusting the rate constant and binding site concentration parameters. Often, during fitting, a set of parameters would provide a good fit for one particular HA concentration, but fail to predict the behaviour of systems with a different HA concentration in the same experiment. In order to avoid the time-consuming comparison of different systems one at a time, a workbook was created that contained a series of worksheets; each one calculating the behaviour of each system in the experiment. A ‘control’ worksheet contained the model parameters, and each system worksheet linked to that. The control worksheet contained a plot of experimental data alongside model data for each dataset in the system of experiments. This setup allowed the immediate comparison of model fit to the experimental data for all datasets in that system simultaneously.

During all modelling, the rate constant $k_{\text{HAb}}$ and amounts of $[M_{\text{exch}}]$ and $[M_{\text{non-exch}}]$ were calculated from the dissociation experiments for each humic fraction.
(described in Chapter 3). These values were also used to calculate the $k_{HAf}$ for each humic sample: the equations that were used were,

$$M_{\text{exch}} \overset{k_{HAf}}{\rightleftharpoons} M_{\text{non-exch}}$$  
Equation 4.15

$$
\frac{k_{HAf}}{k_{HAb}} = \frac{[M_{\text{non-exch}}]}{[M_{\text{exch}}]}
$$  
Equation 4.16

where $k_{HAf}$ and $k_{HAb}$ are the forward and backward rate constants between the exchangeably bound metal ion ($M_{\text{exch}}$) and the non-exchangeable ($M_{\text{non-exch}}$), respectively. Equation 4.16 follows from equation 4.4 when reaction 4.15 is in equilibrium. Equation 4.17 can be rearranged to give,

$$
k_{HAf} = \left(\frac{[M_{\text{non-exch}}]}{[M_{\text{exch}}]}\right) \times k_{HAb}
$$  
Equation 4.17

The values of $k_{HAb}$ and $[M_{\text{non-exch}}]$ are available directly from Chapter 3 (Tables 3.1 - 3.4), and $[M_{\text{exch}}]$ can be calculated by subtracting $[M_{\text{non-exch}}]$ from the total Eu used in the dissociation experiments. Therefore, values of $k_{HAf}$ could be produced, and these are listed in the tables below (Tables 4.1 - 4.5). These rate constants ($k_{HAf}$ and $k_{HAb}$) were then used in Models 1 and 2 to predict the behaviour of the experiments.

Throughout this chapter when modelling the adsorption of Eu$^{3+}$ onto the magnetite surface in the presence of the different humic samples, the sorption of europium onto magnetite without any humic was also fitted (labelled as 0 ppm (w.v) in figures). This data set was the same for all of the different humic samples. It was used to define the rate constants $k_{Sf}$ and $k_{Sb}$.
4.3 Modelling Experimental Sorption Data

4.3.1 Whole Unfractionated HA

Figure 4.1 shows the sorption behaviour of whole HA predicted by Model 1 and Model 2 compared to the experimental data already presented in section 3.2.1 for the whole HA / magnetite binary systems. Example calculations are shown below in Tables 4.1 and 4.2 (Model 1) and Tables 4.3 and 4.4 (Model 2).

![Figure 4.1: Sorption behaviour of whole HA predicted by Models 1 and 2 compared to experimental data (pH 6, I = 0.1 mol dm\(^{-3}\), magnetite concentration = 50 g dm\(^{-3}\)).](image)

From the figure, both predictions of the sorption behaviour by Models 1 and 2 are quite similar. The initial rapid uptake of humic onto magnetite is modelled well, but after day 6 / 518400 s, the slower uptake of humic onto magnetite is underestimated, especially for the 100 ppm (w.v) and 200 ppm (w.v) systems. For the 10 ppm (w.v) system both models correlate well with the data points. It would have been possible to produce a slightly improved fit to the data in Figure 4.3. However, it was an important principle of the modelling that only one set of parameters could be used for each humic sample, and so the fits shown in Figure 4.3 are made with best overall parameters for all of the whole humic experiments.
The sorption behaviour of Eu\(^{3+}\) predicted by Models 1 and 2, compared to the experimental data from section 3.3.3 for the HA / Eu\(^{3+}\) / magnetite ternary system (24 hour pre-equilibration of Eu and HA) is shown in Figure 4.4. Note, as in all of the ternary system experiments, the Model 1 and 2 predictions for the experiment without humic (0 ppm (w.v)) are coincident.

**Example Calculations of the Outputs of Model 1 from Figure 4.3**

Modelling calculations for model 1 with the parameters (Length of Expt (d): 32; Length of Expt (s): 2764800; [HA] init (ppm (w.v)): 100; [S1]: 5; [S2]: 16; \(k_{HAS1}\): 1.00E-06; \(k_{HAS1b}\): 1.00E-05; \(k_{HAS2}\): 2.00E-07; \(k_{HAS2b}\): 1.00E-6; \(k_{SF}\): 3.90E-05; \(k_{SB}\): 1.50E-06; \(k_{HF}\): 3.70E-09; \(k_{HB}\): 1.30E-07; K: 350; \([\text{M}_2]\) t=0: 0; [M\(_{\text{aq}}\)] t=0: 0; [M\(_{\text{exch}}\)] t=0: 7.91E-10; [HA(exch)]\(_T\): 1.00; [M\(_{\text{non-exch}}\)] t=0: 2.51E-13; [S]\(_T\): 1.00) used in Table 4.1 (Humic data) and 4.2 (Metal data).

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<th>[HA(_{\text{z}})]</th>
<th>[S1]</th>
<th>[S2]</th>
<th>(d[\text{HA}_{\text{meq}}]/dt)</th>
<th>(d[\text{HA}_{\text{z}}]/dt)</th>
<th>(d[S1]/dt)</th>
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Table 4.1: Example Humic modelling calculations from Model 1.
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<th>[M₅⁺]</th>
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<th>[M₇⁺]</th>
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<th>d[M₅⁺]/dt</th>
<th>d[M₆⁺ (aq)]/dt</th>
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</table>

Table 4.2: Example Metal modelling calculations from Model 1.

Example Calculations of the outputs of Model 2 from Figure 4.3

Modelling calculations for model 2 with the parameters (Length of Expt (d): 32; Length of Expt (s): 2764800; [HA] init (ppm (w.v)): 100; [S]total: 100; [HA1total]: 40; [HA2total]: 60; k_{HAS1f}: 2.00E-06; k_{HAS1b}: 1.00E-06; k_{HAS2f}/k_{HAS2b}: 2; k_{HAS2f}: 1.5E-07; k_{HAS2b}: 1.0E-07; k_{Sf}: 3.90E-05; k_{Sb}: 1.50E-06; k_{HAf}: 3.70E-09; k_{HAb}: 1.30E-07; K: 350; [M₄⁺] t=0: 0; [M₅⁺] t=0: 0; [M₆⁺ (aq)] t=0: 7.91E-10; [HA(exch)]T: 1.00; [M_{non-exch}] t=0: 2.51E-13; [S]T: 1.00) used in Table 4.3 (Humic data) and 4.4 (Metal data).
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<th>([\text{HA}_\text{free, TOTAL}])</th>
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<th>([\text{HAS}_2])</th>
<th>([\text{S}])</th>
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<th>(\frac{d[\text{HA}_2\text{free}]}{dt})</th>
<th>(\frac{d[\text{HaS}_1]}{dt})</th>
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Table 4.3: Example Humic modelling calculations from Model 2.

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<th>(\frac{d[\text{M}_2]}{dt})</th>
<th>(\frac{d[\text{M}_{\text{aq}}]}{dt})</th>
<th>(\frac{d[\text{M}_{\text{non-exch}}]}{dt})</th>
<th>(\frac{d[\text{M}_{\text{exch}}]}{dt})</th>
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Table 4.4: Example Metal modelling calculations from Model 2.
Figure 4.4: Eu$^{3+}$/HA/magnetite ternary system, comparison of Models 1 and 2 with experimental data, HA/Eu$^{3+}$ equilibration time 24 hours (pH 6, $I = 0.1$ mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

For the europium sorption data in Figure 4.4, the Model 1 and 2 predictions are quite similar at 50 and 100 ppm (w.v), but at 20 ppm (w.v) there is a difference between the two as Model 2 fits the initial sorption well up to day 3 / 259200 s, but then overestimates the amount of Eu$^{3+}$ sorbed for the slower absorption phase. Model 1 gives a good fit to the data across the different humic concentrations.

Figure 4.5 shows the model fits for the Eu$^{3+}$/HA/magnetite ternary system with a humic/Eu pre-equilibration time of 7 days (section 3.3.10).
Figure 4.5: Eu\textsuperscript{3+} / HA / magnetite ternary system, comparison of Models 1 and 2 with experimental data, HA / Eu\textsuperscript{3+} equilibration time 7 days (pH 6, I = 0.1 mol dm\textsuperscript{-3}, magnetite concentration = 50 g dm\textsuperscript{-3}).

As shown in Figure 4.5, the sorption predictions are essentially the same as those in Figure 4.4, with Model 2 again overestimating the amount of metal ions adsorbed for the slow absorption phase in the 20 ppm (w.v) system. This is to be expected as the only difference between the experimental data in the two Figures is the 7 day pre-equilibration time. The only change this will produce is a difference in the relative amounts of Eu in the exchangeable and non-exchangeable, and the experiments in Chapter 3 have shown that only a small part of the Eu population transfers to the non-exchangeable, even after 7 days. Further, as the model parameters for the transfer between the two fractions are based on that dissociation data, there is little difference between the model predictions in Figures 4.4 and 4.5.

The successive sorption of unfractionated HA onto magnetite, where the magnetite was replaced with fresh magnetite twice (section 3.2.4) was simulated with both models, and the results are presented in Figure 4.6. The sorption behaviours predicted by both models are very similar, and both are quite accurate with good
fits to the fast and slow adsorption parts, across the different humic concentrations and for all 3 sorption steps at days 0, 9 (777600 s) and 14 (1209600 s).

Figure 4.6: HA / magnetite binary system successive sorption, comparison of Models 1 and 2 with experimental data (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Figure 4.7: Eu$^{3+}$ / HA / magnetite ternary system successive sorption, comparison of Models 1 and 2 with experimental data (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).
Figure 4.7 shows the successive sorption of $\text{Eu}^{3+}$ onto magnetite in the presence of whole unfractionated HA (section 3.3.6) and the Model 1 and 2 predicted sorption. In Figure 4.7, Models 1 and 2 have similar, reasonable predictions for the first adsorption step up to day 13 / 1123200 s for the 50, 100 and 200 ppm (w.v) systems. Both models struggle to model the 10 ppm (w.v) system as there is a high level of adsorption of $\text{Eu}^{3+}$. When the magnetite is replaced, differences occur between the two models. In the second adsorption step, Model 1 over-predicts the amount $\text{Eu}^{3+}$ sorbing to the magnetite at all humic concentrations, while Model 2 fits well with the 100 and 200 ppm (w.v) data sets. Model 2 slightly overestimates the amount of metal ion adsorbed at 50 ppm (w.v), but not as much as Model 1. At the third step (day 26 / 2246400 s), Model 1 continues to overestimate sorption. Model 2 continues to perform better, and although the fit to the 100 ppm (w.v) system is less good, the fit to the 50 ppm (w.v) system has improved. Overall, Model 2 is significantly better at fitting the data sets in Figure 4.7 than Model 1, which generally overestimates the amount of europium adsorbed to the magnetite.

The parameters used in the Model 1 and 2 predictions in Figures 4.3 to 4.7 are presented in Table 4.5, where $[S1_{\text{total}}]$ and $[S2_{\text{total}}]$ are the total Model 1 binding site concentrations, $[S]_{\text{total}}$ is the total humic binding site concentration for Model 2 and $[HA1_{\text{total}}]$ and $[HA2_{\text{total}}]$ are the percentages of the two types of humic for Model 2.
### Table 4.5: Parameters used for Models 1 and 2 in predicting the experimental data in Figures 4.3 to 4.7.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Model 1 for whole HA</th>
<th>Parameters</th>
<th>Model 2 for whole HA</th>
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<td>$K_{\text{exch}}$ (dm$^3$ mol$^{-1}$)</td>
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<td>$[S]_{\text{total}}$ (µg of humic/mg of magnetite)</td>
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<td>$[S]_{\text{total}}$ (µg of humic/mg of magnetite)</td>
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<td>$[\text{HA}^1_{\text{total}}]$ (%)</td>
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#### 4.3.2 HA<3 kDa Fraction

Figure 4.8 shows the experimental sorption behaviour of the HA<3 kDa fraction (section 3.2.5) compared to the Model 1 and Model 2 predictions.
Both models give reasonable fits to the 100 and 50 ppm (w.v) data, but for the 20 ppm (w.v) system, the Model 1 fit is definitely better. The predicted sorption behaviour by Model 1 has an overall better fit than Model 2 in Figure 4.8.

The sorption behaviours of Eu\(^{3+}\) predicted by Model 1 and Model 2, compared to the experimental data (section 3.3.7) for the HA<3 kDa / Eu\(^{3+}\) / magnetite ternary systems (with a 24 hour pre-equilibration time) are shown in Figure 4.9, whilst the equivalent results for the system with a pre-equilibration time of 7 days are shown in Figure 4.10.
Figure 4.9: Eu\(^{3+}\) / HA<3 kDa fraction / magnetite ternary system, comparison of Models 1 and 2 with experimental data, HA<3 kDa fraction / Eu\(^{3+}\) equilibration time 24 hours (pH 6, I = 0.1 mol dm\(^{-3}\), magnetite concentration = 50 g dm\(^{-3}\)).

Once again, there is no significant difference between the data presented in Figures 4.9 and 4.10, either for the experimental data or for the model predictions. This is to be expected, because the non-exchangeable interaction was shown to be less important for this size fraction in the dissociation experiments. For both figures, both models predict sorption well for the 100 ppm (w.v) systems, however both struggle to predict the 20 ppm (w.v) and 50 ppm (w.v) systems by greatly underestimating the amount of metal ion adsorbed. This is the first time that both models have been used to predict the sorption behaviour of humic size fractions. It is interesting that the size fractionation of the humic sample, which might have been expected to simplify the behaviour, has actually resulted in a poorer fit for the ternary system data. The problem is that the behaviour is too subtle to be addressed by either model in their current forms. The 100 ppm (w.v) data show that the <3kDa fraction is able to bind Eu\(^{3+}\) ions and compete with the surface at this higher concentration. However, at the lower concentrations of humic, the extent of Eu removal from solution is approximately the same as in the humic free system. If the solution phase humic is considered as a competitor for the metal
ions, then we would expect the extent of sorption to increase with decreasing humic concentration. However, it is not possible to define a single binding strength for the sample that allows significant humic enhanced retention in solution at 100 ppm (w.v), but none at 50 ppm (w.v). The problem with the model is that it assumes that all humic molecules have the same binding strength. The 100 ppm (w.v) data show that at least some of the humic molecules in this sample are able to bind the Eu$^{3+}$ relatively strongly, and some of these molecules must be present in the 50 ppm (w.v) system, but since there is no enhanced Eu concentration in solution at this slightly lower humic concentration, the most likely explanation is that a significant proportion of those molecules must be immobilised on the magnetite surface. Therefore, it seems that there is further fractionation of the humic sample (probably chemical fractionation, given the narrow size range) with preferential sorption of the more strongly metal-binding fractions at total humic concentrations below 100 ppm (w.v). At present, the model is unable to simulate such behaviour.

Figure 4.10: Eu$^{3+}$ / HA<3 kDa fraction / magnetite ternary system, comparison of Models 1 and 2 with experimental data, HA<3 kDa fraction / Eu$^{3+}$ equilibration time 7 days (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).
The successive sorption of the HA<3 kDa fraction onto the magnetite surface (section 3.2.8) and the sorption predictions from Model 1 and Model 2 are presented in Figure 4.11.

For the 100 ppm (w.v) system, the fit from Model 1 is better than that of Model 2 for all three sorption steps, as Model 2 underestimates the amount of humic adsorbed in the second and third adsorption steps at days 14 (1209600 s) and 28 (2419200 s), respectively. For the 50 ppm (w.v) data, both models fit the data well across all three adsorption steps.

Figure 4.12 shows the experimental data for the successive sorption of europium onto the magnetite surface in the presence of the HA<3 kDa fraction (section 3.3.10) in comparison with the sorption behaviours predicted by Models 1 and 2.
Figure 4.12: Eu$^{3+}$ / HA<3 kDa / magnetite ternary system successive sorption, comparison of Models 1 and 2 with experimental data (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

For the 100 ppm (w.v) system, both models provide adequate fits across the three sorption steps, however the fits of both models are poor for the 50 ppm (w.v) system, as both models underestimate the amount of europium sorbed to the surface. Given the data in Figures 4.9 and 4.10, this result is expected.

The parameters used for Models 1 and 2 in predicting the sorption trends in Figures 4.8 to 4.12 are presented in Table 4.6.
Table 4.6: Parameters used for Models 1 and 2 in Figures 4.8 to 4.12.

4.3.3 3<HA<10 kDa Fraction

Figure 4.13 shows the sorption behaviour of the 3<HA<10 kDa fraction predicted by Model 1 and Model 2 compared to the experimental data already presented in section 3.2.5.
Figure 4.13: 3<HA<10 kDa fraction / magnetite binary system, comparison of Models 1 and 2 with experimental data (pH 6, I = 0.1 mol dm\(^{-3}\), magnetite concentration = 50 g dm\(^{-3}\)).

This time, for all of the different humic concentrations, Model 2 provides a better fit than Model 1, which slightly over-predicts the amount of humic sorbed to magnetite in the 100 ppm (w.v), but slightly underestimates sorption in the 20 ppm (w.v) system.

The sorption behaviour of Eu\(^{3+}\) predicted by Model 1 and Model 2 compared to the experimental data (section 3.3.7) for the 3<HA<10 kDa / Eu\(^{3+}\) / magnetite ternary system with a pre-equilibration time of 24 hours is shown in Figure 4.14. Figure 4.15 shows the analogous data for the system with a pre-equilibration time of 7 days.
Figure 4.14: Eu$^{3+}$ / 3<HA<10 kDa fraction / magnetite ternary system, comparison of Models 1 and 2 with experimental data, 3<HA<10 kDa fraction / Eu$^{3+}$ equilibration time 24 hours (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

Once again, there is little difference between the 1 day and 7 day data. As for the <3 kDa fraction, the behaviour of this sample is complex. Addition of a small amount of humic actually results in increased sorption. This can happen when the interaction of the metal ion with humic sorbed to the surface is stronger than that directly with the mineral. The models are unable to simulate the 20 ppm (w.v) data, because they both assume that the binding strengths of the sorbed and solution phase humic species are identical. Therefore, as the model binding strength increases, the behaviour of the metal tends towards that of the humic, and so the partition between solid and solution will become the same as that of the humic itself. The problem is that the Eu in the 20 ppm (w.v) systems shows stronger sorption than either the humic itself or the metal in the absence of humic. The only explanation is that the humic that has sorbed in these experiments has a higher affinity for the Eu than that which remains in solution.

For the 50 and 100 ppm (w.v) systems, the amount of Eu sorbed is much lower than in the humic free system. That the 100 ppm (w.v) data come between the 20
and 50 ppm (w.v) systems is unexpected, although the difference between them is small, taking into account the experimental uncertainties. The behaviour of the 3<HA<10 kDa fraction experiments is complex, and as for the previous humic sample, the models cannot cope, and only fit the humic free and 100 ppm (w.v) systems reasonably well. For the 50 ppm (w.v) and 20 ppm (w.v) data both models provide poor fits.

![Figure 4.15: Eu³⁺ / 3<HA<10 kDa fraction / magnetite ternary system, comparison of Models 1 and 2 with experimental data, 3<HA<10 kDa fraction / Eu³⁺ equilibration time 7 days (pH 6, I = 0.1 mol dm⁻³, magnetite concentration = 50 g dm⁻³).](image)

The successive sorption of the 3<HA<10 kDa fraction onto magnetite (section 3.2.8) and the Model 1 and 2 predicted sorption are shown in Figure 4.16.
Figure 4.16: 3<HA<10 kDa / magnetite binary system successive sorption, comparison of Models 1 and 2 with experimental data (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

For the 50 ppm (w.v) system, both models provide a reasonable fit. For the 100 ppm (w.v) data, Model 1 has a better fit for the first sorption step, but in the second sorption step Model 1 overestimates the sorption of humic to magnetite and greatly overestimates the sorption in the third sorption step. Model 2 has a good fit in the second sorption step, but also over-predicts the amount of humic sorbed in the third sorption step.

Figure 4.17 shows the successive sorption of Eu$^{2+}$ in the presence of the 3<HA<10 kDa humic fraction (section 3.3.10) compared with the predicted successive sorption behaviours from Models 1 and 2.
For the 100 ppm (w.v) data, the fit from Model 1 correlates well with the experimental data for all three sorption steps, whilst Model 2 is less effective. Both models struggle to fit the first sorption step in the 50 ppm (w.v) system, but with the second sorption step (day 13 / 1123200 s), Model 1 provides a closer fit than Model 2.

The parameters used in predicting the sorption behaviours for Model 1 and Model 2 in Figures 4.13 to 4.17 are shown in Table 4.7.
<table>
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<th>Model 2 of 3&lt;HA&lt;10 kDa</th>
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<td>$[S]_{\text{total}}$ (µg of humic/mg of magnetite)</td>
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<tr>
<td>$[S1_{\text{total}}]$ (µg of humic/mg of magnetite)</td>
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<td>$[HA1_{\text{total}}]$ (%)</td>
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Table 4.7: Parameters used for Models 1 and 2 in Figures 4.13 to 4.17.

4.3.4 10<HA<100 kDa Fraction

Figure 4.18 shows the sorption behaviour of the 10<HA<100 kDa fraction (section 3.2.5) compared to the model predictions.
Figure 4.18: 10<HA<100 kDa fraction / magnetite binary system, comparison of Models 1 and 2 with experimental data (pH 6, I = 0.1 mol dm⁻³, magnetite concentration = 50 g dm⁻³).

For the 100 ppm (w.v) data, Model 1 shows a slightly better fit than Model 2, which slightly overestimates the sorption of humic from day 1 / 86400 s onwards. Both models provide adequate fits for the 50 ppm (w.v) data, with Model 2 having a better fit for the initial rapid uptake of humic up to day 3 / 259200 s. For the 20 ppm (w.v) system, Model 1 has a much better fit than Model 2, which significantly underestimates the quantity of humic adsorbed, but both models have poor fits for the initial uptake.

The sorption of europium onto the magnetite surface in the presence of the 10<HA<100 kDa fraction for an equilibration time of 1 day (section 3.3.7) and the behaviour predicted by Models 1 and 2 are presented in Figure 4.19, with the 7 day data shown in Figure 4.20.
Figure 4.19: Eu$^{3+}$/10<HA<100 kDa fraction/magnetite ternary system, comparison of Models 1 and 2 with experimental data, 10<HA<100 kDa fraction/Eu$^{3+}$ equilibration time 24 hours (pH 6, $I = 0.1 \text{ mol dm}^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

For the 1 day data (Figure 4.19), both models provide reasonable fits to the 50 ppm (w.v) and 100 ppm (w.v) experimental data, but for the 20 ppm (w.v) data, Model 2 performs much better than Model 1, which over-predicts the sorption of europium.
In Figure 4.20, the performance of the Models is similar to that seen in Figure 4.19, except for the 20 ppm (w.v) system, where Model 1 is able to fit the sorption of metal ions very well (after day 7 / 604800 s). In general, the models have performed much better for this humic sample than for the < 3 kDa and 3 < HA < 10 kDa samples, because the systems are showing simpler behaviour.

The successive sorption of the 10<HA<100 fraction onto magnetite surface (section 3.2.8) and the sorption predicted by Models 1 and 2 are displayed in Figure 4.21.
In the 50 ppm (w.v) system, Model 1 shows a better fit than Model 2, which underpredicts the quantity of humic sorbed for the second and third sorption steps (day 14 / 1209600 s and day 27 / 2332800 s, respectively). For the 100 ppm (w.v) data, neither model is really superior, with Model 1 slightly underestimating sorption, whilst Model 2 overestimates it.

Figure 4.22 shows the successive sorption of europium to magnetite in the presence of the 10< HA< 100 kDa fraction (section 3.3.10) compared with the adsorption behaviour predicted by Model 1 and Model 2.
Figure 4.22: Eu$^{3+}$ / 10<HA<100 kDa / magnetite ternary system successive sorption, comparison of Models 1 and 2 with experimental data (pH 6, I = 0.1 M, magnetite concentration = 50 g L$^{-1}$).

For the 100 ppm (w.v) data, Models 1 and 2 provide reasonable fitting with Model 1 being slightly better as the fit correlates better with the data in the first two adsorption steps. For the 50 ppm (w.v) system, Model 1 is again slightly better, however after day 13 / 1123200 s, both models struggle to fit the data, due to the sorption of metal ions being so high.

The parameters used in predicting the sorption behaviours in Figures 4.18 to 4.22 are presented in Table 4.8.
Table 4.8: Parameters used for Model 1 and Model 2 in Figures 4.18 to 4.22.

4.3.5 HA>100 kDa Fraction

Figure 4.23 presents the experimental data for the sorption of the HA > 100 kDa humic fraction onto the magnetite surface (section 3.2.5) compared with the predicted behaviours from Models 1 and 2.
Figure 4.23: HA>100 kDa fraction / magnetite binary system, comparison of Models 1 and 2 with experimental data (pH 6, I = 0.1 mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

From the 100 and 50 ppm (w.v) data, there is little difference between Model 1 and Model 2, and both provide a reasonable fit. For the 20 ppm (w.v) data, Model 1 is slightly better, with Model 2 slightly under-predicting the quantity of humic adsorbed.

The sorption of Eu$^{3+}$ onto the magnetite surface in the presence of the HA>100 kDa humic fraction (24 hour data; section 3.3.7) and the predicted sorption from Models 1 and 2 are shown in Figure 4.24.
Figure 4.24: Eu$^{3+}$ / HA$>$100 kDa fraction / magnetite ternary system, comparison of Models 1 and 2 with experimental data, HA$>$100 kDa fraction / Eu$^{3+}$ equilibration time 24 hours (pH 6, $I = 0.1$ mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

From Figure 4.24, both models show good fits for the 100 ppm (w.v) system. For the 50 ppm (w.v) data, Model 2 is better than Model 1 as it has a better fit for most of the data points. For the 20 ppm (w.v) system, both models over-predict the sorption.

Figure 4.25 shows the experimental sorption data from section 3.3.9, i.e., europium sorbing to magnetite in the presence of the HA $>$ 100 kDa fraction after 7 days equilibration between HA$>$100 kDa and europium. The figure also shows the predicted sorption patterns from Models 1 and 2.
Figure 4.25: Eu$^{3+}$/HA$>100$ kDa fraction/magnetite ternary system, comparison of Models 1 and 2 with experimental data, HA$>100$ kDa fraction/Eu$^{3+}$ equilibration time 7 days (pH 6, $I = 0.1$ mol dm$^{-3}$, magnetite concentration = 50 g dm$^{-3}$).

In comparison with the previous experiment (Figure 4.24), the predicted sorption behaviours are quite similar. However, this time, the 20 ppm (w.v) data are slightly better fitted by Model 2 with Model 1 still over-predicting the amount of europium adsorbed in comparison.

The successive sorption of the HA$>100$ kDa fraction to the magnetite surface (section 3.2.8) and the sorption behaviours predicted by Models 1 and 2 are presented in Figure 4.26.
Figure 4.26: HA>100 kDa / magnetite binary system successive sorption, comparison of Models 1 and 2 with experimental data (pH 6, I = 0.1 mol dm\(^{-3}\), magnetite concentration = 50 g dm\(^{-3}\)).

For the 100 ppm (w.v) system, both models provide reasonable fits for the first sorption step, but Model 2 has a slightly better fit during the second and third sorption steps. For the 50 ppm (w.v) data, Model 1 provides a very slightly better fit than Model 2 during the first sorption step, but for the 2\(^{nd}\) and 3\(^{rd}\) steps, both models perform very well.

Figure 4.27 shows the successive sorption of europium to magnetite in the presence of the HA>100 kDa fraction (section 3.3.10), compared with the sorption behaviours predicted by Models 1 and 2.
From Figure 4.27, Model 1 and Model 2 show reasonably good sorption predictions of the 100 ppm (w.v) data across the three adsorption steps. For the 50 ppm (w.v) system, Model 2 has a better fit than Model 1 during the first sorption step, but after day 13 / 1123200 s both models underestimate the sorption of Eu$^{3+}$.

The parameters used for Model 1 and Model 2 in predicting sorption trends in Figures 4.23 to 4.27 are presented in Table 4.9.
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Table 4.9: Parameters used for Model 1 and Model 2 in Figures 4.23 to 4.27.

4.4 The Best Model

It is hard to make a single decision about whether Model 1 or 2 is better for fitting all of the data, since the behaviour varies significantly between the different humic sample systems. However, we can try to define a best model for each humic sample instead.

For the unfractionated humic data, there was no significant difference between the models in predicting the behaviour of the humic itself (Figures 4.3 and 4.6). For the Eu data, Model 1 was better at fitting the single stage batch data than Model 2 (Figure 4.4 and 4.5). For the Eu sequential sorption data (Figure 4.7) Model 2 performed much better than Model 1 in predicting the successive sorption of Eu
onto magnetite. Overall Model 1 provides better fits in the unfractionated HA data than Model 2.

For the HA<3 kDa size fraction data, Model 1 is overall better than Model 2 at predicting the behaviour of the humic itself, although both struggle to cope with the Eu data. For the 3<HA<10 kDa size fraction, again both cannot cope properly with the Eu sorption data, but this time for the humic sorption, Model 2 is slightly better than Model 1 overall. In the case of the 10<HA<100 kDa size fraction, Model 1 has better sorption predictions across the board. For the largest HA size fraction (HA>100 kDa), the two models give comparably good overall fits to the behaviour of the humic itself. However, for the Eu data, Model 2 does give a better fit than Model 1.

The overall result is that Model 1 appears to be more appropriate more often than Model 2, and so for predicting the speciation in these systems, Model 1 is likely to give a better overall fit than Model 2 in predicting sorption behaviours in HA / magnetite binary and HA / Eu / magnetite ternary systems.

The model parameters, $k_{Sf}$ and $k_{Sb}$ remained constant for both Model 1 and 2 when fitting the experimental data, while the other parameters such as $k_{HAS1f}$, $k_{HAS1b}$, $k_{HAf}$, etc. differed with each humic size fraction within each model but no clear trend can be seen. However, both models have the $K_{exch}$ parameter increasing in same order as for the relative binding powers determined using the DOWEX ion exchange experiment (Table 3.17). $K_{exch}$ increases with humic fraction size, except for the 3<HA<10 kDa fraction, which has the lowest $K_{exch}$. The unfractionated HA has the highest values. Therefore, the order is whole HA > (HA>100 kDa) > (10<HA<100 kDa) > (HA<3 kDa) > (3<HA<10 kDa). It cannot be a coincidence that the order is the same. By comparing the values of $K_{exch}$, we can compare the relative binding powers of the humic samples required to best fit the ternary data with the values measured directly with the DOWEX resin technique in
Chapter 3: the values are given in Table 4.10. The experimental and model values in the table agree well for the <3 kDa data. For the larger size fractions and the unfractionated data, although the order is the same, the binding powers increase more quickly for the model predictions than for the experimental data. The origin of the effect may be that the values used in the model are those that give the best overall fit to the ternary system data, where there is evidence that the solution and sorbed humics show different binding strengths, but the models only use a single value.

<table>
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<td>3.6 (± 0.2)</td>
<td>3.8 (± 0.2)</td>
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<td>1</td>
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<td>10</td>
<td>70</td>
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</table>

Table 4.10: Relative binding powers of the unfractionated HA and HA size fractions w.r.t. to 3<HA<10 kDa fraction comparison of experimental values and Model predictions (errors = 1σ, for experimental data).

4.5 Previous Work

In previous studies, Farrelly (2007) and Abrahamsen (2009) developed similar Models to predict sorption data with equations that either included surface binding site heterogeneity (like Model 1 here) or humic heterogeneity (like Model 2 here). In Farrelly (2007) and Abrahamsen (2009) unfractionated humic acid was used in all the experiments, and therefore only comparisons with unfractionated HA can be made with this study. Farrelly (2007) found that for the binary systems and ternary systems involving goethite and quartz, neither approach was superior, but for hematite systems, Model 1 provided better fits for the data.

Compared with the modelling in this chapter both models were able to fit the binary data for all concentrations with little difficulty. Overall the modelling in this chapter has shown better fittings of the data than Farrelly (2007), despite the fact that
Farrelly did not use sequential sorption experiments, which are harder to model. Therefore, it seems that the magnetite system is ‘better behaved’ than those of goethite or hematite.

In Abrahamsen (2009), the binary/ternary systems of sand and montmorillonite at humic concentrations of 10 - 200 ppm (w.v) were modelled. Abrahamsen (2009) found that Model 1 was slightly better at fitting the sand systems than Model 2; however Model 2 provided better fits for the montmorillonite data. Not only were simple batch uptake experiments fitted, but also successive HA sorption experiments were also fitted this time. Abrahamsen (2009) found that both models gave adequate fits for the sand system; however Model 1 was better overall.

4.6 Limitations of the Models
This is the first time that ternary behaviour for HA size fractions has been modelled using any approach, yet alone using Models 1 and 2, and so limitations might be expected. For the HA<3 kDa and 3<HA<10 kDa ternary systems, only the Eu behaviour in the 100 ppm (w.v) system could be fitted. This failure of the linear additive approach is almost certainly due to chemical fractionation, and the humics on the surface and in solution appear to have different binding strengths. Given that the samples have been size fractionated already, and that the samples showing the most challenging behaviour have very narrow size ranges, it seems probable that the problems are due to chemical fractionation. Such fractionation has been observed previously (Claret et al., 2007, 2008). Other authors (Yamamoto et al., 2005, 2006; Sonke and Salters, 2006; Pourret et al., 2007; Stern et al., 2007) have proposed that the variability of lanthanide-HA binding patterns is due to the presence of two distinct fractions with different affinities for the lanthanides, which occur in distinct proportions. This could help to explain why the ternary model does not always work. The models only have a single metal ion binding strength, but if the two fractions partition differently between solid and solution, then a ternary model like ours has to fail.
It is important to note that not all of the modelling failed in fitting the HA size fraction data and in fact overall, a majority of the experiments were fitted by Models 1 and 2 across a variety of experiments (simple uptake in binary and ternary; successive sorption in binary and ternary) and conditions, which shows both models to be quite resilient and adaptable.
Chapter 5

Conclusions and Future Work
5.1 Kinetics

First order dissociation rate constants have been determined for the whole HA and HA size fractions. The dissociation rate constants are independent of HA fraction size. The HA fraction size only affects the amount of Eu$^{3+}$ in the non-exchangeable. The largest HA size fraction (HA>100 kDa) contained the highest amount of Eu$^{3+}$ bound non-exchangeably. Longer pre-equilibration times (from 24 hours to 7 days) do result in higher amounts non-exchangeably bound. For a given sample, the amounts of Eu$^{3+}$ in the non-exchangeable at 20 and 100 ppm (w.v) are not significantly different, and the rate constants are the same too. Therefore, humic concentration does not have an effect on the non-exchangeable binding of Eu$^{3+}$ by humics (in the concentration range 20 - 100 ppm (w.v)).

Time series ultrafiltration of Eu$^{3+}$/whole humic mixtures has shown a shift in the distribution of metal ions between different size fractions. There is a distinct shift to larger fractions with time. After 24 hours, the 3<HA<10 kDa size fraction contains the most Eu$^{3+}$, but after 3 days the HA>100 kDa fraction has the largest amount of Eu$^{3+}$. Beyond 3 days, the larger HA fractions are mainly responsible for binding the metal ion. This shift in the distribution over the course of a week occurs on the same timescale as the development of the non-exchangeable effect, and it is tempting to associate the two observations.

5.2 Humic Interactions in the Magnetite / Eu$^{3+}$ / Humic Ternary System

The sorption of HA onto magnetite revealed that there is a rapid sorption of HA followed by slower sorption with time across the humic concentration range 10 - 200 ppm (w.v). Successive sorption of HA onto magnetite at 50 - 200 ppm (w.v) has shown evidence of rapid and slow uptake of humic in all the sorption steps, the relative magnitude of the rapid and slow uptake changes for each ‘sorption step’ for all of the humic samples, suggesting a complex mechanism. There is considerable irreversibility in the interaction of the humic with the magnetite surface (for the whole humic and the humic size fractions). This is a significant result, since any
metal ion associated non-exchangeably with a sorbed humic is likely to show similar slow desorption kinetics. This could complicate the prediction of radionuclide mobility in the geosphere.

The presence of Eu$^{3+}$ (at concentrations in the range $1 \times 10^{-5}$ to $1 \times 10^{-8}$ mol dm$^{-3}$) seems to have no effect on the sorption of whole HA and HA size fractions onto magnetite. This means that model parameters for predicting humic behaviour derived from binary systems should be valid in ternary systems as well, and so the same parameters to describe humic sorption may be used regardless of radionuclide concentration at any level that would realistically be expected in the far-field of a radioactive waste repository. The results also suggest that ternary complexes of the type mineral-metal ion-humic are not significant in these systems, since we would have expected to see an effect of the presence of Eu in the data if they were important.

The strength of the sorption to magnetite increases with HA fraction size. This result supports the previous suggestion in the literature (Pitois et al., 2008; Chorover and Amistadi 2001; Vermeer and Koopal, 1998; Schmitt et al., 1996; Gu et al., 1995) that larger HA species should show preferential sorption to mineral surfaces. The difference in sorption strength is important for radionuclide behaviour, as it suggests that a radionuclide attached to a larger humic species is more likely to be retarded. The whole HA shows greater sorption than the smaller HA fractions (HA $<3$ kDa and $3<$HA$<10$ kDa), which suggests that the larger fractions (10<$HA<100$ and HA$>100$ kDa) dominate the humic sorption behaviour in the unfractionated humic and that they are mainly responsible for sorption in the ternary systems at low humic concentration. The sorption of combinations of HA size fractions onto magnetite may be predicted from the average behaviour of the individual size fractions, which suggests that the mixed fractions are behaving like simple, non-interacting mixtures.
Sorption increases with increasing humic fraction size for all ionic strengths between 0.01 and 3 mol dm$^{-3}$. The whole humic adsorbs the most at $I = 0.01$ and 0.1 mol dm$^{-3}$, however at $I = 1$ and 3 mol dm$^{-3}$, the largest humic fraction (HA>100 kDa) adsorbs more. For all humic size fractions and the whole humic, sorption increases with increasing ionic strength ($I = 0.01 - 3$ mol dm$^{-3}$). The explanation cannot be as simple as increased electrolyte concentration resulting in the shielding of magnetite (and humic) charge, because the experiments were performed under conditions where the magnetite carries a positive charge. Instead, it seems that the humic contracts with increasing ionic strength, reducing the surface area required to bind a given mass of humic and also allowing the humic and its negative charges to approach closer to the positively charged magnetite surface.

The analysis of humic sorption onto magnetite by Asymmetric Flow Field Flow Fractionation found initial sorption of intermediate molecular weight fractions, but after 1 day there is a shift in weight average MW to higher mass, which indicates preferential sorption of lower molecular weight fractions. The behaviour is qualitatively similar to the behaviour in hematite systems (Hur and Schlautman 2003) and confirms the complexity of the interaction with magnetite.

**5.3 Europium / Magnetite / Humic Ternary Systems**

Eu$^{3+}$ sorption onto magnetite was studied as a function of Eu concentration at ionic strengths of 0.01 and 0.1 mol dm$^{-3}$. For both ionic strengths, there is a general increase in the relative sorption of Eu$^{3+}$ as Eu concentration decreases from $1 \times 10^{-5}$ to $7.91 \times 10^{-10}$ mol dm$^{-3}$. Significantly, there is some evidence that the sorption of europium (bound to the humic exchangeably) in the Eu$^{3+}$/humic/magnetite ternary system may be reversible, unlike that of the humic itself. During the successive sorption of Eu$^{3+}$ onto magnetite in the presence of humic (whole and size fractions), the relative magnitudes of the sorption (rapid and slow components) generally decrease with each successive ‘sorption step’.
In the whole humic/europium ternary systems, there is initial, rapid adsorption of Eu$^{3+}$, followed by a slower uptake with time. The sorption of Eu$^{3+}$ onto magnetite increases as humic concentration decreases for the whole humic and the larger humic size fractions. This is ‘simple ternary system’ behaviour, and the humic appears to be acting primarily as a ligand that competes with the magnetite surface, and so reduces sorption. The order of addition of the components to the ternary system does affect the partition of the Eu between solid and solution, which is probably due to the irreversible nature of the humic sorption to magnetite.

The behaviour of the Eu in the ternary system is independent of Eu concentration for \([\text{Eu}] < 10^{-6} \text{ mol dm}^{-3}\). This result is significant, as it suggests that the same parameters could be used to describe the effect of humics on radionuclide partition between solid and solution up to radionuclide concentrations far higher than would be expected in the far-field of a radioactive waste repository.

The larger humic fractions \((10<\text{HA}<100 \text{ kDa}; \text{HA}>100 \text{ kDa})\) are more effective at retaining Eu$^{3+}$ in the solution than the smaller fractions. The separation of whole HA into sub-fractions reduces the overall binding strength. It seems that studies of metal ion behaviour in whole HA in ternary systems may not reveal fully the complexity of the interactions of the individual components in the humic population. This is important, as the results above have shown that fractionation of the whole humic is likely during transport. The order of Eu$^{3+}$ sorption was \((3<\text{HA}<10 \text{ kDa}) > (\text{HA}>3 \text{ kDa}) > (10<\text{HA}<100 \text{ kDa}) > (\text{HA}>100 \text{ kDa}) > \text{whole HA}\). This order is consistent with the different binding strengths of the HA size fractions determined separately.

Pre-equilibration time (24 hours and 7 days) between the humic samples and the Eu$^{3+}$ before the introduction of magnetite has little effect on the sorption behaviour of Eu$^{3+}$. However, pre-equilibration time between humic and magnetite does effect
the initial sorption of europium when it is introduced, but after a few days, it appears that equilibrium is established.

The experimental data contain direct evidence for the formation of ternary complexes, and that these can affect the partition of the metal ion between solid and solution. In the effect of Eu concentration on the Eu\(^{3+}\) sorption onto magnetite in the presence of whole humic, there is some evidence for ternary complexes in the system, as the presence of humic increases sorption of Eu\(^{3+}\) onto magnetite at [Eu] = 10\(^{-6}\) mol dm\(^{-3}\). The behaviour of the Eu in the 20 ppm (w.v) 3<HA<10 kDa ternary system is another example: i.e., there is stronger sorption in the presence of the humic than without. Further, they become more important as the humic concentration tends towards the values expected in the environment. Hence, they must be considered in the prediction of radionuclide mobility.

### 5.4 Modelling

Two ternary system kinetic speciation models have been developed. Both treat the interaction of HA and metal ion with 2 components: one exchangeable and one non-exchangeable. The binary interaction between metal ion and mineral surface has been described here with a single kinetic reaction. The two differ in their description of the multi-component behaviour of the binary HA-mineral interaction. Model 1 assumes a single HA species and two surface binding sites, whilst Model 2 has a single surface sorption site and two HA species in solution.

Models 1 and 2 were able to predict the sorption behaviours of unfractionated humic data in humic / magnetite binary and humic / Eu / magnetite ternary systems, but overall Model 1 provided better fits. Model 1 continued to perform better than Model 2 in fitting the HA size fraction data.

The exchangeable binding strengths required to explain the experimental data in both models (K\(_{\text{exch}}\)) varied for the different humic samples in the order: whole HA >
(HA>100 kDa) > (10<HA<100 kDa) > (HA<3 kDa) > (3<HA<10 kDa), which is the same order found experimentally using an ion exchange technique.

When evaluating the performance of the models, it is important to remember that they are both very simple approaches to describing a complex system. In previous studies, a large majority of experimental and modelling studies have only examined single stage sorption with unfractionated humic. For the whole humic / HA size fractions, both models do well in predicting the behaviour of humic and metal in the first stage of sorption. However, it is important to test the models rigorously with other types of experiments such as successive sorption. The successive sorption experiments used here provide a much more rigorous test of a ternary system speciation model than simple batch uptake experiments, because in the environment, as the groundwater moves, it will encounter fresh mineral surfaces, and the successive experiments simulate this. In fact, the results from the modelling show that for many conditions, although the model could simulate the behaviour in a simple batch uptake experiment, it failed in the successive sorption experiments. This suggests that speciation models and parameters defined using simple batch $K_d$ experiments may not provide a good description of the system during transport calculations.

The two models have been kept as simple as possible, so that they would be more useful for a radiological performance assessment study or general prediction of radionuclide transport in the environment. However, the parameters that have been derived here could not be applied to a real RPA calculation, because the conditions at the site would be different to those studied here.

The experimental results (Chapter 3) and the modelling (Chapter 4) strongly suggest that, despite the fact that size fractionation has been shown to accompany sorption of the humic to mineral surfaces (e.g. Pitois et al 2008), this is probably not the origin of the failure of the linear additive approach to predicting the
behaviour of radionuclides in ternary systems. The most likely reason for the failure of the linear additive approach is that the humic in solution has a different binding strength to that sorbed on the mineral surface. It would be tempting to associate this difference with the well documented size fractionation. However, the size fraction data presented here show that this is unlikely to be correct for magnetite systems at least, because the single size fractions show behaviour that is harder to model than that of the whole humic, even for very narrow fractions (for example the very complex behaviour of the Eu in the 3<HA<10 kDa system). Hence, the data suggest that the origin of the effect is chemical fractionation that must accompany the size fractionation, and Pitois et al (2008) have suggested that in addition to the size differences, there are chemical differences between the solution phase and sorbed humic molecules. In the magnetite system at least, it seems that these chemical differences translate into differences in metal ion binding strengths, which in turn lead to the failure of the linear additive approach.

For the magnetite systems, where the linear additive approach fails, the sorbed humic always seems to show stronger binding than that in solution. Therefore, if these effects cannot be included easily in a model for RPA, then the good news is that assuming an average binding strength over the whole of the humic population will always overestimate the amount of radionuclide in solution (underestimate sorption), and so will give a conservative prediction of radionuclide transport.

Although the whole humic system behaviour appears simpler than some of the individual fractions, this must be because of an averaging process. The differences in binding strength between sorbed and solution phase humic that are very clear in the separate fraction data must still be there in the whole humic samples, and so the apparently simpler behaviour has significant underlying complexity.
5.5 Future Work

Further experiments with HA size fractions could be performed, such as HA size fraction-induced desorption of Eu\(^{3+}\) under a variety of conditions (pH, ionic strength, humic concentration).

The effect of pH on the sorption of humic onto magnetite in binary humic fractions systems and the effect of pH on the sorption of Eu in HA size fraction / Eu / magnetite ternary systems could be studied.

Further variations in the humic size fraction combinations experiments under various conditions could be studied to test if various fraction combinations can be predicted accurately using the average behaviour of the individual size fractions.

The experiments reported here could be repeated with various magnetite samples from the environment so the sorption behaviour of Aldrich magnetite can be compared with that of the environmental magnetite. This would give a better idea of the interactions occurring in the environment.

\(^{152}\)Eu has been used here as it has similar properties to Am. However, \(^{152}\)Eu is not an important constituent of radioactive waste. It would, therefore, be useful to apply the techniques developed here to systems involving radionuclides of interest in RPA calculations, such as U, Np or Pu.

Model 1 has been able to fit certain data that Model 2 cannot and vice versa. A combined Model 1 and 2 could be developed to overcome the limitations of both models to give better predictions of radionuclide partition and hence, transport in the environment.
As would be expected, the behaviour in the ternary systems is more complex than in the separate binary systems. The behaviour of the humic is much easier to simulate than that of the metal ion. The model fits are not always perfect for the humic, and for some samples, one model performs better than the other, but generally, it is possible to get a decent fit. That is not the case with the metal ion, where often a reasonable fit is not always possible (e.g. Eu behaviour in the <3 kDa and 3<HA<10 kDa ternary systems). Therefore, future modelling work should concentrate on improving the performance of the prediction of metal ion behaviour. The issue is not with the binary interaction of Eu$^{3+}$ with the magnetite, where the models can simulate the behaviour easily with a single chemical equation. It seems clear that it is the fractionation of the humic that is responsible for the failure of the models, and the models need to be adapted to account for this. An obvious first step would be to introduce different values of $K_{\text{exch}}$ for the two types of humic in Model 2. Adapting Model 1 would be much more difficult, since there is only a single humic fraction. Introducing different equilibrium constants for the single humic species in solution and on the solid phase might produce a fit to the data, but the implication would be that the intrinsic affinity of a humic molecule for a metal ion changes when it is bound to a mineral surface. In the magnetite case, the humic molecule would need to become much more attractive to the metal ion when it bound to the surface.
References


