

The effect of humic acid on the adsorption of REEs on kaolin

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Abstract

For a better understanding of adsorption of the rare earth elements (REEs) onto minerals and its controlling factors, adsorption experiments were performed at pH range of from 3 to 10 with kaolin (1500 mg/L) in a matrix of various concentration of NaNO₃ and about 20 μg/L of the total REEs as well as various amounts of humic acid (HA). The adsorption of HA onto the kaolin occurred over a wide pH range and decreases with increasing pH and with increasing HA concentration. The results show that humic acid has ability to either increase or decrease the adsorption of the REEs onto kaolin, depending on pH, which may be related to their speciation distribution, interaction of HA with the mineral surface. Furthermore, the light REEs are more adsorbed onto kaolin in presence of higher concentration of HA, presumably because the increase in HA concentration in the solution enhance stronger complexing of HA with heavy REEs as compare to light REEs. The ionic strength has strong effect on the adsorption of HA and REEs onto the kaolin but little on the REEs fractionation. The results presented here indicate that mineral/water adsorption may generate the enrichment of the dissolved heavy REEs in the presence of a significant amount of humic acid, which is consistent with the fractionation of REEs in the most of natural waters.

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1. Introduction

The rare earth element (REE) series is an excellent natural probe of many fundamental geochemical processes taking place in both of the interior and at the surface of the earth. In recent decades, geochemical processes controlling metal migration and deposition in the earth's surface environment has been intensively and increasingly attracting much interests of scientists [1–5], largely due to importance of understanding geochemistry of surface processes of the earth. Because of much concern especially about environmental pollution by heavy metals and the storage/disposal of nuclear waste (i.e. Am³⁺, Cm³⁺, and Cf³⁺) in recent years, it is of great importance to understand the geochemical behaviors of the REEs and their controlling factors in the earth's surface environment [6–8].

It has been proposed by many researchers [1,2] that water/particle adsorption/desorption and water/rock (soil) interactions play a major role in establishing the lanthanide

composition of freshwater. Inorganic particles in natural fresh waters are mainly composed of clays (silicates), carbonates and hydrous oxides of Al, Fe, Mn and Si [9], and can adsorb a great lot of trace metals especially in aquatic environment. However, adsorbed organics appear to be capable of dramatically transforming the surface characteristics of particles in natural waters and thereby affect the interactions with trace metals in solution [4,5,10]. Humic acid (HA), naturally occurring organic polyacid and having a strong complexing capacity for cations and a high affinity for mineral surfaces, has been recognized as an important factor controlling the behavior of various elements in the natural aquatic environment [9,11]. The affinity of lanthanides for mineral surfaces can be strongly affected by thin organic coatings [12,13]. Although extensive experimental studies have been carried out on the control of particle/water interaction on the distribution of the REEs in the aquatic environment, the studies have mainly focused on REE adsorption onto inorganic colloids [14–19]. Now, there are Several studies concerning the effect of HA on the REE distribution between the mineral and the solution with a main purpose to study the treatment of radioactive waste products [20–25], but the experiments have been generally conducted with a single lanthanide. It is,

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therefore, still quite uncertain how the sorption/desorption leads to fractionation of the REEs in aquatic system in the presence of the HA. To get a better understanding of role of humic acid in controlling the REEs adsorption and fractionation between light and heavy REEs, we performed adsorption experiments using solutions containing REEs and kaolin within pH range of 3–10 at normal temperature and pressure conditions in both the absence and presence of humic acid and discuss the effect of ionic strength and HA concentration on pH dependence of the REEs adsorption onto kaolin.

2. Materials and methods

Water was obtained from a Milli-Q (Millipore) purification apparatus. All other reagents used were of analytical grade or better. All equipment (polythene) were leached with acid (20% HNO₃) for overnight and thoroughly rinsed with Milli-Q water prior to use. Traces of acids from the washing procedure were removed by drying in oven. The pH of all solutions and suspensions were measured with Orion Model 818 pH-meter using Orion CHNO 60 electrode. All experiments were conducted at room temperature and atmospheric pressure.

2.1. Materials

The humic acid used was Fluka humic acid with technical grade, and used without further purification. Concentrated stock solutions were prepared by dissolution and filtration through glass fiber filter membranes. The solutions were allowed to store in the dark at 4 °C in amber glass bottles. Absorbance spectra were taken of the HA and absorbance was measured at wavelength 254 nm on Shimadzu UV3000 Dual-wavelength/Double-beam recording spectrophotometer.

REEs spiking in 0.45 M HNO₃ was prepared from nitrate standards and the composition of the REEs is similar to that of the shale (NASC). Kaolin was used without further purification, and simply added dry by weight, directed into the polythene bottles. The kaolinite was KGa-1 presented by Clay Minerals Society Source Clays Repository, the chemical and physical properties of which are previously investigated. The specific surface area of the kaolin is 10.05 ± 0.02 m²/g determined by BET method using N₂. And also characterized for cation exchange capacity (CEC) is 2.0 meq/100 g.

2.2. Adsorption experiment

All REEs and HA adsorption experiments were conducted in batches in acid-washed polythene bottles. All ionic strengths (*I*) were set to vary from 0 to 0.35 using NaNO₃, and pH was adjusted to between 3 and 10 using dilute HNO₃ and NaOH. The concentrations of HA varied between 0 and 50 mg L⁻¹. The concentration of total REEs in the solutions used for the experiments is 20 μg L⁻¹. Kaolin was used at a final concentration of 1500 mg L⁻¹. Phase separation was achieved by filtration. The efficiency of the supernatant was checked by measurement of the blank.

The adsorption of HA to the kaolin as a function of pH or ionic strength was studied by adjusting to the required pH or *I* after adding the desired concentration of HA to the kaolin dispersions. Before final pH measurement and phase separation, the suspensions were allowed to equilibrate for at least 24 h, which are considered to be long enough to equilibrate adsorption/desorption according to previous experiments conducted by many authors. The absorbance of the supernatant was then determined by spectrophotometer. Corresponding concentrations of HA were determined from calibration curves of absorbance versus humic acid concentration, taking into account variations in HA absorbance and removal by the influence of NaNO₃.

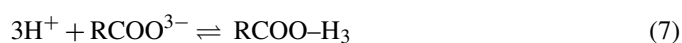
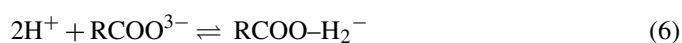
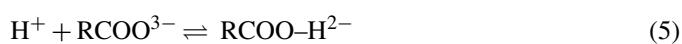
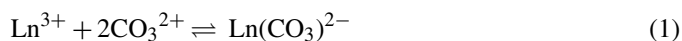
The adsorption of REEs as a function of pH, HA or *I* was studied by a similar procedure. After the equilibration of kaolin with the required concentration of HA, REEs was added and the samples were left to equilibrate for a further 24 h. After measurement of the final pH, the solutions were filtered through 0.22 μm membranes. The membrane filters were flushed and rinsed with HNO₃, which stripped the REEs adsorbed. The REEs concentration in these solutions were determined by ICP-MS. Triplicate blanks (REEs-containing solution without solid present, REEs-free solution with 1500 mg L⁻¹ kaolin) were run for each solution type.

2.3. Data treatment

The adsorption of HA to the kaolin surface was calculated as the difference between the initial and final concentrations of HA. The REE sorption ratio, *Rd* (%), was calculated from $Rd = (C_f - C_b)/C_o \times 100$, where *C_o* is the REE concentration in the REE-containing blank, in μg/L, at the end of the sorption period; *C_b* is the REE concentration in the REE-free blank, in μg/L, at the end of the sorption period; and *C_f* is the final REE concentration in the filter in μg/L, at the end of the sorption period. The final REE and HA concentration in the blanks was used in calculating sorption coefficients, thereby automatically correcting for any vial wall sorption and/or precipitation that may have occurred during the sorption period. The relative standard deviations of distribution coefficients for most REEs are between 5.0 and 6.6 [26].

2.4. Speciation calculation

The equilibrium in the solution may be as follow in the absence or presence of HA:



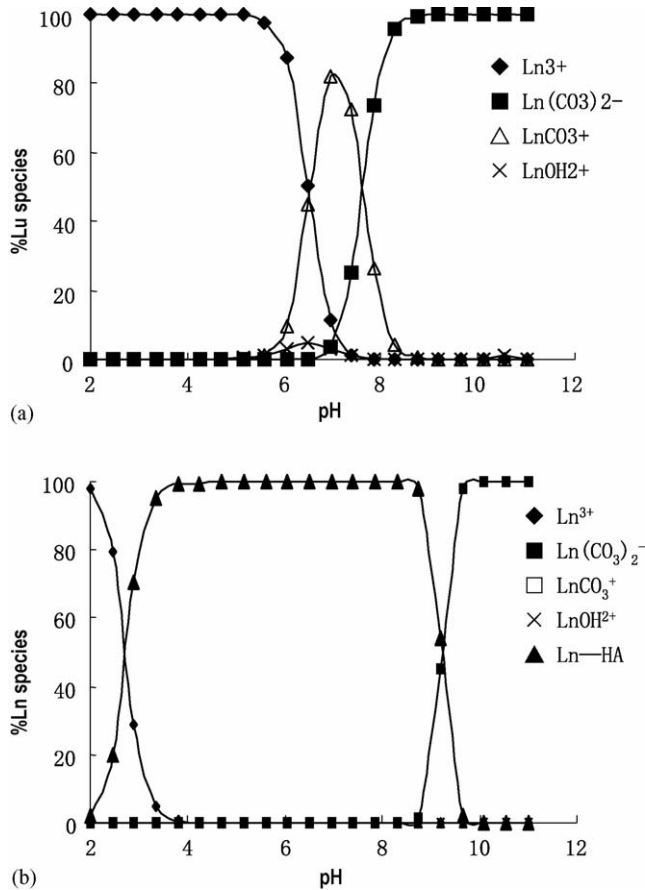


Fig. 1. Speciation calculation for REE in the absence (a) and presence (b) of humic acid in MINEQL⁺.

where Ln^{3+} and RCOO^- show Ln free ion and ligands for humic acid, respectively.

The percentages of dissolved species calculated by taking account of free ions, hydroxide, carbonate, and humate complexes in the absence or presence of HA at I 0.01 mol/L by MINEQL⁺ software are shown in Fig. 1. The stability constants of hydroxide and carbonate complex were taken from the literature [11,27,28]. The results show it have great influence on the REE speciation in the presence of HA. It is similar to other reports [11,12,21]. The results in speciation calculation show HA have a great influence on REE adsorption on the mineral due to REE–HA complex dominating in wide pH range. The results of the adsorption experiments are mostly explained by the present results on speciation calculation, as discussed later.

3. Results and discussion

3.1. Adsorption of humic acid

Fig. 2 shows the results of adsorption experiments with HA, which were conducted on kaolin at a range of HA concentrations of between 2 and 10 mg L⁻¹, over a pH range of between 3 and 10. The adsorption behavior of the HA in all cases are characterized by the general trend of decrease in HA adsorption with increasing pH, as well as a decrease in the percentages of

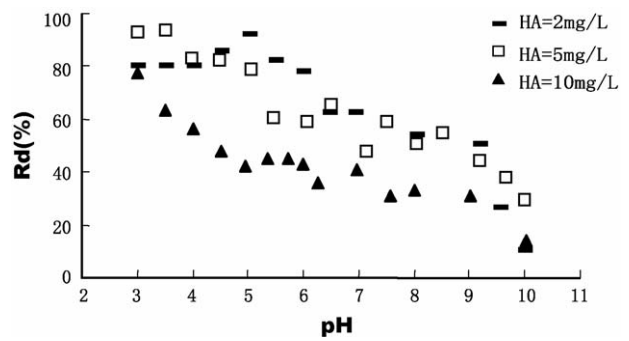


Fig. 2. The effect of pH on the adsorption of HA onto the Kaolin at $I=0.01$.

adsorbed HA with increasing HA concentration. This observation indicates the progressive saturation of the surface at all HA values and a strong dependence of adsorption on pH. The sorption behavior of the humic substances (HS) is consistent with the zeta-potential and structure change as a function of pH. With pH increasing, the hydrophobicity of HA decreases, while negative charge of HA increases, and the surface charge of colloid becomes more negative. In this case, the electrostatic attraction between the HA and colloid turns into the electrostatic repulsion, leading to reduced adsorption of HA with pH increasing. Generally, anion or/and ligand exchange between anion group on the HA and the surface hydroxyl group (e.g. $-\text{OH}_2^+$, $-\text{OH}$) on the kaolin is believed to be the main reason why sorption of humic substances increases with decreasing pH. Protonation of the surface hydroxyl initiates that less $-\text{OH}_2^+$ and $-\text{OH}$ would bind with the group of HA at higher pH in the ligand-exchange reaction.

The HA adsorption of kaolin shows the effect of ionic strength in Fig. 3. It shows the HA sorption is generally higher at higher ionic strength at all pH studied and the effect is remarkable especially at intermediate pH values. This result indicated that increasing of pH increases the polarity of HA, while increasing of ionic strength increases the hydrophobicity of HA.

3.2. Adsorption of REEs

3.2.1. The adsorption of REEs in the absence of HA

Fig. 4 shows the adsorption of Nd and Yb as function of pH in the absence and presence of HA. The sorption ratio (Rd)

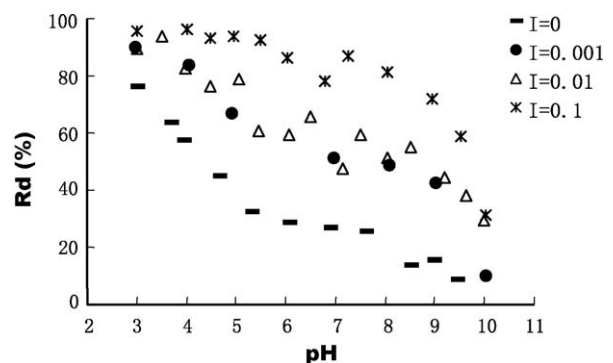


Fig. 3. The influence of pH on the adsorption of HA onto the Kaolin at $\text{HA} = 5 \text{ mg L}^{-1}$.

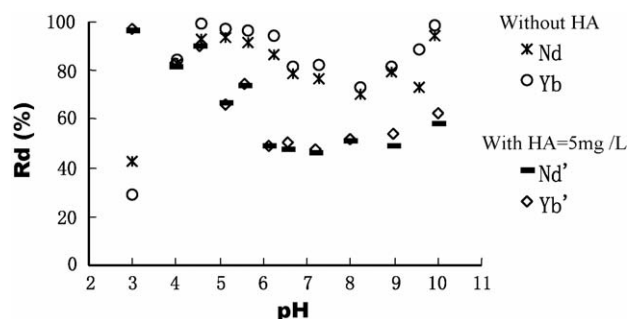


Fig. 4. Dependence of adsorption ratio (Rd%) on pH for REEs both in the absence and presence (5 mg L^{-1}) of HA, with $I=0$.

increases from about 20% at pH 3 to nearly 100% above pH 5, and then slightly decreases to nearly 70% around pH 8. It is observed from Fig. 4 that the adsorption of REEs onto kaolin is of less dependence on higher pH (higher than pH 5) as compared to that on lower pH. The measurement of the zeta potential of kaolin shows that the kaolin is negatively charged across the pH range and become more negatively charged with increasing pH, which may be due to deprotonation of hydroxyl groups on the surface of the mineral [21]. Accordingly, we expect that the kaolin studied here would be negatively charged almost over the whole pH range studied and of strong adsorption of REEs mainly by electrostatic attraction, though the zeta potential of the studied kaolin was not measured. However, an additional mechanism of adsorption is needed to explain the slight drop in adsorption of REEs from pH 5–8. We tentatively have no definite explanation for this drop, but consider that this mechanism could be the ion exchange reaction that competition of formation of REECO_3^+ with strong surface coordination complexes (AlOLn^{2+}) leads to a decrease in adsorption. At pH higher than alkaline pH (higher than 8), where the $\text{REE}(\text{CO}_3)_2^-$ becomes predominant, the adsorption increase again possibly due to the $\text{REE}(\text{CO}_3)_2^-$ forms complexes at the surface site (AlO^-) of kaolin.

3.2.2. The adsorption of REEs in the presence of HA

Fig. 4 shows the adsorption curve observed in this study, which is clearly different from that obtained in the absence of HA. Comparing this adsorption curve with that of HA especially at the same concentration and low ionic strength (Figs. 2 and 3), we suggest that the HA adsorbed onto the kaolin exerts an important role on controlling the adsorption of REEs on the mineral surface or edge, since the adsorption curves of HA and REEs are of very similar variation as function of pH.

Enhancement of REEs adsorption at low pH range (pH <4) would be expected owing to complexation of REEs with the HA sorbed onto kaolin surface. Another possible factor would be that adsorption of HA onto the surface of the kaolin produces a more negative zeta-potential which could lead to the more static favorable adsorption of any free REE^{3+} . In both cases, HA sorbed onto the minerals govern the adsorption of the REEs, and hence the adsorption of HA dominates the REEs adsorption at low pH range, because humic complexation is minimal at this pH range as carboxylic functions are not entirely ionized.

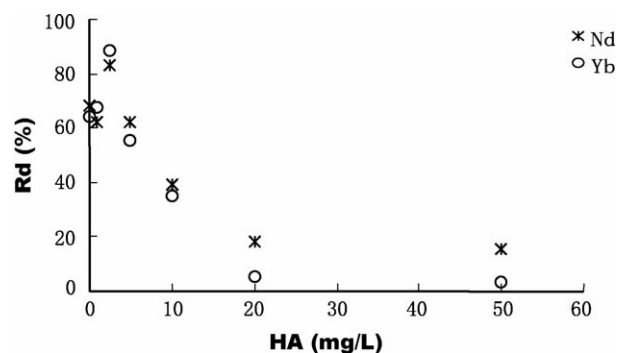


Fig. 5. The effect of HA concentration on REE adsorption on kaolin at pH 6.00 and $I=0.01$.

At most of the pH range, the REEs adsorption in the presence of HA is much lower than that in the absence of HA, presumably due to competition for REEs between HA in solution and HA sorbed onto the surface of the kaolin. At the pH range of from 3 to 7, the sorption of REEs onto the kaolin is significantly decreased with increasing pH in the presence of HA. The decrease in REEs adsorption can be explained by the increase in HA concentration and hence complexation of REEs by HA in solution. At the pH range of higher than 7, the adsorption of REEs onto the mineral surface shows a slight increase with increasing pH, very similar to the experimental results of previous authors [10,12] for adsorption of tetravalent elements onto hematite and kaolinite. The authors ascribe the increase in adsorption of the tetravalent elements to the competition between the surface sites of minerals and HA in solution.

HA concentration affects significantly the adsorption of REEs onto the kaolin (Fig. 5). The REEs adsorption increases from nearly 60% in the absence of HA to about 90% at $\text{HA} = 2.5 \text{ mg L}^{-1}$, and then decreases vastly to below 20% at $\text{HA} = 20 \text{ mg L}^{-1}$ at constant pH 6. At low HA concentration, REEs adsorption increases presumably due to the HA adsorption increasing and hence to the complexation of adsorbed HA with REEs. At HA concentrations higher than 2.5 mg L^{-1} , the REEs adsorption decreases with increasing HA concentration at pH 6. The effect of HA concentration on REEs adsorption is attributable to the competition for REEs between the HA in solution and the HA sorbed onto the minerals surface. As the surface of the mineral is saturated with HA, the more the concentration of HA present, the more free humic complexing sites are present in solution and the more efficient is the screening of the mineral surface. Under these conditions, the REEs is more predominately in solution as REE–HA complexes.

3.2.3. The effect of ionic strength

The effect of ionic strength on REEs adsorption is shown in Fig. 6. It indicates that in the presence of HA, the REEs adsorption increases sharply at low ionic strengths and slightly or become stable at high ionic strength at constant pH 6 and constant HA concentration ($\text{HA} = 5 \text{ mg/L}$). This is in accordance with the adsorption of HA at different ionic strength, which increases with increasing ionic strengths (Fig. 3) and suggests a control of HA–REEs complexing on the mineral surface.

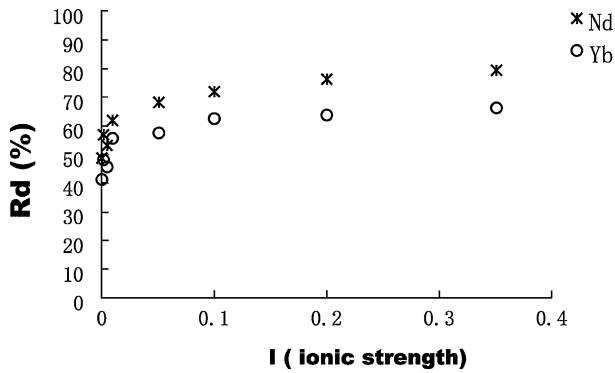


Fig. 6. The effect of ionic strength on REE adsorption, pH 6, HA = 5 mg L⁻¹.

3.3. REEs fractionation

The REE–HA complexes play the important role in REE adsorption and fractionation. In the presence of HA, HA distribution between the aqueous phase and the solid surface govern REE distribution due to REE exist as REE–HA as discussed in Section 3.2.2. The gradual decrease in REE Rd from HA 0 to 50 mg/L, apart from HA 2.5 mg/L in Fig. 7a, which are consistent with Fig. 5.

It modeled the lanthanides speciation as a whole due to lack of the complex constant for each rare earth element in Fig. 1. In fact, Takahashi et al. [12] considered humate complex with less ionic radius are more stable, therefore, heavy REE (Yb and Lu) can form more stable complex with humate compared to light REE (Ce and Eu) due to difference in ionic radius, which result in the REEs fractionation during adsorption in the presence of HA as function of HA concentration (Fig. 7a). Among REEs, the heavy REEs seems to favor humic substances slightly more than lighter REEs, which can explain the preference of light

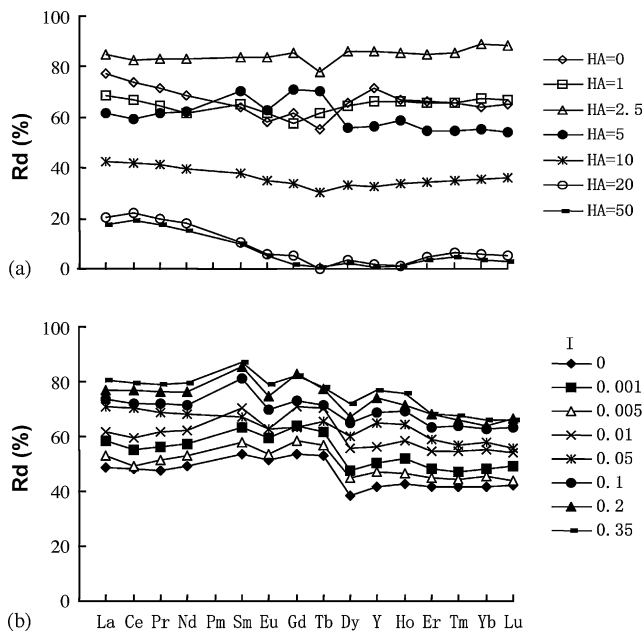


Fig. 7. Distribution patterns of REE adsorption ratios experimentally derived at various HA concentrations and $I=0.01$ (a) and various ionic strengths (b) with HA = 5 mg L⁻¹ and pH 6.

REEs adsorption at high HA concentration when more heavy REE–HA complexes forming in the aqueous phase.

As seen from the Fig. 7b, in the presence of HA with a constant concentration, the ionic strength shows little effect on fractionation of the REEs at certain pH, which is clearly different from the results of the experiments conducted in the absence of HA by Coppin et al. [18]. As the effect of ionic strength on fractionation of REEs adsorption in the absence of HA onto kaolinite and smectite, there are two explanations: one is that the high density of sorbed Na⁺ at high ionic strength reduces REEs sorption and the steric constraint inhibits the sorption of competitors with a larger ionic radius but the steric effect of Na⁺ is negligible at low ionic strength; another is that sorption at high ionic strength corresponds to chemisorption on the pH-dependent variably charged edge of the particles, indicating desolvation of cations to form inner-sphere complexes and hence the fractionation due to the variation in desolvation energy with atomic number of the REEs. In the REE–HA–mineral ternary system, competition among REE–HA in the solution and mineral–REE together with mineral–HA–REE complexation will most likely regulate the relative differences among the REEs adsorption. From the effect of HA concentration on the fractionation of the REEs adsorption, we know that higher HA concentration makes more light REEs be adsorbed onto mineral surface but low HA concentration has almost no effect on the fractionation of the REEs adsorption. Therefore, when the HA is present, the fractionation of the REEs adsorption is greatly dependent on HA concentration instead of ionic strength.

4. Conclusion

The adsorption of HA onto the kaolin occurred over a wide pH range and decreases with increasing pH and with increasing HA concentration. The pH dependence of adsorption of HA can be significantly affected by ionic strength and the adsorption of HA onto kaolin increases with increasing ionic strength at the whole range of pH studied, with the effect of ionic strength most significant at the pH range from 6 to 8.

The presence of HA shows clearly effect on pH dependence of the REEs adsorption onto kaolin. At lower pH from 3 to 4, the presence of HA enhances the REEs adsorption because of dominant electrostatic interaction and specific site binding due to negatively charged surface of the mineral, but will reduce the adsorption at pH values higher than about 5 as compared with the adsorption in the absence of HA, which could be ascribed specifically to the speciation of the REEs and the surface coverage of HA. This clearly suggests that the presence of organic materials in the aquatic environment generally lowers the adsorption of trace metals onto particles and enhances the dissolution of trace metals in waters, which might facilitate the long-distance migration of trace metals in the aquatic environment. The ionic strength affects the adsorption of the REEs in the presence of HA, and its increasing will increase the adsorption.

The fractionation of the REEs during adsorption/desorption in the presence of HA is not remarkable as function of ionic strength, but occurs as a function of HA concentration. In general, high concentration of HA in the solution increases the

adsorption of light REEs onto the kaolin. The results are experimental verification of a process that may generate the enrichment of light REEs in the particulate phase in the presence of humic acid, which is in consistence with the fractionation of REEs in most of natural waters [29]. To improve our understanding of the mechanisms controlling the REEs sorption and fractionation processes, the interaction between HA–REE–mineral ternary phases should be systematically investigated.

Acknowledgment

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