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Influence of pH, soil humic/fulvic acid, ionic strength and foreign ions on sorption of thorium(IV) onto γ-Al_2O_3

C.L. Chen, X.K. Wang *

Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei, Anhui 230031, People's Republic of China

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Abstract

The sorption of Th(IV) onto γ-Al_2O_3 in the absence and presence of soil humic acid (HA)/fulvic acid (FA) was studied by batch technique. The influence of pH from 2 to 12, ionic strength from 0.01 M to 0.1 M KNO_3, soil HA/FA concentrations from 2.5 mg/L to 17.5 mg/L, and foreign cations (Li^+, Na^+, K^+) and anions (NO_3^-, Cl^-) on the sorption of Th(IV) onto γ-Al_2O_3 was also tested. The sorption isotherms of Th(IV) were determined at pH 3.50 (±0.02) and analyzed with the linear, Freundlich, and Langmuir sorption models, respectively. The results demonstrated that the sorption of Th(IV) onto γ-Al_2O_3 increases steeply with increasing pH from 2 to 4. HA/FA was shown to enhance Th(IV) sorption at low pH, but to reduce Th(IV) sorption at high pH. It was assumed that the significantly positive influence of HA/FA on Th(IV) sorption onto γ-Al_2O_3 at pH 2–4 is attributable to the strong surface binding of HA/FA on γ-Al_2O_3 and subsequently to the formation of ternary surface complexes such as $\equiv$SO–O–HA–Th or $\equiv$SO–O–FA–Th. The results also demonstrated that the sorption is strongly dependent on the concentration of HA/FA, and slightly dependent on ionic strength. The sorption of Th(IV) onto γ-Al_2O_3 was also dependent on foreign ions in solution under the experimental conditions.

1. Introduction

The fate and transport of radionuclides and toxic metal ions in the environment is generally controlled by sorption reactions, complexation, colloid formation, etc. These interactions may be complicated by the presence of natural organic matter, such as humic substances (HSs), which are not stoichiometric chemical species, but rather macromolecular colloidal phases. Their compositions are variable and differ greatly from one sample to another (Stevenson, 1994). Based upon their solubility in acidic and alkaline solutions, HSs are classified as follows: (a) humin is the insoluble fraction at whatever pH, (b) humic acids (HAs) are soluble above a pH of approximately 3.5 and (c) fulvic acids (FAs) are the soluble fraction at all pH values. Previous work has demonstrated that HSs carry a large number of functional groups that bind strongly with both dissolved metal ions in solution and functional groups at oxide surfaces (e.g., carboxylate, phenolate, amino, thiol) (Davis, 1982; Choppin, 1998; Moulin et al., 2001; Plancque et al., 2001; McIntyre et al., 2002). Because of their high functionality, HSs can form strong complexes with transition

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* Corresponding author. Fax: +86 551 5591310.
E-mail address: xkwang@ipp.ac.cn (X.K. Wang).

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elements, and lanthanide and actinide ions, and therefore modify metal ion sorption by minerals and oxides (Davis, 1984; Zachara et al., 1994; Labonne-Wall et al., 1997; Takahashi et al., 1999; Reiller et al., 2002). In earlier studies (Wang et al., 2000, 2002, 2003), the sorption of Cs^+, Eu(III), Yb(III) and Co^{2+} onto alumina was investigated. The results indicated that the sorption of Cs on alumina was independent of pH (Wang et al., 2003), while that of Eu, Yb and Co was strongly dependent on pH values (Wang et al., 2000, 2002). The results also indicated that FA had a positive effect on Eu and Yb sorption at low pH, but a negative effect on Co sorption. The sorption of metal ions by alumina has been studied intensively in geochemistry, oceanography, limnology and pollution control (Niven and Moore, 1993; Chu et al., 1996; Baumgarten and Kirchhausen-Düsing, 1997; Rabung et al., 2000; Montavon et al., 2002). The chemical processes of HSs have to be taken into account in modeling migration of fission products and actinides in radioactive waste disposal. With regard to the influence of HSs on metal ion sorption on mineral and oxide surfaces, it is generally considered that sorption is enhanced at low pH and reduced at high pH (Montavon et al., 2002), but the influence of HSs on the sorption mechanism of different metal ions in aquifer systems is still different and the comparison of the influence of FA and HA on metal ion sorption is still scarce (Xu et al., 2006b), and needs to be studied, especially for actinides.

Thorium is only stable at its valence +IV in solution, and is usually regarded as a chemical analogue for tetravalent actinides (Choppin, 1999), despite the fact that it has no 4f electron. The association of Th(IV) with HSs is strong and has been observed in the field (Miekeley et al., 1985; Guo et al., 1997; Labonne-Wall et al., 1997; Choppin, 1999; Dai and Benitez-Nelson, 2001) and quantified (Nash and Choppin, 1980; Choppin and Allard, 1985; Murphy et al., 1999; Reiller et al., 2002, 2003, 2005). Niven and Moore (1993) investigated the sorption of Th in seawater suspensions of γ-Al_2O_3 particles. However, the methodical study of the effect of HA/FA on the sorption of Th onto γ-Al_2O_3 is still scarce, and needs to be studied.

The objectives of the present work are: (a) to compare the different influences of HA and FA, which are extracted from the same soil samples, on Th(IV) sorption, (b) to determine Th(IV) sorption isotherms and to analyze experimental data with the linear, Freundlich, and Langmuir sorption models, (c) to investigate the influence of HA/FA (from 2.5 mg/L to 17.5 mg/L), pH (from 2 to 12), ionic strength (from 0.01 M to 0.1 M KNO_3), and foreign cations and anions on the sorption and complexation of Th(IV) on the γ-Al_2O_3 surface; and (d) to discuss the sorption/complexation mechanism of Th(IV) in the ternary systems Al_2O_3–HA–Th(IV) or Al_2O_3– FA–Th(IV).

2. Experimental

2.1. Materials

The hydrous γ-Al_2O_3 (Degussa, Aluminium Oxide C) was the same as the one used in previous sorption experiments (Rabung et al., 2000; Montavon et al., 2002; Wang et al., 2003). Prior to its use, the sample was firstly washed with 0.1 M HNO_3, then with 0.1 M NaOH up to pH 10 and finally rinsed with Milli-Q water until the conductivity of the washing solution reached that of water (Wang et al., 2003). The N_2-BET measurement of the surface area of the free dried sample was 105 m^2/g, and the average particle radius measured by PCS was about 150 nm. The point of zero charge of the sample was pH_{pzc} 9.2 ± 0.1 (Wang et al., 2003). Soil humic and fulvic acids were extracted from the soil of Hua-Jia county (Gansu province, China), and have been characterized in detail in an earlier report (Zhang et al., 1999). In that report, cross-polarization magic angle spinning (CPMAS) ^{13}C NMR spectra of FA and HA was divided into four chemical shift regions, 0–50 ppm, 51–105 ppm, 106–160 ppm and 161–200 ppm. These regions were referred to as aliphatic, carbohydrate, aromatic and carboxyl regions. The percentage of total intensity for each region is estimated by integrating the CPMAS ^{13}C NMR spectra with each region and the total aromaticities calculated by expressing aromatic C as a percentage of aliphatic C (0–105 ppm) + aromatic C (106–160 ppm) and are listed in Table 1.

All other chemicals were reagent grade, except for additional illustration, and used without any

Table 1
^{13}C NMR characteristics (chemical shift ppm)% of HSs

HSs	0–50	51–105	106–160	161–200	Aromaticity
HA	15	21	47	17	57
FA	16	28	19	39	30

treatment. Water used in all experiments was doubly distilled.

2.2. Design of sorption experiments

The sorption behavior of Th(IV) onto γ-Al_2O_3 was investigated by using a batch technique in polyethylene centrifuge tubes sealed with a screw-cap under ambient conditions. In all experiments, no attempt was made to exclude air. The stock solutions of γ-Al_2O_3 and KNO_3 were pre-equilibrated for 12 h and then Th stock solution was added to achieve the desired concentration of the different components. In addition, in the studies of the influence of HA/FA on Th(IV) sorption, HA/FA and γ-Al_2O_3 were pre-equilibrated for 24 h. A stock solution of $Th(NO_3)_4$ was prepared by dissolving ThO_2 in HNO_3. The pH values of the system were adjusted by adding negligible volumes of 0.01 M HNO_3, 0.01 or 0.1 M KOH to achieve the desired pH values. Ionic strengths were adjusted to desired values with 0.1 mol/L or 1 mol/L KNO_3 solution. Samples were gently shaken for 24 h (which was enough to achieve equilibrium), and then centrifuged for 30 min at 8000 rpm for the separation of solid phase from aqueous phase. The detailed procedures are given in previous reports (Wang et al., 2000, 2002).

The concentration of Th was determined by spectrophotometry at 650 nm by using the Th arsenazo(III) complex. The amount of Th(IV) sorbed was calculated from the difference between the initial concentration and the equilibrium one. The blank experiments demonstrated that the sorption of Th(IV) on the test tube walls was negligible.

All experiments were conducted at room temperature (25 ± 2 °C) and atmospheric pressure. All the experimental data were the average of duplicate experiments. The relative errors of data were about 5%.

3. Results and Discussion

3.1. Solubility and species of Th(IV) in aqueous solutions

The solubility limiting phases of Th(IV) are $Th(OH)_4$ and, possibly, ThO_2 at relatively low pH and low carbonate concentration; the solubility product for $Th(OH)_4$ has been estimated as 10^{-42} mol/L and 10^{-39} mol/L (Katzin and Sonnenberger, 1986). At low pH, the solubility data for ThO_2(cr) are essentially lower than those for $Th(OH)_4$(am), But at pH >5 equal Th concentrations are observed (Neck and Kim, 2001). Similar observations are reported by Östhols et al. (1994). The total solubility of microcrystalline ThO_2 as a function of pH at different partial pressures of CO_2 was determined by Östhols et al. (1994). It was found that the total solubility would have a minimum of about 10^{-6}–$10^{-6.5}$ mol/L at about pH 5, and in the absence of CO_2, the total solubility rapidly decreases from $\sim 10^{-3.5}$ mol/L at pH 3.5 to $\sim 10^{-4.6}$ at pH 4. However, the solubility of ThO_2 was greatly increased by adding 2–3 drops HF (1:20) during the course of preparation of the Th stock solution in the experimental conditions. The total concentration of Th(IV) in aqueous solutions used at pH <4 was smaller than the experimental solubility of microcrystalline ThO_2 and than the calculated solubility of $Th(OH)_4$. Consequently, the sorption data of Th(IV) obtained herein at pH <4 are not due to precipitation.

Thorium(IV) is the least hydrolyzed tetrapositive ion, the uncomplexed cation is stable at pH 3 or less (Sarrin, 1961). Cromières et al. (1998) calculated the distribution diagram for Th species at an ionic strength of 0.1 mol/L $NaClO_4$ from the following hydrolysis constants ($\log\beta_1 = -3.86$, $\log\beta_2 = -8.01$, $\log\beta_3 = -12.99$, and $\log\beta_4 = -17.16$) and found that at pH $\leqslant 3$, Th(IV) is the prevailing species ($\geqslant 88\%$) and $Th(OH)^{3+}$ is less than 12%; at pH ≈ 3.5, Th(IV) is about 26.5%, $Th(OH)^{3+}$ is less than 42.8%, $Th(OH)_2^{2+}$ is less than 29%, $Th(OH)_3^+$ and $Th(OH)_4$ are less than 1.7%, respectively, at pH $\leqslant 4.5$, $Th(OH)_4$ is less than 25%, $Th(OH)_3^+$ is less than 12%, $Th(OH)_2^{2+}$ is less than 40% and $Th(OH)^{3+}$ is less than 18%, at pH >10, $Th(OH)_4$ is the prevailing species ($\geqslant 99\%$). From continuous titration experiments, Östhols et al. (1994) found that even at $p(CO_2) = 0.1$ atm, $Th(OH)_3(CO_3)^-$ is less than 3% at pH $\leqslant 4.5$. Therefore, in this work, at pH from 2 to 4, $Th(OH)_3(CO_3)^-$ and $Th(CO_3)_5^{6-}$ are negligible.

3.2. Influence of pH

Fig. 1 shows the removal percentage, R, of Th(IV) as a function of pH values in the absence and presence of HA/FA. The value of R was calculated as follows:

$$R = (C_0 - C_{eq}) \times 100/C_0(\%) \tag{1}$$

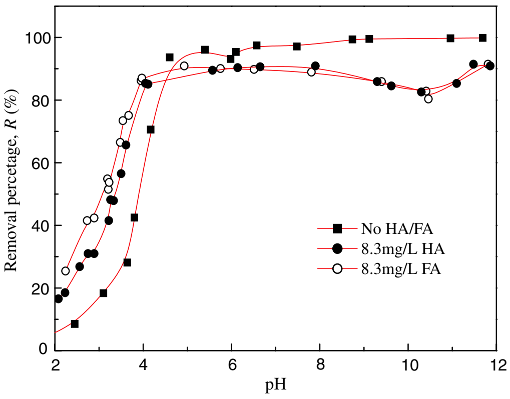

Fig. 1. Influence of pH on the sorption of Th(IV) onto γ-Al_2O_3 in the absence and presence of HA/FA, at $m/V = 0.1485$ g/L, $C_0(\mathrm{Th(IV)}) = 3.23 \times 10^{-5}$ mol/L, $I = 0.02$ M KNO_3.

where C_0 is the initial concentration of Th(IV) (mol/L), C_{eq} is the concentration of Th(IV) in the supernatant after sorption and centrifugation (mol/L). The results show that Th(IV) sorption increases with increasing pH, showing a distinct sorption edge at pH 2.5 to 4.5 for γ-Al_2O_3 in the absence of HA/FA, and that the sorption of Th(IV) in the presence of HA/FA is obviously enhanced at low pH (~2 to 4), but reduced at intermediate and high pH (~pH >5). The sorption and complexation of inorganic species onto γ-Al_2O_3 and other hydrous oxides have been investigated by numerous authors (James and Healy, 1972a,b,c; Righetto et al., 1988; Östhols, 1995). As early as 1988, the adsorption of Th(IV) onto alumina was studied by using ^{228}Th at an ionic strength 0.1 mol/L $NaClO_4$ (Righetto et al., 1988). It was found that the adsorption increases sharply with increasing pH from 1 to 4 and that the presence of humic acid leads to reduction of the sorption of Th(IV) at relatively high pH values (6.5–10.5). The shape of sorption edges in Fig. 1 is also similar to those for SiO_2 (Östhols, 1995) and α-Fe_2O_3 (Cromières et al., 1998). This common pattern is characteristic of the adsorption of hydrolyzable metal ions on oxides (James and Healy, 1972a,b,c; Davis, 1984; Wang et al., 2000).

The sorption properties of γ-Al_2O_3 depend on its crystal structure and the chemical properties of the surface. Since the surface of γ-Al_2O_3 contains OH groups, with respect to the sorption of ions, these surface OH groups represent the functional sites of γ-Al_2O_3. In aqueous systems, the surface groups of γ-Al_2O_3 can be protolyzed in two different ways. First, at pH < $\mathrm{pH_{pzc}}$, the surface may be protonated according to $\equiv SOH + H^+ \leftrightarrow \equiv SOH_2^+$. Secondly, at pH > $\mathrm{pH_{pzc}}$, the surface hydroxyl groups can dissociate and release protons to the liquid phase $\equiv SOH \leftrightarrow \equiv SO^- + H^+$. Therefore, the concentrations of surface species ($\equiv$SOH uncharged surface group, $\equiv SOH_2^+$ positively charged surface group, $\equiv SO^-$ negatively charged group) of γ-Al_2O_3 change with different pH values. With increasing pH, the negatively charged group $\equiv SO^-$ increases and the hydrolysis of Th(IV) also increases. Consequently, it is not surprising that the sorption of Th(IV) increases with increasing pH.

In Fig. 1, HA/FA influences the sorption of Th(IV) onto γ-Al_2O_3, showing that the sorption of Th(IV) is obviously enhanced at low pH (~2–4), but is reduced at intermediate and high pH (~pH >5). In the presence of HA/FA, (HA/FA)-Th complexes may form. At low pH, these complexes are easily sorbed by γ-Al_2O_3 leading to enhancement of the sorption of Th(IV). Additionally, sorbed HA/FA may induce greater negative surface charge on γ-Al_2O_3, allowing more Th(IV) to be sorbed due to favorable electrostatic interaction. At high pH, the negatively charged FA/HA is weakly sorbed onto γ-Al_2O_3, because as pH increases, γ-Al_2O_3 becomes progressively more negatively charged, and thereby hinders the sorption of FA/HA due to electrostatic repulsion, and makes the strong stable complex (HA/FA)-Th easily dissolved in solution, leading to the decrease in the sorption of Th(IV) on γ-Al_2O_3. According to the previously proposed mechanisms of HSs sorption on oxides or clays (Takahashi et al., 1999; Xu et al., 2006a), the complex mechanism between γ-Al_2O_3 and HA/FA can be expressed as follow:

$$\begin{aligned}&\equiv S - OH_2^+ + {}^-OOC - HA/FA\\&\quad \leftrightarrow \equiv S - OOC - HA/FA + H_2O \qquad (2)\end{aligned}$$

$$\begin{aligned}&\equiv S^{-OH_2^+}_{-OH} + HOO - HA/FA\\&\quad \leftrightarrow \equiv S^{-O-}_{-O-}C - HA/FA + 2H_2O \qquad (3)\end{aligned}$$

The presence of HA/FA in solution affects the sorption of Th(IV) on γ-Al_2O_3, and the species of Th(IV) on γ-Al_2O_3 depend mainly on both HA/FA and γ-Al_2O_3. Ternary complexes, such as $\equiv$SO–O–HA–Th or $\equiv$SO–O–FA–Th, are probably formed on the surface of γ-Al_2O_3 in the presence of HA/FA (Wang et al., 2004).

From Fig. 1, one can also see that the influence of FA on the sorption of Th(IV) is much stronger than that of HA at low pH when the concentration of FA was identical to that of HA. FA has far more carboxylic groups than HA (Table 1), and these functional groups provide more available complex sites and form complexes with Th(IV) species. In earlier reports (Schnitzer, 1977; Milne et al., 2001), typically, the amount of reactive functional groups ranges from ~4 mol/kg to 14 mol/kg with the tendency toward higher values for fulvic acids compared to humic acids. According to Choppin (1998), generally, the structures of FA have somewhat more aliphatic and less aromatic character than HA and lower molecular weights ~300–2000 amu typically compared to 1000–5000 amu for aquatic HA and 5000–100 000 amu for soil HA.

From Fig. 1, it is interesting that at ~pH >10, Th(IV) sorption rises again slightly, which could be due to the following factors: at pH >10, $Th(OH)_3(CO_3)^-$ and $Th(CO_3)_5^{6-}$ are expected to begin forming and $Th(OH)_4$ is the pre-dominating species (Östhols et al., 1994; Altmaier et al., 2005). These species may be sorbed by HA/FA–Al_2O_3. However, the sorption of Th(IV) does not reach the level achieved in systems free from HA/FA, which could be due to either residual Th–HA/Th–FA remaining in solution, thus reducing $Th(OH)_3(CO_3)^-$, $Th(CO_3)_5^{6-}$ and $Th(OH)_4$ concentrations available for sorption, or residual HA/FA on γ-Al_2O_3 surface enhancing electrostatic repulsion of the $Th(OH)_3(CO_3)^-$ and $Th(CO_3)_5^{6-}$, or blocking potential sorption sites on γ-Al_2O_3 surface. In general, the sorption behavior of Th(IV) in the presence of HA/FA may be explained by a competition between surface complex (from the γ-Al_2O_3 surface and/or sorbed HA/FA) and non-sorbed species in solution. Sorbed HA/FA may also affect the sorption of Th(IV) by altering surface charges and/or blocking available sites for the sorption of Th(IV). The experimental result mentioned above is similar to that of the influence of humic acid on Eu-mineral interactions (Fairhurst and Warwick, 1998).

3.3. Sorption isotherms

The experimental data obtained at pH 3.50 ± 0.02 were analyzed with the linear, Freundlich, and Langmuir models (Atkins, 1978). The linear isotherm indicates a partitioning process of the solutes from a liquid to a solid surface; the Freundlich model is an empirical relationship describing the sorption of solutes from a liquid to a solid surface; the Langmuir model assumes that there is no interaction between the adsorbate molecules and the sorption is localized in a monolayer. The equations of the above three types of sorption isotherms are expressed as follow:

$$C_s = K_d C_{eq} \tag{4}$$

$$\log C_s = n \log C_{eq} + \log k \tag{5}$$

$$1/C_s = b/C_{eq} + 1/Q_0 \tag{6}$$

where C_s is the amount of Th(IV) sorbed per mass unit of γ-Al_2O_3 (mol/g), C_{eq} is the concentration of Th(IV) in the supernatant after sorption and centrifugation (mol/L), K_d is the distribution coefficient (L/g), n and k are empirical constants, Q_0 is the saturated amount (mmol/g) and b is the Langmuir constant (g/L). The sorption isotherms are shown in Figs. 2a, b and c, respectively. Sorption equations

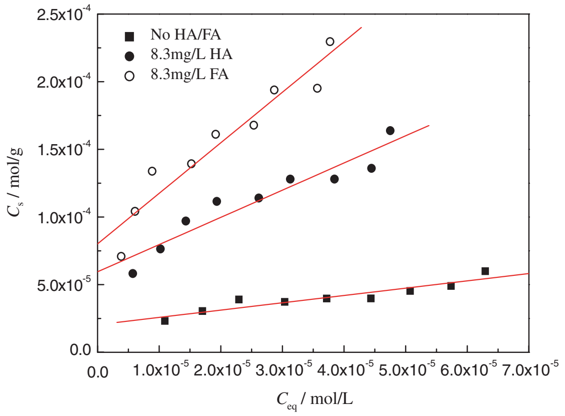

Fig. 2a. Linear sorption isotherm of Th(IV) onto γ-Al_2O_3 in the absence and presence of HA/FA, at $m/V = 0.1485$ g/L, $I = 0.02$ M KNO_3, pH 3.50 ± 0.02.

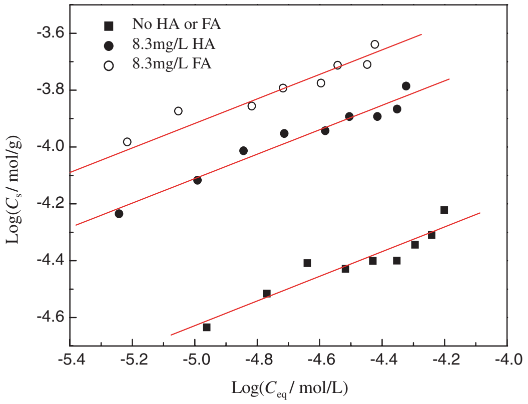

Fig. 2b. Freundlich sorption isotherm of Th(IV) onto γ-Al_2O_3 in the absence and presence of HA/FA, at $m/V = 0.1485$ g/L, $I = 0.02$ M KNO_3, pH 3.50 ± 0.02.

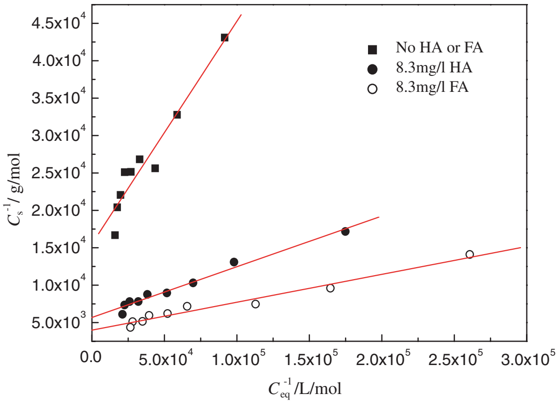

Fig. 2c. Langmuir sorption isotherm of Th(IV) onto γ-Al_2O_3 in the absence and presence of HA/FA, at $m/V = 0.1485$ g/L, $I = 0.02$ M KNO_3, pH 3.50 ± 0.02.

and their correlation coefficients (R^2) are listed in Table 2. The results indicate that the linear model poorly describes the sorption of Th(IV) onto γ-Al_2O_3 in the absence and presence of HA/FA, and the Langmuir model is the only model which correctly fits the sorption of Th(IV) onto bare γ-Al_2O_3. The Freundlich model and the Langmuir model fit well the sorption of Th(IV) onto γ-Al_2O_3 in the presence of HA/FA, and this shows that the sorption behavior of Th(IV) is very complicated and might be affected by many factors in the presence of HA/FA. From the data in Table 2, it can be seen that the saturated amounts of Th(IV) at a pH value of 3.50 ± 0.02 are in the following sequence: (bare γ-Al_2O_3) < (HA + γ-Al_2O_3) < (FA + γ-Al_2O_3). In the presence of HA/FA, HA/FA is sorbed onto γ-Al_2O_3, leading to the enhancement of complex sites available on the γ-Al_2O_3 surface and therefore enhancing the saturated amount of sorbed Th(IV). FA has far more carboxylic groups than HA, and these functional groups have more complex sites available and thereby can form stronger complexes with Th(IV) species, and therefore the saturated amount of Th(IV) in the presence of FA is higher than that in the presence of HA.

3.4. Influence of ionic strength

Influence of ionic strength on the sorption of Th(IV) onto γ-Al_2O_3 in the absence and presence of HA/FA is shown in Fig. 3. The sorption of Th(IV) onto γ-Al_2O_3 in the absence and presence of HA/FA is slightly dependent on ionic strength. The sorption decreases weakly with increasing

Table 2
Equations of sorption isotherms of Th(IV) onto γ-Al_2O_3 in the absence and presence of HA/FA

Samples	Linear model	R^2	Freundlich model	R^2	Langmuir model	R^2	Q_0 (mmol/g)
γ-Al_2O_3	$C_s = 0.540 \cdot C_{eq} + 2 \times 10^{-5}$	0.87	$\log C_s = 0.434 \cdot \mathrm{Log}\, C_{eq} - 2.458$	0.89	$1/C_s = 0.297/C_{eq} + 1/(6.44 \times 10^{-5})$	0.93	0.0644
γ-Al_2O_3 + HA	$C_s = 2.01 \cdot C_{eq} + 6 \times 10^{-5}$	0.90	$\log C_s = 0.43 \cdot \mathrm{Log}\, C_{eq} - 1.962$	0.96	$1/C_s = 0.0678/C_{eq} + 1/(1.76 \times 10^{-4})$	0.98	0.176
γ-Al_2O_3 + FA	$C_s = 3.375 \cdot C_{eq} + 8 \times 10^{-5}$	0.92	$\log C_s = 0.431 \cdot \mathrm{Log}\, C_{eq} - 1.760$	0.94	$1/C_s = 0.0373/C_{eq} + 1/(2.51 \times 10^{-4})$	0.97	0.251

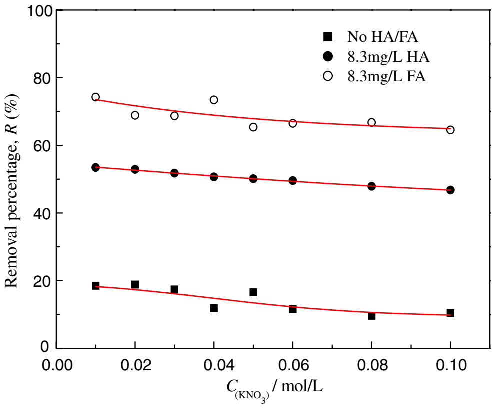

Fig. 3. Influence of ionic strength on the sorption of Th(IV) onto γ-Al_2O_3 in the absence and presence of HA/FA, at $m/V =$ 0.1485 g/L, C_0(Th(IV)) = 3.23×10^{-5} mol/L, pH 3.50 ± 0.02.

KNO_3 concentration, which suggests that the K^+ ion weakly affects Th(IV) sorption. The ions in solution may influence the double layer thickness and interface potential, and thereby affect the binding of the sorbed species. Outer-sphere complexes may be affected by the variations of ionic strength more easily than inner-sphere complexes, since the background electrolyte ions are placed in the same plane as outer-sphere complexes. Consequently, during sorption Th(IV) is assumed to form inner-sphere complexes with carbonyl and/(or) hydroxyl groups. Jakobsson (1999) investigated the sorption of Th(IV) onto bare TiO_2 and found that the sorption was independent of ionic strength. Reiller et al. (2002, 2005) studied the sorption of Th(IV) on hematite and Fe oxide, and also found that the sorption of Th(IV) was not influenced by ionic strength drastically in the presence of HA. Guo et al. (2005) found that the sorption of Th(IV) on alumina decreased drastically with increasing ionic strength from 0.05 to 0.5 mol/L KNO_3 at Th(IV) aqueous solution concentrations ranging from 7.5×10^{-5} to 2×10^{-4} mol/L in the absence of HSs. In contrast, the sorption of Th(IV) increased with increasing ionic strength, from 0.05 mol/L to 0.1 mol/L KNO_3, at Th(IV) aqueous solution concentrations $<7.5 \times 10^{-5}$ mol/L in the absence of HSs.

The present results show that the sorption of Th(IV) onto γ-Al_2O_3 in the absence and presence of HA/FA is influenced by ionic strength weakly and by pH values strongly. This suggests that surface complexation mainly contributes to the sorption of Th(IV) (Niven and Moore, 1993; Dai and Benitez-Nelson, 2001). In general, surface complexation is influenced by pH values, whereas ion exchange is mainly influenced by ionic strength.

3.5. Influence of soil HA/FA concentration

Fig. 4 shows the influence of HA/FA concentration on Th(IV) sorption onto γ-Al_2O_3. From Fig. 4, one can see that Th(IV) sorption increases with increasing concentration of HA/FA, which is consistent with the properties of humic substances. At higher concentrations of HA/FA, there are more functional groups of HA/FA, such as carboxylic and phenolic groups, and these groups could form strong complexes with Th(IV). Similar experimental results were reported by Kim et al. (2005). They should be interpreted from the fact that the proportion of HA/FA is not sufficient to saturate the mineral or oxide surface sites. Reiller et al. (2002, 2005) reported that the sorption of Th(IV) on HA coated hematite decreases with increasing concentration of HA in solution, when the concentration of HA/FA exceeds the saturation of the minerals or oxides. Therefore, the extent of these effects depends upon the relative ratio between HA/FA and mineral phases or oxide sites. This ratio has to be smaller than a critical value in order to enhance the sorption of Th(IV).

3.6. Influence of foreign ions

In order to investigate the influence of background electrolyte foreign cations and anions, the sorption of Th(IV) on bare γ-Al_2O_3 was investigated

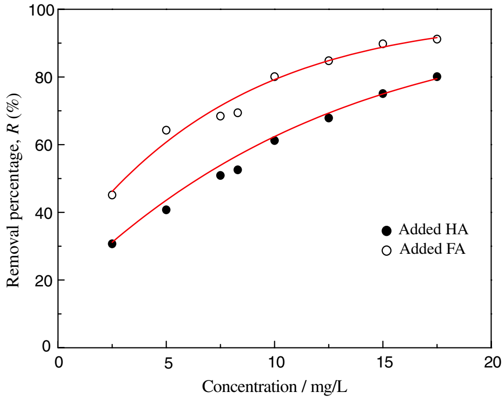

Fig. 4. Influence of FA/HA concentration on the sorption of Th (IV) onto γ-Al_2O_3, at $m/V = 0.1485$ g/L, C_0(Th(IV)) = 3.23×10^{-5} mol/L, $I = 0.02$ M KNO_3, pH 3.50 ± 0.02.

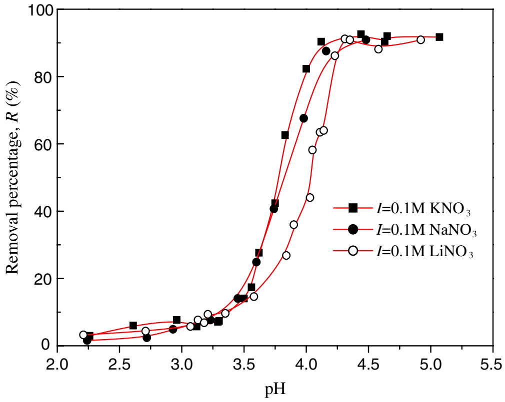

Fig. 5. Influence of cations and pH on the sorption of Th(IV) onto γ-Al_2O_3, at $m/V = 0.1485$ g/L, C_0(Th(IV)) $= 3.23 \times 10^{-5}$ mol/L.

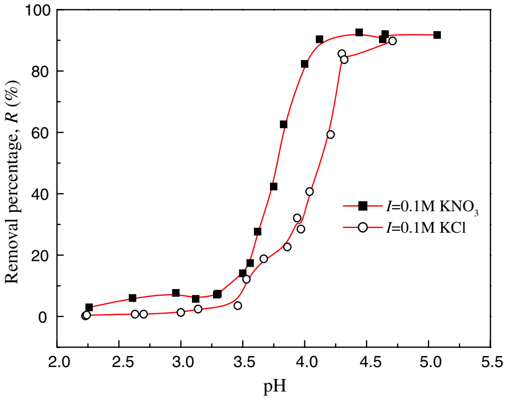

Fig. 6. Influence of anions and pH on the sorption of Th(IV) onto γ-Al_2O_3, at $m/V = 0.1485$ g/L, C_0(Th(IV)) $= 3.23 \times 10^{-5}$ mol/L.

in 0.1 M $LiNO_3$, $NaNO_3$, KNO_3, and KCl solutions, respectively. Fig. 5 indicates that foreign cations influence the sorption of Th(IV) slightly, whereas Fig. 6 shows that foreign anions affect Th(IV) sorption drastically. Cations in solution may compete with Th(IV) for interaction with the surface groups of γ-Al_2O_3. From Fig. 5, as supported by this competition principle, the order of decrease in the sorption of Th(IV) is highest for Li^+ and lowest for K^+, which might be due to the fact that the radius of Li^+ is the smallest one. Hence Li^+ has the highest affinity to the surface of γ-Al_2O_3 and the highest tendency for counter-ion exchange with the surface groups of γ-Al_2O_3, which reduces ion interaction sites of the surface of γ-Al_2O_3 with Th(IV). However, the influence of monovalent alkali metal ions on the tetravalent Th(IV) ion sorption is weak. Experimental results are well consistent with the influence of ionic strength on the sorption of Th(IV). From Fig. 6, one can see that the sorption of Th(IV) on γ-Al_2O_3 in KCl solution is lower than that in KNO_3 solution at the same pH values. This phenomenon could be attributed to two reasons: (1) Th(IV) can complex with inorganic acid radicals (e.g. Cl^-, NO_3^-) and form soluble complex species (e.g. $ThCl_3^+$, $Th(NO_3)^+$). Since the radius of Cl^- is smaller than that of NO_3^-, Th(IV) has higher affinity to Cl^- and a higher tendency for complexation with Cl^- compared to NO_3^-, leading to a stronger decrease of Th(IV) concentration. (2) In general, idiocratic adsorption of Cl^- is easier on the solid phase than NO_3^-, and Cl^- adsorption on the surface of γ-Al_2O_3 changes the surface state of γ-Al_2O_3 and decreases the availability of binding sites. The interpretations mentioned above are reasonable in principle.

Experimental results mentioned above provide the evidence that the sorption of Th(IV) onto bare or HA/FA bound γ-Al_2O_3 may be mainly attributed to chemical sorption or surface complexation and not to ion exchange.

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