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Sorption of Th(IV) on Na-rectorite: Effect of HA, ionic strength, foreign ions and temperature

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Abstract

The sorption of Th(IV) on Na-rectorite as a function of pH, ionic strength, temperature, soil humic acid (HA) and foreign ions was studied by using a batch technique under ambient conditions. The results indicated that the sorption of Th(IV) on Na-rectorite is strongly depended on pH, ionic strength and temperature. The presence of HA enhanced Th(IV) sorption at low pH and had no obvious effect on Th(IV) sorption at high pH. The sorption of Th(IV) decreased with increasing temperature, indicating that the sorption process of Th(IV) on rectorite was exothermic. Sodium-rectorite and HA were characterized by acid–base titration to obtain the pK_a, and the constant capacitance model (CCM) modeled the sorption data very well with the aid of FITEQL 3.2. HA/Th(IV) addition sequences affected Th(IV) sorption in the ternary systems. The sorption of Th(IV) on Na-rectorite may be dominated by surface complexation, while cation exchange also contributes partly to the sorption.

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 affected by many factors, such as the surface oxygen complexes content, the pH at the point of zero charge (pH_{pzc}), the pore texture of the material, the solution pH, and ionic strength, temperature, the nature of the metal ion, its solubility and the presence of natural organic matter.

Thorium is only stable at its valence +IV in solution, and is usually used as a chemical analogue of tetravalent radionuclides such as Zr, Hf, Np, U and Pu, which are difficult to study and to keep in the tetravalent form (Choppin, 1999; Jakobsson, 1999). In recent decades, sorption of Th(IV) on different sorbents as a function of pH, ionic strength, sorbate and humic substances have been studied extensively (Östhols, 1995; Guo et al., 1997, 2005; Cromières et al., 1998; Murphy et al., 1999; Jakobsson, 1999; Dai and Benitez-Nelson, 2001; Reiller et al., 2002, 2003, 2005; Zhang et al., 2006; Xu et al., 2006; Chen and Wang, 2007a,b; Tan et al., 2007a,b).

Rectorite is an uncommon natural clay, which is represented by regular (1:1) interstratification of

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dioctahedral mica and dioctahedral montmorillonite layers. Rectorite has been used as an adsorbent for metal ions. Zhang et al. (2004, 2005) studied the sorption of Cu(II) and Zn(II) on rectorite and found that adsorption achieved equilibrium quickly and a magnetic treatment promoted the sorption of Cu and Zn on rectorite. Properties such as a strong adsorptive capacity, good stability in water and an easy regeneration of the rectorite has led to this material being tested as a remover of many anions and cations from the environment (Ma et al., 2003; Murakami et al., 2005). Most studies on rectorite have focused on its mineral structure, components and relationship with other clays. However, research work on its adsorption of heavy metal ions and more especially its interaction with radionuclides in the presence of humic substances, which represent the major fraction of dissolved organic compounds present in freshwater, are still scarce.

In this work, the effect of pH, ionic strength, HA concentration and HA/Th(IV) addition sequences on the sorption of Th(IV) on Na-rectorite has been investigated. The sorption thermodynamics of Th(IV) on Na-rectorite have also been investigated. Rectorite and HA were characterized by acid–base titration to obtain the $\mathrm{p}K_{\mathrm{a}}$ values, and the constant capacitance model (CCM) was applied to model the experimental data with the aid of FITEQL 3.2. The desorption of Th(IV) from Na-rectorite in the absence and presence of HA was also investigated.

2. Methodology

2.1. Materials

All chemicals used in the experiments were analytical purity grades and were used without any further purification. The Na-rectorite sample was derived from Zhongxiang county (Hubei, China). The water content of 5.7% was taken into account in the calculation of the Na-rectorite content. The N_2-BET surface area was 11.9 m^2/g, and the average particle size was 7.4 μm.

Soil HA was extracted from a soil from Gansu province (China), and was characterized by NMR and pyrolysis-capillary gas chromatography electron impact mass spectrometry (Py-GC/MS) (Zhang et al., 1999). The main constituents of the HA are: C 60.44%, H 3.53%, N 4.22%, O 31.31% and S 0.50%.

A stock solution of $\mathrm{Th(NO_3)_4}$ was prepared by dissolving $\mathrm{ThO_2}$ in $\mathrm{HNO_3}$.

2.2. Experimental procedures

Selected samples doped with Th(IV) were characterized using Fourier Transform Infrared sorption (FT-IR) (Perkin Elmer spectrum 100, America) in pressed KBr pellets. For FT-IR spectroscopy, the samples were washed three times with ethanol for 5 min, filtered and dried at 343 K for 24 h.

X-ray powder diffraction analysis (XRD) was performed with Cu K_α radiation ($\lambda = 0.15406$ nm) with a Rigaku X-ray diffractometer. Patterns were identified by comparison to the JCPD standards.

The acid–base titrations of rectorite and HA, with a rectorite suspension (7.5 g/L) and HA suspension (45 mg/L) were carried out using a DL50 Automatic Titrator (Mettler Toledo) in 0.01 M $\mathrm{NaNO_3}$ under Ar gas at $T = 298$ K. Initially, the suspensions were titrated to about pH 3 and purged with Ar gas for about 1 h. Then, titrations were completed from about pH 3–10.5 using 0.04668 M NaOH.

The sorption of Th(IV) on Na-rectorite 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 Na-rectorite and $\mathrm{NaNO_3}$ were pre-equilibrated for 24 h and then Th stock solution was added to achieve the desired concentration of the different components. The system was adjusted to the desired pH by adding negligible volumes of 0.01 or 0.1 M $\mathrm{HNO_3}$, or 0.01 or 0.1 M NaOH. Ionic strengths were adjusted to desired values with 0.1 or 1 M $\mathrm{NaNO_3}$ solution.

For HA adsorption at different pH values, rectorite and $\mathrm{NaNO_3}$ were pre-equilibrated for 24 h, then HA was added and the pH was adjusted. Samples were gently shaken for 24 h, and then centrifuged for 50 min at 8500 rpm for the separation of solid phase from aqueous phase, pH was measured, and HA absorbance concentrations were determined at 299 nm with UV spectrophotometry.

For the HA effect, Na-rectorite and $\mathrm{NaNO_3}$ were pre-equilibrated for 24 h, then HA was added to equilibrate for 24 h and, finally, Th stock solution was added to achieve the desired concentration of the different components. Preliminary studies indicated that sorption of Th(IV) on rectorite achieved equilibrium after several hours. Samples were gently shaken for 24 h, and then centrifuged for 50 min at 8500 rpm for the separation of solid phase from aqueous phase. The efficiency of separation was checked by photo-correlation spectroscopy (PCS), which showed no colloidal particles in the supernatant solution.

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 degree of sorption of Th on the test tube walls was determined at $C_o(\mathrm{Th(IV)}) = 4.31 \times 10^{-5}$ mol/L, $I = 0.01$ M $NaNO_3$ and without rectorite. Results demonstrated that the sorption of Th(IV) on the test tube walls was negligible. All experimental data were the average of duplicate or triplicate experiments. The relative errors of the data were about 5%.

For the desorption experiments, at the end of the sorption experiments after centrifugation, half of the supernatant was removed by pipette and an equal volume of background electrolyte solution with the same pH was added. The pH was adjusted to obtain the same pH values as in the sorption experiments. Then the mixture was shaken and centrifuged under the same conditions as in the sorption experiments.

In addition to testing for the effect of HA concentration and HA/Th(IV), the effect of the sequence of additions on the sorption of Th(IV) was also studied. The sequences of addition were: (1) HA and Th(IV) were pre-equilibrated for 24 h before the addition of Na-rectorite (called batch 1); (2) Na-rectorite and Th(IV) were pre-equilibrated for 24 h before the addition of HA (called batch 2); (3) HA and Na-rectorite were pre-equilibrated for 24 h before the addition of Th(IV) (called batch 3).

3. Results and discussion

3.1. Characterization of Na-rectorite before and after Th(IV) sorption

Fig. 1 shows the XRD patterns of the four samples. The basal spacing was 23.9 Å for Na-rectorite, 25.7 Å for HA-rectorite hybrids, and 25.8 and 26.1 Å for Na-rectorite after Th(IV) sorption in the absence and presence of HA, respectively, which indicates their different structures. After Th(IV) sorption on Na-rectorite in the absence and presence of HA, the basal spacing of rectorite becomes larger. Some of Th(IV) ions and HA may intercalate into the interlayer space of Na-rectorite. The basal spacing of each sample was calculated using Bragg's law:

$$2d \sin\theta = n\lambda, \qquad (1)$$

where d is the basal spacing (Å), θ the angle of diffraction (°), λ the wavelength (nm), and n is the path differences between the reflected waves which equal an integral number of wavelengths (λ).

No other reflection peak is observed in the XRD pattern of samples (b), (c) and (d). None of the peaks corresponds to Th solids (e.g., ThO_2).

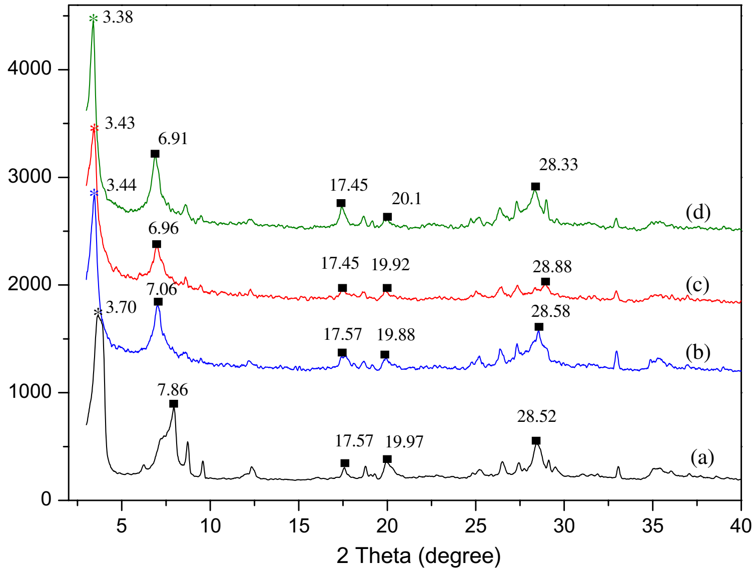

Fig. 1. XRD spectra of samples: (a) rectorite, (b) HA-sorbed rectorite, (c) Th-sorbed rectorite and (d) Th–HA-rectorite hybrids.

The samples were also characterized by FT-IR spectroscopic analysis before and after Th(IV) sorption in the absence and presence of HA (Fig. 2). Before the sorption, the broad bands of Na-rectorite at 3642 and 3430 cm^{-1} are due to the O–H stretching vibration of the silanol (Si–OH) groups from the solid and HO–H vibration of the water molecules adsorbed on the silica surface. The spectral band at 1640 cm^{-1} reflects bending of the HO–H bond of water molecules, which is retained in the silica matrix. The strong band at 1052 cm^{-1} represents the Si–O groups of the tetrahedral sheet. The spectral band at 932 cm^{-1} reflects the stretching vibration of Al–O–(OH)–Al. The bands at 695, 543, and 481 cm^{-1} are due to the deformation and bending modes of the Si–O bond. As also seen in Fig. 2, after the sorption of HA on rectorite the peak at 1382 cm^{-1} is due to the symmetric COO$^-$ stretching mode.

After HA and Th(IV) sorption, the O–H stretching vibration band of the silanol (Si–OH) at 3642 cm^{-1} becomes weaker due to the formation of Th and HA complexes with silanol. The Si–O bond of rectorite has shifted from 1052 to 1043 cm^{-1}, the deformation and bending bands of the Si–O bond at 695 cm^{-1} has also shifted to 669 cm^{-1} and bending bands of the Si–O bond at 543 and 481 cm^{-1} have become broader and weaker, or have even disappeared. The stretching vibration of Al–O–(OH)–Al at 932 cm^{-1} has shifted to 909 cm^{-1} and has become much weaker, or has even disappeared. Intercalations of Th and HA within rectorite lamellae cause a change in the position of the basal spacing and result in the variations in adsorption position and intensity of the Si–O bond in the SiO_4 tetrahedral sheet and adsorption position and intensity of Al–O–(OH)–Al in the Al–O–OH octahedron.

3.2. Results of acid–base titrations

Acid–base titration data of rectorite and HA are shown in Figs. 3a and 4a, respectively. TOTH is the total concentration of consumed protons in the titration process, which is calculated from the following equation:

$$\mathrm{TOTH} = \frac{-(V_\mathrm{b} - V_\mathrm{eb1}) \cdot C_\mathrm{b}}{V_0 + V_\mathrm{b}}, \tag{2}$$

where V_b is the volume of NaOH used in titration at each point, V_0 is the initial volume of the suspension, C_b is the concentration of NaOH, V_eb1 is the volume of NaOH used in titration at Gran point to zero on the acidic side.

For experimental data, various surface complexation models (SCMs) have been developed and extensively utilized to interpret and predict the interfacial procedures. The commonly adopted forms include the CCM, the diffusion layer model (DLM) and triple layer model (TLM). Assuming that surface sites ($\equiv$SOH) are amphoteric, i.e., can either be protonated to form ($\equiv$SOH$_2^+$) or

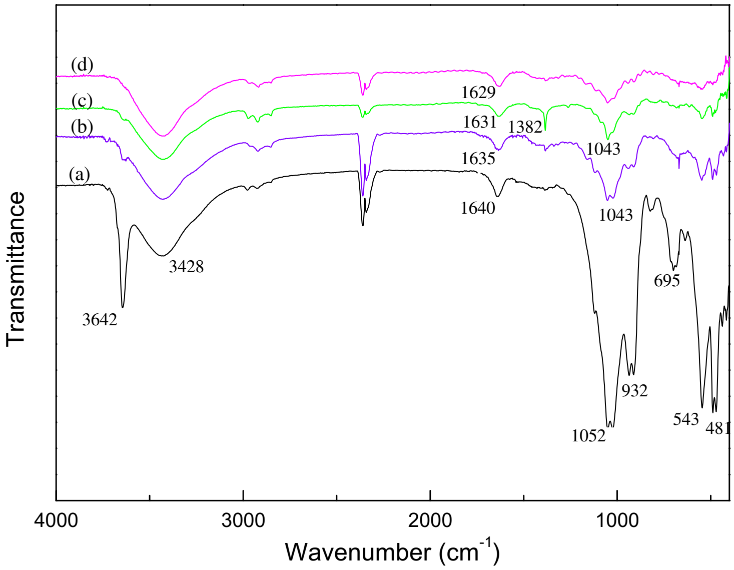

Fig. 2. FT-IR spectra of samples: (a) rectorite, (b) Th-sorbed rectorite, (c) HA-sorbed rectorite and (d) Th–HA-rectorite hybrids.

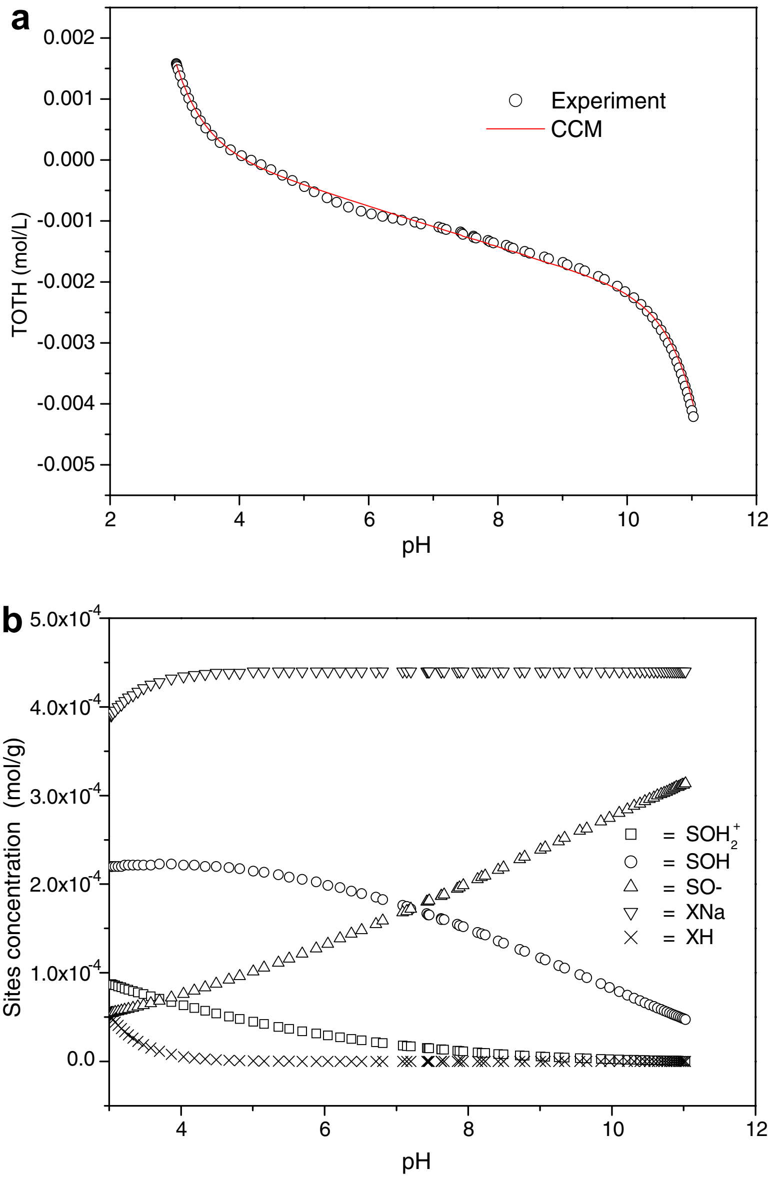

Fig. 3. (a) Model description and actual acid–base titration and (b) distribution of surface sites concentration, of rectorite sample (7.5 g/L) as a function of pH, at $I = 0.01$ M $NaNO_3$ and $T = 298$ K.

deprotonated to form ($=SO^-$), concentration of protonated and deprotonated sites, and hence site density, can be estimated from acid–base titration (Naveau et al., 2006). The different sites' concentrations calculated with the aid of FITQEL 3.2 as a function of pH are shown in Fig. 3b. The site ($=SO^-$) concentration increases with increasing pH, whereas site ($=SOH$) concentration decreases with increasing pH. The sites density of the sample calculated from the titration curve is 0.32 mmol/g. The consecutive acidity constants of $=SOH$ sites of rectorite as pK_a are optimized to be 3.29 for $=SOH_2^+$, −4.26 for $=SO^-$, 1.99 for $=SH$ and 2.13 for $=SNa/K$, respectively, with WSOS/DF = 21.68.

HA is chemically heterogeneous compound having different types of functional groups at different proportions and configurations. It contains carboxyl (–COOH), amine ($–NH_2$), hydroxyl (–OH), and phenol (Ar–OH) functional groups, and has negative charge in weakly acidic-to-basic media because of deprotonation (Brady, 1990). Distribution of surface sites concentration of HA (45 mg/L) as a function of

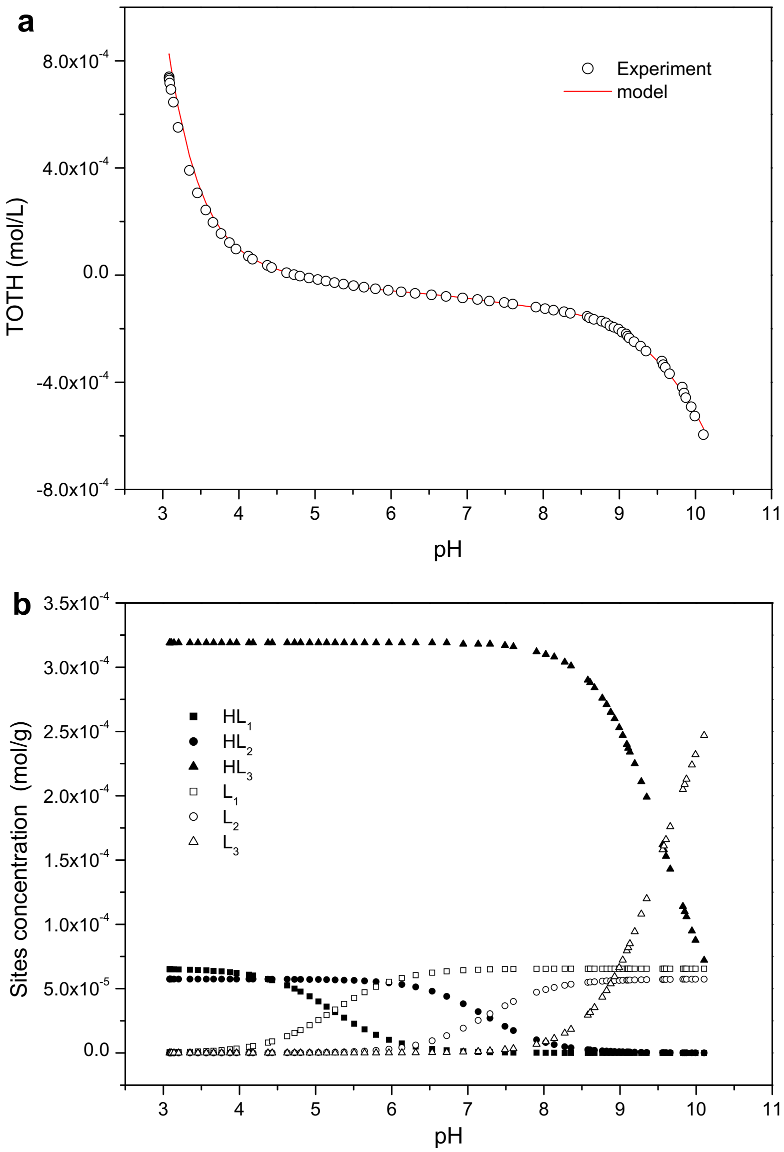

Fig. 4. (a) Acid–base titration of HA and (b) distribution of surface sites concentration, of HA (45 mg/L) as a function of pH at $I = 0.01$ M $NaNO_3$ and $T = 298$ K.

pH values are shown in Fig. 4b. The acidity constant pK_a values of HL_1 (due to carboxyl groups), HL_2 (due to amine groups), and HL_3 (due to phenolic groups), are optimized to be −5.23, −7.24, and −9.57 with WSOS/DF = 4.61, respectively.

3.3. *Effect of pH and HA*

HA adsorption decreases with increasing pH in a manner typical of ligand-like adsorption (Fig. 5). Both rectorite surfaces and HA lose their protons with increasing pH and become negatively charged, causing repulsive interactions. On the other hand, because both rectorite and HA are in a hydrogenated form at lower pH, the functional groups of rectorite and HA may attract each other via protons and electronegative O atoms probably in the form of H bonds. From Fig. 5, HL_1 and HL_3 are the leading species adsorbed, while adsorption of HL_2 species is not observed. HA adsorption on rectorite is modeled to obtained pK_a3.72 for $\equiv SOHHL_1$, and 0.79 for $\equiv SOHHL_3$, respectively, with WSOS/DF = 4.14.

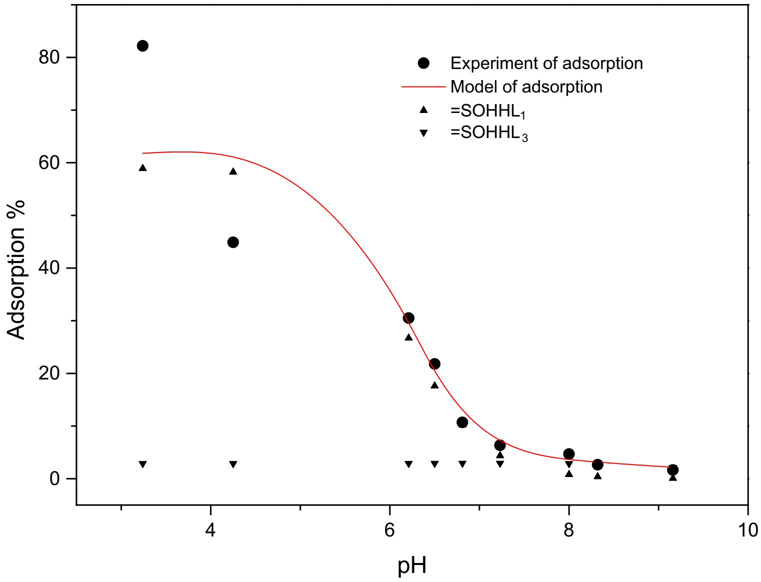

Fig. 5. HA adsorption on rectorite as a function of pH, at $C_o(HA) = 10$ mg/L, $m/V = 0.21$ g/L, $I = 0.01 NaNO_3$ $T = 293$ K.

The sorption of Th(IV) is strongly dependent on pH in the absence and presence of HA (Fig. 6). The sorption of Th(IV) increases from ~30% to ~96% at pH 1–4.5, and then remains constant with increasing pH. 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 ($\log \beta_1 = -2.8$, $\log \beta_2 = -7.6$, $\log \beta_3 = -13.1$ and $\log \beta_4 = -18$) and found that at pH $\leqslant 3$, Th^{4+} is the prevailing species ($\geqslant$ 88%) and $Th(OH)^{3+}$ is less than 12%; 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,

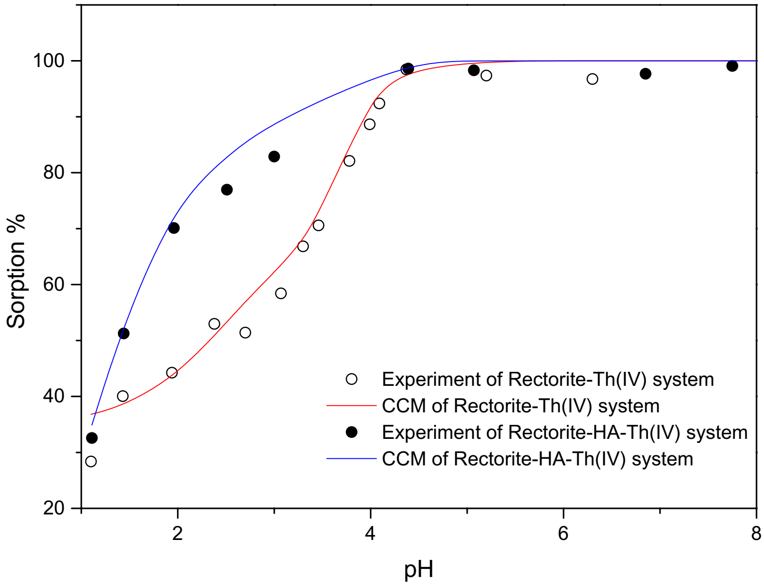

Fig. 6. Effect of pH on Th(IV) sorption on Na-rectorite in the absence and presence of HA, at $C_{Th(IV)(initial)} = 4.31 \times 10^{-5}$ mol/L, $m/V = 0.21$ g/L, $I = 0.01$ M $NaNO_3$, $C_{HA(initial)} = 10$ mg/L and $T = 293$ K.

$Th(OH)_4$ is the prevailing species($\geqslant$99%). From continuous titration experiments, Östhols (1995) 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 a pH from 1 to 4, $Th(OH)_3(CO_3)^-$ and $Th(CO_3)_5^{6-}$ can be neglected. In aqueous systems, with increasing pH, the number of negatively charged =SO^- groups increases and the hydrolysis of Th(IV) also increases.

At pH < 4, the presence of HA increases the sorption of Th(IV) on rectorite, while at pH > 4, little effect of HA on the sorption of Th(IV) is observed. HA has a macromolecular structure, only a small fraction of the "sorbed" carboxylic and phenolic groups of HA directly interact with rectorite surface sites and the remaining "sorbed" groups being free to interact with metal ions (Strathmann and Myneni, 2005). The complexation between HA and Th(IV) is stronger than that between Th(IV) and rectorite. Therefore, the presence of HA increases the sorption of Th(IV) on Na-rectorite at low pH. At pH > 4, about 96% of the added Th(IV) is sorbed on Na-rectorite. As the sorption of Th(IV) on Na-rectorite increases with increasing pH, the complexation between Th(IV) and Na-rectorite increases correspondingly. The strong pH dependent sorption indicates that the sorption is dominated by surface complexation (Baeyens and Bradbury, 1997; Wang et al., 2005).

Here, CCM is applied to fit experimental data on Th(IV) sorption in the absence and presence of HA. Screen "II. Species" in FITEQL 3.2 are tabulated in Tables 1 and 2. The WSOS/DF = 1.2 and 0.87 are obtained for the fit of Th(IV) sorption on Na-rectorite in the absence and presence of HA, which is indicative of a satisfactory optimization procedure.

Table 1
Screen "II. Species" in FITEQL3.2 for Rectorite-Th(IV) system

	Log*K*	PSI	=XOH	=XNa/K	Th^{4+}	Th(ads)	H^+
H^+	0	0	0	0	0	0	1
OH^-	−13.8	0	0	0	0	0	−1
Th^{4+}	0	0	0	0	1	0	0
$Th(OH)^{3+}$	−2.8	0	0	0	1	0	−1
$Th(OH)_2^{2+}$	−7.6	0	0	0	1	0	−2
$Th(OH)_3^+$	−13.1	0	0	0	1	0	−3
$Th(OH)_4$	−18	0	0	0	1	0	−4
=SOH	0	0	1	0	0	0	0
=SOH_2^+	3.25	1	1	0	0	0	1
=SO^-	−4.26	−1	1	0	0	0	−1
=XNa/K	2.13	0	0	1	0	0	0
=XOTh^{3+}	0.40	0	1	0	1	1	−1
=XOHTh^{4+}	2.57	0	1	0	1	1	0
$\text{=X}_4\text{Th}$	9.07	0	0	4	1	1	−4

To illustrate the three variables, Q_e, C_e, and pH, and their relationships, the experimental data in Fig. 6 are again represented as a three-dimensional plot of Q_e, C_e, and pH, and its respective projections on Q_e–C_e, C_e–pH, and Q_e–pH, planes (Fig. 7). As shown in Fig. 7, on the Q_e–pH plane, the projection is two curves similar to both curves in Fig. 6; on the Q_e–C_e plane, the projection is a straight line containing sorption data in the absence and presence of HA, and the straight line results from the constrained relationship, $V\,C_0(\text{Th}) = V\,C_e(\text{Th}) + \text{m}Q_e$. On the C_e–pH plane, there are two curves for the absence and presence of HA, respectively, C_e sharply decreases with increasing pH in the pH ranges 1–3 and 3–4.5. Fig. 7 also shows that the projection on the C_e–pH plane is the inverted image of the projection on the Q_e–pH plane. Thus, the complexity of the sorption edge relative to sorption isotherm at constant pH is demonstrated. The positive effect of HA on Th(IV) sorption on Na-rectorite is also demonstrated in Fig. 7.

3.4. Effect of ionic strength and foreign ions

The ionic strengths of 0.001, 0.01 and 0.1 M $NaNO_3$ were chosen to investigate their effect on Th(IV) sorption onto Na-rectorite. The sorption of Th(IV) decreased with increasing ionic strength (Fig. 8). This phenomenon could be attributed to two reasons: (1) Th(IV) ions form electrical double layer complexes with Na-rectorite, which favors the sorption when the concentration of the competing salt is decreased. This may indicate that the sorption interaction between the functional groups of Na-rectorite and Th(IV) ions is mainly an ionic interaction in nature, which is in agreement with an ion exchange mechanism; (2) ionic strength of solution influences the activity coefficient of Th(IV) ions, which limits their transfer to Na-rectorite surfaces (Reddad et al., 2002). In the authors' earlier reports (Chen and Wang, 2007a,b), the sorption of Th(IV) onto γ-Al_2O_3 and SiO_2 in the absence and presence of HA/FA was weakly dependent on ionic strength. 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, 2003, 2005) studied the sorption of Th(IV) on hematite and Fe oxide, and also found that the sorption of Th(IV) was not strongly influenced by ionic strength in the presence of HA.

A comparison of Na^+, Mg^{2+} and Ca^{2+} influence on the sorption of Th(IV) can be seen in the plots

Table 2
Screen “II. Species” in FITEQL3.2 for Rectorite-HA–Th(IV) system

	Log K	PSI	=XOH	=XNa/K	Th^{4+}	HL_1	HL_2	HL_3	Th(ads)	H^+
H^+	0	0	0	0	0	0	0	0	0	1
OH^-	−13.8	0	0	0	0	0	0	0	0	−1
Th^{4+}	0	0	0	0	1	0	0	0	0	0
$Th(OH)^{3+}$	−2.8	0	0	0	1	0	0	0	0	−1
$Th(OH)_2^{2+}$	−7.6	0	0	0	1	0	0	0	0	−2
$Th(OH)_3^+$	−13.1	0	0	0	1	0	0	0	0	−3
$Th(OH)_4$	−18	0	0	0	1	0	0	0	0	−4
=XOH	0	0	1	0	0	0	0	0	0	0
$=XOH_2^+$	3.25	1	1	0	0	0	0	0	0	1
$=XO^-$	−4.26	−1	1	0	0	0	0	0	0	−1
=XNa/K	2.13	0	0	1	0	0	0	0	0	0
HL_1	0	0	0	0	0	1	0	0	0	0
HL_2	0	0	0	0	0	0	1	0	0	0
HL_3	0	0	0	0	0	0	0	1	0	0
L_1	−5.22	0	0	0	0	1	0	0	0	−1
L_2	−7.24	0	0	0	0	0	1	0	0	−1
L_3	−9.57	0	0	0	0	0	0	1	0	−1
ThL_2	4.29	0	0	0	1	0	1	0	0	−1
$=XOThL_2$	6.03	0	1	0	1	0	1	0	1	−2
$=XOHHL_1$	3.72	0	1	0	0	1	0	0	0	0
$=XOHHL_3$	0.79	0	1	0	0	0	0	1	0	0
$=XOHTh^{4+}$	0	1	1	0	1	0	0	0	1	0
$=XOTh^{3+}$	0	0	1	0	1	0	0	0	1	−1
$=X_4Th$	0	0	0	4	1	0	0	0	1	−4

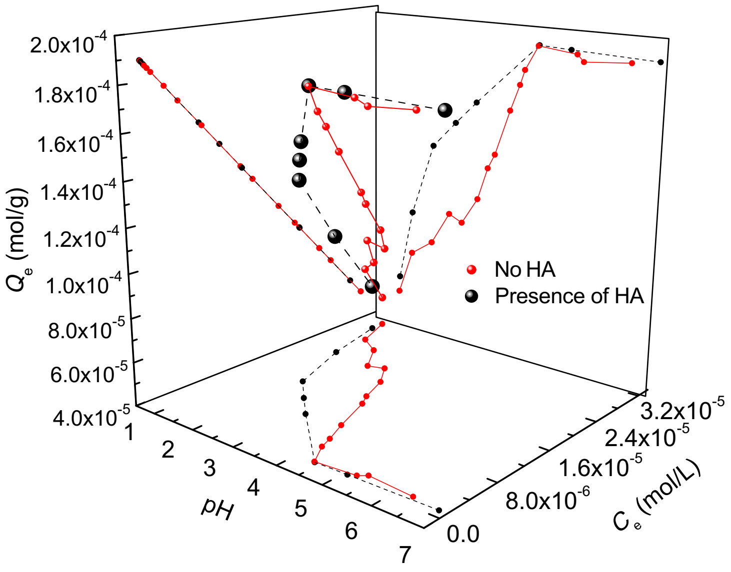

Fig. 7. Three-dimensional plot of both phase concentrations (Q_e, C_e) and pH for Th(IV) sorption on Na-rectorite, at $C_{Th(IV)(initial)} = 4.3 \times 10^{-5}$ mol/L, $m/V = 0.21$ g/L, $I = 0.01$ M $NaNO_3$, $C_{HA(initial)} = 10$ mg/L and $T = 293$ K.

presented in Fig. 9. The distribution coefficient, K_d, is derived from the following equation:

$$K_d = \frac{C_0 - C_e}{C_e} \cdot \frac{V}{m}, \qquad (3)$$

where C_0 is the initial Th(IV) concentration, C_e is the Th(IV) concentration in the supernatant after centrifugation, m is the mass of Na-rectorite and V is the volume of the suspension. The low K_d values of Th(IV) sorption on Na-rectorite at high ionic

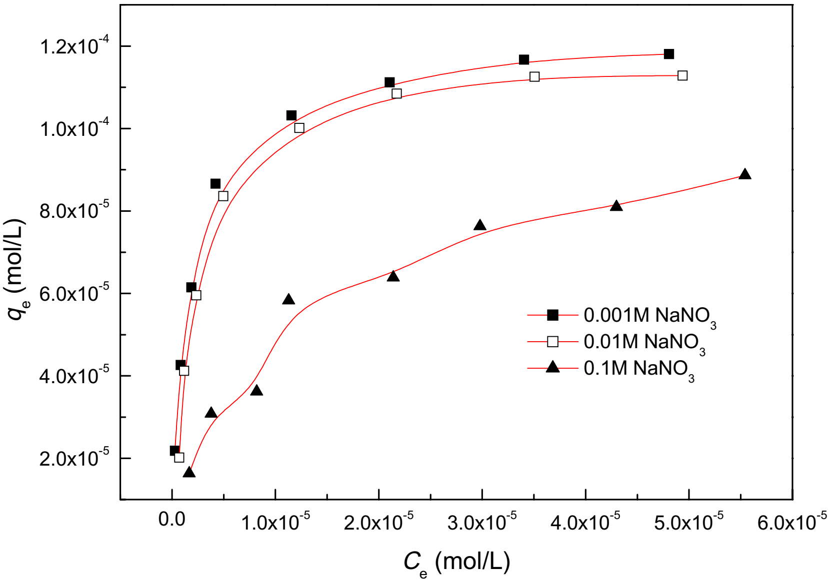

Fig. 8. Isotherms of Th (IV) sorption at different ionic strength, at initial pH 1.7 ± 0.1, $C_{\mathrm{Th(IV)(initial)}} = 4.31 \times 10^{-5}$ mol/L, $m/V = 0.25$ g/L and $T = 293$ K.

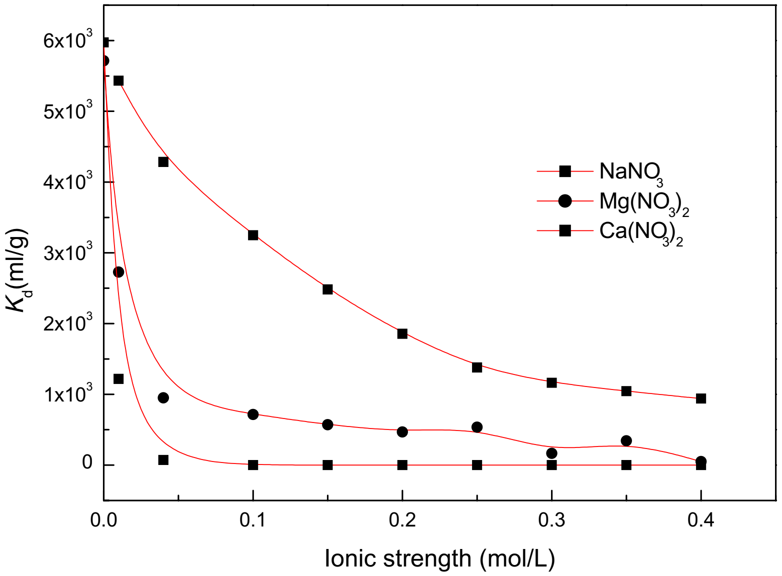

Fig. 9. Effect of ionic strength comparison of $NaNO_3$, $Mg(NO_3)_2$ and $Ca(NO_3)_2$ on Th(IV) sorption on Na-rectorite, at initial pH 2.0 ± 0.1, $C_{\mathrm{Th(IV)(initial)}} = 4.31 \times 10^{-5}$ mol/L, $m/V = 0.21$ g/L and $T = 293$ K.

strength indicate that the sorption of Th(IV) on Na-rectorite is influenced by the foreign cations in the solution. The order in which the cations influence Th(IV) sorption is $Na^+ < Mg^{2+} < Ca^{2+}$. The sorption ability of the three cations on Na-rectorite is $Na^+ < Mg^{2+} < Ca^{2+}$, and therefore the influence of Ca^{2+} on Th(IV) sorption is stronger than those of Mg^{2+} and Na^+. However, tetravalent Th(IV) ion sorption on Na-rectorite should be weakly affected by the monovalent Na^+ and bivalent Mg^{2+} and Ca^{2+}, as the higher valence ion is much more easily and strongly sorbed by clay minerals. pH and ionic strength dependent sorption of Th(IV) on Na-rectorite suggests that the sorption of Th(IV) can be attributed to surface complexation and cation exchange under the experimental conditions.

3.5. Sorption thermodynamics

Increase in temperature appears to decrease the maximum sorption of Th(IV) on Na-rectorite. The thermodynamic parameters, the values of enthalpy, ΔH^o, and entropy, ΔS^o, were calculated from the slopes and intercepts of the plot of $\ln K_d$ vs. 1000/T (Fig. 10) by using the equation

$$\ln K_d = \Delta S^o/R - \Delta H^o/RT. \tag{4}$$

The Gibbs free energy, ΔG^o, of specific adsorption was calculated from the equation

$$\Delta G^o = \Delta H^o - T\Delta S^o, \tag{5}$$

where R (8.3145 J mol^{-1} K^{-1}) is the ideal gas constant, and T (K) is the temperature in Kelvin. Relevant data calculated from Eqs. (4) and (5) are listed in Table 3. The sorption process of Th(IV) onto Na-rectorite is exothermic, i.e. the sorption of Th(IV) decreases with increasing temperature. One possible interpretation of exothermicity of the enthalpy of sorption is that Th(IV) ions with low hydration energies are weakly solvated in water. The sorption of Th(IV) ions may require at least a partial decomposition of their hydration shell, a process that requires energy input. If the exothermicity associated with the sorption of Th(IV) ions on Na-rectorite exceeds the dehydration energy of Th(IV) ions, then the overall energy balance will lead to exothermic behavior. ΔG^o is negative as expected for a spontaneous process under the conditions applied. The decrease in ΔG^o with decreasing temperature indicates more efficient adsorption at lower temperature. The positive values of entropy change (ΔS^o) reflects the affinity of Na-rectorite toward Th(IV) ions in the solutions and may suggest some structural changes in the sorbents (Altundoğan et al., 2000; Genc-Fuhrman et al., 2004). The decomposition of the hydration shell will increase the entropy of the solvent.

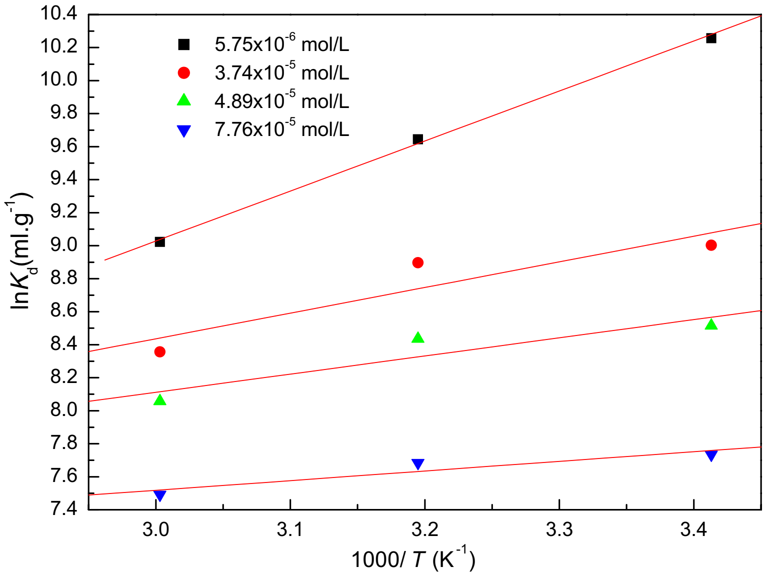

Fig. 10. Plot of $\ln K^o$ vs. $1/T$ for Th(IV) sorption on Na-rectorite, at initial pH 1.7 ± 0.1, $I = 0.01$ M NaNO$_3$ and $m/V = 0.25$ g/L.

Table 3
Thermodynamic parameters for Th(IV) sorption onto rectorite

C_o (Th(IV)) (mol/L)	ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1} K^{-1})	$-\Delta G^o$ (kJ mol^{-1})		
			$T = 293$ K	$T = 313$ K	$T = 333$ K
5.75×10^{-6}	−24.942	0.125	24.978	24.981	24.984
3.74×10^{-5}	−12.887	31.427	22.095	22.723	23.352
4.89×10^{-5}	−9.145	40.655	21.057	21.871	22.684
7.76×10^{-5}	−4.822	47.972	18.878	19.837	20.797

3.6. Effect of HA concentration and HA/Th(IV) addition sequences

The effect of HA concentration and addition sequences on Th(IV) sorption on Na-rectorite is shown in Fig. 11. The sorption of Th(IV) increases with increasing initial concentration of HA in the solution, which is consistent with the properties of humic substances. At higher concentration of HA, there are more functional groups, such as carboxylic and phenolic groups, and these groups could form strong complexes with Th(IV). Whereas, Reiller et al. (2002, 2005) reported that the sorption of Th(IV) on HA bound hematite decreased with increasing concentration of HA in solution.

Fig. 11 also shows that HA/Th(IV) addition sequences affect Th(IV) sorption obviously. The decrease in metal sorption when HA is pre-equilibrated with the solid is a classical observation (Davis, 1984; Zachara et al., 1994; Ticknor et al., 1996; Takahashi et al., 1999). Under the experimental conditions, some humic sites are present in the solution, and when Th(IV) is added to the system, competition occurs between free humic sites and Na-rectorite surfaces sites. This competition is strongly in favor of HA in the acidic pH range and strong complexation between Th(IV) and HA. Hence in this system, where Na-rectorite is pre-equilibrated with HA, organic matter controls Th(IV) behavior. Given the preferential complexation of Th(IV) by the highest molecular mass fraction of NOM (Zhang et al., 1997; Quigley et al., 2001) and the kinetic control of the NOM sorption by mineral surfaces (Gu et al., 1994; van de Weerd et al., 1999), a tentative explanation of this behavior can be proposed. van de Weerd et al. (1999) modeled the results of Gu et al. (1994) and proposed different sorption kinetics for six fractions representing NOM, namely, hydrophobic and hydrophilic fractions of size <3 kDa, 3–100 kDa, and >100 kDa. The lower mass fraction and the more hydrophobic fraction have faster kinetics. Through this modeling, the higher mass fractions reach sorption equilibrium in times ranging from 100 h to more than 900 h. These modeling results were experimentally confirmed by Hur and Schlautman (2003) in the case of purified Aldrich humic acid. Given the short time of the present experiments (24 h), the sorption of these fractions had not reached equilibrium. This is further confirmed by the observation of Hur and Schlautman (2003). Therefore, when HA is pre-equilibrated with Na-rectorite over 24 h, the higher mass fractions are not in equilibrium with the Na-rectorite surfaces and are thus present in the solution. When Th(IV) is added to this suspension, the complexation with higher mass fractions would lead to its presence in solution.

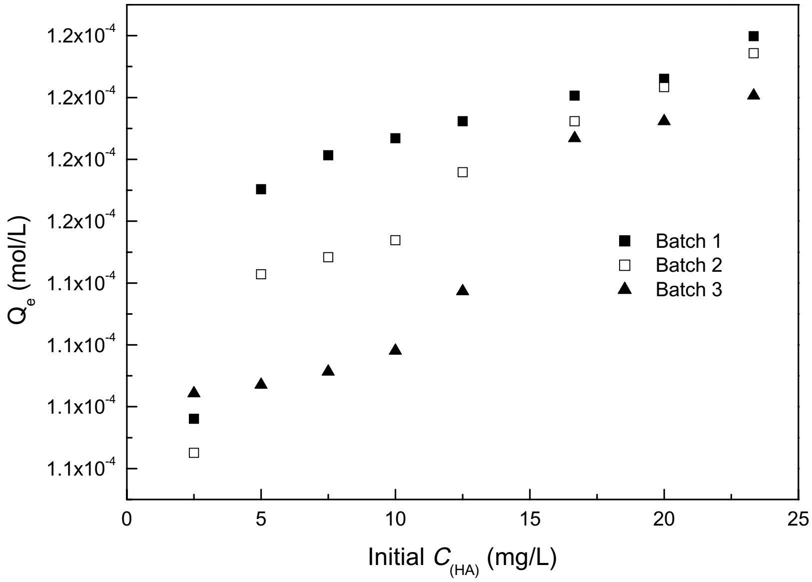

Fig. 11. Effect of the addition sequences of the component and of HA concentration on Th(IV) sorption, at initial pH 1.7 ± 0.1, $C_{\mathrm{Th(IV)(initial)}} = 4.31 \times 10^{-5}$ mol/L, $I = 0.01$ M $NaNO_3$, $m/V = 0.25$ g/L and $T = 293$ K.

When Th(IV) is pre-equilibrated with Na-rectorite, the complexation between the higher mass fraction in the solution and sorbed Th(IV) seems less probable in the time frame of the experiment, and Th(IV) sorption by Na-rectorite would be more important. The sorption of Th(IV) is higher in batch 1 than in batch 2 and batch 3. Reiller et al. (2005) reported a similar observation. The differences cannot be reasonably interpreted, and further work is necessary to understand this behavior.

3.7. Sorption and desorption isotherms

The sorption and desorption isotherms of Th(IV) on Na-rectorite in the absence and presence of HA are shown in Fig. 12a and b. The desorption isotherms overlap the sorption isotherms at low Th(IV) concentrations, which indicates that the sorption of Th(IV) on Na-rectorite in the absence and presence of HA is reversible at low Th(IV) concentrations. Whereas, at high

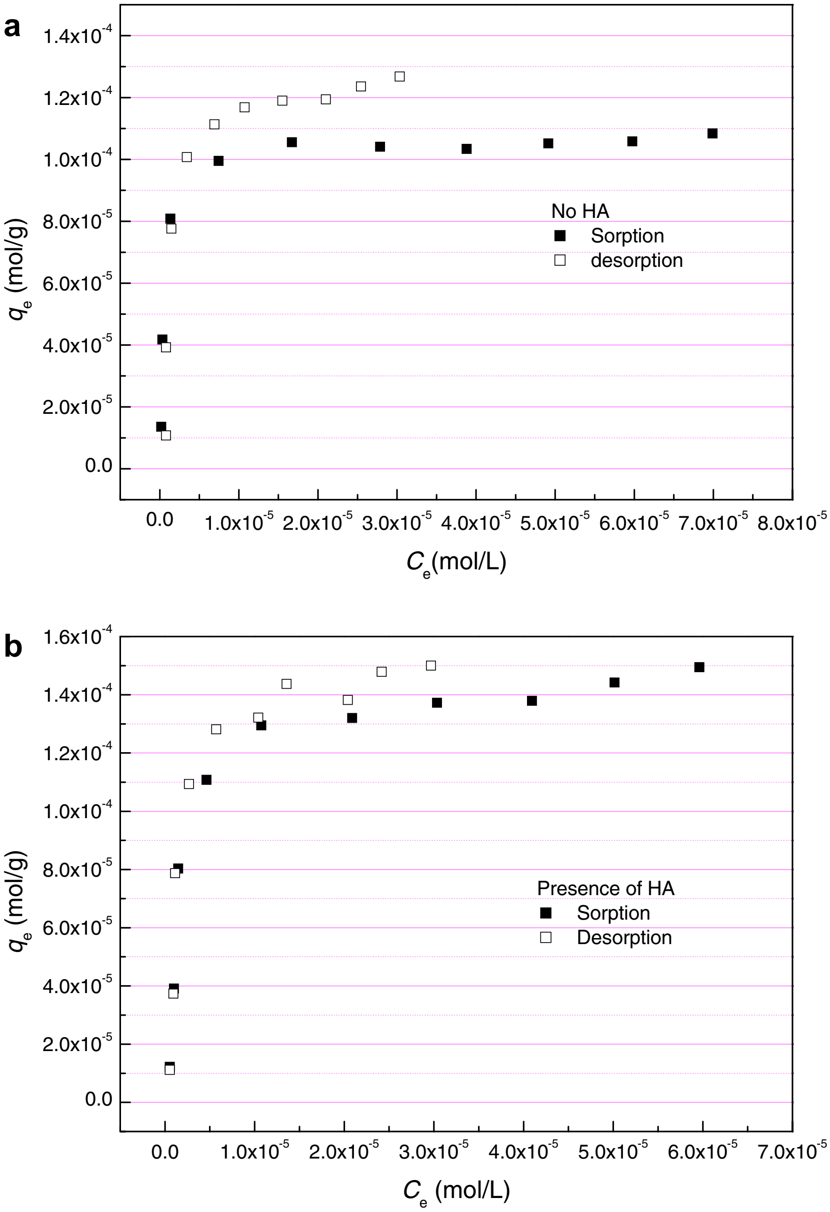

Fig. 12. Sorption and desorption isotherms of Th(IV) on Na-rectorite: (a) no HA and (b) HA added, $C_{(HA)initial} = 10$ mg/L, at initial pH 2.0 ± 0.1, $I = 0.01$ mol/L $NaNO_3$, $m/V = 0.21$ g/L and $T = 293$ K.

Th(IV) concentrations, the desorption isotherms are obviously higher than the sorption isotherms which indicates that sorption–adsorption hysteresis actually occurs and the sorption is irreversible. The concentration of Th(IV) in the solid phase does not change after the concentration of Th(IV) in the solution decreases. This indicates that Th(IV) ions sorbed on solid particles are not desorbed from solid to liquid phase to reestablish equilibrium under the experimental conditions. The irreversible sorption also suggests that strong surface complexation contributes to the sorption of Th(IV) on rectorite in the absence and presence of HA.

4. Conclusions

In the light of this work, the following main conclusions can be drawn:

(I) Th(IV) sorption onto Na-rectorite was strongly dependent on ionic strength and temperature in the experiments.
(II) The presence of HA enhanced Th(IV) sorption at low pH and had no obvious effect on Th(IV) sorption at high pH.
(III) The sorption process of Th(IV) on Na-rectorite was exothermic.
(IV) HA/Th(IV) addition sequences affected Th(IV) sorption in the ternary systems.
(V) The sorption of Th(IV) on Na-rectorite may be dominated by surface complexation and CCM modeled the experimental data very well, while cation exchange also contributed partly to Th(IV) sorption.

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