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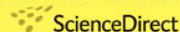
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Sorption–desorption of Th(IV) on attapulgite: Effects of pH, ionic strength and temperature

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Abstract

The sorption of Th(IV) on attapulgite was studied as a function of pH, ionic strength, temperature, attapulgite contents and Th(IV) concentrations under ambient conditions using a batch technique. The results indicated that sorption of Th(IV) on attapulgite was strongly affected by pH values, and weakly dependent on ionic strength. Sorption of Th(IV) was dominated by surface complexation, although ion exchange also contributed to this sorption. Sorption of Th(IV) increased with increasing temperature of the system. Enthalpy (ΔH^0), entropy (ΔS^0) and Gibbs free energy (ΔG^0) were calculated from the temperature-dependent sorption data; the results indicated that the sorption of Th(IV) on attapulgite was a spontaneous process. Sorption–desorption hysteresis indicated that the sorption of Th(IV) was irreversible, and that the Th(VI) adsorbed on attapulgite was difficult to be desorbed from solid to liquid phases. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Th(IV); Sorption; Attapulgite; pH; Ionic strength; Temperature

1. Introduction

Sorption and desorption of Th(IV) on all kinds of clay minerals and oxides are very important in determining the mobility and bioavailability of Th(IV) in the natural environment (Xu et al., 2006a; Tan et al., 2007a, b; Chen et al., 2007; Chen and Wang, 2007). Many mechanisms have been postulated for Th(IV) and other actinides' sorption, including surface complexation, chemisorption, cation exchange, surface precipitation, colloid formation at surface and diffusion into the particle micropores (Jakobsson, 1999; Reiller et al., 2005). The results of the previous studies indicated that sorption of Th(IV) is strongly pH-dependent and weakly ionic strength-dependent. Xu et al. (2006a) studied the sorption of Th(IV) on MX-80 bentonite in the presence and absence of humic/fulvic acids, and found that sorption of Th(IV) on humic substances bound MX-80 bentonite was strongly

enhanced at low pH values, although little influence of humic substances was found at high pH values. Tan et al. (2007a) investigated the sorption of Th(IV) on TiO₂ nanoparticles using SEM, XRD, IR and Raman spectroscopy, and found that sorption of Th(IV) was mainly dominated by surface complexation and Ti–O–Th was formed at the surfaces of TiO₂ colloids.

Desorption of the adsorbed metal ions from solid surface can control the availability of the adsorbed metal ions to the natural environment. Distribution coefficients derived from sorption and desorption isotherms (i.e., $K_{d(sorp)}$ and $K_{d(desorp)}$) can be used to evaluate the sorption–desorption hysteresis of the adsorbed ions on the solid phase (Wang and Liu, 2005; Shirvani et al., 2006a). Hysteresis and irreversibility have been interchangeably used to describe the “reversible” or “irreversible” sorption properties of metal ions on solid surfaces. Strawn and Sparks (1999) thought that “true-hysteresis” arises from a shift in the equilibrium from the desorption direction rather than from sorption. The irreversibility is a result of the time-wise incomplete desorption experiment failing to reach true-equilibrium, due to the slow kinetics involved.

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Attapulgite is a hydrated octahedral layered magnesium aluminum silicate present in nature as a fibrillar silicate clay mineral. It has permanent negative charges on its surface, which enable it to be modified by cationic surfactants, to enhance contaminant retention and to retard contaminant migration. In addition, some isomorphous substitutions in the tetrahedral layer, such as Al^{3+} for Si^{4+} , develop negatively charged adsorption sites able to electrostatically adsorb cations (Zhang et al., 2006; Shirvani et al., 2006b). In the last decades, attapulgite has been intensively investigated as an adsorbent in the removal of organic contaminants and heavy metal ions from the solutions and heavy metal polluted soils in the natural environment (Galan, 1996; Murray, 2000; Visera and Lopez-Galindo, 1999; Álvarez-Ayuso and García-Sánchez, 2003). There are large reserves of attapulgite in South China. It was first utilized in the 1940s, and has been mainly used as an absorbent, catalyst carrier, densifying agent, adhesive and food additive. In this paper, we will report our use of attapulgite as a sorbent to study the sorption properties of Th(IV) at different experimental conditions. The purposes are: (1) to investigate the effect of pH on Th(IV) sorption; (2) to study the influence of ionic strength on Th(IV) sorption; (3) to measure the sorption and desorption isotherms and to calculate the distribution coefficient and sorption–desorption hysteresis; (4) to study the sorption of Th(IV) at different temperatures and to achieve the adsorption thermodynamic data (i.e., ΔG^0 , ΔH^0 , ΔS^0); (5) to study the possibility of attapulgite in waste solution treatment; and (6) to discuss the sorption mechanism.

2. Experimental

All chemicals used in the experiments were purchased as analytically pure and were used without any further purification. The sample of attapulgite micro-powder was supplied by Kaixi Co. (Gansu, China). It was treated with 5% hydrochloric acid for 24 h, followed by washing with distilled water until no chloride was detectable in supernatant with 0.01 M AgNO_3 . Then the sample was dried at 105 °C in oven for 2 h in order to remove free water. Each thus prepared sample was calcined for 2 h at 360 °C in muffle to eliminate the zeolitic water and part of crystal water. At last the sample was milled through a 320-mesh screen and used in the experiments (Zev and Bruno, 1978; Chessick and Zettlemoyer, 1956; Haden and Schwint, 1967). The N2-BET surface area of the thus-derived sample is 115 m²/g.

All the experiments were carried out at ambient conditions. Stock suspensions of attapulgite, NaNO_3 , and thorium stock solution were added in the polyethylene tubes to achieve the desired concentrations of different components. It is necessary to note that before the addition of thorium stock solution, attapulgite and NaNO_3 were first shaken for 2 days to achieve the equilibration of Na^+

with attapulgite. The pH values of the solution were adjusted by adding negligible volumes of 0.1 or 0.01 M HNO_3 or NaOH . After the suspensions were stirred for 24 h, the solid and liquid phases were separated by centrifugation at 7500 rpm for 30 min.

The concentration of Th(IV) was analyzed by spectrophotometry at a wavelength of 650 nm by using Th Arsenazo III complex. All the experimental data were the averages of duplicate or triplicate experiments. The relative errors of the data were about 5%.

For desorption experiments, the suspension of attapulgite was centrifuged (7500 rpm, 30 min) at the end of the sorption experiments; half of the supernatant was pipetted out and an equal volume of background electrolyte solution with the same pH value was added. Then the mixture was shaken and centrifugation was done under the same conditions as in the sorption experiments.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns of untreated attapulgite (not calcined for 2 h at 360 °C in muffle to eliminate the zeolitic water and part of crystal water) and activated attapulgite (calcined for 2 h at 360 °C). From Fig. 1, one can see that no difference of the peaks is found in the two different samples, which indicates that the crystal structure does not change after treatment at 360 °C. The peak positions at 2θ values of 8.34, 25.42, 42.6 and 54.97 are correspondence to the crystal structure of attapulgite. Other clay minerals such as montmorillonite and quartz are also found in attapulgite. It is necessary to note that the attapulgite sample used in the following experiments was calcined for 2 h at 360 °C.

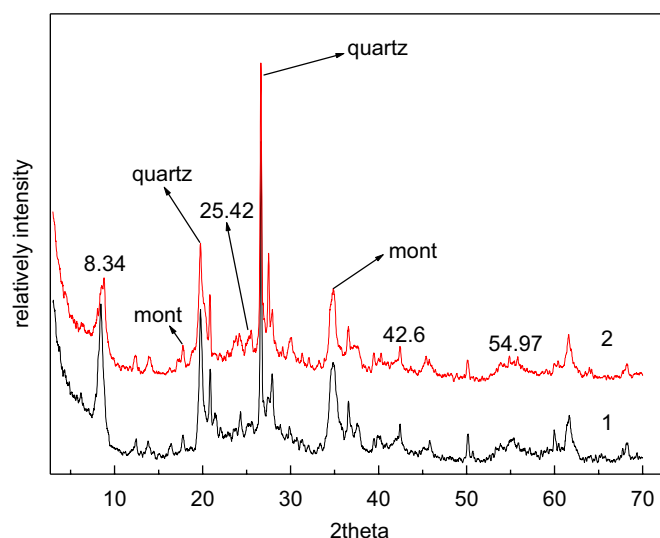


Fig. 1. XRD of untreated attapulgite (named 1) and activated attapulgite (named 2).

3.2. Equilibration time

The removal of Th(IV) from solution to attapulgite as a function of contact time is shown in Fig. 2. As can be seen from Fig. 2, the sorption of Th(IV) is quick and 2 h is enough to achieve the sorption equilibration. After 2 h contact time, the removal percent of Th(IV) from solution to attapulgite remains level with increasing contact time. In the following experiments, we shook the test tubes for 24 h. The high sorption capacity of attapulgite and fast sorption velocity indicate that strong chemisorption or strong surface complexation contributes to the sorption of Th(IV) on attapulgite (Wang et al., 2005b). The high sorption and fast sorption velocity also suggest that attapulgite is suitable for sorption and pre-concentration of Th(IV) from large volume of solutions.

3.3. Effect of attapulgite concentration

The sorption of Th(IV) on attapulgite as a function of attapulgite concentrations is shown in Fig. 3. The distribution coefficient (K_d) was calculated from the concentration of Th(IV) in suspension (C_0) and that of Th(IV) in supernatant (C_{eq}) according to the following equation:

$$K_d = \frac{C_0 - C_{eq}}{C_{eq}} \cdot \frac{V}{m}, \quad (1)$$

where V is the volume of the solution and m is the mass of the attapulgite. One can see that the removal percent of Th(IV) increases with increasing attapulgite contents in the suspension. The distribution coefficient, K_d , values as a function of the attapulgite concentration are also plotted in Fig. 3. Comparing to the strong dependence of Th(IV)

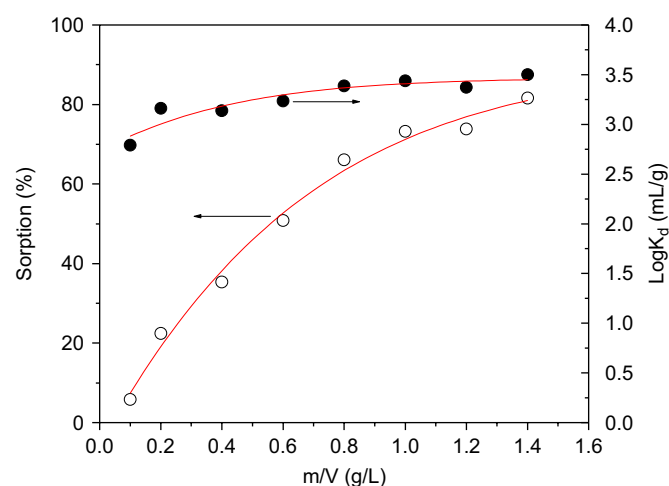


Fig. 3. Effect of solid content on the sorption of Th(IV) to attapulgite. $C[\text{Th(IV)}]_{\text{initial}} = 4.3 \times 10^{-5} \text{ mol/L}$, $\text{pH} = 1.68 \pm 0.01$, $I = 0.01 \text{ M NaNO}_3$, $T = 22 \pm 2^\circ \text{C}$.

removal on solid content, we see that the K_d value is weakly dependent on attapulgite content under our experimental conditions. With increasing attapulgite content in the suspension, the number of sites of attapulgite which participate in the sorption of Th(IV) increases and thereby the removal percent of Th(IV) increases reasonably. However, the K_d value is theoretically independent of solid content if the solid content in the suspension is not high. Herein, our results show that the K_d value increases slightly with increasing attapulgite content. Xu et al. (2006b) studied the sorption of Co(II) on bentonite and found that the K_d value of Co(II) decreases slightly with increasing bentonite content. Nevertheless, the weak K_d dependence on solid content is reasonable. However, the results of the sorption of Sr(II), Eu(III) and U(VI) (Wang and Liu, 2004; Wang et al., 2004a,b, 2005c) in compacted bentonite indicated that distribution coefficient decreases with increasing bulk density of the compacted bentonite.

3.4. Effects of pH and ionic strength

Removal percent of Th(IV) from solution to attapulgite as a function of pH values in 0.001, 0.01 and 0.1 M NaNO_3 solutions are shown in Fig. 4. Sorption of Th(IV) occurs at low pH value and a sharp increase in sorption from ~5% to ~100% of the added Th(IV) concentration occurs over the pH range from 1 to 4. Then the sorption of Th(IV) on attapulgite remains level with increasing pH values. In comparison to the sorption of Th(IV) on bentonite (Xu et al., 2006a), on TiO_2 (Tan et al., 2007a,b) and on carbon nanotubes (Chen and Wang, 2007), the sorption of Th(IV) mainly occurs at $\text{pH} < 4$. The results of Th(IV) sorption on TiO_2 indicated that the sorption started from pH 0.5 and increased quickly to ~100% at pH 5 (Tan et al., 2007a,b; Jakobsson, 1999). Murphy et al. (1999) studied the sorption of Th(IV) on hematite and found that ~100% Th(IV) was adsorbed on hematite at pH ~3.5. The results

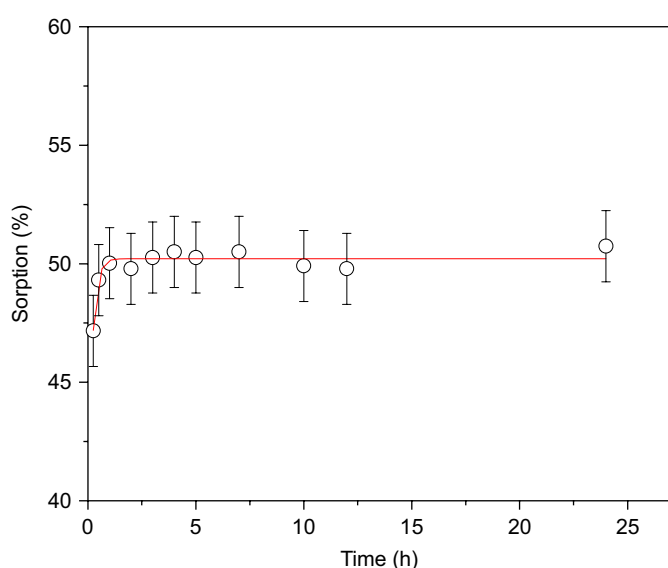


Fig. 2. Effect of time on the sorption of Th(IV) to attapulgite. $C[\text{Th(IV)}]_{\text{initial}} = 4.3 \times 10^{-5} \text{ mol/L}$, $\text{pH} = 1.68 \pm 0.01$, $I = 0.01 \text{ M NaNO}_3$, $m/V = 0.6 \text{ g/L}$, $T = 22 \pm 2^\circ \text{C}$.

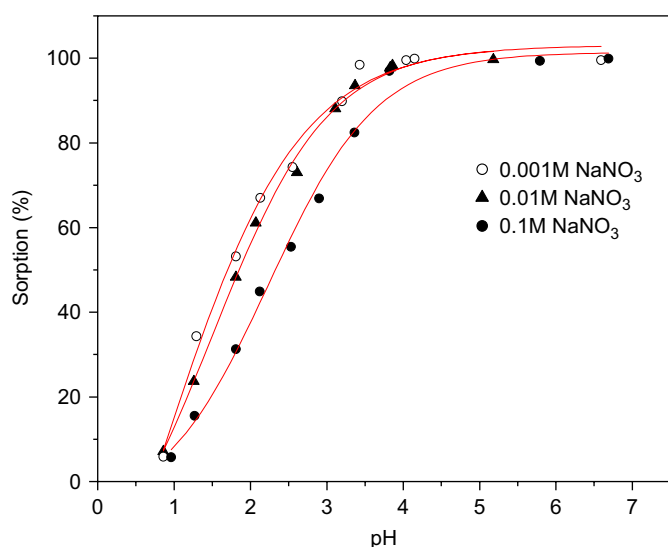


Fig. 4. Effect of pH and ionic strength on the sorption of Th(IV) to attapulgite. $C[\text{Th(IV)}]_{\text{initial}} = 4.3 \times 10^{-5} \text{ mol/L}$, $m/V = 0.6 \text{ g/L}$, $T = 20 \pm 2^\circ \text{C}$.

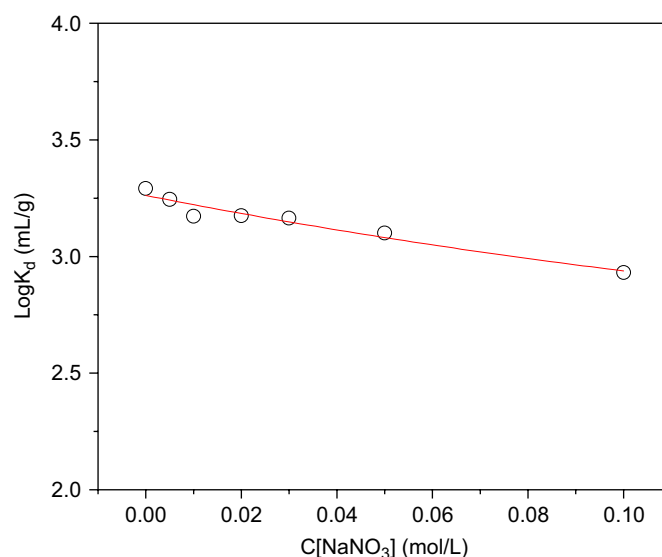


Fig. 5. Effect of ionic strength on the sorption of Th(IV) to attapulgite. $C[\text{Th(IV)}]_{\text{initial}} = 4.3 \times 10^{-5} \text{ mol/L}$, $m/V = 0.6 \text{ g/L}$, $\text{pH} = 1.85 \pm 0.01$, $T = 22 \pm 2^\circ \text{C}$.

of the references (Xu et al., 2006a; Tan et al., 2007a,b; Murphy et al., 1999) are very similar to the results of this work. The strongly pH-dependent sorption of Th(IV) on attapulgite suggests that surface complexation contributes mainly to the sorption of Th(IV) on attapulgite (Wang et al., 2004a,b, 2005a,b; Baeyens and Bradbury, 1997).

From Fig. 4, one can also see that sorption of Th(IV) on attapulgite is also affected by the concentration of NaNO_3 weakly. The influence of monovalent Na^+ ions on sorption of tetravalent Th(IV) indicates that outer-sphere complexes are formed at the surface of attapulgite. There is little difference in the sorption data of Th(IV) at 0.01 and 0.001 M NaNO_3 concentrations; this result suggests that inner-sphere complexes are also formed. The formation of an inner-sphere complex is independent of ionic strength (Hayes et al., 1991; Wang et al., 2004b). In general, surface complexation is influenced by pH values obviously, whereas ion exchange is influenced by ionic strength (Wang et al., 2004b, 2005b,c; Baeyens and Bradbury, 1997). Sorption of Th(IV) on attapulgite forms outer- and inner-sphere complexes, and the sorption mechanism of Th(IV) on attapulgite is similar to that of Th(IV) on bentonite (Xu et al., 2006b; Jakobsson, 1999).

The influence of NaNO_3 concentration on the sorption of Th(IV) on attapulgite is shown in Fig. 5. From Fig. 5, one can see that the sorption of Th(IV) on attapulgite is weakly dependent on the ionic strength. The distribution coefficient decreases with increasing NaNO_3 concentration, which suggests that the ions at the attapulgite surface contribute to the sorption and complexation of Th(IV) on attapulgite. Outer-sphere complexes were formed on attapulgite. The results in Figs. 4 and 5 are consistent with each other.

3.5. Effect of temperature

Fig. 6 shows the sorption isotherms (i.e., the quantity of Th(IV) in solid phase (C_s , mol/g) vs. the equilibrium concentration of Th(IV) in solution (C_{eq} , mol/l) at different temperatures. One can see that the sorption increases with rise in temperature. Bikerman (1958) attributes this phenomenon to a negative temperature coefficient of solubility of solutes or to a steep simultaneous decrease of real adsorption of solvent. The values of enthalpy, ΔH^0 , and entropy, ΔS^0 , were calculated from the slope and intercept of the plot of $\ln K_d$ vs. $1/T$ (Fig. 7) by using the equation

$$\ln K_d = \Delta S^0/R - \Delta H^0/RT. \quad (2)$$

The Gibbs free energy, ΔG^0 , of specific adsorption was calculated from the equation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0, \quad (3)$$

where R ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$) is the ideal gas constant, and T (K) is the temperature. Relevant data calculated from Eqs. (2) and (3) are listed in Table 1. It is evident that the values of ΔH^0 are positive, i.e., the process is endothermic. The removal of water molecules from ions is essentially an endothermic process, and it appears that the endothermicity of the desolvation process exceeds that of the enthalpy of adsorption to a considerable extent. The Gibbs free energy change (ΔG^0) is negative, as expected for a spontaneous process under the conditions applied. The decrease in ΔG^0 with the increase of temperature indicates more efficient adsorption at higher temperature. The positive values of entropy change (ΔS^0) reflect the affinity of attapulgite toward Th(IV) ions in aqueous solutions and may suggest some structure changes in the adsorbents

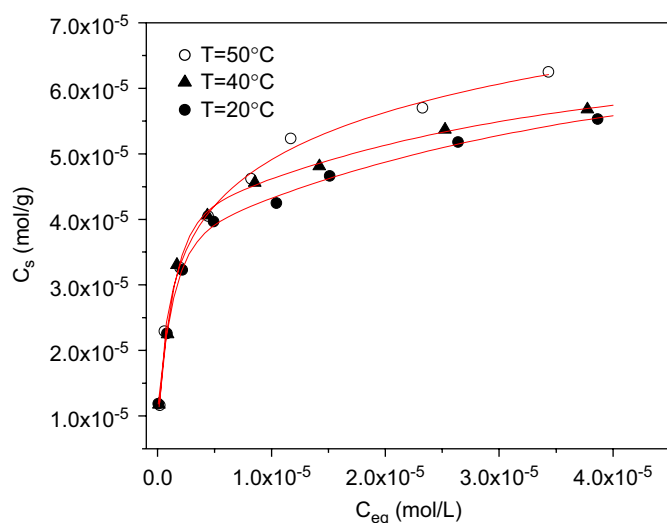


Fig. 6. Sorption isotherms of Th(IV) on attapulgite at three different temperatures. pH = 2.50 ± 0.01 , $m/V = 0.6$ g/L, $I = 0.01$ M NaNO_3 .

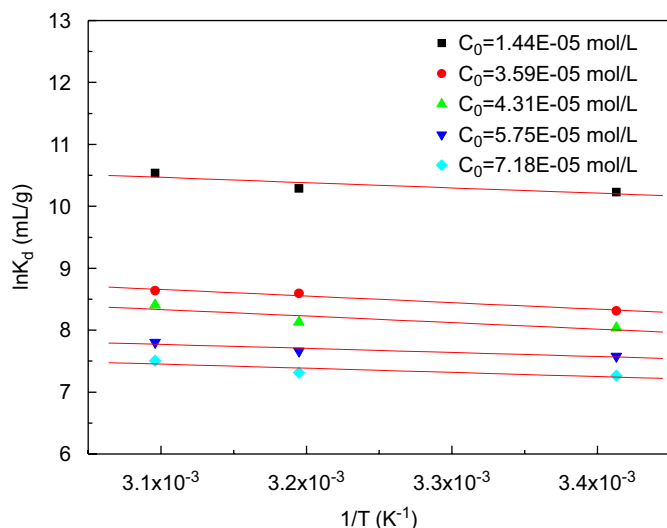


Fig. 7. Effect of temperature on the distribution coefficients of Th(IV) on attapulgite at different solution concentration. pH = 2.50 ± 0.01 , $m/V = 0.6$ g/L, $I = 0.01$ M NaNO_3 .

Table 1
The thermodynamic data of Th(IV) sorption on attapulgite at different Th(IV) initial solution concentrations

C^0 (mol/L)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	ΔG^0 (kJ mol ⁻¹)		
			293	313	323
1.44E-05	7.06	99.44	-22.07	-24.06	-25.05
3.59E-05	8.86	87.05	-16.64	-18.38	-19.25
4.31E-05	8.72	96.43	-19.53	-21.46	-22.42
5.75E-05	5.41	81.37	-18.43	-20.06	-20.88
7.18E-05	5.56	79.18	-17.64	-19.23	-20.02

(Genc-Fuhrman et al., 2004; Chen and Wang, 2006). It will be necessary to study the species and structures of Th(IV) on attapulgite in future research (Wang et al., 2004b, 2006).

3.6. Sorption isotherms

The distribution coefficients (K_d) of Th(IV) on attapulgite as a function of Th(IV) concentration at pH 1.00 ± 0.01 and 2.50 ± 0.01 , respectively, are shown in Fig. 8. From Fig. 8, one can see that the distribution coefficient decreases with increasing Th(IV) concentration, which indicates that the sorption of Th(IV) on attapulgite is influenced by the extent of Th(IV) on attapulgite surface. The sorption isotherm at pH 2.50 is much higher than that at pH 1.00 (see Fig. 8), which suggests that sorption of Th(IV) is strongly influenced by pH values at these pH range (the results are consistent with the results in Fig. 4). The decrease of K_d with increasing Th(IV) concentration indicates that the sorption ability of attapulgite decreases with the increasing of Th(IV) concentration in solution. The K_d values at low solution concentration are higher than those at high loading. Th(IV) may initially be adsorbed on high-energy (high-affinity) sites at low surface coverage and on high- and low-energy sites at higher surface coverage (Shirvani et al., 2006a). The sorption of Th(IV) on attapulgite can be considered to be a result of the competition among Th(IV) with other cations (including Th(IV) ions) in solution and on the surface of attapulgite. With increasing Th(IV) concentration, the competition of Th(IV) with Th(IV) and other ions increases, and thereby the sorption of Th(IV) on attapulgite decreases reasonably.

3.7. Sorption and desorption isotherms

Sorption and desorption isotherms of Th(IV) on attapulgite at pH 1.93 ± 0.01 are shown in Fig. 9. The isotherm of desorption is much higher than that of sorption, which indicates that sorption–desorption hysteresis occurs in the

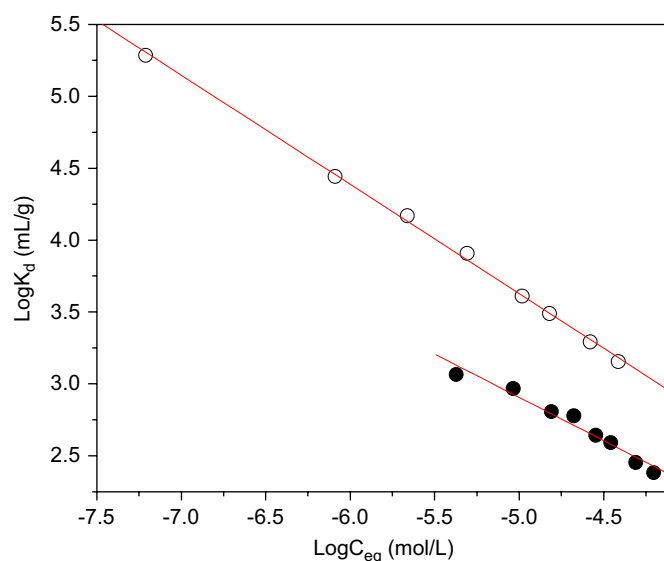


Fig. 8. Sorption isotherms of Th(IV) on attapulgite at two different pH values. $m/V = 0.6$ g/L; $T = 20 \pm 2$ °C; $I = 0.01$ M NaNO_3 , solid point: pH = 1.00 ± 0.01 ; open point: pH = 2.50 ± 0.01 .

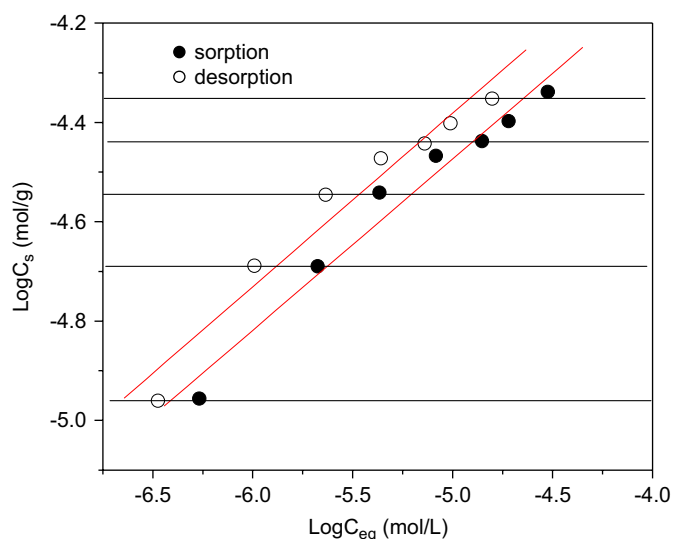


Fig. 9. Sorption and desorption isotherms of Th(IV) on attapulgite. $m/V = 0.6 \text{ g/L}$, $T = 20 \pm 2^\circ\text{C}$, $I = 0.01 \text{ M NaNO}_3$, $\text{pH} = 1.93 \pm 0.01$.

sorption–desorption process. Inner-sphere adsorption and nucleation processes might have caused the hysteresis observed in the study, since the presence of 0.01 M Na^+ in the background solutions likely inhibited the Th(IV) outer-sphere adsorption via weak ion exchange process (Shirvani et al., 2006a). Some structural changes in forward-sorption and backward-desorption process may also result in the hysteresis. It is necessary to study this structural change using spectroscopic methods (such as TEM, XAFS, XRD, etc.) in further works. Nusinelli et al. (2003) stated that lead desorption hysteresis by montmorillonite was due to irreversible Pb inner-sphere binding to the mineral edge sites and its precipitation at pH values higher than the hydrolysis point of Pb.

The desorption isotherm is higher than the sorption isotherm, demonstrating that the affinity of Th(IV) for the sorbents increases from the forward (sorption) to the reverse (desorption) direction. The average distribution coefficient of sorption and desorption isotherms and the sorption–desorption hysteresis coefficient (HC) are listed in Table 2. The \bar{K}_d value indicates the average quantity of Th(IV) in forward-binding process (i.e., sorption) and/or backward-release from solid phase (i.e., desorption) under our experimental conditions. It is an indirect value to evaluate the quantity of Th(IV) binding on solid phase. The value of HC can be calculated as (Wang et al., 2005d)

$$HC\% = \frac{\bar{K}_{d(\text{desorb})} - \bar{K}_{d(\text{sorb})}}{\bar{K}_{d(\text{desorb})}} \times 100\%. \quad (4)$$

Ma et al. (1993) calculated the hysteresis using another equation to describe the sorption–desorption properties:

$$W\% = \frac{\bar{K}_{d(\text{desorb})} - \bar{K}_{d(\text{sorb})}}{\bar{K}_{d(\text{sorb})}} \times 100\%. \quad (5)$$

The value of $W\%$ is also listed in Table 2. From Table 2, one can see that the value of $\bar{K}_{d(\text{desorb})}$ is almost 2 times that

Table 2

The \bar{K}_d values, sorption–desorption hysteresis and Freundlich sorption constants of Th(IV) sorption on attapulgite

	Sorption isotherm	Desorption isotherm
$\bar{K}_d \text{ (mL/g)}$	6030	10850
$HC\%$		44.4
$W\%$		79.9
A	1.78×10^{-3}	2.31×10^{-3}
N	0.345	0.349
r	0.984	0.977

of $\bar{K}_{d(\text{sorb})}$, which indicates that the adsorbed Th(IV) on attapulgite is very difficult to be desorbed from attapulgite to solution after decreasing the equilibration concentration is decreased. The irreversible sorption indicates that chemisorption rather than physical sorption contributes to Th(IV) sorption, and also suggests that inner-sphere complexes rather than outer-sphere complexes are formed.

Both sorption and desorption isotherms can be fitted to Freundlich equation using the non-linear least-square analysis. The Freundlich equation can be presented as

$$C_s = A_{\text{sorb}} \times C_{\text{eq}}^{N_{\text{sorb}}}, \quad (6)$$

$$C_s = A_{\text{desorb}} \times C_{\text{eq}}^{N_{\text{desorb}}}, \quad (7)$$

where C_s is the quantity of Th(IV) in solid phase (mol/g), C_{eq} is the equilibrium Th(IV) concentration (mol/L), A_{sorb} and N_{sorb} are Freundlich sorption constants and A_{desorb} and N_{desorb} are Freundlich desorption constants. The Freundlich A constant is a quantity parameter, i.e., the amount of Th(IV) retained on the solid phase when the Th(IV) concentration is 1 mol/L. The value of A_{desorb} is significantly higher than that of A_{sorb} (see Table 2). The coefficient of determinations (r) listed in Table 2 shows that the sorption and desorption isotherms can be fitted well by the Freundlich model.

4. Conclusions

From the results of Th(IV) sorption on attapulgite at different experimental conditions, the following conclusions can be drawn:

1. Sorption of Th(IV) on attapulgite is strongly dependent on pH values, and weakly dependent on ionic strength.
2. Sorption of Th(IV) is mainly dominated by surface complexation and ion exchange.
3. Inner-sphere and outer-sphere complexes are formed on attapulgite.
4. The sorption of Th(IV) is influenced by temperature obviously. Sorption of Th(IV) on attapulgite is a spontaneous process.
5. The sorption of Th(IV) on attapulgite is irreversible, and the sorption of Th(IV) can be described by a Freundlich model.

6. Attapulgite is a promising candidate for pre-concentration and solidification of heavy metal ions from large volumes of solutions because of its negative surface charge.

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References

- Álvarez-Ayuso, E., García-Sánchez, A., 2003. Palygorskite as a feasible amendment to stabilize heavy metal polluted soils. *Environ. Pollut.* 125, 337–344.
- Baeyens, B., Bradbury, M.H., 1997. A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part I: titration and sorption measurements. *J. Contam. Hydrol.* 27, 199–222.
- Bikerman, J.J., 1958. *Surface Chemistry: Theory and Applications*, Segunda Edition. Academic Press Inc., New York, p. 294.
- Chen, C.L., Wang, X.K., 2006. Adsorption of Ni(II) from aqueous solution using oxidized multi-walled carbon nanotubes. *Ind. Eng. Chem. Res.* 45, 9144–9149.
- Chen, C.L., Wang, X.K., 2007. Sorption of Th (IV) to silica as a function of pH, humic/fulvic acid, ionic strength, electrolyte type. *Appl. Radiat. Isot.* 65, 155–163.
- Chen, C.L., Li, X.L., Wang, X.K., 2007. Application of oxidized multi-wall carbon nanotubes for Thorium ions sorption. *Radiochim. Acta* 95, 261–266.
- Chessick, J.J., Zettlemoyer, A.C., 1956. Studies of the surface chemistry of silicate minerals. IV. Adsorption and heat of wetting measurements of attapulgite. *J. Phys. Chem.* 60, 1181–1184.
- Galan, E., 1996. Properties and applications of palygorskite-sepiolite clays. *Clay Miner.* 31, 443–453.
- Genc-Fuhrman, H., Tjell, J.C., Mcconchie, D., 2004. Adsorption of arsenic from water using activated neutralized red mud. *Environ. Sci. Technol.* 38, 2428–2434.
- Haden, W.L., Schwint Jr., I.A., 1967. Attapulgite: its properties and applications. *Ind. Eng. Chem.*, 58–69.
- Hayes, K.F., Redden, G., Ela, W., Leckie, J.O., 1991. Surface complexation models: an evaluation of model parameter estimation using FITEQL and oxide mineral titration data. *J. Colloid Interface Sci.* 142, 448–469.
- Jakobsson, A.M., 1999. Measurement and modeling of Th sorption onto TiO₂. *J. Colloid Interface Sci.* 220, 367–373.
- Ma, L., Southwick, L.M., Willis, G.H., Selim, H.M., 1993. Hysteretic characteristics of atrazine adsorption-desorption by a Sharkey soil. *Weed Sci* 41, 627–663.
- Murphy, R.J., Lenhart, J.J., Honeyman, B.D., 1999. The sorption of thorium (IV) and uranium (VI) to hematite in the presence of natural organic matter. *Colloids Surf. A* 157, 47–62.
- Murray, H.H., 2000. Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. *Appl. Clay Sci.* 17, 207–211.
- Nusinelli, M., Cascisri, F., Businelli, D., Gigliotti, G., 2003. Mechanisms of Pb(II) sorption and desorption at some clays and goethite-water interfaces. *Agronomie* 23, 219–225.
- Reiller, P., Casanova, F., Moulin, V., 2005. Influence of addition order and contact time on thorium(IV) retention by hematite in the presence of humic acids. *Environ. Sci. Technol.* 39, 1641–1648.
- Shirvani, M., Kalbasi, M., Shariatmadari, H., Nourbakhsh, F., Najafi, B., 2006a. Sorption-desorption of cadmium in aqueous palygorskite, sepiolite, and calcite suspensions: isotherm hysteresis. *Chemosphere* 65, 2178–2184.
- Shirvani, M., Shariatmadari, H., Kalbasi, M., Nourbakhsh, F., Najafi, B., 2006b. Sorption of cadmium on palygorskite, sepiolite and calcite: equilibria and organic ligand affected kinetics. *Colloids Surf. A* 287, 182–190.
- Strawn, D.G., Sparks, D.L., 1999. Sorption kinetics of trace elements in soils and soil materials. In: Selim, H.M., Iskandar, I. (Eds.), *Fate and Transport of Heavy Metals in the Vadose Zone*. Lewis Publishers, Chelsea, MI, pp. 1–28.
- Tan, X.L., Wang, X.K., Fang, M., Chen, C.L., 2007a. Sorption and desorption of Th(IV) on nanoparticles of anatase studied by batch and spectroscopy methods. *Colloids Surf. A* 296, 109–116.
- Tan, X.L., Wang, X.K., Chen, C.L., Sun, A.H., 2007b. Effect of soil humic and fulvic acids, pH and ionic strength on Th(IV) sorption to TiO₂ nanoparticles. *Appl. Radiat. Isot.* 65, 375–381.
- Visera, C., Lopez-Galindo, A., 1999. Pharmaceutical applications of some Spanish clays (sepiolite, palygorskite, bentonite): some preformulation studies. *Appl. Clay Sci.* 14, 69–82.
- Wang, X.K., Liu, X.P., 2004. Effect of pH and concentration on the diffusion of radiostromium in compacted bentonite—a capillary experimental study. *Appl. Radiat. Isot.* 61, 1413–1418.
- Wang, X.K., Chen, Y.X., Wu, Y.C., 2004a. Diffusion of Eu(III) in compacted bentonite—effect of pH, solution concentration and humic acid. *Appl. Radiat. Isot.* 60, 963–969.
- Wang, X.K., Rabung, Th., Geckeis, H., Panak, P.J., Klenze, R., Fanghaenel, Th., 2004b. Effect of humic acid on the sorption of Cm(III) onto γ -Al₂O₃ studied by the time resolved laser fluorescence spectroscopy. *Radiochim. Acta* 92, 691–695.
- Wang, X.K., Liu, X.P., 2005. Sorption and desorption of radioselenium on calcareous soil and its solid components studied by batch and column experiments. *Appl. Radiat. Isot.* 62, 1–9.
- Wang, X.K., Chen, C.L., Du, J.Z., Tan, X.L., Xu, D., Yu, S.M., 2005a. Effect of pH and aging time on the kinetic dissociation of ²⁴³Am(III) from humic acid coated γ -Al₂O₃: a chelating resin exchange study. *Environ. Sci. Technol.* 39, 7084–7088.
- Wang, X.K., Chen, C.L., Hu, W.P., Ding, A.P., Xu, D., Zhou, X., 2005b. Sorption of ²⁴³Am(III) to multi-wall carbon nanotubes. *Environ. Sci. Technol.* 39, 2856–2860.
- Wang, X.K., Chen, C.L., Zhou, X., Tan, X.L., Hu, W.P., 2005c. Diffusion and sorption of U(VI) in compacted bentonite studied by a capillary method. *Radiochim. Acta* 93, 273–278.
- Wang, X.K., Tan, X.L., Chen, C.L., Chen, L., 2005d. The concentration and pH dependent diffusion of ¹³⁷Cs in compacted bentonite by using capillary method. *J. Nucl. Mater.* 345, 184–191.
- Wang, X.K., Zhou, X., Du, J.Z., Hu, W.P., Chen, C.L., Chen, Y.X., 2006. Using of chelating resin to study the kinetic desorption of Eu(III) from humic acid-Al₂O₃ colloid surfaces. *Surf. Sci.* 600, 478–483.
- Xu, D., Wang, X.K., Chen, C.L., Zhou, X., Tan, X.L., 2006a. Influence of soil humic acid and fulvic acid on sorption of thorium(IV) on MX-80 bentonite. *Radiochim. Acta* 94, 429–434.
- Xu, D., Shao, D.D., Chen, C.L., Ren, A.P., Wang, X.K., 2006b. Effect of pH and fulvic acid on sorption and complexation of cobalt onto bare and FA bound MX-80 bentonite. *Radiochim. Acta* 94, 97–102.
- Zev, G., Bruno, Y., 1978. Adsorption and desorption of parathion by attapulgite as affected by the mineral structure. *J. Agric. Food Chem.* 26, 569–573.
- Zhang, J., Li, A., Wang, A., 2006. Study on superabsorbent composite. VI. Preparation, characterization and swelling behaviors of starch phosphate-graft-acrylamide/attapulgite superabsorbent composite. *Carbohydr. Polym.* 65, 150–158.