Chemical Engineering Journal 150 (2009) 188–195

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Effect of pH, ionic strength, temperature and humic substances on the sorption of Ni(II) to Na–attapulgite

Qiaohui Fan [a,b], Dadong Shao [a], Yi Lu [a], Wangsuo Wu [b], Xiangke Wang [a,*]

[a] Key Lab of Novel Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, 230031, Hefei, PR China
[b] Radiochemistry Laboratory, Lanzhou University, 730000, Lanzhou, PR China

ARTICLE INFO

Article history:
Received 27 June 2007
Received in revised form 14 December 2008
Accepted 16 December 2008

Keywords:
Ni(II)
Sorption
Attapulgite
pH
Humic substances
Temperature

ABSTRACT

Sorption of Ni(II) on Na–attapulgite as a function of pH and ionic strength is investigated under ambient conditions. The results indicate that sorption of Ni(II) is strongly dependent on ionic strength at pH < 8, and independent of ionic strength at pH > 8. Results of the desorption tests of Ni(II) from bare and HA bound attapulgite hybrids indicate that the sorption is reversible at pH 6.0. Outer-sphere complexation or ion exchange may be the main sorption mechanism of Ni(II) to attapulgite at pH < 8, whereas the uptake of Ni(II) at pH > 8 is mainly dominated by inner-sphere complexation. The presence of FA and HA decreases Ni(II) sorption to FA/HA–attapulgite hybrids at pH > 7 obviously, and the influence at pH < 7 is weakly. Sorption of Ni(II) to Na–attapulgite increases with increasing temperature. The thermodynamic data (ΔH^0, ΔS^0, ΔG^0) are calculated from the temperature-dependent sorption isotherms, and the results suggest that sorption process of Ni(II) on attapulgite is spontaneous and endothermic.

1. Introduction

Attapulgite [$(Mg, Al)_4(Si)_8(O,OH,H_2O)_{26}\cdot nH_2O$] is a hydrated magnesium aluminum silicate present in nature as fibrillar mineral [1,2]. It presents in natural environment and its structure was illustrated in 1940, and later refined by many authors [3–6]. Attapulgite is a kind of di-octahedral clay mineral, formed by discontinuous octahedral layers elongated in the *C*-direction alternated with continuous tetrahedral ones. The apex of SiO_4 tetrahedral point upward and downward conforms two chains which causes the special micro-aperture and micro-channel structures in the *C*-direction. Under ambient conditions and room temperature, three kinds of water generally present on attapulgite particles: (i) sorption water on the mineral surface by physical effect; (ii) zeolitic water in the micro-channel by weakly bound effect; and (iii) crystalline water that tightly bound water-molecules completing with the coordination of the (Mg and Al) cations at the borders of each octahedral layer (i.e., structural water). Besides the three kinds of water, attapulgite also contains structural hydroxyl groups (Al–OH and Mg–OH) [4,5,7,8] and other sorption sites such as cations of tetrahedron, and the fringe complex water of structure with Mg^{2+} and silicic-hydroxyl groups (Si–OH) [9]. Because of its special structure, attapulgite can be modified by cationic surfactant and has permanent negative charges on its surface, to enhance the contaminant retention, to adsorb and to retard contaminant migration on its surface or in its micro-channel. In addition, some isomorphic substitutions in the tetrahedral layer, such as Al^{3+} for Si^{4+}, develop negatively charged adsorption sites able to electro-statically adsorb cation ions [10,11]. In last decades, attapulgite has been intensively investigated as adsorbent in the removal of organic contaminants and heavy metal ions from the solutions and heavy metal polluted soils in the natural environment [12–15].

Nickel is a toxic metal ion present in wastewater and most of nickel is used in steel factories, electroplating and ceramic industry, battery and accumulator manufacturing [16,17]. Sorption of Ni(II) on clay minerals, which are ubiquitous in the environment, has been widely studied in the last decades. Many kinds of sorbents such as solid humic acid, chelating resins, raw rice bran, hematite, and montmorillonite have been used to remove Ni(II) [18–20]. Many mechanisms have been synchronously postulated for Ni(II) sorption, including surface complexation, ion exchange, surface precipitation/coprecipitation and diffusion into particle micropores [21–23]. The property of negatively surface charge of attapulgite makes it a suitable material for preconcentration and solidification of metal ions from large volume of solutions. To the best of our knowledge, the study of Ni(II) on attapulgite, especially the thermodynamic data of Ni(II) sorption on attapulgite and the effect of humic substances on Ni(II) uptake to humic–attapulgite hybrids, is still scarce.

The main purposes of this paper are: (1) to investigate the sorption behavior of Ni(II) on attapulgite; (2) to study the influence of

---

* Corresponding author. Tel.: +86 551 5592788; fax: +86 551 5591310.
E-mail address: xkwang@ipp.ac.cn (X. Wang).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.12.024

ionic strength on Ni(II) sorption; (3) to evaluate the effect of pH on Ni(II) sorption; (4) to study the effect of temperature on Ni(II) sorption and to calculate the thermodynamic parameters of Ni(II) sorption on attapulgite; (5) to compare the influence of humic acid and fulvic acid on Ni(II) sorption in the ternary systems; (6) to study the sorption and desorption behavior of Ni(II) at different experimental conditions; and (7) to discuss the sorption mechanism of Ni(II) on attapulgite.

2. Experimental

2.1. Materials

All chemicals used in the experiments were purchased in analytic purity and used without any purification. The sample of attapulgite was achieved from KaiXi Co. (Gansu, China), and was treated with 5% hydrochloric acid for 24 h, then was immersed into 20% NaCl solution for 60 h; followed by washing with distilled water until no chloride was detected in supernatant with 0.01 M $AgNO_3$. Thus achieved sample was dried at 105 °C for 2 h in order to eliminate the free water. At last the sample was milled and passed through a 320-mesh screen and then used in the experiments [8,24,25].

Soil humic and fulvic acids were extracted from the soil of Gansu province (China), and have been characterized in detail. The main elements of HA are: C 60.44%, H 3.53%, N 4.22%, O 31.31% and S 0.50%; and those of FA are: C 50.15%, H 4.42%, N 5.38%, O 39.56% and S 0.49%.

2.2. Experimental procedure

All the experiments were carried out under ambient conditions. The stock suspension of attapulgite, $NaNO_3$, and nickel stock solution were added in the polyethylene tubes to achieve the desired concentrations of different components. It was necessary to note that before the addition of nickel solution, attapulgite and $NaNO_3$ were first shaken for 2 days to achieve the equilibration of Na^+ with attapulgite. For the experiments in the presence of HA/FA, HA/FA was equilibrated with attapulgite for 2 days before the addition of nickel solution. 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 2 days, the solid and liquid phases were separated by centrifugation at 7500 rpm for 30 min.

The concentration of Ni(II) was analyzed by spectrophotometry at wavelength of 530 nm by using Ni butanedione dioxime complex. The concentration of FA and HA was analyzed by UV–vis spectrophotometry at wavelength of 294 nm. 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. Result and discussion

3.1. XRD analysis

XRD analysis (Fig. 1) showed that the crystal structures of untreated attapulgite and attapulgite treated with NaCl did not undergo any changes. One can see that there is no difference in the peak positions ($2\theta = 8.34$, 27.49, 35.01 and 42.6) of the two samples. It must be noticed that the peak at $2\theta = 8.34$ has interplanar distance (d) = 1.064 nm and is attributed to the basal plane of attapulgite structure [26]. The intergrowth-minerals of montmorillonite and quartz are also found in the sample, and have been marked in Fig. 1.

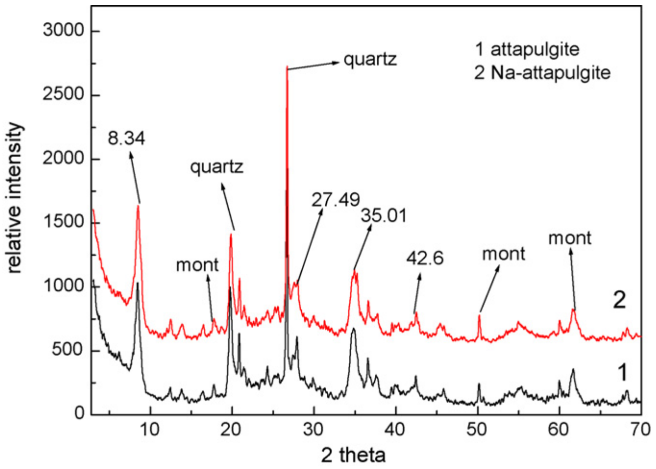

Fig. 1. XRD of attapulgite and Na–attapulgite.

3.2. Effect of contact time

The removal of Ni(II) from solution to Na–attapulgite as a function of contact time was shown in Fig. 2. The removal of Ni(II) by Na–attapulgite was calculated by the following equation:

$$Sorption\% = \frac{C_0 - C_{eq}}{C_0} \times 100\% \qquad (1)$$

where C_0 is the initial concentration of Ni(II), and C_{eq} is the equilibrium one in supernatant after centrifugation. As can be seen from Fig. 2, the sorption of Ni(II) on attapulgite was very quickly and the removal of Ni(II) to attapulgite maintained level after 2 h contact time. The quickly removal of Ni(II) from aqueous solution to attapulgite is essential for the application of attapulgite in the removal of Ni(II) from large volume of solutions. After the addition of attapulgite to solution, the sorption of Ni(II) to attapulgite occurs immediately and can be followed by the separation of attapulgite from solution quickly. In the following experiments, 2 days

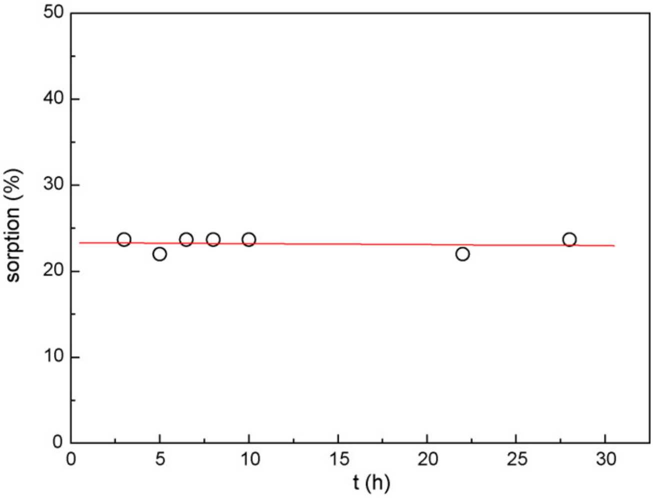

Fig. 2. Effect of time on the sorption of Ni(II) to Na–attapulgite. $C_{[Ni]initial} = 8.52 \times 10^{-5}$ mol/L, pH 6.0 ± 0.1, $T = 18 \pm 2$ °C, $I = 0.01$ M $NaNO_3$, $m/V = 0.8$ g/L.

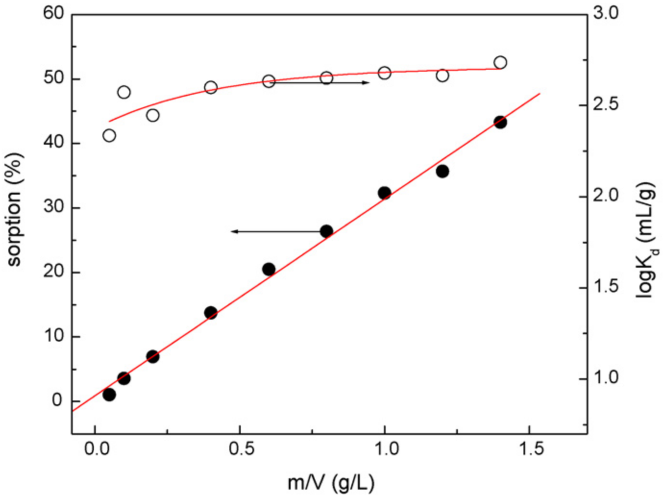

Fig. 3. Effect of solid content on the sorption of Ni(II) to Na–attapulgite. $C_{[\text{Ni}]\text{initial}} = 1.7 \times 10^{-4}$ mol/L, pH 6.0 ± 0.1, $T = 18 \pm 2\,^\circ$C, $I = 0.01$ M NaNO$_3$.

is selected to shake the test tubes to achieve the sorption equilibration. The high sorption capacity and quick sorption velocity indicate that quite strong chemisorption or strong surface complexation contributes to the sorption of Ni(II) on Na–attapulgite. Generally, ion exchange reactions or physical sorption of metal ions on solid particles is slow as compared to surface complexation.

3.3. *Effect of Na–attapulgite content*

The sorption of Ni(II) on Na–attapulgite as a function of solid content was shown in Fig. 3. The distribution coefficient (K_d) was calculated from the concentration of Ni(II) in suspension (C_0) and that of Ni(II) in supernatant (C_{eq}) according to the following equation:

$$K_d = \frac{C_0 - C_{eq}}{C_{eq}} \frac{V}{m} \tag{2}$$

where V is the volume of the suspension and m is the mass of attapulgite. It can be seen that the removal of Ni(II) from solution to Na–attapulgite increases with the increasing of Na–attapulgite content as a linear relationship. With increasing solid content, the functional groups at attapulgite surfaces increases and thereby provides more sites to cooperate with metal ions. This result is very consistent with Ni(II) sorption on Na–rectorite [27]. The distribution coefficient (K_d) as a function of attapulgite content was also plotted in Fig. 3. However, it is interesting to notice that the K_d values increase weakly with increasing attapulgite content under our experimental conditions. Xu et al. [28] reported that the K_d values of Co(II) on bentonite decreased slightly with the increasing solid content, and Chang et al. [27] found that the K_d values of Ni(II) sorption on rectorite decreased with the increasing solid content. Considering the physico-chemical properties of the distribution coefficient, the K_d values should be independent of solid content at very low solid content. It is well known that attapulgite presents in solution as fibrillar structures and the sites which participates the sorption of metal ions locate not only on the surfaces but also in the channel of the colloids. With increasing attapulgite content, local high concentration of Ni(II) may be formed on solid surfaces and results the precipitation or macromolecular colloids to be formed, and thereby causes distribution coefficient increases slightly with increasing solid content. Nevertheless, the interpretation is still questionably. Further investigation is necessary.

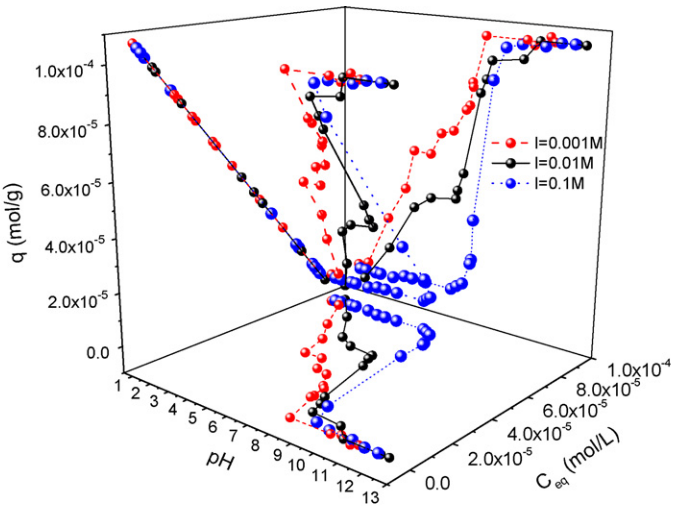

Fig. 4. Effect of pH and ionic strength on the sorption of Ni(II) to Na–attapulgite. $C_{[\text{Ni}]\text{initial}} = 8.52 \times 10^{-5}$ mol/L, $T = 18 \pm 2\,^\circ$C, $m/V = 0.8$ g/L.

3.4. *Influence of pH and ionic strength*

The pH of the system is a very important parameter for metal ions sorption. The removal percent of Ni(II) onto Na–attapulgite as a function of pH values in 0.1, 0.01 and 0.001 M NaNO$_3$, respectively, were investigated. To illustrate the variation and relationship of pH, C_{eq}, and q, experimental data are plotted as three-dimensional plots of q, C_{eq}, and pH (Fig. 4). On the pH–q plane, one can see that sorption of Ni(II) on attapulgite is strongly dependent on pH values, and also dependent on ionic strength. The removal of Ni(II) in 0.01 M NaNO$_3$ solutions at pH 2–8 is higher than that at $I = 0.1$ M and lower than that at $I = 0.001$ M. No drastic difference can be found under the three different ionic strength conditions at pH > 8. On the pH–C_{eq} plane, the concentration of Ni(II) remained in solution decreases with increasing pH to about pH 8, and then maintains level with increasing pH at pH > 10. The data in pH–C_{eq} plane and pH–q plane are in agreement with each other; On the C_{eq}–q plane, the projection is a straight line containing sorption data under the three ionic strength conditions. It is known that the initial concentration of Ni(II) in each experimental point is same. The following equation can describe the relationship of C_{eq}–q:

$$VC_0 = mq + VC_{eq} \tag{3}$$

Eq. (3) can be rearranged as:

$$q = C_0 \frac{V}{m} - C_{eq} \frac{V}{m} \tag{4}$$

C_0 is the initial concentration of Ni(II), V is the volume and m is the mass of attapulgite. Thereby, the experimental data of C_{eq}–q lies in a straight line with slope ($-V/m$) and intercept ($C_0(V/m)$). The slope and the intercept calculated from C_{eq}–q line are ($-1.25 \pm 9 \times 10^{-7}$) L/g and ($1.065 \times 10^{-4} \pm 6 \times 10^{-11}$) mol/g, which are quite in agreement with the values of $m/V = 0.8$ g/L and $C_0 = 8.52 \times 10^{-5}$ mol/L (i.e., the values calculated from V/m and C_0 are 1.25 and 1.065×10^{-4}). The 3D plots show the relationship among C_{eq}, q and pH very clearly.

Comparing to Ni(II) sorption on oxidized carbon nanotubes [29], on Na–rectorite [27] and on palygorskite clay [30], the results of this work are consistent with the results of the references. The sorption of Ni(II) on carbon nanotubes increased from ~10% (pH 3.8) to ~80% (pH 8). Chang et al. [27] studied the Ni(II) sorption on Na–rectorite and found that the removal of Ni(II) increased slowly at pH 2–7, then increased sharply at pH 7–9, and then maintained level at pH > 9. Potgieter et al. [30] reported the Ni(II) ions adsorption onto palygorskite increased with the pH values increasing, and the increasing became abruptly at pH > 5; and it was in agreement with those found by Demirba et al. [31].

It is well known that the surface charge of attapulgite is negative at pH > 4 [32]. The electrostatic attraction between Ni^{2+} and adsorbent particles would lead to increase the adsorption of Ni(II) onto Na–attapulgite [27,30,33]. Adsorption of Ni^{2+} can be described by ion exchange with hydrogen and sodium ions that saturate the exchange sites on attapulgite surfaces [34]. The sorption edges over three pH values suggest that the sorption of Ni^{2+} on Na–attapulgite is complicated and dominated by many mechanisms [35,36]. The pH-dependent sorption indicates that surface complexation is one main sorption mechanism. Whereas the ionic strength dependent sorption indicates that ion exchange is also one main mechanism. Below pH 8, adsorption is via ion exchange with hydrogen and sodium ions that saturate the exchange sites [34]. At pH > 8, surface complexation contributes the uptake of Ni(II) to attapulgite surface. The exchange involving hydrated Ni^{2+} can be depicted by two elementary reactions:

(I) to exchange with hydronium ions:

$$2 \equiv S-OH + Ni^{2+} \rightarrow (\equiv S-O)_2Ni + 2H^+ \tag{5}$$

(II) to exchange with Na^+ ions at attapulgite surfaces:

$$2 \equiv S-ONa + Ni^{2+} \rightarrow (\equiv S-O)_2Ni + 2Na^+ \tag{6}$$

(III) hydrolysis of Ni^{2+} in solution:

$$Ni^{2+} + nH_2O \rightarrow Ni(OH)_m(H_2O)_{n-m}^{2-m} + mH^+ \tag{7}$$

(IV) Being $n > m$, and to exchange with hydrolyzed species:

$$\equiv S-ONa + Ni(OH)_m(H_2O)_{n-m}^{2-m} \rightarrow \equiv S-ONiOH + Na^+ \tag{8}$$

It is necessary to note that the hydroxylated surface groups vary at different pH values because of the protonation/deprotonation processes as follows:

$$\equiv SOH + H^+ \leftrightarrow \equiv SOH_2^+ \tag{9}$$

$$\equiv SOH \leftrightarrow \equiv SO^- + H^+ \tag{10}$$

With increasing pH values, the concentrations of surface species ($\equiv$SOH uncharged surface groups; $\equiv SOH_2^+$ positively charged surface groups; $\equiv SO^-$ negatively charged surface groups) become different. The concentration of $\equiv SOH_2^+$ decreases with increasing pH, whereas $\equiv SO^-$ increases with increasing pH.

As can be seen from pH–*q* plane in Fig. 4, sorption of Ni(II) on Na–attapulgite is affected obviously by ionic strength at low pH values. Chen and Wang [29] studied Ni(II) sorption on oxidized carbon nanotubes and found the Ni(II) removal by oxidized carbon nanotubes decreased with ionic strength increasing. Chang et al. [27] also found that Ni(II) sorption onto Na–rectorite was affected by ionic strength at pH < 7, and concluded that the sorption was mainly dominated by ion exchange low pH values and formed inner-sphere complexes at high pH values. Sorption of Ni(II) onto Na–attapulgite decreased with increasing of $NaNO_3$ concentration at pH 6.0 ± 0.1 (see Fig. 5). Because ion exchange or outer-sphere complexation is influenced by ionic strength obviously [37–40], and inner-sphere complexes is not affected by ionic strength [41,42]. One can conclude that sorption of Ni(II) on Na–attapulgite is dominated by ion exchange or outer-sphere complexation at low pH, and by inner-sphere surface complexation at high pH.

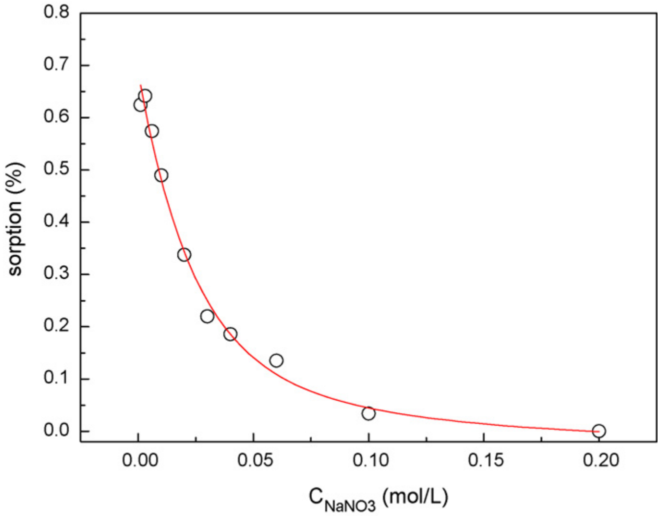

Fig. 5. Effect of ionic strength on the sorption of Ni(II) to Na–attapulgite. $C_{[Ni]initial} = 8.52 \times 10^{-5}$ mol/L, pH 6.0 ± 0.1, $T = 18 \pm 2\,^{\circ}C$, $m/V = 0.8$ g/L.

3.5. Effect of temperature and thermodynamic data

It is well known that temperature is one of most important parameters which dominate metal ions physicochemical behavior in environment. Fig. 6 shows the sorption isotherms at different temperatures. As can be seen from Fig. 6, the sorption of Ni(II) increases with rise of temperature. The results indicate that the sorption reaction is an endothermic process. Tertre et al. [43] and Chang et al. [27] studied the sorption of Ni(II) onto montmorillonite and Na–rectorite, respectively, and found that the sorption was weakly dependent on temperature at pH < 6.

The thermodynamic parameters of Ni(II) sorption on Na–attapulgite was calculated from the temperature-dependent sorption. 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 following equation:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{11}$$

The change of Gibbs free energy (ΔG^0) was calculated from the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{12}$$

where R (8.3145 J mol^{-1} K^{-1}) is the ideal gas constant, and T (K) is the temperature in Kelvin. The thermodynamic data calculated by Eqs. (11) and (12) are listed in Table 1. The positive enthalpy change

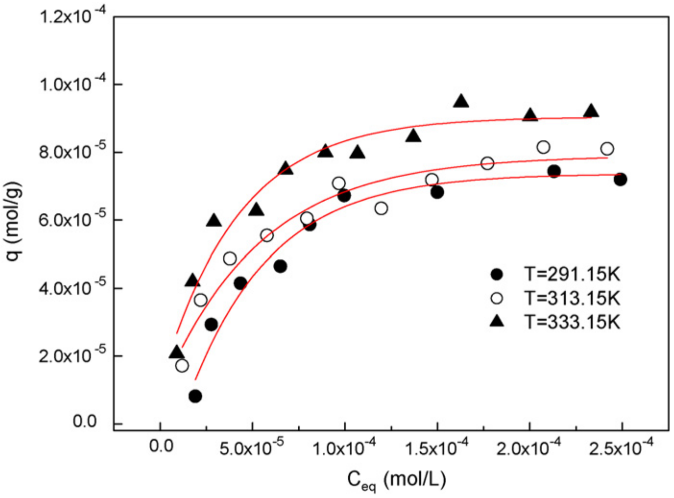

Fig. 6. Sorption isotherms of Ni(II) on Na–attapulgite at three different temperatures. pH 6.0 ± 0.1, $I = 0.01$ M $NaNO_3$, $m/V = 0.8$ g/L.

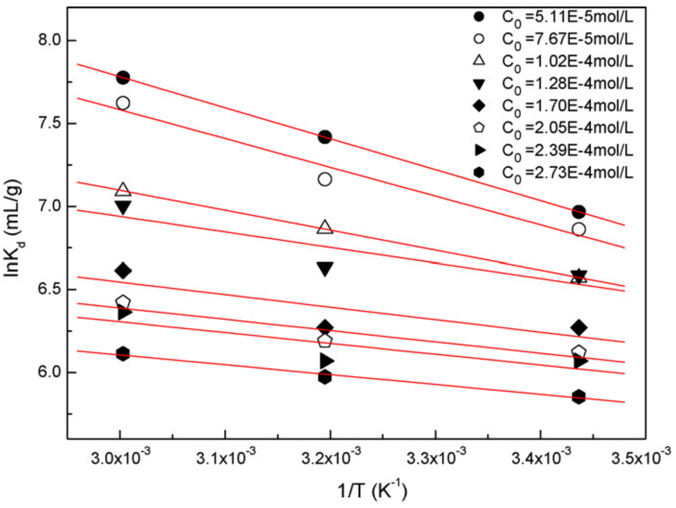

Fig. 7. Effect of temperature on the distribution coefficient of Ni(II) sorption on Na–attapulgite at different initial concentrations. pH 6.0 ± 0.1, I = 0.01 M $NaNO_3$, m/V = 0.8 g/L.

(ΔH^0) means that the holistic process of Ni(II) removal from solution to Na–attapulgite is endothermic. One possible explanation to this positive entropy is that Ni^{2+} is solved well in water, and the hydration sheath of Ni^{2+} has to be destroyed before its adsorption to attapulgite. This dehydration process needs energy, and it is favored at high temperature. This energy exceeds the exothermicity of cations to attach to the solid surface. This assumption indicated that the endothermicity of the desolvation process is higher than the enthalpy of adsorption by a considerable extent. The Gibbs free energy change (ΔG^0) is negative as expected for a spontaneous process under the conditions applied. The value of ΔG^0 becomes more negative with the increase of temperature indicates more efficient adsorption at higher temperature. At higher temperature, cations are readily desolvated and hence its sorption becomes more favorable [19]. The positive values of entropy change (ΔS^0) reflects the affinity of attapulgite toward Ni(II) ions in aqueous solutions and may suggest some structure changes on the adsorbents [29,44]. It is also interesting to note that the values of ΔH^0 and ΔS^0 decrease with increasing initial solution concentration. It could be qualitatively explained by considering that the sorption occurs initially in the most active available sites involving high interaction energies. At low concentration of Ni(II), Ni(II) is mainly governed by interaction between the Ni(II) and absorbent surface, a plausible reason could be the differences in attractive forces between Ni(II) and sorption sites of attapulgite. It indicates that a greater propensity for Ni(II) sorption probably due to the cooperative and non-cooperative ability of macromolecules resulting in higher binding energy at lower concentration level [45]. This indicates that the sorption percentage of Ni(II) on attapulgite decreases at high solution concentration as compared to the relative values at low solution concentration, although the high Ni(II) concentration results in high adsorption.

Table 1
Thermodynamic parameter of Ni(II) sorption on Na–attapulgite.

C_0 (mol/L)	ΔH^0 (kJ/mol)	ΔS^0 J/(mol K)	ΔG^0 (kJ/mol)		
			291.15 K	313.15 K	333.15 K
C_0 = 5.11E−05	15.53	111.29	−47.92	−50.37	−52.59
C_0 = 7.67E−05	14.43	106.33	−45.37	−47.71	−49.83
C_0 = 1.02E−04	9.99	88.98	−35.88	−37.84	−39.62
C_0 = 1.28E−04	7.75	80.94	−31.30	−33.08	−34.70
C_0 = 1.70E−04	6.28	73.25	−27.59	−29.21	−30.67
C_0 = 2.05E−04	5.67	70.13	−26.08	−27.62	−29.02
C_0 = 2.39E−04	5.42	68.70	−25.41	−26.93	−28.30
C_0 = 2.73E−04	4.94	65.59	−24.03	−25.47	−26.78

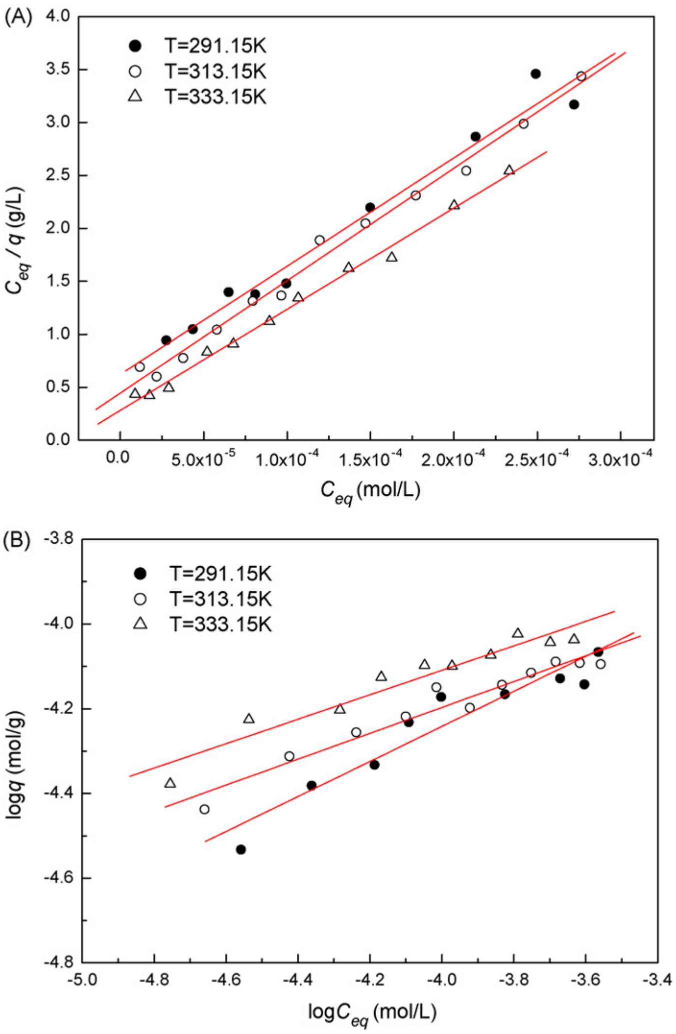

Fig. 8. (A) Langmuir sorption isotherms of Ni(II) on Na–attapulgite at different temperatures. pH 6.0 ± 0.1, I = 0.01 M $NaNO_3$, m/V = 0.8 g/L. (B) Freundlich sorption isotherms of Ni(II) on Na–attapulgite at different temperatures. pH 6.0 ± 0.1, I = 0.01 M $NaNO_3$, m/V = 0.8 g/L.

The sorption isotherms of Ni(II) at T = 291.15, 313.15 and 333.15 K are correlated by the Langmuir and Freundlich models, respectively, and the results are shown in Fig. 8A and B. The form of Langmuir isotherm can be represented by the following equation [46]:

$$q = \frac{bq_{\max} C_{eq}}{1 + bC_{eq}} \tag{13}$$

Eq. (11) can be represented in linear form as:

$$\frac{C_{eq}}{q} = \frac{1}{bq_{\max}} + \frac{C_{eq}}{q_{\max}} \tag{14}$$

where C_{eq} is the equilibrium concentration of metal ions remained in the solution (mol L^{-1}); q is the amount of metal ions adsorbed on per weight unit of solid after equilibrium (mol g^{-1}); q_{max} and b are Langmuir constants related to sorption capacity and sorption energy, respectively. q_{max}, the maximum sorption capacity, is the amount of metal ions at complete monolayer coverage (mol g^{-1}) and b (L mol^{-1}) is a constant that relates to the heat of adsorption.

Freundlich isotherm model allows for several kinds of sorption sites on the solid and represents properly the sorption data at low and intermediate concentrations on heterogeneous surfaces [46].

Table 2
Langmuir and Freundlich isotherm parameter.

Temperature (K)	Langmuir			Freundlich		
	q_{max} (mol/g)	b (L/mol)	R	k_F (mol^{1-n} L^n/g)	n	R
291.15	9.42×10^{-5}	1.71×10^4	0.986	0.0026	0.41	0.956
313.15	9.78×10^{-5}	2.27×10^4	0.996	0.0011	0.31	0.972
333.15	1.05×10^{-4}	3.42×10^4	0.997	0.0011	0.29	0.962

The model has the following form:

$$q = k_F C_{eq}^n \tag{15}$$

Eq. (13) can be expressed in linear form as:

$$\log q = \log k_F + n \log C_{eq} \tag{16}$$

where k_F (mol^{1-n} g^{-1} L^n) represents the sorption capacity when metal ion equilibrium concentration equals to 1, and n represents the degree of dependence of sorption with equilibrium concentration.

The related parameters are listed in Table 2. One can see that Langmuir model fitted the experimental data better than Freundlich model. However, Chang et al. [27] and Potgieter et al. [30] reported that Ni(II) sorption onto Na–rectorite and palygorskite could be described by Freundlich model well. The values of q_{max} obtained from the Langmuir model are highest at T = 333.15 K and lowest at T = 291.15 K, which indicates that the sorption is favored at high temperature. In the Freundlich model, the value of n is less than unity, which indicates that metal ions are favorably adsorbed by attapulgite.

3.6. Sorption and desorption isotherms

Sorption and desorption isotherms of Ni(II) on Na–attapulgite at pH 6.0 ± 0.1 in the absence and presence of HA are shown in Fig. 9A and B, respectively. One can see that no drastic difference in the sorption and desorption isotherms, which indicates that the sorption is nearly reversible. The reversible sorption–desorption of Ni(II) at pH 6.0 indicates that the sorption of Ni(II) is mainly dominated by outer-sphere complexation or ion exchange with Na$^+$/H$^+$ at the outer-sphere of Na–attapulgite. The results are consistent with the results shown in Figs. 4 and 5. Outer-sphere

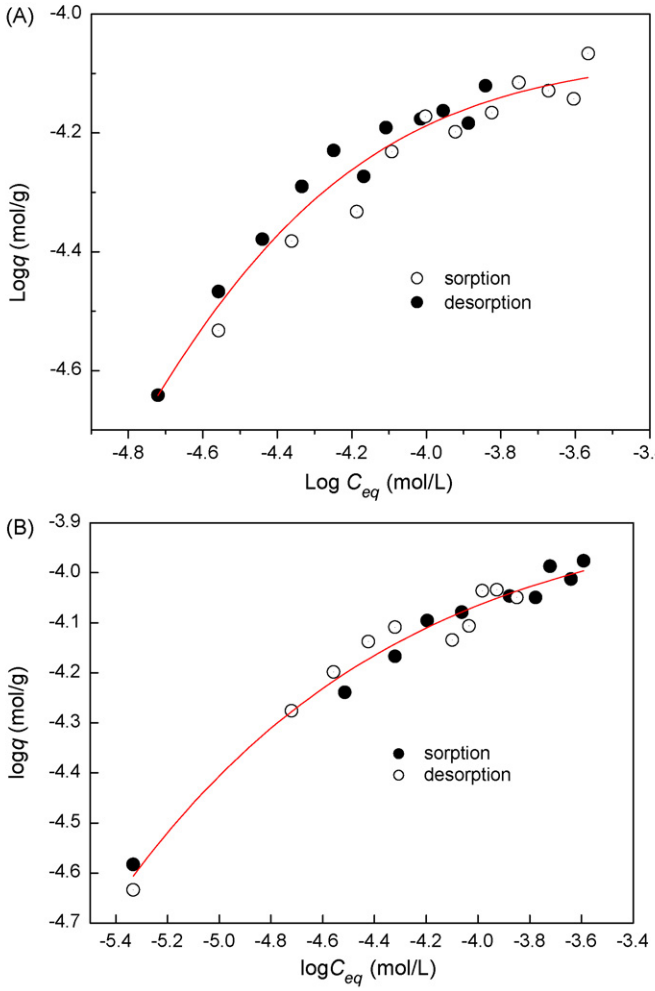

Fig. 9. Sorption and desorption isotherms of Ni(II) on Na–attapulgite. pH 6.0 ± 0.1; I = 0.01 M NaNO$_3$; T = 20 ± 2 °C; m/V = 0.8 g/L. (A) no HA; (B) $C_{HA(initial)}$ = 3.7 mg/L.

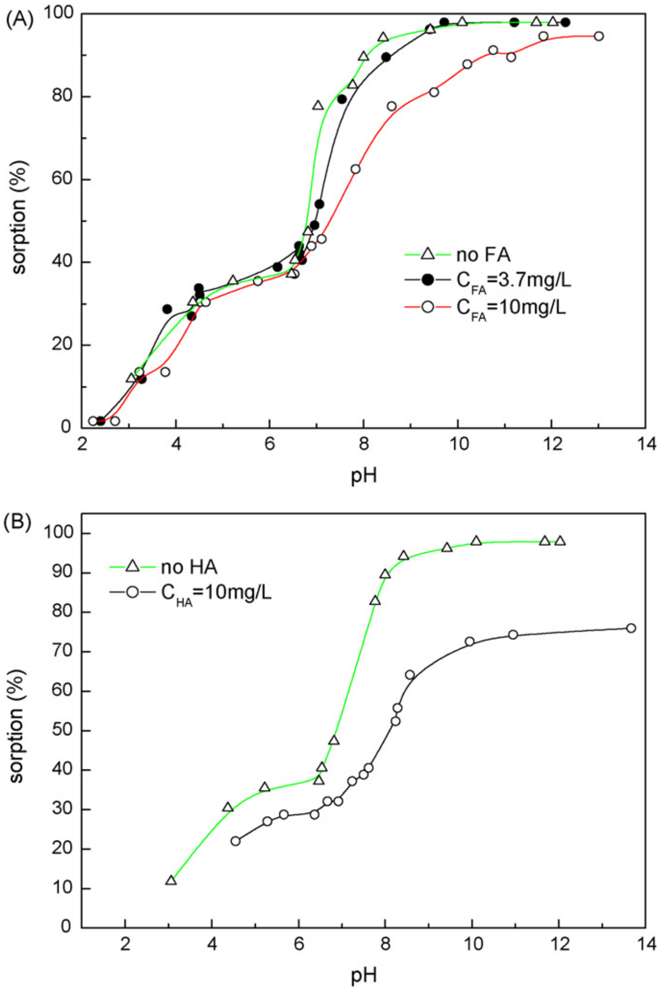

Fig. 10. (A) Influence of pH and FA on Ni(II) sorption on Na–attapulgite. $C_{[Ni(II)]initial}$ = 8.52 × 10^{-5} mol/L, I = 0.01 M NaNO$_3$, T = 18 ± 2 °C, m/V = 0.8 g/L. (B) Influence of pH and HA on Ni(II) sorption on Na–attapulgite. $C_{[Ni(II)]initial}$ = 8.52 × 10^{-5} mol/L, I = 0.01 M NaNO$_3$, T = 18 ± 2 °C, m/V = 0.8 g/L.

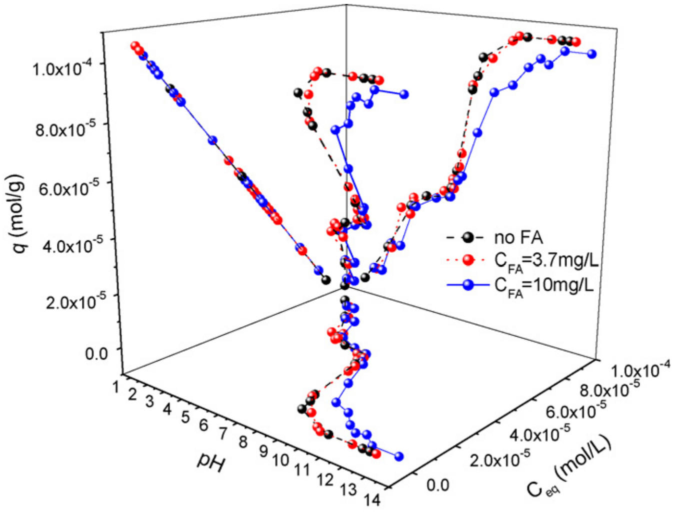

Fig. 11. 3D-plots of pH, C_{eq} and q of Ni(II) sorption on Na–attapulgite in the presence and absence of FA. $C_{[\mathrm{Ni(II)}]\mathrm{initial}} = 8.52 \times 10^{-5}$ mol/L, $I = 0.01$ M NaNO$_3$, $T = 18 \pm 2$ °C, $m/V = 0.8$ g/L.

adsorption/ion exchange causes the reversible process of Ni(II) sorption–desorption on Na–attapulgite [10,27].

3.7. *Influence of humic substances*

Sorption of Ni(II) on Na–attapulgite in the presence of FA as a function of pH are shown in Fig. 10A. No drastic effect of FA on Ni(II) uptake to FA–attapulgite hybrids at pH < 7 is observed. At pH > 7, the presence of FA decreases the sorption of Ni(II) to FA–attapulgite hybrids. At low pH values, FA generally presents as spherical shapes in solution or adsorbed on solid particles. The spherical structure makes most of the functional groups not available to form complexes with metal ions [47]. The presence of FA does not affect Ni(II) uptake to attapulgite drastically. With increasing pH values, the negatively charged FA is difficult to be adsorbed on the negatively charged surface of attapulgite. The competition among the soluble FA and attapulgite with Ni(II) ions thereby increases and results the reduction of Ni(II) uptake to attapulgite. With increasing FA concentration, the fraction of FA remained in solution increases and the soluble complexes FA–Ni reasonably decreases Ni(II) sorption.

Effect of HA on Ni(II) sorption as a function of pH is shown in Fig. 10B. It can be seen that the presence of HA reduces the sorption of Ni(II) to HA–attapulgite hybrids at the whole pH values of our investigation. Comparing to the influence of FA on Ni(II) sorption, the influence of HA is stronger than FA at same pH values under the same FA/HA concentrations. It is necessary to note that the samples of FA and HA were extracted from the same soil sample, and had similar function groups such as carboxylic and phenolic groups. The influence of FA and HA on Ni(II) sorption to attapulgite should be very similar. It may be drawn that the presence of FA/HA decreases Ni(II) sorption to FA/HA–attapulgite hybrids at pH > 7, the influence of FA/HA on Ni(II) sorption at pH < 7 is weaker rather than that of FA/HA at pH > 7. The complicated structures of FA, HA and attapulgite make it difficult to get an unambiguous and exact conclusion of FA/HA influence on Ni(II) sorption to attapulgite. Nevertheless, humic substances presents in environment ubiquitously as a kind of natural organic compounds and its influence on metal ions behavior can not be neglected. The influence of humic substances on metal ions' sorption to clay minerals is essential to control the mobility and bioavailability of metal ions.

To illustrate the variation and relationship of pH, C_{eq}, and q, experimental data (in Fig. 10A) are plotted again as 3D plots of q, C_{eq}, and pH (Fig. 11). On the pH–q plane, the lines are very similar to that of pH-sorption % (in Fig. 10A); On the pH–C_{eq} plane, the concentration of Ni(II) remained in solution decreases with increasing pH; On the C_{eq}–q plane, the projection is a straight line containing all sorption data, which is quite same as shown in Fig. 4. The slope and the intercept calculated from C_{eq}–q line are $(-1.25 \pm 6 \times 10^{-7})$ L/g and $(1.065 \times 10^{-4} \pm 3 \times 10^{-11})$ mol/g, which are quite same as those calculated in Fig. 4. The projection on the pH–C_{eq} plane is the inverted image of the projection on the pH–q plane. Thus, the complexity of the sorption edge relative to sorption isotherm is demonstrated.

4. Conclusions

From the results derived from the experiments, the following conclusions may de drawn:

1. Sorption of Ni(II) on attapulgite is strongly influenced by pH values.
2. Sorption of Ni(II) on attapulgite is dependent on ionic strength at pH < 8, and independent of ionic strength at pH > 8.
3. At same initial concentrations, the relationship of Ni(II) concentration adsorbed on solid phase and Ni(II) concentration remained in solution can be described by a straight line with slope $(-V/m)$ and intercept $(C_0(V/m))$, which are independent of other experimental parameters.
4. Outer-sphere complexation or ion exchange may be the main sorption mechanism of Ni(II) on attapulgite at pH < 8, where as inner-sphere complexation is the main sorption mechanism at pH > 8.
5. Sorption of Ni(II) is favored with increasing temperature. The uptake reactions of Ni(II) to attapulgite is a spontaneous process, and the reaction is endothermic.
6. The presence of humic substances does not enhance the removal of Ni(II) to attapulgite. Especially at pH > 7, the presence of humic substances decreases Ni(II) sorption obviously, and the influence of humic substances on Ni(II) sorption to HS–attapulgite hybrids becomes stronger with increasing humic substances concentration.
7. The results indicate that sorption of Ni(II) on attapulgite is complicated. It cannot be described by simple sorption models. The physicochemical behavior of Ni(II) is dominated by the nature of attapulgite, nature of humic substances, nature of solution (i.e., pH, ionic strength, temperature etc.), nature of metal ion etc.

Acknowledgements

Financial supports from National Natural Science Foundation of China (J0630962, 20871062, 20501019) and 973 Project (2007CB936602) are acknowledged.

References

[1] R. Giustetto, F.X.L. Xamena, G. Ricchiardi, S. Bordiga, A. Damin, R. Gobetto, M.R. Chierotti, A Blue: a computational and spectroscope study, J. Phys. Chem. B 109 (2005) 19360–19368.
[2] J. Huang, Y. Liu, Q. Jin, X. Wang, J. Yang, Adsorption studies of a water soluble dye, Reactive Red MF-3B, using sonication surfactant-modified attapulgite clay, J. Hazard. Mater. 143 (2007) 541–548.
[3] W.F. Bradley, The structural scheme of attapulgite, Am. Mineral. 25 (1940) 405–410.
[4] J.E. Chisholm, An X-ray powder-diffraction study of palygorskite, Can. Mineral. 28 (1990) 329–339.
[5] G. Chiari, R. Giustetto, G. Ricchiardi, Crystal structure refinement of palygorskite and Maya Blue from molecular modeling and powder synchrotron diffraction, Eur. J. Mineral. 15 (2003) 21–33.
[6] A. Preisinger, Sepiolite and related compounds: its stability and application, Clays Clay Miner. 10 (1963) 365–371.
[7] J.E. Chisholm, Powder-diffraction patterns and structural models for palygorskite, Can. Mineral. 30 (1992) 61–73.
[8] W.L. Haden Jr.I.A., Schwint, Attapulgite: its properties and applications, Ind. Eng. Chem. 59 (1967) 58–69.

[9] C.L. Serratosa, Surface properties of fibrous clay mineral (palygorskite and sepiolite), in: Proceedings of the Sixth International Clay Conference, 1978.

[10] M. Shirvani, H. Shaiatmadari, M. Kalbasi, F. Nourbakhsh, B. Najafi, Sorption of cadmium on palygorskite, sepiolite and calcite: equilibria and organic ligand affected kinetics, Colloid Surf. A 287 (2006) 182–190.

[11] J. Zhang, A. Li, A. Wang, Study on superabsorbent composite. VI. Preparation, characterization and swelling behaviors of starch phosphate-graft-acrylamide/attapulgite superabsorbent composite, Carbohydr. Polym. 65 (2006) 150–158.

[12] E. Galan, Properties and applications of palygorskite–sepiolite clays, Clay Miner. 31 (1996) 443–453.

[13] M.H. Murray, Traditional and new applications for kaolin, smectite, and palygorskite: a general overview, Appl. Clay Sci. 17 (2000) 207–211.

[14] C. Visera, A. Lopez-Galindo, Pharmaceutical applications of some Spanish clays (sepiolite, palygorskite, bentonite): some preformulation studies, Appl. Clay Sci. 14 (1999) 69–82.

[15] E. Álvarez-Ayuso, A. García-Sánchez, Palygorskite as a feasible amendment to stabilize heavy metal polluted soils, Environ. Pollut. 125 (2003) 337–344.

[16] H. Parab, S. Joshi, N. Shenoy, A. Lali, U.S. Sarma, M. Sudersanan, Determination of kinetic and equilibrium of Co(II), Cr(III), and Ni(II) onto coirpith, Process Biochem. 41 (2006) 609–615.

[17] X.S. Wang, J. Huang, H.Q. Hu, J. Wang, Y. Qin, Determination of kinetic and equilibrium parameters of the batch adsorption of Ni(II) from aqueous solutions by Na-mordenite, J. Hazard. Mater. 142 (2007) 468–476.

[18] F.D. Mendes, A.H. Martins, Selective sorption of nickel and cobalt from sulphate solutions using chelating resins, Int. J. Miner. Process. 74 (2004) 359–371.

[19] S.S. Tahir, N. Rauf, Thermodynamic studies of Ni(II) adsorption onto bentonite from aqueous solution, J. Chem. Thermodyn. 35 (2003) 2003–2009.

[20] E.A. Oliveira, S.F. Montanher, A.D. Andrade, J.A. Nóbrega, M.C. Rollemberg, Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran, Process Biochem. 40 (2005) 3485–3490.

[21] T.J. Strathmann, S.C.B. Myneni, Effect of soil fulvic acid on nickel(II) sorption and bonding at the aqueous-boehmite (γ-AlOOH) interface, Environ. Sci. Technol. 39 (2005) 4024–4034.

[22] W. Stumm, Chemistry of the Slid–Water Interface: Processes at the Mineral–Water and Particle–Water Interface in Natural System, John Wily and Sons, New York, 1992.

[23] D.L. Sparks, A.M. Scheidegger, D.G. Strawn, K.G. Scheckel, in: D.L. Sparks, T.J. Grundl (Eds.), Kinetics and Mechanisms of Metal Sorption at the Mineral–Water Interface. Mineral–Water Interfacial Reactions: Kinetics and Mechanisms, American Chemistry Society, Washington, DC, 1998, pp. 108–135.

[24] Z. Gerstl, B. Yaron, Adsorption and desorption of parathion by attapulgite as affected by the mineral structure, J. Agric. Food Chem. 26 (1978) 569–573.

[25] J.J. Chessick, A.C. Zettlemoyer, Studies of the Surface Chemistry of Silicate Minerals. IV. Adsorption and Heat of Wetting Measurements of Attapulgite, J. Phys. Chem. 60 (1956) 1181–1184.

[26] E. Cao, R. Bryant, D.J.A. Willianms, Electrochemical properties of Na–palygorskite, J. Colloid Interface Sci. 179 (1996) 143–150.

[27] P. Chang, X. Wang, S. Yu, W. Wu, Sorption of Ni(II) on Na–rectorite from aqueous solution: effect of pH, ionic strength and temperature, Colloids Surf. A: Physicochem. Eng. Aspects 302 (2007) 75–81.

[28] D. Xu, D.D. Shao, C.L. Chen, A.P. Ren, X.K. Wang, Effect of pH and fulvic acid on sorption and complexation of cobalt onto bare and FA bound MX-80 bentonite, Radiochim. Acta 94 (2006) 97–102.

[29] C.L. Chen, X.K. Wang, Adsorption of Ni(II) from aqueous solution using oxidized multiwall carbon nanotubes, Ind. Eng. Chem. Res. 45 (2006) 9144–9149.

[30] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, Miner. Eng. 19 (2006) 463–470.

[31] E. Demirba, M. Kobya, S. Öncel, Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated. carbon: equilibrium studies, Bioresource Technol. 84 (2002) 291–293.

[32] A. Neaman, A. Singer, Rheological properties of aqueous suspensions of palygorskite, Soil Sci. Soc. Am. J. 64 (2000) 427–436.

[33] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith, Separ. Purif. Technol. 24 (2001) 497–505.

[34] J. Echeverría, J. Indurain, E. Churio, J. Garrido, Simultaneous effect of pH, temperature, ionic strength, and initial concentration on the retention of Ni on illite, Colloids Surf. A 218 (2003) 175–187.

[35] D.A. Dzombak, F.M.M. Morel, Surface Complexation Modeling: Hydrous Ferric Oxide, John Wiley & Sons, New York, 1990.

[36] A. Kowal-Fouchard, R. Drot, E. Simoni, J.J. Ehrhardt, Use of spectroscopic techniques for uranium(VI)/montmorillonite interaction modeling, Environ. Sci. Technol. 38 (2004) 1399–1407.

[37] X.K. Wang, X.P. Liu, Effect of pH and concentration on the diffusion of radiostrontium in compacted bentonite—a capillary experimental study, Appl. Radiat. Isot. 61 (2004) 1413–1418.

[38] X.K. Wang, C.L. Chen, X. Zhou, X.L. Tan, W.P. Hu, Diffusion and sorption of U(VI) in compacted bentonite studied by a capillary method, Radiochim. Acta 93 (2005) 273–278.

[39] X.K. Wang, X.L. Tan, C.L. Chen, L. Chen, The concentration and pH dependent diffusion of ^{137}Cs in compacted bentonite by using capillary method, J. Nucl. Mater. 345 (2005) 184–191.

[40] B. Baeyens, M.H. Bradbury, A mechanistic description of Ni and Zn sorption on Na–montmorillonite. Part I. Titration and sorption measurements, J. Contam. Hydrol. 27 (1997) 199–222.

[41] K.F. Hayes, G. Redden, W. Ela, J.O. Leckie, Surface complexation models: an evaluation of model parameter estimation using FITEQL and oxide mineral titration data, J. Colloid Interface Sci. 142 (1991) 448–469.

[42] X.K. Wang, Th. Rabung, H. Geckeis, P.J. Panak, R. Klenze, Th. Fanghaenel, Effect of humic acid on the sorption of Cm(III) onto γ-Al_2O_3 studied by the time resolved laser fluorescence spectroscopy, Radiochim. Acta 92 (2004) 691–695.

[43] E. Tertre, G. Berger, S. Castet, M. Loubet, E. Giffaut, Experimental study of adsorption of Ni^{2+}, Cs^{+} and Ln^{3+} onto Na–montmorillonite up to 150 °C, Geochim. Cosmochim. Acta 69 (2005) 4937–4948.

[44] H. Genc-Fuhrman, J.C. Tjell, D. Mcconchie, Adsorption of arsenic from water using activated neutralized red mud, Environ. Sci. Technol. 38 (2004) 2428–2434.

[45] D. Mihoubi, A. Bellagi, Thermodynamic analysis of sorption isotherms of bentonite, J. Chem. Thermodyn. 38 (2006) 1105–1110.

[46] X. Tan, X. Wang, M. Fang, C. Chen, Sorption and desorption of Th(IV) on nanoparticles of anatase studied by batch and spectroscopy methods, Colloid Surf. A: Physicochem. Eng. Aspects 296 (2007) 109–116.

[47] C.L. Chen, X.K. Wang, H. Jiang, W.P. Hu, Imaging of humic acid macromolecular structures observed by atomic force microscopy and scanning electron microscope, Colloid Surf. A: Physicochem. Eng. Aspects 302 (2007) 121–125.