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Solution chemistry effects on sorption behavior of radionuclide ^{63}Ni(II) in illite–water suspensions

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ABSTRACT

In this work, a naturally occurring illite was characterized by using FTIR and XRD to determine its chemical constituents and crystal structure. A series of batch experiments were carried out to investigate the effect of various environmental factors such as contact time, pH, ionic strength, foreign ions, coexisting humic substances and temperature on the sorption behavior of illite towards radionuclide ^{63}Ni(II). The sorption of ^{63}Ni(II) on illite was strongly dependent on pH and ionic strength. A positive effect of HA/FA on ^{63}Ni(II) sorption was found at pH < 6.5, whereas a negative effect was observed at pH > 6.5. The Langmuir, Freundlich, and D-R models were used to simulate the sorption isotherms of ^{63}Ni(II) at three different temperatures of 293, 313 and 333 K. The thermodynamic parameters (ΔH^0, ΔS^0 and ΔG^0) of ^{63}Ni(II) sorption on illite were calculated from the temperature dependent sorption isotherms, and the results indicated that the sorption of ^{63}Ni(II) on illite was endothermic and spontaneous. At low pH, the sorption of ^{63}Ni(II) was dominated by outer-sphere surface complexation and ion exchange with Na^+/H^+ on illite surfaces, whereas inner-sphere surface complexation was the main sorption mechanism at high pH. From the experimental results, it is possible to conclude that illite has good potentialities for cost-effective treatments of ^{63}Ni(II)-contaminated wastewaters.

1. Introduction

The increasing levels of toxic metals and radionuclides that are discharged to the environment as industrial wastes represent a serious threat to human health, living resources and ecological systems. Among the potentially pollutants, nickel is one of the most widespread contaminants in the environment. The wastewater containing nickel mainly derives from industrial production processes such as mining, electrolysis, electroplating, batteries dyes metallurgy and pesticides [1]. ^{63}Ni(II) ($T_{1/2} = 96$a) is an important product of the neutron activation of the reactor materials. The important radionuclide ^{63}Ni(II) is present in liquid wastes released from pressurized water from the nuclear power reactors, and it is also widely used in research and medical applications. The presence of nickel in drinking water above the permissible limit of 0.02 mg/L (WHO drinking-water quality standards) may cause adverse health impacts such as anemia, diarrhea, encephalopathy, hepatitis and the dysfunction of central nervous system. For the sake of ecosystem stability and public health, it is of great imminence to eliminate nickel ions from wastewaters.

Sorption technique has been widely used all over the world for the disposal of wastewater and retention of nuclear waste due to its simplicity of design, high sorption efficiency, low cost and wide adaptability. In Sweden, the Svensk Kärnbränslehantering AB (SKB, the Swedish Nuclear Fuel and Waste Management Co.) presents an R&D program every 3 years to manage and dispose of spent nuclear fuel and other radioactive waste [2]. The studies on the sorption and retention of nuclear waste have been conducted extensively. Many R&D programs and various results have been reported [3–8]. For the long-term performance assessment of nuclear waste retention, it is imperative to acquire more in-depth understanding on the sorption mechanisms of radionuclides on mineral surfaces.

Clay minerals have been found to be low cost, effective materials for the removal of metal ions from various effluents owing to their high cation exchange capacity and high specific surface area associated with their small particle sizes [9]. Thereby, the removal of heavy metal ions and radionuclides from various effluents by using multifarious clay minerals has been studied extensively in the recent years and many mechanisms have been postulated such as ion exchange, outer-sphere surface complexation, inner-sphere surface complexation, precipitation, and diffusion into particle micropores [10–14]. However, to the best of our knowledge, few researches were focused on the sorption behavior of illite towards radionuclides. Therefore, it is of great value to do the present study,

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which has a quite important reference value in appraising the elimination capacity of illite for the treatment of radionuclide-contained water.

The basic objectives of this paper are: (1) to characterize illite using XRD and FTIR to determine its chemical constituents and crystal structure; (2) to study the sorption of ^{63}Ni(II) on illite as a function of environmental factors such as pH, ionic strength, solid content, foreign ions and coexisting humic substances (i.e., humic acid (HA) and fulvic acid (FA)); (3) to determine the thermodynamic parameters of ^{63}Ni(II) sorption on illite; and (4) to presume the sorption mechanism of ^{63}Ni(II) on illite and to estimate the possible application of illite in wastewater disposal.

2. Experimental

2.1. Materials

The illite sample was purchased from ChengMing illite Co., LTD. and was ground to <200 mesh (<0.065 mm). The CEC was determined to be 70 mmol/100 g by using the ammonia electrode method [15]. Gu et al. [16] studied the acid–base surface chemistry of illite by using potentiometric titration method with 0.1, 0.01, and 0.001 M $NaNO_3$ solutions as the background electrolyte and found the point of zero charge (pH_{pzc}) of illite ranged from 6.0 to 7.5 at the three different ionic strengths. The specific surface area of illite sample was determined to be 65.91 m^2/g by using N_2-BET method.

HA and FA were extracted from the soil of Hua-Jia county (Gansu province, China) near 35°N and 105°E, which is very near to the site of nuclear weapon test. Tan et al. [17] had characterized HA and FA in detail as a suite of 3 discrete acids with pK_a values and the surface site densities of HA and FA determined by fitting the potentiometric titration data using FITEQL 3.1 are given in Table 1.

All chemicals used in the experiments were purchased as analytical purity and used directly without any further purification. All the reagents were prepared with high-purity deionized water from a Millipore Synthesis A10 water system (18.2 MΩ, <8 ppb total organic carbon (TOC), UV light treated, ultrafiltration membrane, 0.2 μm filtered).

2.2. Characterization

The sample of illite was characterized using Fourier transform infrared sorption (FTIR) (Perkin Elmer spectrum 100, America) in pressed KBr pellets. The spectral resolution was set to 1 cm^{-1}, and 150 scans were collected for each spectrum. The X-ray powder diffraction (XRD) pattern of illite crystal was recorded on a MAC Science Co., M18XHF diffractometer. XRD analysis was performed with Cu Kα radiation ($\lambda = 0.15406$ nm) with a Rigaku diffractometer. The 2θ-scanning rate was 2° min^{-1}.

2.3. Experimental procedures

All the experiments were carried out by using batch technique in polyethylene centrifuge tubes under ambient conditions. The stock solutions of illite and $NaClO_4$ were pre-equilibrated for 24 h and then ^{63}Ni(II) stock solution was added to achieve the desired concentrations of different components. The pH was adjusted to desired values by adding negligible volumes of 0.1 or 0.01 M $HClO_4$ or NaOH. After the suspensions were oscillated for 24 h, the solid and liquid phases were separated by centrifugation at 7788 g for 30 min. To take into the account of ^{63}Ni(II) loss from procedures except for illite sorption (i.e., ^{63}Ni(II) sorption on tube wall), calibration curves were obtained separately under otherwise identical conditions as the sorption process but no illite. Based on the obtained calibration curves, the amount of ^{63}Ni(II) adsorbed on illite was calculated by subtracting the mass in the solution from the mass spiked.

The concentration of radiotracer ^{63}Ni(II) used in the experiments was analyzed by Liquid Scintillation counting using a Packard 3100 TR/AB Liquid Scintillation analyzer (Perkin Elmer). The sorption percentage (Sorption, $\% = (C_0 - C_{eq})/C_0 \times 100\%$) and distribution coefficient ($K_d = (C_0 - C_{eq})/C_{eq}\ V/m$) of ^{63}Ni(II) on illite were derived from the initial concentration of ^{63}Ni(II) (C_0), the equilibrium concentration of ^{63}Ni(II) (C_{eq}), the mass of illite (m) and the volume of the suspension (V). All experimental data were the average of triplicate determinations and the relative errors of the data were about 5%.

3. Results and discussion

3.1. Microstructure characterization of illite sample

The FTIR spectrum of illite sample is shown in Fig. 1. The band at 427 cm^{-1} is corresponded to δ (AlAlOH) of surface hydroxyl layer. The bands at 466 and 527 cm^{-1} are corresponded to δ (SiO) of siloxamic cavity. The bands at 665, 752 and 795 cm^{-1} are assigned to the δ (MgAlOH), δ (Si–O–Al) and δ (FeMgOH), respectively. The band at 1024 cm^{-1} corresponds to ν(Si–O) in plane stretch. The band at 1638 and 3445 cm^{-1} are assigned to the *δ (OH) and* ν(OH) of water, respectively. The sorption band at 3623 cm^{-1} is due to the ν(OH) in Fe-rich illites [18]. The δ (Al–O–Al) at 694 cm^{-1} and ν(AlAlO–H) at 3695 cm^{-1} are typical of kaolinite clays and are likely the result of impurities in the illite system.

The XRD pattern of illite sample shown in Fig. 2 corresponds to illite-2M#2. The main peaks at $2\theta = 9°$, 19° and 26.5° (marked by I) are the characteristic diffraction peaks for natural illite [19]. The other peaks are corresponded to the impurities of kaolinite (marked by *K*) and quartz (marked by *q*).

3.2. Macroscopic experimental results

3.2.1. Sorption kinetics analysis

Fig. 3 shows the sorption of ^{63}Ni(II) on illite as a function of contact time. One can see that sorption of ^{63}Ni(II) on illite increases rapidly at the first 5 h and then the sorption percentage maintains at an aptotic value with increasing contact time. This result symptomatizes that ^{63}Ni(II) sorption on illite surface is attributed to chemical sorption rather than physical sorption [20,21]. The whole sorption dynamics process can be divided into two distinct steps: an initial fast sorption, followed by a much slower sorption. The fast ^{63}Ni(II) removal rate in the beginning is attributed to the rapid diffusion of ^{63}Ni(II) from the solution to the external surfaces of il-

Table 1
The concentrations of functional groups of HA and FA calculated from potentiometric titration by using FITEQL 3.1 [17].

	Log K_a			C (mol/g)[a]			Surface sites density (mol/g)	WSOS/DF
	L_1	L_2	L_3	HL_1	HL_2	HL_3		
HA	−5.04	−7.40	−9.60	2.20×10^{-3}	1.08×10^{-3}	3.18×10^{-3}	6.46×10^{-3}	2.37
FA	−5.19	−7.77	−10.53	1.83×10^{-3}	1.08×10^{-3}	2.42×10^{-2}	2.71×10^{-2}	0.10

[a] HL1, HL2 and HL3 represent the carboxyl groups (–COOH), the phenolic groups (Ar–OH) and the amine groups (–NH2) of HA and FA, respectively.

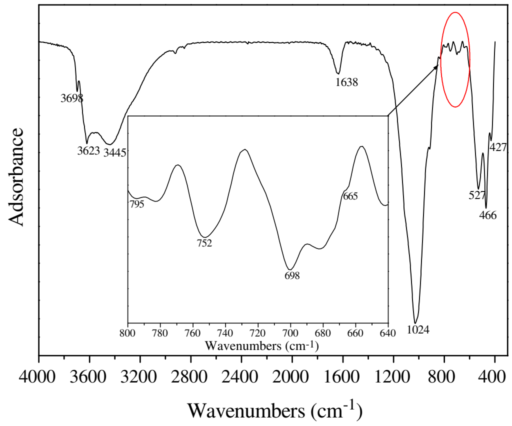

Fig. 1. FTIR spectrum of illite sample.

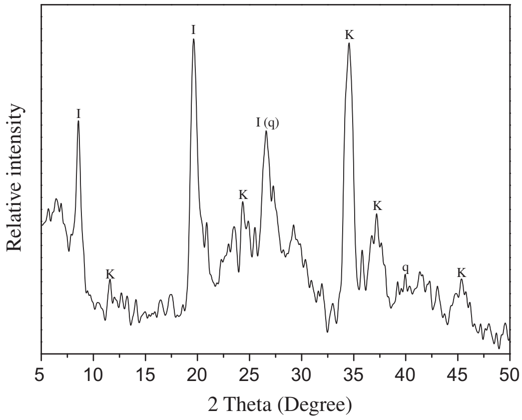

Fig. 2. XRD pattern of illite sample.

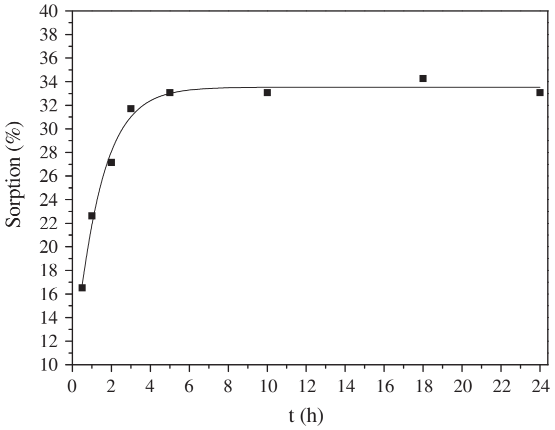

Fig. 3. Sorption of ^{63}Ni(II) on illite as a function of contact time. $T = 293 \pm 2$ K, pH = 6.4 ± 0.1, C(Ni)initial = 1.59 × 10−4 mol/L, $m/V = 0.8$ g/L, $I = 0.01$ M $NaClO_4$.

lite. The subsequent slow sorption process is attributed to the longer diffusion range of ^{63}Ni(II) into the inner-sphere pores of illite or the exchange with cations in the inner surface of illite. Such slow diffusion will lead to a slow increase in the sorption curve at later stages [22]. According to the above results, the oscillating time is fixed at 24 h in the following experiments to ensure that the sorption reaction can achieve complete equilibrium. The fast sorption kinetics observed with this clay sorbent is an advantage for continuous water treatment systems.

3.2.2. Effect of pH

Fig. 4 shows the pH dependence of ^{63}Ni(II) sorption on illite in 0.001 M, 0.01 M and 0.1 M $NaClO_4$ solutions, respectively. As can be seen from Fig. 4A, the sorption of ^{63}Ni(II) on illite is obviously affected by pH values. The sorption curve of ^{63}Ni(II) on illite can be divided into three regions. The sorption of ^{63}Ni(II) increases gradually from about ∼5% to ∼25% when the pH of the solution increases from 2 to 6 (region I). In region II, from pH 6 to 8.5, the sorption performance of ^{63}Ni(II) on illite increases sharply from 25% to a maximum value of 96%. Above pH 8.5, the removal of ^{63}Ni(II) maintains unchanged at 96% (region III). The phenomenon that the sorption edges spread over three pH units implies the formation of multifarious surface complexes and represents different sorption mechanisms [23]. The changes of distribution coefficient (K_d) as a function of pH values is shown in Fig. 4B. One can see that the K_d values increase with increasing pH and then remain the same, which is consistent with the trend of sorption percent. With increasing pH, the sorption of ^{63}Ni(II) on illite increases and thus the concentration of ^{63}Ni(II) in solution (C_{eq}) diminishes, which leads to the increase of sorption capacity ($C_s = (C_0 - C_{eq})\ V/m$) and the uptrend of distribution coefficient ($K_d = (C_0 - C_{eq})/C_{eq}\ V/m$).

The exact speciation of ^{63}Ni(II) has a significant impact on the removal efficiency of illite, thus the removal selectivity of ^{63}Ni(II) by illite is influenced by the character of ^{63}Ni(II) complex that predominates at a particular solution pH. It is known that nickel

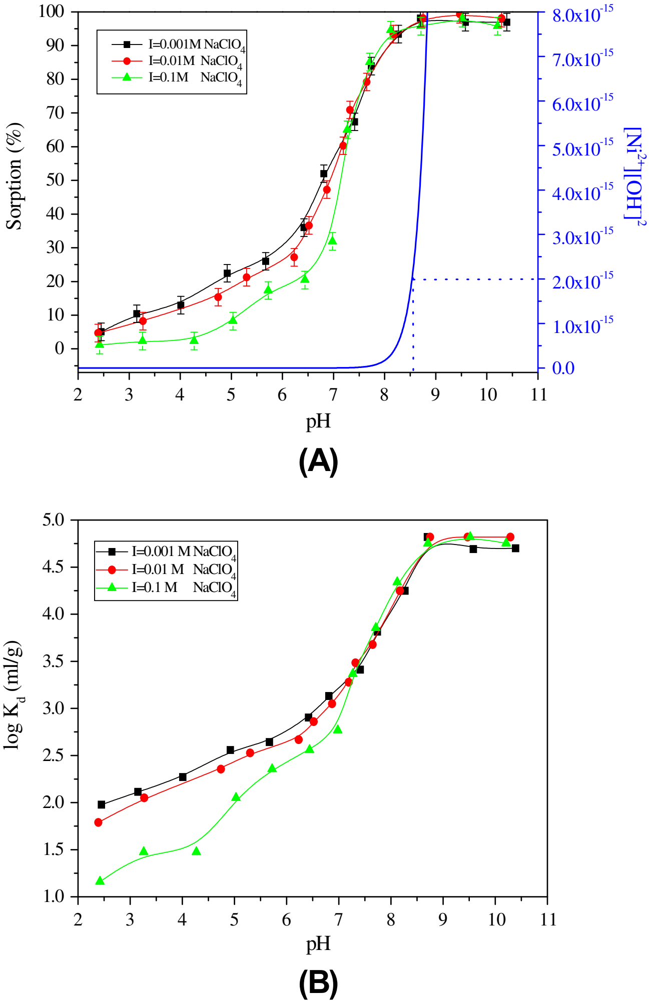

Fig. 4. Effect of ionic strength on ^{63}Ni(II) sorption to illite as a function of pH values. $T = 293 \pm 2$ K, $C_{(Ni)initial} = 1.59 \times 10^{-4}$ mol/L, $m/V = 0.8$ g/L.

species present in the forms of Ni^{2+}, $Ni(OH)^+$, $Ni(OH)_2$, $(Ni(OH)_3^-$ and $Ni(OH)_4^{2-}$ at different pH values (Fig. 5). The predominant nickel specie is Ni^{2+} and the removal of $^{63}Ni(II)$ is mainly accomplished by sorption reaction at pH < 8.5. Therefore, the low $^{63}Ni(II)$ sorption that takes place at pH < 6 (region I) can be attributed partly to the competition between H^+/Na^+ and Ni^{2+} on the surface sites. It is noteworthy that the drastic increasing in the uptake of $^{63}Ni(II)$ on illite at 6 < pH < 8.5 (region II) is not attributed to the precipitation of $Ni(OH)_2(s)$ because of the low precipitation constant (2.0×10^{-15}). The precipitation curve of $^{63}Ni(II)$ at the concentration of 1.59×10^{-4} mol/L is also shown in Fig. 4A. It is clear that $^{63}Ni(II)$ begins to form precipitation at pH ~ 8.5 in the absence of illite. However, more than 90% $^{63}Ni(II)$ is adsorbed on illite at pH 8.5. Thereby the sorption of $^{63}Ni(II)$ on illite at pH below 8.5 is not attributed to the surface precipitation of $Ni(OH)_2$. However, the formation of $^{63}Ni(II)$ species with OH^- plays an important role in the increase of $^{63}Ni(II)$ removal above pH 8.5 (region III). Depending on the pH and metal concentration, the hydrolytic actions of $^{63}Ni(II)$ may generate various complexes such as $Ni(OH)^+$, $Ni(OH)_2$, $Ni(OH)_3^-$ and $Ni(OH)_4^{2-}$ at high pH values (pH > 8.5), which participates in the sorption and precipitate onto the illite [24].

3.2.3. Effect of ionic strength

The effect of ionic strength on $^{63}Ni(II)$ sorption on illite as a function of pH values is also shown in Fig. 4A. One can see that the sorption of $^{63}Ni(II)$ is obviously affected by ionic strength, especially at low pH values. The sorption is strongly affected by ionic strength at pH < 7.5 and no effect is approximately found on $^{63}Ni(II)$ sorption at pH > 7.5. The ionic strength can influence the double electrode layer thickness and interface potential, thereby can affect the binding of the adsorbed species. Outer-sphere surface complexes are expected to be more impressionable to ionic strength variations than inner-sphere complexes as the background electrolyte ions are placed in the same plane for outer-sphere surface complexes [25]. Based on the theory mentioned above, one can deduce that cation exchange or outer-sphere surface complexation mainly contribute to $^{63}Ni(II)$ sorption on illite at pH < 7.5, while inner-sphere surface complexation is the main sorption mechanism of $^{63}Ni(II)$ on illite at pH > 7.5 [11,26].

As can be seen from Fig. 4A, the sorption of $^{63}Ni(II)$ on illite increases with decreasing ionic strength at pH < 7.5. This phenomenon could be attributed to three reasons: (1) $^{63}Ni(II)$ ions form electrical double layer complexes with illite, 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 illite and $^{63}Ni(II)$ ions is mainly an ionic interaction in nature, which is in agreement with the ion exchange mechanism; (2) the ionic strength of solution influences the activity coefficient of $^{63}Ni(II)$ ions, which limits their transfer to illite surfaces [27,28]; (3) ionic strength effects can impact particle aggregation by affecting electrostatic interactions. Increased ionic strength has been shown to reduce electrostatic repulsion and thereby increases particle aggregation of illite, which reduces the amount of available binding sites and thereby decreases the sorption of $^{63}Ni(II)$ on illite [29].

3.2.4. Effect of solid content

The sorption of $^{63}Ni(II)$ on illite as a function of solid content is shown in Fig. 6. One can see that the sorption percentage of $^{63}Ni(II)$ increases with increasing illite content. With increasing solid content, the amount of functional groups at illite surface increases and thereby increases the available sites for binding $^{63}Ni(II)$, which enhances the formation of complexes between $^{63}Ni(II)$ and illite. The results also clearly indicate that the removal efficiency increases up to the optimum dosage beyond which its increase is negligible.

As can be seen from Fig. 6, the sorption capacity of $^{63}Ni(II)$ on illite decreases gradually with the increase of solid content. This may be attributed to the overcrowding of particles which may be termed as a kind of solid concentration effect [30]. A large amount of sorbent effectively reduces the unsaturation of the sorption sites and accordingly, the number of such sites per unit mass comes down leading to comparatively less sorption at higher solid content. Besides, higher sorbent amount increases the probability of collision between solid particles and therefore creates particle aggregation, resulting in a decrease in the total surface area and an increase in diffusional path length, both of which contribute to the decrease in amount adsorbed per unit mass. Particle interaction may also desorb some of the $^{63}Ni(II)$ that is only loosely and reversibly bound to the illite surface [31]. Another possible interpretation is that the increase ratio of net sorption quantity of $^{63}Ni(II)$ on illite surface is lower than that of the solid content, which can also lead to the decrease in amount adsorbed per unit mass.

This experimental phenomenon indicates that the augmentation of sorbent dosage could not unboundedly increase the contact area between metal ions and solid surface. Meanwhile, the competition sorption between the sorbent molecules will also reduce the sorption quantity of solid per unit mass. Thus, for the sake of reducing the cost of pollution management in actual application, one should choose appropriate sorbent dosage according to the initial concentrations and required removal efficiency of the specific pollutant.

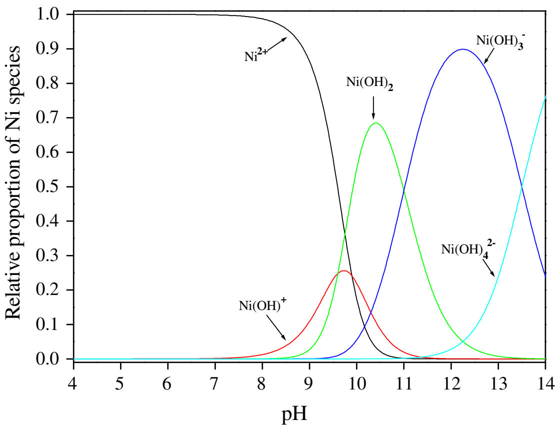

Fig. 5. Relative proportion of $^{63}Ni(II)$ species as a function of pH.

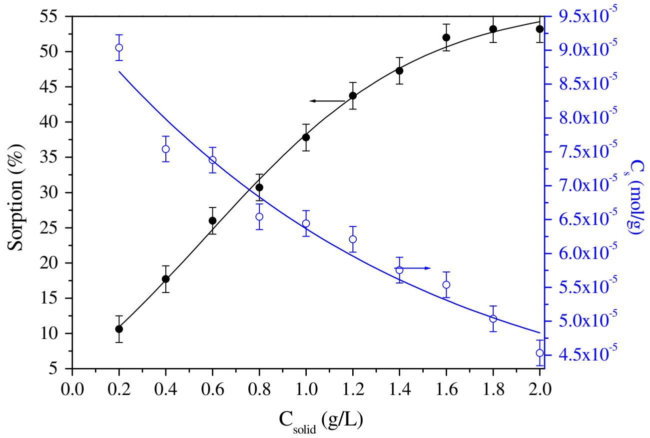

Fig. 6. Sorption of $^{63}Ni(II)$ on illite as a function of solid content. $T = 293 \pm 2$ K, pH = 6.4 ± 0.1, $C_{(Ni)initial} = 1.59 \times 10^{-4}$ mol/L, $I = 0.01$ M $NaClO_4$.

3.2.5. Effect of foreign ions

Fig. 7 shows the effect of foreign ions on the removal of ^{63}Ni(II) from aqueous solution to illite in 0.01 M $LiClO_4$, $NaClO_4$, $KClO_4$, $NaNO_3$ and NaCl electrolyte solutions, respectively, as a function of pH values. From Fig. 7A, one can see that the influence of foreign anions on the sorption of ^{63}Ni(II) on illite at pH < 7.5 is the sequence of $Cl^- > NO_3^- > ClO_4^-$. The inorganic acid radicals radium order is $Cl^- < NO_3^- < ClO_4^-$, the smaller radium negative charged inorganic acid radicals may form complexes with the oxygen-containing functional groups on the surfaces of illite and thereby results in the decrease of ^{63}Ni(II) sorption. In addition, NO_3^- and Cl^- can form soluble complexes with ^{63}Ni(II) (e.g. $Ni(NO_3)_x^{(2-x)-}$, $NiCl_x^{(2-x)-}$), whereas ClO_4^- cannot. Compared with NO_3^- and ClO_4^-, Cl^- is easier to form idiocratic sorption on the solid surface, which changes the surface state of illite and decreases the availability of binding sites. The result is consistent with the sorption of Ni(II) on attapulgite and Pb(II) on diatomite [32,33]. However, other literatures reported that the influence of foreign ions on the sorption of Ni(II) on Na-bentonite and Pb(II) on oxidized MWCNTs can be neglected due to the formation of surface complexes on sorbent surfaces [34,35]. The differences may be attributed to the surface properties of sorbent and the physicochemical properties of metal ions.

As can be seen from Fig. 7B, the sorption of ^{63}Ni(II) on illite is somewhat influenced by the cations in suspension, especially at low pH values. One can see that the sorption of ^{63}Ni(II) on illite with the same pH values is in the sequence of $Li^+ > Na^+ > K^+$ at pH < 7.5. This phenomenon can be easily interpreted by the competition between different positive ions and ^{63}Ni(II) for the binding sites on illite surfaces. The radii of hydration of these three cations are K^+ = 2.32 Å, Na^+ = 2.76 Å and Li^+ = 3.4 Å, respectively [36]. The radius of K^+ is smaller than the radii of the other two cations and therefore the influence of K^+ on ^{63}Ni(II) sorption is more obvious than the influences of Na^+ and Li^+. Generally, the cations may follow an order of increasing selectivity for binding to solid surfaces of alkali metal cations < H^+ < alkaline earth cations < transitional group monovalent cations (e.g. Ag^+) < transitional group divalent cations (e.g. Cu^{2+} and Ni^{2+}) < trivalent cations [31]. Thus, the influence of monovalent alkali ions on the sorption of bivalent ^{63}Ni(II) should be weak. However, the influence of Li^+, Na^+ and K^+ on ^{63}Ni(II) sorption is a little drastic at pH < 7.5. In the experiments, the concentration of the monovalent alkali ions (1.00×10^{-2} mol/L) is much higher than that of ^{63}Ni(II) (1.59×10^{-4} mol/L). Before the addition of ^{63}Ni(II) ions, the illite has been pre-equilibrated with alkali ions. The sorption of ^{63}Ni(II) on illite is attributed to the exchange of ^{63}Ni(II) ions with alkali ions and other reactions. Thereby, it is reasonable that the alkali ions can affect ^{63}Ni(II) sorption.

3.2.6. Effect of HA/FA

The pH dependence of ^{63}Ni(II) sorption on illite in the absence and presence of HA/FA is shown in Fig. 8. One can see that the presence of HA/FA enhances the sorption of ^{63}Ni(II) on illite at pH < 6.5, while a negative effect of HA/FA on ^{63}Ni(II) sorption is observed at pH > 6.5. Fig. 9 shows the sorption of HA and FA to illite as a function of pH. One can see that about 90% HA/FA is adsorbed on illite at pH < 6.5, and then the sorption decreases with increasing pH. HA and FA were determined to have ζ potentials at pH > 2 [37,38], which were in agreement with previous potentiometric titration results [17]. Therefore, at low pH values, the negatively charged HA/FA can be easily adsorbed on the positively charged surfaces of illite due to electrostatic attraction, which results in a more favorable electrostatic environment for ^{63}Ni(II) sorption and enhances the formation of Ni-HS-illite ternary surface complexes. However, at high pH values, the negatively charged HA/FA is difficult to be adsorbed on the negatively charged surfaces of illite due to electrostatic repulsion. The competition between the soluble HA/FA and illite with ^{63}Ni(II) ions increases the formation of strong HA/FA-Ni complexes in solution, thereby competitively diminishing the extent of ^{63}Ni(II) sorption on HA/FA-illite hybrids [39].

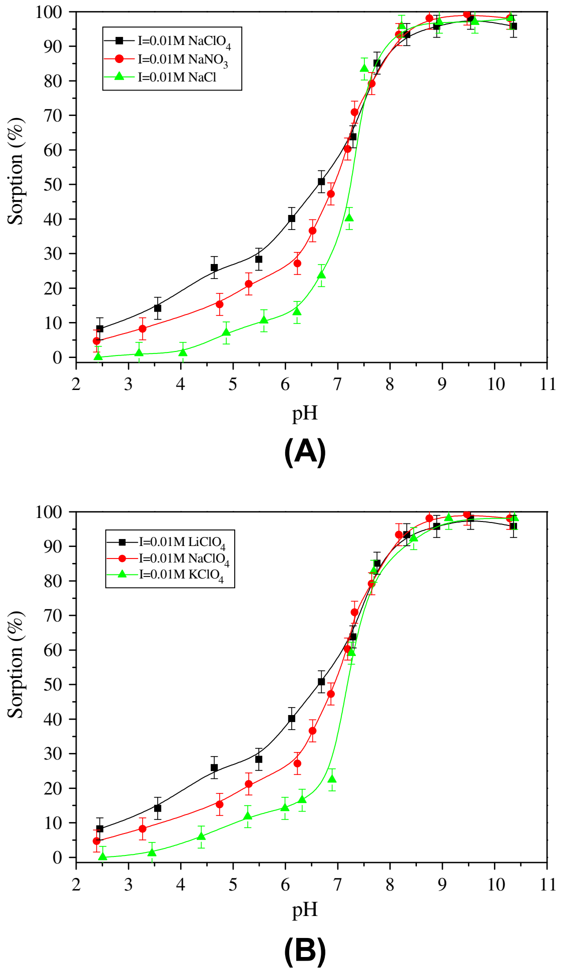

Fig. 7. Influence of foreign anions (A) and cations (B) on ^{63}Ni(II) sorption to illite as a function of pH values. $T = 293 \pm 2$ K, $C_{(Ni)initial} = 1.59 \times 10^{-4}$ mol/L, m/V = 0.8 g/L.

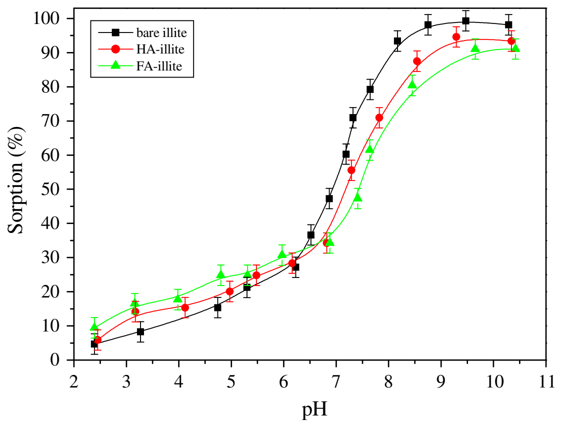

Fig. 8. Effect of pH on sorption of ^{63}Ni(II) on bare and HA/FA bound illite. $T = 293 \pm 2$ K, $C_{(Ni)initial} = 1.59 \times 10^{-4}$ mol/L, $C_{[HA/FA]}$ = 10 mg/L, m/V = 0.8 g/L, I = 0.01 M $NaClO_4$.

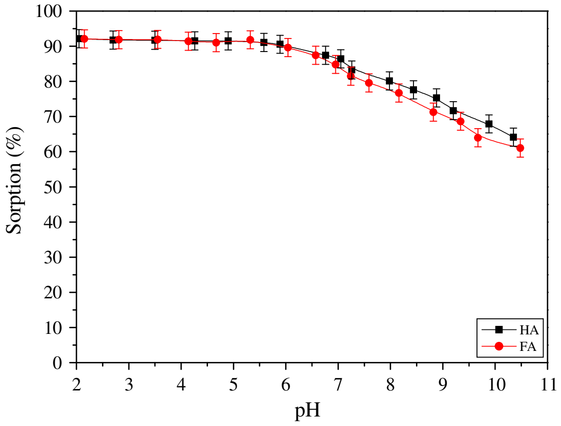

Fig. 9. Sorption of HA and FA on illite as a function of pH values. $T = 293 \pm 2$ K, $C_{[HA/FA]} = 10$ mg/L, $m/V = 0.8$ g/L, $I = 0.01$ M $NaClO_4$.

From Fig. 8, one can also see that the influence of FA on the sorption of ^{63}Ni(II) is a little stronger than that of HA at the whole pH range when the mass concentrations of HA and FA are the same. Although the samples of HA and FA were extracted from the same soil samples and both of them contain functional groups such as carboxyl, amine and phenolic, the proportions and configurations of these functional groups and surface sites density are different. As is illustrated in Table 2, the surface sites density of FA (i.e., 2.71×10^{-2} mol/g) is higher than that of HA (i.e., 6.46×10^{-3} mol/g), which can provide more available surface sites for binding ^{63}Ni(II). Therefore, it is reasonable that FA has a stronger effect on ^{63}Ni(II) sorption than HA at the whole pH range.

3.2.7. Sorption isotherms and thermodynamic studies

The sorption isotherms for ^{63}Ni(II) sorption on illite at 293, 313 and 333 K are shown in Fig. 10. It can be seen from Fig. 10 that the sorption isotherm is the highest at $T = 333$ K and is the lowest at $T = 293$ K. The result indicates that high temperature is advantageous for ^{63}Ni(II) sorption on illite. Several factors may account for the increase of ^{63}Ni(II) sorption on illite with increasing temperature. Increased diffusion rate of ^{63}Ni(II) into the illite pores due to increased temperature may account for the observed behavior [40]. Changes in the illite pore sizes as well as an increase in the number of sorption sites due to the breaking of some internal bonds near illite surface edge are expected at higher temperatures. The increase in temperature may lead to the increase in proportion and activity of ^{63}Ni(II) ions in solution, the affinity of ^{63}Ni(II) ions to the surface, or the charge and the potential of illite surface [41].

For isotherm modeling, herein, the Langmuir, Freundlich and D-R isotherm equations are conducted to simulate the sorption isotherms and to establish the relationship between the amount of ^{63}Ni(II) adsorbed on illite and the concentration of ^{63}Ni(II) remained in solution.

Table 2
The parameters for the three isotherm models at different temperatures.

Correlation parameters		$T = 293$ K	$T = 313$ K	$T = 333$ K
Langmuir	C_{smax} (mol/g)	1.54×10^{-4}	1.59×10^{-4}	1.63×10^{-4}
	b (L/mol)	9.39×10^{3}	1.25×10^{4}	2.29×10^{4}
	R_L	0.207–0.758	0.164–0.702	0.096–0.561
	CC (R^2)	0.990	0.991	0.991
Freundlich	k_F (mol^{1-n}·L^n/g)	4.53×10^{-3}	3.52×10^{-3}	2.08×10^{-3}
	n	0.451	0.407	0.325
	CC (R^2)	0.974	0.962	0.971
D-R	β (mol^2/kJ)	4.69×10^{-3}	3.81×10^{-3}	2.58×10^{-3}
	C_{smax} (mol/g)	5.61×10^{-4}	5.94×10^{-4}	7.03×10^{-4}
	E (kJ/mol)	10.32	11.46	13.92
	CC (R^2)	0.990	0.985	0.989

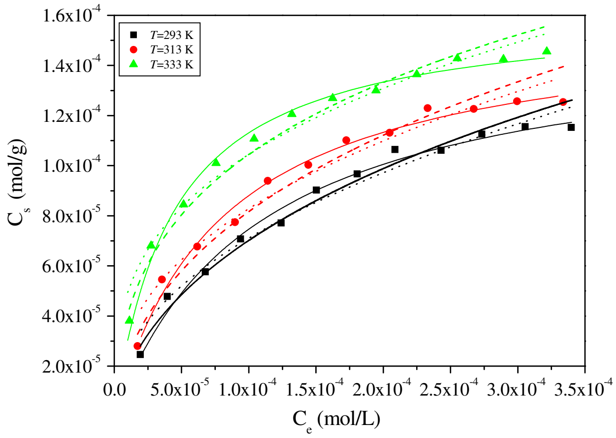

Fig. 10. Sorption isotherm (symbols) and Langmuir (solid lines), Freundlich (dash lines), D-R (dotted lines) models fitting for ^{63}Ni(II) sorption on illite at three different temperatures. pH = 6.4 ± 0.1, $C_{(Ni)initial} = 1.45 \times 10^{-5} \sim 1.74 \times 10^{-4}$ mol/L, $m/V = 0.8$ g/L, $I = 0.01$ M $NaClO_4$.

The Langmuir model assumes that sorption occurs in a monolayer or that sorption may only occur at a fixed number of localized sites on the surface with all sorption sites identical and energetically equivalent [42]. Its form can be described by the following equation:

$$C_s = \frac{bC_{smax}C_{eq}}{1 + bC_{eq}} \tag{1}$$

where C_{eq} is the equilibrium concentration of metal ions remained in the solution (mol/L); C_s is the amount of metal ions adsorbed on per weight unit of solid after equilibrium (mol/g); C_{smax}, the maximum sorption capacity, is the amount of sorbate at complete monolayer coverage (mol/g), and b (L/mol) is a constant that relates to the heat of sorption. Furthermore, the essential characteristics of Langmuir equation to predict whether a sorption system is 'favorable' or 'unfavorable' could be expressed by dimensionless constant called equilibrium parameter R_L, which is defined from the following relation:

$$R_L = \frac{1}{1 + bC_0} \tag{2}$$

where b is Langmuir constant (L/mol), and C_0 is the initial concentration of ^{63}Ni(II) in solution (mol/L). The value of R_L indicates the shape of the isotherms to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [43].

The Freundlich expression is an exponential equation with the assumption that as the sorbate concentration increases so too does the concentration of sorbate on the heterogeneous sorbent surface [46]. The equation is commonly represented by:

$$C_s = k_F C_{eq}^n \tag{3}$$

where k_F (mol^{1-n}·L^n/g) 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 D-R isotherm model is more general than the Langmuir isotherm since it does not have the restriction of surface properties or constant sorption potential [34]. It is valid at low concentration ranges and can be used to describe sorption on both homogeneous and heterogeneous surfaces with a general expression as follows:

$$C_s = C_{smax} \exp(-\beta\varepsilon^2) \tag{4}$$

where C_s and C_{smax} are defined above, β is the activity coefficient related to mean adsorption energy (mol^2/kJ^2), and ε is the Polanyi potential, which is equal to:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_{eq}}\right) \tag{5}$$

where R is ideal gas constant (8.3145 J/(mol K)), and T is the absolute temperature in Kelvin (K).

E (kJ/mol) is defined as the free energy change, which requires to transfer 1 mol of ions from solution to the solid surfaces. Its value can be calculated from the following equation:

$$E = \frac{1}{\sqrt{2\beta}} \tag{6}$$

The magnitude of E is an important parameter for estimating the mechanism of the sorption reaction. Sorption is dominated by chemical ion exchange if E is in the range of 8–16 kJ/mol, whereas physical forces may affect the sorption in the case of $E < 8$ kJ/mol [42,44].

The experimental data of ^{63}Ni(II) sorption are regressively simulated with the Langmuir, Freundlich and D-R models and the results are given in Fig. 10. The relative values calculated from the three models are listed in Table 2. The correlation coefficients for the Langmuir, Freundlich and D-R isotherms are very close to 1. It can be concluded from R^2 values that Langmuir and D-R models simulate the experimental data better than Freundlich model. The fact that the sorption data of ^{63}Ni(II) according with Langmuir isotherm indicates that the binding energy on the whole surface of illite is uniform. In other words, the whole surface has identical sorption activity and therefore the adsorbed ^{63}Ni(II) ions do not interact or compete with each other, and they are adsorbed by forming an almost complete monolayer coverage of the illite particles. This phenomenon, at the same time, indicates that chemosorption is the principal uptake mechanism in sorption process [45]. Moreover, illite has a limited sorption capacity, thus the sorption could be better described by Langmuir model rather than by Freundlich model, as an exponentially increasing sorption was assumed in the Freundlich model. At all temperatures, the value of C_s was found to be smaller than C_{smax}, which confirms that ^{63}Ni(II) sorption on illite is by a monolayer type in which the surface of sorbent is not saturated. The values of C_{smax} obtained from the Langmuir model for ^{63}Ni(II) sorption on illite are the highest at $T = 333$ K and the lowest at $T = 293$ K, which indicates that the sorption is enhanced with increasing temperature. The fact that all the R_L values for the sorption of ^{63}Ni(II) on illite at the three temperatures are in the ranges of 0.096–0.758 implies that the sorption process is favorable. The value of n calculated from the Freundlich model is from unity, indicating that a nonlinear sorption of ^{63}Ni(II) takes place on illite surfaces. The E values obtained from Eq. (14) are 10.32 ($T = 293$ K), 11.46 ($T = 313$ K) and 13.92 kJ/mol ($T = 333$ K), which are in the sorption energy range of chemical ion-exchange reaction. The sorption capacities (C_{smax}) derived from the D-R model are higher than those derived from the Langmuir model. This may be attributed to the different assumptions considered in the formulation of the isotherms. The parameters calculated from the analysis of the three isotherm models concertedly manifest that sorption of ^{63}Ni(II) on the surfaces of illite is a favorable and chemisorption process.

The thermodynamic parameters (ΔH^0, ΔS^0, and ΔG^0) for ^{63}Ni(II) sorption on illite can be determined from the temperature dependence. Free energy change (ΔG^0) is calculated from the relationship:

$$\Delta G^0 = -RT \ln K^0 \tag{7}$$

where K^0 is the sorption equilibrium constant. Values of $\ln K^0$, obtained by plotting $\ln K_d$ versus C_{eq} for ^{63}Ni(II) sorption on illite and extrapolating C_{eq} to zero, are 7.08 ($T = 293$ K), 7.31 ($T = 313$ K) and 7.79 ($T = 333$ K). Standard entropy change (ΔS^0) is calculated from the equation:

Table 3
Values of thermodynamic parameters for ^{63}Ni(II) sorption on illite.

T (K)	ΔG^0 (kJ/mol)	ΔS^0 (J/(mol K))	ΔH^0 (kJ/mol)
293	−17.25	108.02	14.41
313	−19.03	108.02	14.79
333	−21.57	108.02	14.42

$$\left(\frac{\partial \Delta G^0}{\partial T}\right)_P = -\Delta S^0 \tag{8}$$

The average standard enthalpy change (ΔH^0) is then calculated from the expression:

$$\Delta H^0 = \Delta G^0 + T\Delta S^0 \tag{9}$$

The values obtained from Eqs. (7)–(9) are tabulated in Table 3. A positive value of the standard enthalpy change indicates that the sorption is endothermic. One possible explanation to this positive entropy is that ^{63}Ni(II) is solved well in water, and the hydration sheath of ^{63}Ni(II) has to be destroyed before its sorption on illite. This dehydration process needs energy, and it is favored at high temperature [46]. The implicit assumption here is that after sorption the environment of ^{63}Ni(II) ions is less aqueous than it was in the solution state. The removal of water from ions is essentially an endothermic process, and it appears that the endothermicity of the desolvation process exceeds that of the enthalpy of sorption 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, which indicates that the reaction is more favorable at higher temperatures. At high temperature, cations are readily desolvated and hence its sorption becomes more favorable. The positive value of entropy change (ΔS^0) shows some structural changes in sorbate and sorbent during the sorption process, causing an increase in the disorderness of the solid-solution system [47,48]. A positive entropy change for ^{63}Ni(II) sorption on illite is due to the fixation of ions on the exchange sites of the randomly distributed surface species. The ΔS^0 value is also an indication of whether or not a reaction is an associative or dissociative mechanism. The large ΔS^0 values for ^{63}Ni(II) sorption on illite at the three temperatures are in the range of a dissociative mechanism ($\Delta S^0 > -10$ kJ/mol) [49]. The analysis of ^{63}Ni(II) sorption isotherms and model fitting indicates that the reaction of ^{63}Ni(II) sorption on illite is an endothermic process. However, Duong et al. [50] investigated the sorption of Ni(II) on high-yield kraft fibers and found that the sorption is spontaneous and exothermic. The biosorption process of Pb(II) and Ni(II) ions onto C. furcata biomass was feasible, spontaneous and exothermic [51]. The results derived from this work and the above-mentioned references indicate that the thermodynamic parameters are related not only on the nature of sorbate, but also on the nature of solid particles.

4. Conclusions

Batch technique was adopted to investigate the sorption of ^{63}Ni(II) from aqueous solutions onto illite as a function of various environmental factors such as contact time, pH, ionic strength, coexisting electrolyte ions, humic substances and temperature under ambient conditions. The sorption increases with increasing pH values at pH < 8.5, and then maintains high level at pH > 8.5. The sorption of ^{63}Ni(II) is dependent on ionic strength and foreign ions at low pH values, and independent of these factors at high pH values. The presence of HA/FA enhances the sorption of ^{63}Ni(II) at pH < 6.5, while reduces ^{63}Ni(II) sorption at pH > 6.5. The thermodynamic analysis derived from temperature dependent sorption isotherms suggests that the sorption process of ^{63}Ni(II) on illite is spontaneous and endothermic. By integrating all the above-mentioned analysis results together, one can conclude that the sorption of ^{63}Ni(II) on illite is dominated by ion exchange or outer-sphere surface complexation at low pH values, and by inner-sphere surface complexation at high pH values. Considering the accessibility and low cost of illite, one can conclude that this material has a great application potential for the cost-effective disposal of ^{63}Ni(II)-contaminated wastewaters.

Based on the results noted for ^{63}Ni(II), illite may also be suitable for the removal of other heavy metals and radionuclides. Hence, more investigations on the sorption property of illite towards various environmental pollutants are ongoing in our laboratory so as to have a more thorough view of the possibility of using illite as a high-efficiency material for wastewater disposal.

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References

[1] H. Parab, S. Joshi, N. Shenoy, A. Lali, U.S. Sarma, M. Sudersanan, Process Biochem. 41 (2006) 609–615.
[2] B. Rosborg, L. Werme, J. Nucl. Mater. 379 (2008) 142–153.
[3] D. Cui, T.E. Eriksen, Reduction of Tc(VII) and Np(V) in Solution by Ferrous Ion. A Laboratory Study of Homogeneous and Heterogeneous Redox Processes. SKB Technical Report, TR-96-03, 1996.
[4] F. El Aamrani, I. Casas, J. de Pablo, L. Duro, M. Grivé, J. Bruno, Experimental and Modeling Study of the Interaction Between Uranium (VI) and Magnetit. SKB Technical Report, TR-99-21, 1999.
[5] M.A. Glaus, B. Baeyens, M. Lauber, T. Rabung, L.R. Van Loon, Water-extractable Organic Matter from Opalinus Clay: Effect on Sorption and Speciation of Ni(II), Eu(III) and Th(IV). Nagra Technical Report 01-07, 2001.
[6] N. Marmier, A. Delisée, F. Fromage, J. Colloid Interface Sci. 211 (1999) 54–60.
[7] Å. Gustafsson, M. Molera, I. Puigdomenech, Study of Ni(II) sorption on chlorite – a fracture filling mineral in granites, in: Scientific Basis for Nuclear Waste Management XXVIII, Materials Research Society Symposium Proceedings vol. 824, 2004, pp. 373–378.
[8] S. Holgersson, Oskarshamn Site Investigation. Batch Experiments of I, Cs, Sr, Ni, Eu, U and Np Sorption onto Soil from the Laxemar Area. SKB P-09-29, 2009.
[9] E. Álvarez-Ayuso, A. García-Sánchez, Sci. Total Environ. 305 (2003) 1–12.
[10] D.G. Strawn, D.L. Sparks, J. Colloid Interface Sci. 216 (1999) 257–269.
[11] G.D. Sheng, J. Hu, X.K. Wang, Appl. Radiat. Isot. 66 (2008) 1313–1320.
[12] J. Hu, D. Xu, L. Chen, X.K. Wang, J. Radioanal. Nucl. Chem. 279 (2009) 701–708.
[13] R.G. Ford, A.C. Scheinost, D.L. Sparks, Adv. Argon. 74 (2001) 41–62.
[14] L.R. Van Loon, B. Baeyens, M.H. Bradbury, Appl. Geochem. 20 (2005) 2351–2363.
[15] D. Borden, R.F. Giese, Clays Clay Miner. 49 (2001) 444–445.
[16] X.Y. Gu, L.J. Evans, J. Colloid Interface Sci. 307 (2007) 317–325.
[17] X. Tan, X. Wang, H. Geckeis, T. Rabung, Environ. Sci. Technol. 42 (2008) 6532–6537.
[18] R.A. Alvarez-Puebla, D.S. dos Santos Jr., C. Blanco, J.C. Echeverria, J.J. Garrido, J. Colloid Interface Sci. 285 (2005) 41–49.
[19] W.X. Liu, Water Res. 35 (2001) 4111–4125.
[20] X.K. Wang, C.L. Chen, W.P. Hu, A.P. Ding, D. Xu, X. Zhou, Environ. Sci. Technol. 39 (2005) 2856–2860.
[21] J. Hu, C.L. Chen, X.X. Zhu, X.K. Wang, J. Hazard. Mater. 162 (2009) 1542–1550.
[22] M.H. Al-Qunaibit, W.K. Mekhemer, A.A. Zaghloul, J. Colloid Interface Sci. 283 (2005) 316–321.
[23] A. Kowal-Fouchard, R. Drot, E. Simoni, J.J. Ehrhardt, Environ. Sci. Technol. 38 (2004) 1399–1407.
[24] C. Cabrera, C. Gabaldon, P. Marzal, J. Chem. Technol. Biotechnol. 80 (2005) 477–481.
[25] C.L. Chen, X.K. Wang, Appl. Radiat. Isot. 65 (2007) 155–163.
[26] P.P. Chang, X.K. Wang, S.M. Yu, W.S. Wu, Colloids Surf., A 302 (2007) 75–81.
[27] Z. Reddad, C. Gerente, Y. Andres, L.P. Cloirec, Environ. Sci. Technol. 36 (2002) 2067–2073.
[28] C.L. Chen, X.K. Wang, Ind. Eng. Chem. Res. 45 (2006) 9144–9149.
[29] K.L. Mercer, J.E. Tobiason, Environ. Sci. Technol. 42 (2008) 3797–3802.
[30] K.G. Bhattacharyya, S.S. Gupta, Colloids Surf., A 317 (2008) 71–79.
[31] A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, J. Hazard. Mater. 95 (2002) 137–152.
[32] Q.H. Fan, D.D. Shao, J. Hu, W.S. Wu, X.K. Wang, Surf. Sci. 602 (2008) 778–785.
[33] G.D. Sheng, S.W. Wang, J. Hu, Y. Lu, J.X. Li, Y.H. Dong, X.K. Wang, Colloids Surf., A 339 (2009) 159–166.
[34] S.T. Yang, J.X. Li, Y. Lu, Y.X. Chen, X.K. Wang, Appl. Radiat. Isot. 67 (2009) 1600–1608.
[35] D. Xu, X.L. Tan, C.L. Chen, X.K. Wang, J. Hazard. Mater. 154 (2008) 407–416.
[36] F. Esmadi, J. Simm, Colloids Surf., A 104 (1995) 265–270.
[37] W.L. Yan, R.B. Bai, Water Res. 39 (2005) 688–698.
[38] K. Yang, B.S. Xing, Environ. Pollut. 157 (2009) 1095–1100.
[39] I. Christl, R. Kretzschmar, Geochim. Cosmochim. Acta 65 (2001) 3435–3442.
[40] H. Genc-Fuhrman, J.C. Tjell, D. McConchie, Environ. Sci. Technol. 38 (2004) 2428–2434.
[41] F. Partey, D. Norman, S. Ndur, R. Nartey, J. Colloid Interface Sci. 321 (2008) 493–500.
[42] A. Ozcan, E.M. Oncu, A.S. Ozcan, Colloids Surf., A 277 (2006) 90–97.
[43] R.P. Han, W.H. Zou, Y. Wang, L. Zhu, J. Environ. Radioact. 93 (2007) 127–143.
[44] R. Donat, A. Akdogan, E. Erdem, H. Cetisli, J. Colloid Interface Sci. 286 (2005) 43–52.
[45] Y.T. Zhou, H.L. Nie, C. Branford-White, Z.Y. He, L.M. Zhu, J. Colloid Interface Sci. 330 (2009) 29–37.
[46] S.S. Tahir, N. Rauf, J. Chem. Thermodyn. 35 (2003) 2003–2009.
[47] M. Ajmal, R.A.K. Rao, S. Anwar, J. Ahmad, R. Ahmad, Bioresour. Technol. 86 (2003) 147–149.
[48] Q.H. Fan, X.L. Tan, J.X. Li, X.K. Wang, W.S. Wu, G. Montavon, Environ. Sci. Technol. 43 (2009) 5776–5782.
[49] K.G. Scheckel, D.L. Sparks, Soil Sci. Soc. Am. J. 65 (2001) 719–728.
[50] T.D. Duong, K.L. Nguyen, M. Hoang, J. Colloid Interface Sci. 303 (2006) 69–74.
[51] A. Sarı, M. Tuzen, Ö.D. Uluözlü, M. Soylak, Biochem. Eng. J. 37 (2007) 151–158.