Natural illite as an Efficient Adsorbent for Thorium Removal

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Abstract: *In this paper，the natural illite is used as low-cost sorbent for investigating the sorption of Th(IV). The sorbent is characterized by titration, N_2-BET, FTIR, XRD, SEM/EDS and XPS. The sorption behavior of Th(IV) on the sorbent is investigated by batch method. The kinetics of Th(IV) adsorption process on the sorbent is fitted well by the pseudo-second order rate equation. The sorption capacity of Th(IV) is increased with the solid-to-liquid ratio increasing. The sorption of Th(IV) is strongly dependent on pH(pH<5) and ionic strength. The negative effects on sorption of cations shown from strong to weak is: $Mg(NO_3)_2 > KNO_3 > NaNO_3$. The influence of the anions are: PO_4^{3-} obviously promoted Th(IV) sorption, while the existence of SO_4^{2-} inhibited Th(IV) adsorption. Gibbs free energy (ΔG^0), Enthalpy (ΔH^0) and entropy (ΔS^0) and are calculated from the temperature-dependent sorption data and the results indicate that the sorption of Th(IV) on natural illite was a spontaneous process. Isotherms of Th(IV) adsorption to natural illite could be described well by Langmuir model. Through the desorption experiments, the adsorption process on natural illite was reversible reaction. The sorption mechnism of Th(IV) on natural illite is ion exchange reaction with its potassium ions that are trapped in its interlayer spaces; as well as outer sphere complexes formation (pH<5) and inner sphere complexes(pH>5) through ≡Si−O- and ≡Al−O- groups are located at the edges.*

Keywords: *natrual illite; Th(IV); sorption; kinetics; isotherm.*

1. INTRODUCTION

With the development of nuclear energy, the nuclear critical safety problem becomes more and more significant. In particular, some long-lived radionuclides have attracted people (Yu *et aL*, 2015; Kitamura and Kirishima, 2015). Radionuclides with high mobility in contaminated water will transfer into soil and plant materials. The radionuclides will enter the food chain, which will potentially produce serious damage to human beings(Wen *et aL*, 2014). Among these nuclear waste and fission products, one of the elements that cause people to pay attention to is thorium. Thorium, which is a potential nuclear fuel and fertile in mining tailings and wastewater from disposal plants, is one of the most significant radioactive contaminations in environmental medium(Pan *et aL*, 2011; Xu *et aL*, 2016). Additionally, It is only stable at its valence +4 in solution, and is usually selected as a chemical analogue for other tetravalent actinides(Choppin, 1999). Since that is not biodegradable and tends to accumulate in living organisms, causing various diseases and disorders, the separation and enrichment of Th(IV) from aqueous solutions are crucial in protecting environment and reutilizing thorium as a resource (Pan *et aL*, 2011; Xu *et aL*, 2016). Th(IV) on all kinds of clay minerals and oxides are most important for determining the mobility and bioavailability of Th(IV) in the natural environment (Chen and Wang, 2007; Chen *et aL*, 2007; Tan *et aL*, 2007; Xu *et aL*, 2007). In recent decade years, the sorption of Th(IV) on all kinds of minerals as a function of pH, ionic strength, temperature was studied extensively (Xu *et aL,* 2007; Fan *et aL*, 2008; Pan *et aL*, 2011; Hu and Tan, 2012; Zhang *et aL*, 2015). Many mechanisms have been postulated for Th(IV) and other actinides of sorption, such as

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surface complexation, chemi-complexation, chemisorption, cation exchange, surface precipitation, colloid formation at surface and diffusion into the particle micropores (Jakobsson,1999; Reiller *et aL*, 2005; Wang *et aL*, 2005a; Wang *et aL*, 2005b; Wang *et aL*, 2005c) .

Illite is 2:1 layer type clays: its structure consists of two tetrahedral sheets that sandwich an octahedral sheet, and non-expanding, aluminous, and contains nonexchangeable K as the major interlayer cation. The potassium balances a negative layer charge, generated by Al for Si substitution in the tetrahedral sheet and (Mg, Fe^{2+}) for Al in the octahedral sheet. (Rieder *et aL*, 1998; Jan Środoń, 2005) Usually, illite is white, but when containing impurities it will become yellow, green, brown and other colors. Because illite has specific surface area, microcellular structure and high cation exchange capacity, it has a strong affinity for metallic pollutants in the environment. In the last decades, illite has been intensively investigated as an adsorbent in the removal of heavy metal ions from the solutions and heavy metal polluted soils in the natural environment, e.g. Pb(II), Ni(II), Cu(II), Co(II), Eu(II) and Zn(II) on illite (Echeverría *et aL*, 2005; Elzinga and Sparks, 2001; Bradbury and Baeyens, 2009; Turan *et aL*, 2011). There are large reserves of illite in China. Illite 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 the use of illite as a sorbent to study the sorption properties of Th(IV) at different experimental conditions.

In this work, natrual illite sample is characterized by a variety of detection means, such as powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) SEM/EDS, and XPS. The effect of contact time, temperature, solid-to-liquid ratio, pH, ionic strength and foreign ions on Th(VI) sorption on natural illite is investigated using batch experiments. The sorption and desorption isotherms are measured. Study the sorption of Th(IV) at different temperatures and achieve the adsorption thermodynamic data (i.e., ΔG^0, ΔS^0, ΔH^0). Finally, discuss the sorption mechanisms of Th(IV) on natural illite.

2. EXPERIMENTAL

2.1 Materials

All chemicals and reagents used in this study are purchased as analytically pure and are used without any further purification. The natural micro-powder illite is supplied by Sushan Co. (Henan, China). It is treated with 5% hydrochloric acid for 24 h, and then followed by washing with distilled water until no chloride is detectable in supernatant with 0.01M $AgNO_3$. After the sample dried, it is crushed to pass through 160-mesh screen and is stored in glass bottles for further use.

2.2 Characterizations

The content of elements and composite was obtained by XRF and XRD(X-Strata920, Oxford, Shanghai). The pore structure parameters relating to surface area, pore volume and average pore size were measured from N_2 adsorption–desorption isotherms using a Micromeritics ASAP2020 instrument. Fourier transform infrared (FT-IR) spectroscopy was obtained in the wavenumber region of 4000–400cm^{-1} with a Nicolet IS10 spectrometer using KBr pellets. The surface morphologies and the elemental composition of samples were observed using the S-4800 field-emission scanning electron microscope with energy dispersive spectrometer (SEM-EDS, Oxford, Shanghai). XPS (Thermo, US) was used to measure the elemental composition and chemical state of the surface elements on the natural illite. The surface charge and point of zero charge of natural illite was obtained by titrations (Zhang *et aL*, 2016).

2.3 Batch Sorption Experiments

The sorption behavior of Th(IV) onto the sorbent is investigated by using batch technique in polyethylene centrifuge tubes sealed with screw-cap under ambient conditions. A stock solution of $Th(NO_3)_4$ is prepared by dissolving $Th(NO_3)_4 \cdot 6H_2O$ in Milli-Q water. The stock solutions of $NaNO_3$, Th(IV), and natural illite are added in the polyethylene centrifuge test tubes to achieve the desired concentration of different components. The pH values of the solution are adjusted by adding negligible volume of HNO_3 or NaOH solution. After the suspension is stirred, the solid and liquid phases are separated by centrifugation. The concentration of Th(IV) is analyzed by using a spectrophotometer at wavelength of 662nm by using Th(IV) arsenazo(III) complex. The sorption of Th(IV) on the test tube walls is neglected (Chen and Wang, 2007).

For desorption experiments, after centrifugation at the end of sorption experiments, two-thirds of the supernatant is pipetted out and the equal volume of background electrolyte solution with same pH is added. Then the mixture is shaken and centrifuged at the same conditions as in sorption experiments.

The amount of adsorbed Th(IV) is determined from the difference between the Th(IV) concentration in the aqueous before and after the sorption. The percent sorption (%) of Th(IV) from aqueous solution is calculated as follows:

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

where C_0 (mol/L) and C_e (mol/L) are the concentrations of Th(IV) at initial and equilibrium time, respectively. The sorption capacity (q_e, mol/g) of Th(IV) on natrual illite is calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

where V is the volume of the solution (L) and m is the mass of dry sorbent (g).

Conformity between experimental data and kinetic models and thermodynamic model was determined by the correlation coefficient (R^2) and the residual root mean square errors (RMSE) which can be written as follows (Yari *et aL*, 2015):

$$RMSE = \sqrt{\left(\frac{1}{n-1}\right)\sum_{i=1}^{n}\left(q_{i,\exp} - q_{i,cal}\right)^2} \qquad (3)$$

where $q_{i,cal}$ and $q_{i,exp}$ (mmol/g) are the calculated and the experimental values of the sorption capacity, respectively, and n is the number of data points.

3. RESULTS AND DISCUSSION

3.1 Characterizations

The N_2-BET surface area and the chemical components of the micro-powder as analyzed by X-ray fluorescence diffraction is listed in Table.1.

Table 1. *Chemical Composition of Natural Illite Sample (Wt%, not including C and H_2O)*

Components	Content (wt%)
SiO_2	63.74
Al_2O_3	18.40
K_2O	7.92
MgO	1.87
Fe_2O_3	7.36
CaO	1.11
Na_2O	0.05
Parameter	test data
BET surface area	21.97m^2/g
Pore volume	0.047ml/g
pore size	12.55nm

The XRD characterization of the natural illite is shown in Fig.1. The XRD peak shows the sample consists mainly of illite, with associated quartz, goethite, calcite and montmorillonite. From Table 1，the higher amount of Si in natural clay is due to the quartz content, which is supported by the XRD results (in Fig.1). The presence of relatively high concentration of Iron, Mg and Ca can be partly attributed to the presence of calcite and goethite, as indicated by XRD.

The FT-IR spectrum of natural illite sample is shown in Fig.2. According to the FTIR spectrum, the bands at 3,619 cm^{-1} and 3,629 cm^{-1} are assigned to the presence of the stretching vibration of Al–OH groups. The bend vibration of H_2O is observed at 1,635 cm^{-1}. The strong stretching vibration sorption band at 1,025 cm^{-1} corresponds to Si–O (stretching vibration). The bands at 538 and 479 cm^{-1} are

attributed to the bending vibration of Si–O groups (Giustetto *et aL*, 2005; Boyd *et aL*, 1988; Xu and Boyd, 1994; Potgieter *et aL*, 2006). Besides, it is noted that the bands of 801 cm^{-1} and 830 cm^{-1} are matched with Al/Mg/Fe-OH stretching, which only exists in natural illite FT-IR spectrum. It indicates that natural illite is mixed with some impurities that contain Mg or Fe element. This result is in conformity with Table.1.
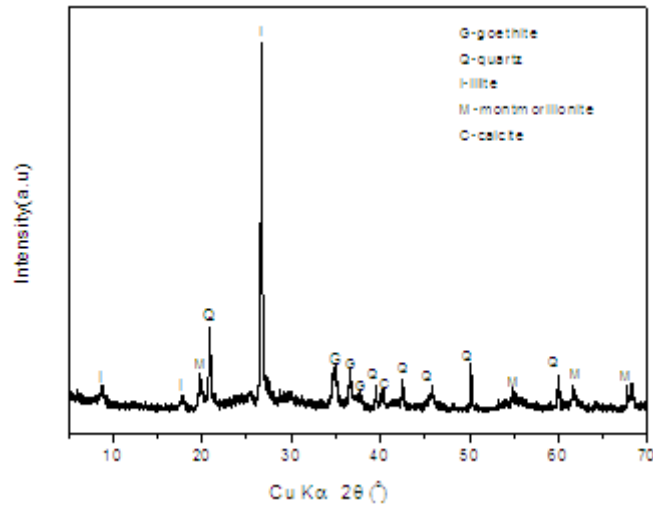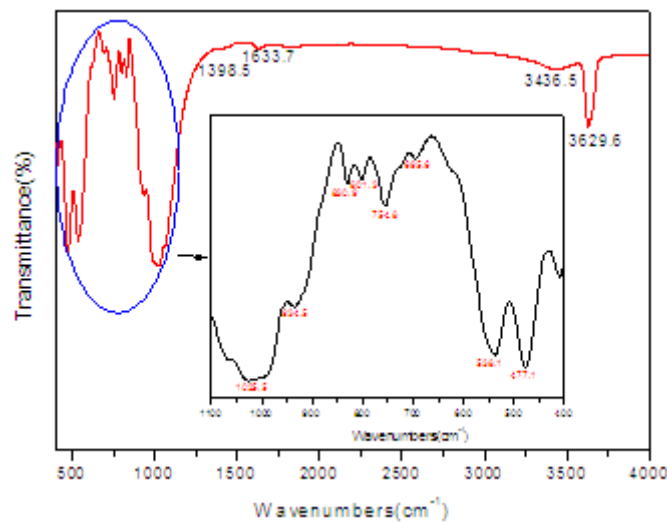

Fig. 1 *The XRD spectra of the natural illite*

Fig 2. *The FT-IR spectrum of natural illite*

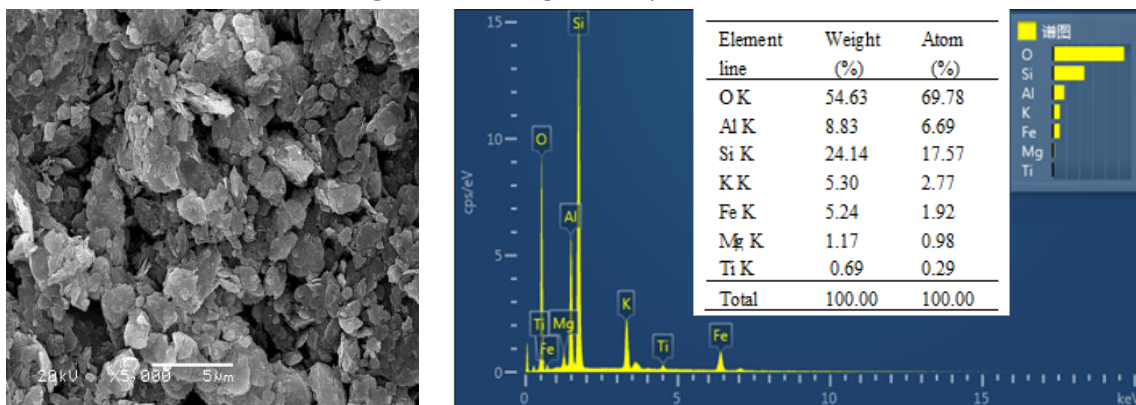| Element line	Weight (%)	Atom (%)
O K	54.63	69.78
Al K	8.83	6.69
Si K	24.14	17.57
K K	5.30	2.77
Fe K	5.24	1.92
Mg K	1.17	0.98
Ti K	0.69	0.29
Total	100.00	100.00

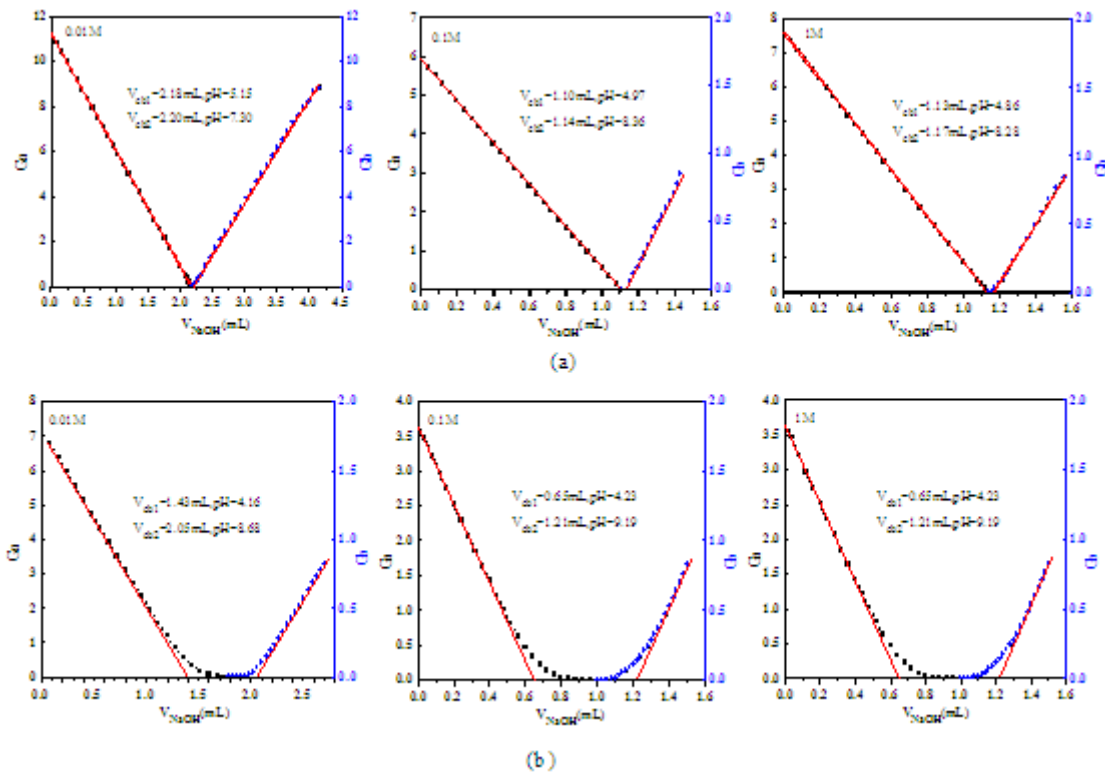**Fig 3.** *SEM/EDS of natural illite surface*

Fig.3 shows the SEM image of natural illite. It can be seen they were flat, but the surface of natural illite is rougher because of impurities, which might influence the surface properties of sorbent. It may increase the specific surface area and provide more active sites. This conclusion is conformed to the results of N$_2$-BET. EDS show the elements of natural illite surface, and the result is consistent with the result of X-ray fluorescence diffraction.

Potentiometric titration can be employed to determine the nature of the surface charge and to calculate the density of active sites(H_s) (liu *et aL*, 1999). The natural illite is characterized by potentiometric titration. The Gran function (G) is expressed as follows(Zhao *et aL*, 2007):

at acidic regime :
$$G_a = (V_0 + V_a + V_b) \times 10^{-pH} \times 100 \tag{4}$$

at alkaline regime:
$$G_b = (V_0 + V_a + V_b) \times 10^{-(13.8-pH)} \times 100 \tag{5}$$

where G_a and G_b are the Gran functions in the acidic and alkaline regimes of the titration, respectively. Meanwhile, V_0 (mL) denotes the initial solution volume, and V_b (mL) corresponds to the volume of NaOH added at the different titration points. The two equivalence points, V_{eb1} and V_{eb2}, which were obtained from linear regression analysis of the Gran plot's terminals, can be considered as the zero point and the end-point of the natural illites titration (seen Fig.4).

Fig 4. *Gran plots of natural illite in 0.01, 0.1 and 1.0 M NaNO₃ solutions at 20 ± 1 °C. (a) blank; (b)Natural illite.*

The surface site density of natural illite is calculated from Eq. (6) (Wagner *et aL*, 1979):

$$H_s = \frac{(V_{eb2} - V_{eb1})_{sample} \times C_b - (V_{eb2} - V_{eb1})_{blank} \times C_b}{m} (mol/g) \tag{6}$$

where C_b (mol/L) denotes the concentration of NaOH. The H_s values of illite in different ionic strength are listed in Table 2. It can be seen that the H_s values of natural illite becomes smaller as the ionic strength increases from 0.01M to 1.0M. This can predict the metal sorption on natural illite will significantly dependent on ionic strength. The TOTH refers to the concentration of protons consumed during the titration process. This value can be calculated from Eq. (7) (Wagner *et aL*, 1979)

$$TOTH = \frac{-(V_b - V_{eb1}) \times C_b}{V_0 + V_b} (mol/L) \tag{7}$$

Table 2. *H_s values of natural illite*

C $_{NaNO3}$ (mol/L)	0.01	0.1	1.0
Hs(mol/g)	1.20×10^{-4}	1.04×10^{-4}	8.99×10^{-5}

Got from the value of TOTH as a function of pH(seen in Fig.5), the pH$_{pzc}$ (point of zero charge) is measured to be 4.2 for natural illite, and the result is consistent with the result of previous study(Zhang *et aL*, 2016). This indicates that the surface of natural illite is likely neutral or positively charged at pH ≤ 4.2 and negatively charged at pH > 4.2.
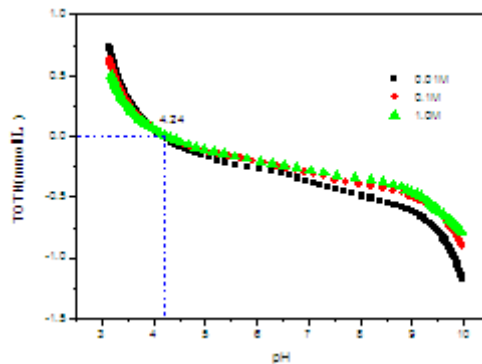

**Fig 5.** *The surface site relative distribution calculated from titration curve of the natural illite, T=25°C,I=0.01, 0.1, 1.0mol/L, m/V=5.0(g/l)*

3.2 Effect of solid-to-liquid (m/V) ratio

The influence of solid-to-liquid ratio (m/V) on Th(IV) sorption to natural illite is shown in Fig.6. As expected, a higher m/V is desirable for Th(IV) sorption on natural illite within the range 1–8 g/L. A probable explanation is that more sorption sites are available for Th(IV) sorption with increasing the content of natural illite (Asci *et aL*, 2007). However, the sorption of Th(IV) on natural illite arrived to the top quickly and kept stable with the m/V increasing. This phenomenon can be explained because the natural illite has more sorption sites than of pure illite in the same m/V and the sorbent concentration is more over the Th(IV) concentration(Zhang *et aL*, 2016). When the sorbent concentration is high, the sorbent cannot disperse well and thus reduces the effective sites of functional groups at illite surface and results in the sorption and complexation ability of natural illite decreases as the m/V increasing (Xu *et aL*, 2006). The m/V dependence is actually consistent with the prediction of the pseudo-second-order model in the kinetic estimation above. The distribution coefficient (K$_d$, L/g) is also plotted as a function of m/V in Fig.6. K$_d$ can be calculated from the concentration of Th(IV) in suspension (C$_0$) and in the supernatant liquid (C$_e$) according to Eq. (8) (Xu *et aL*, 2006):
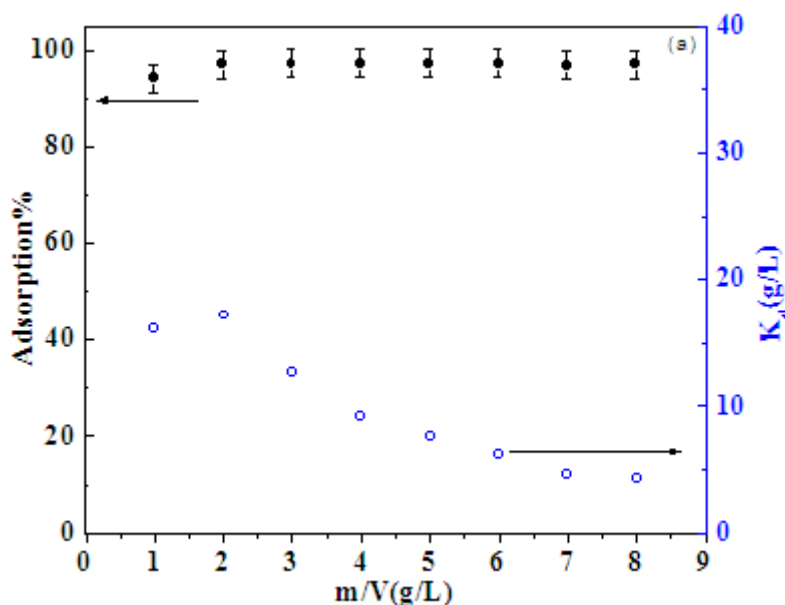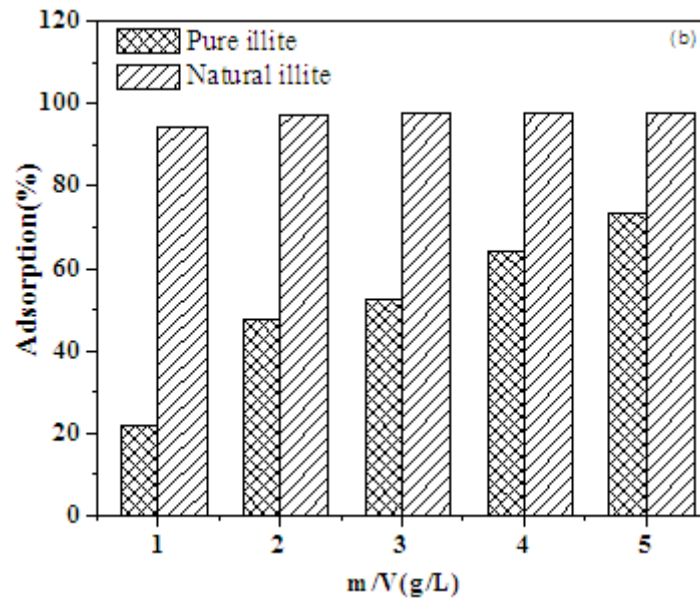
Fig. 6 *(a)The effect of m/V on the adsorption of Th(IV) on natural illite (b)comparison of percentage of Th(IV) adsorbed on pure illite and natural illite*

pH=3.50±0.03, *t*=20h, *I*=0.01M NaNO$_3$, T=25±2℃, $C_{Th(IV)}$=2.0×10^{-4}mol/L

$$K_d = \frac{(C_0 - C_{eq})V}{mC_{eq}} \tag{8}$$

where V is the volume of the suspension (L) and m is the mass of the natural illite(g). It should be noted that the value of K_d is weakly dependent on the ratio of m/V, which is consistent with the physicochemical properties of the K_d value. However, the value of K_d of natural illite is getting smaller gently, which has the same reason as the phenomenon of the sorption rate of natural illite.

3.3 Sorption Kinetics

The time-dependent experiment was conducted to evaluate the effect of contact time and understand the adsorption mechanism, especially the kinetic aspect. As can be seen from Fig.7(a), the sorption of Th(IV) was quick. The sorption achieved equilibration in less than 5h, and then the sorption of Th(IV) from solution to natural illite maintained level off with increasing contact time. In the following experiments, more than 20h was selected to make the sorption equilibration of Th(IV) on natural illite.
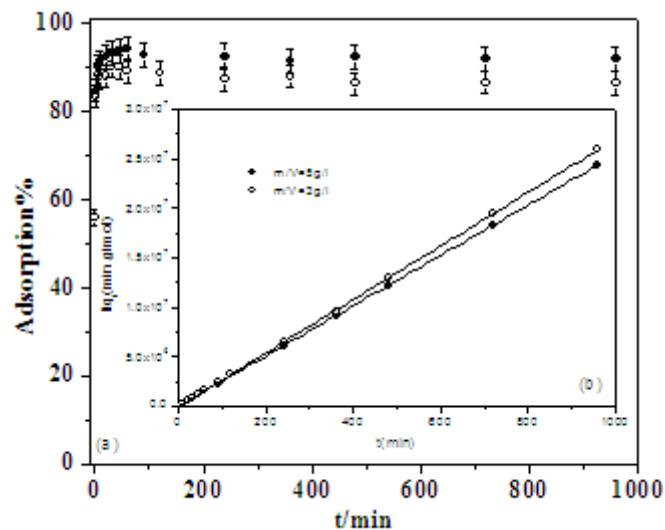
Fig 7. *(a) Kinetics of Th(IV) sorption onto the natural illite at 0.01 M ionic strength, pH=3.50±0.03, T=25±2 ℃, $C_{Th(IV)}$=2.0×10^{-4}mol/L, pH=4,*
(b) Pseudo-second-order kinetics of Th(IV) adsorption onto the natural illite

A suitable kinetics model can provide useful information in determining the underlying mechanism during the sorption process. To analyze the adsorption rate and mechanism of Th(IV) on illite, a pseudo-second-order rate equation was applied to simulate the kinetic sorption (Ho Y.S., 2006):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{9}$$

where k (gmol^{-1}min^{-1}) is the pseudo-second-order rate constant of adsorption, q_t (gmol^{-1})is the amount of Th(IV) adsorbed on illites at time t (h), and q_e (gmol^{-1}) is the equilibrium adsorption capacity. Linear plot feature of t/qt vs. t is shown in Fig.7(b). The k and q_e values at different m/V are calculated from the slope and intercept, respectively, and the results list in Table 3. A smaller RMSE and higher R^2 values indicated that the kinetic adsorption could be described by a pseudo-second-order rate equation well. The process of the Th(IV) sorption on illites may be chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate (Ho and Makay, 2000). A smaller RMSE and higher R^2 values indicate a better curve fitting (Keshtkar and Abbasizadeh, 2016; Yari et aL, 2015b).

Table 3. *The values of parameters obtained from the pseudo-second-order rate equations*

Pseudo-second-order model	m/V (g/L)	K (g/(mol·min))	q_e (mmol/g)	R^2	RMSE
$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$	5	2.85×10^4	0.0393	0.9999	0.0004
	3	1.99×10^4	0.0377	0.9998	0.0007

3.4 Effects of pH and Ionic Strength

Removal percent of Th(IV) from solution to natural illite as a function of pH values in 0.1 and 1M NaNO$_3$ solutions is shown in Fig.8(a). Sorption of Th(IV) occurs at low pH value and a sharp increase in sorption from 25% to 90% of the added Th(IV) concentration occurs over the pH range from 1 to 4. Then the sorption of Th(IV) on illite remains level with increasing pH value. The strongly pH-dependent sorption of Th(IV) on natural illite suggests that surface complexation contributes mainly to the sorption of Th(IV) on natural illite.(Wu et aL, 2007; Baeyens and Bradbury,1997)
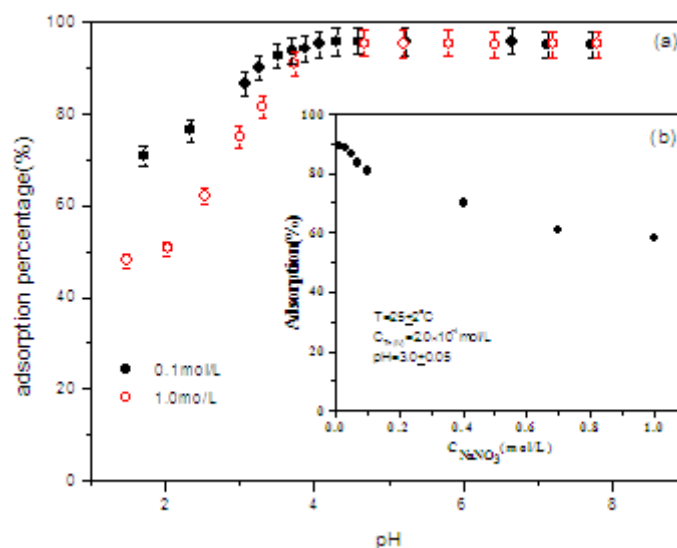
Fig 8. (a) Effect of pH on the adsorption of Th(IV) on natural illite.

(b) Effect of ionic strength on the adsorption of Th(IV) on natural illite

T=25$\pm$2℃, $C_{Th(IV)}$=2.0×10^{-4}mol/L, pH=3.0$\pm$0.03, m/V=5g/L, t=20h

From Fig.8(b), sorption of Th(IV) on natural illite is affected by the concentration of NaNO$_3$ strongly. This result is in conformity with the values of natural illite H$_s$. The sorption of Th(IV) decreases with increasing NaNO$_3$ concentration, which suggests that there is the strong competition between Na$^+$ and Th(IV) at the natural illite surface. It is well known that outer-sphere complexes and ion exchange can be can be affected by ionic strength, while inner-sphere complexes cannot be influenced by ionic

strength and be affected by pH(Pan *et aL,* 2011; Baeyens and Bradbury, 1997). Therefore, the results manifested ion exchange and outer-sphere complexes contribute to Th(IV) sorption on natural illite at low pH value. At high pH value, inner-sphere complexes and/or precipitation may dominate Th(IV) sorption on natural illite.

In general, surface complexation is influenced by pH values obviously, whereas ion exchange is influenced by ionic strength (Baeyens and Bradbury, 1997). The sorption mechanism of Th(IV) on natural illite is outer-sphere complexation or ion exchange (Yu *et aL*, 2007; Esmadi and Simm,1995) .

3.5 Influence of Foreign Ions

To investigate the influence of background electrolyte foreign cations, sorption of Th(IV) on natural illite were investigated in 0.1M $NaNO_3$, KNO_3 and $Mg(NO_3)_2$ solutions, respectively. Fig.9(a) indicates that the negative influence on the sorption of Th(IV) from strong to weak is $Mg(NO_3)_2 > KNO_3 > NaNO_3$ under the same pH values, and the influence is more obvious on the sorption on natural illite, which indicating that cations can alter the surface properties of natural illite and thus can affect the sorption of Th(IV) on natural illite. The sorption of Th(IV) is affected by K^+ since the sorption capability of K^+ is stronger than Na^+. The hydrated radii of K^+ is greater than of Na^+, hence the hydrated K^+ is easier to interact with the surface functional groups of natural illite. This results is similar to Th(IV) sorption on Na-bentonite(Pan *et aL*, 2011). Fig.9(a) also shows the effect of divalent cation (Mg^{2+}) on the sorption of Th(IV) on illite is stronger than Na^+ and K^+. The sorption of cation was decreasing with the increasing valence of competitive cation, because the increasing cation valence made the potential in the plane of sorption less negative at $pH<pH_{PZC}$(Harter and Naidu, 2001). The higher valent ions are much more easily and strongly adsorbed by natural illite, and the divalent cations would occupy twice sites more competitively by forming $(\equiv SO)_2$-Mg. This conclusion is similar to Th(IV) adsorbed on Na-bentonite(Pan *et aL*, 2011). Therefore, the ionic valence plays a more important role in the sorption process than ionic radius. In short, At pH<6, the sorption of Th(IV) on natural illite can be attributed to the exchange of Th(IV) with alkali metal cations or alkaline earth cations. One can also see that the sorption of Th(IV) on illite at pH>6 is not affected by competing cations, which may be due to the formation of surface precipitates at high pH values(Yu *et aL*, 2015).
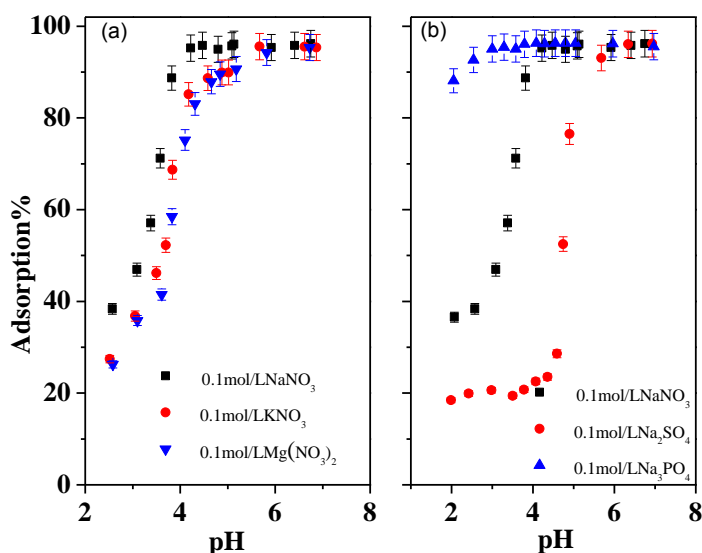

Fig.9 Effect of background electrolyte the adsorption of Th(IV) on natural illite,

(a) foreign cations (b) foreign anions. *T*=25±2℃,*C*$_{Th(IV)}$=2.0×10^{-4}mol/L,*m/V*=3g/L,*t*=20h

To investigate the influence of background electrolyte foreign anions, sorption of Th(IV) on natural illite were investigated in 0.1M $NaNO_3$, Na_2SO_4 and Na_3PO_4 solutions, respectively. The influences of anions on Th(IV) sorption are plotted in Fig.9(b). The sorption of Th(IV) is obviously enhanced in the presence of PO_4^{3-}, while inhibited in the presence of SO_4^{2-}. This can be interpreted by the fact that, phosphate ions are more easily to be sorbed to natural illite surface than sulfate ions. In the presence

of PO_4^{3-}, the ternary complexes of SO–Th–PO_4 and/or SO–PO_4–Th cause more Th(IV) ions to be sorbed(Pan *et aL*, 2011). Sulfate has less affinity to surface of clay and oxide comparing with phosphate (Weijden *et aL*, 1997). Therefore, residual sulfate ions in aqueous favorably form soluble binary complexes reducing Th(IV) sorption on natural illite.

In general, the effect of cations on sorption of Th(IV) may be attributed to competitive sorption, while anions attributed to the strong complex abilities with Th(IV) (Xu *et aL*, 2007; Chen and Wang, 2007).

3.6 Sorption Isotherm and Thermodynamic Data

Sorption isotherm experiments at different temperatures are performed and the results are shown in Fig.10. It is found that the sorption amount of Th(IV) by natural illite increased with increasing temperature, indicating that high temperatures favored Th(IV) sorption.

In order to obtain a better understanding of the Th(IV) sorption mechanism, the Langmuir, Freundlich and D–R sorption isotherms of Th(IV) at the three different temperatures are used to fit the experimental data, and the results are shown in Table 4, respectively. The relative parameters and the correlation coefficients calculated from Eqs.(10)–(14) are listed as follows (Chen *et aL*, 2007):

$$\text{Langmuir:} \qquad \frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \tag{10}$$

$$\text{Freundlich:} \qquad lgq_e = lgK_F + nlgC_e \tag{11}$$

$$\text{D-R:} \qquad lgq_e = lgq_{max} - \beta \varepsilon^2 \tag{12}$$

$$\varepsilon = -RTlg(1 + 1/C_e) \tag{13}$$

$$E = \frac{1}{\sqrt{2\beta}} \tag{14}$$

Table 4. *The parameters of Langmuir, Freundlich and D-R models*

Model	Parameters	T(K)		
		298.15	318.15	338.15
Langmuir	q_{max} (mmol/g)	0.0649	0.0731	0.1065
	K_L(L/mol)	137.29	129.49	91.84
	R^2	0.9991	0.9975	0.9934
	RMSE	0.0008	0.0015	0.0043
Freundlich	K_F(mol^{1-n}L^n/g)	4.19×10^{-4}	6.64×10^{-4}	7.04×10^{-3}
	n	0.18	0.21	0.38
	R^2	0.9482	0.9591	0.9721
	RMSE	0.0358	0.0318	0.0917
D-R	q_{max} (mmol/g)	0.1261	0.1593	0.4825
	E(kJ/mol)	14.35	14.18	13.09
	R^2	0.9682	0.9763	0.9791
	RMSE	0.0298	0.0276	0.0253

where q_{max}, the maximum sorption capacity, is the amount of Th(IV) at complete monolayer coverage (mol/g), K_L is the constant that relates to the heat of sorption (L/mol). K_F and *n* are represents the sorption capacity when Th(IV) equilibrium concentration equals to 1, and *n* represents the degree of dependence of sorption with equilibrium concentration. ε is the Polanyi potential, *R* is ideal gas constant, and *T* is the absolute temperature(K). The value of β is the activity coefficient related to mean sorption energy (mol^2/kJ^2). It is related with the adsorption mean free energy, E(kJ/mol), defined as the free energy change required to transfer one mole of ions from infinity in solution to the solid surfaces. The linear plots of Langmuir Freundlich and D–R equation representing Th(IV) sorption are shown in Fig.10.
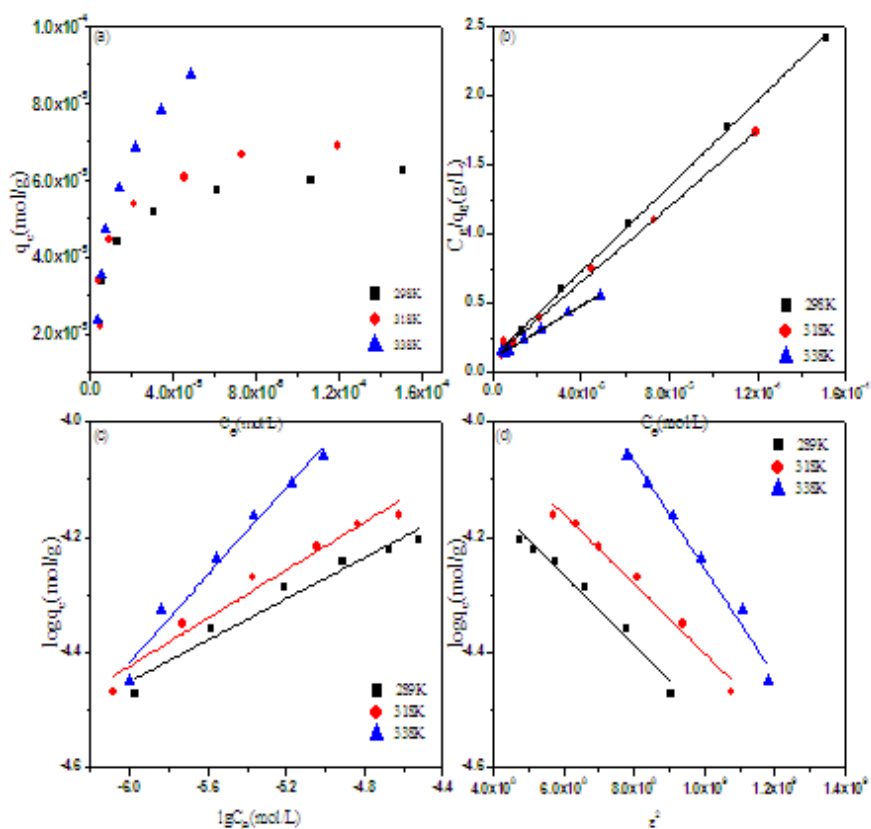
Fig 10. The effect of temperature on the adsorption adsorption isotherm of Th(IV) on natural illite. pH=3.5±0.03, m/V=5g/L, t=20h, I=0.01M NaNO$_3$.

(b)Langmuir, (c)Freundlich, (d) D–R

The higher correlation coefficients and a smaller RMSE indicate that the sorption can be fitted by the Langmuir model better than by the Freundlich and D–R models. From Langmuir model, the maximum sorption (q_{max}) increases with increasing temperature, which suggests that sorption of Th(IV) on illite increases with increasing temperature. Similar results are also found in D–R model. The maximum sorption of Th(IV) calculated from Langmuir model are about 10^{-5}~10^{-4}mol/g, and the results calculated by the two models are not an exact match maybe attributed to the different assumptions considered in the formulation of the isotherms. Adsorption mean free energy (E) shows that Th(IV) adsorption on the natural illite is chemical adsorption.

The thermodynamic parameters for Th(IV) sorption on natural illite can be calculated from the temperature dependent sorption isotherms. The relevant data (ΔG^0, ΔS^0, ΔH^0) are listed in Table 5. It is evident that the values of ΔH^0 are positive, *i.e.* endothermic. 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 increasing temperature indicates more efficient adsorption at higher temperature. The positive values of entropy change (ΔS^0) reflect the affinity of illite toward Th(IV) ions in aqueous solutions and may suggest some structure changes in the adsorbents(Fan *et aL*, 2012; Fan *et aL*, 2009).

Table 5. *The thermodynamic data of Th(IV) adsorption on natural illite*

T(K)	ΔG^0(kJ/mol)	ΔH^0(kJ/mol)	ΔS^0(J/mol·K)
298.15	-20.74	11.24	
318.15	-22.64	11.48	107.25
338.15	-25.03	11.24	

3.7 Adsorption and desorption of Th(IV) on natural illite

The desorption behavior is conducive to understand the interaction mechanism between thorium and natural illite. Sorption and desorption isotherms of Th(IV) on natural illite at 25±2℃ and 45±2℃ are shown in Fig.11(a)(b), respectively. The reversible process is complete desorption without any

interventions, while irreversible process indicates that complete desorption cannot occur without intervention(Xu *et aL*, 2016). For the sorption of Th(IV) on natural illite, the isotherm of desorption at different temperatures obviously overlaps that of sorption. The sorption process on natural illite was reversible process with no desorption hysteresis. The adsorbed Th(IV) on natural illite can be easily desorption. Moreover, from Fig.11a and b, high temperatures favor Th(IV) sorption because Th(IV) sorption increased with increasing temperatures, and indicating that the sorption process was endothermic.
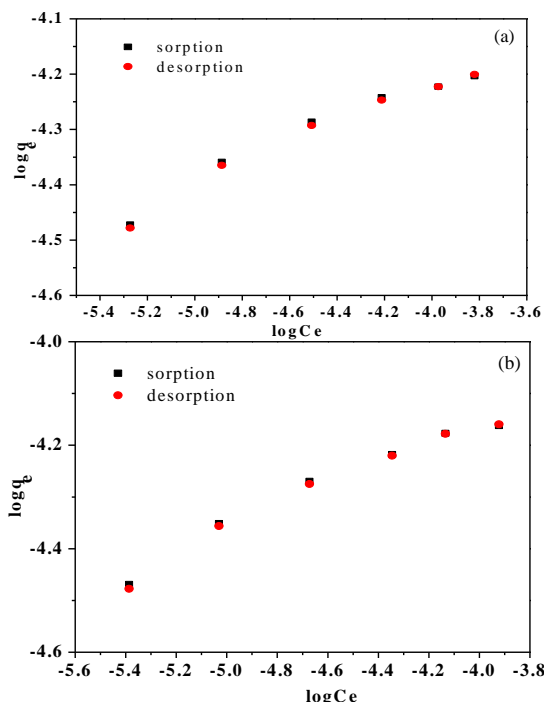
Fig 11. Adsorption and desorption isotherms of Th(IV) on natural illite.(a) T=25±2℃,

(b)45±2℃，pH=3.5±0.03，m/V=5g/L, t=24h, I=0.01mol/L NaNO$_3$.

3.8 X-ray photoelectron spectroscopy analysis

The XPS spectroscopy technique is used to determine the interaction mechanism between Th(IV) and natural illite. Fig.12 showed the total scans of XPS spectrum of illite before and after the adsorption experiments. The figure revealed that oxygen was the predominant element observed on the surface of illite. After adsorption, the peaks of Th are observed, indicating that Th(IV) was adsorbed on natural illite and the intensity of Th(IV) peak was higher in pH 5.5, which illustrates that the adsorption capacity of Th(IV) was larger than that of higher pH.
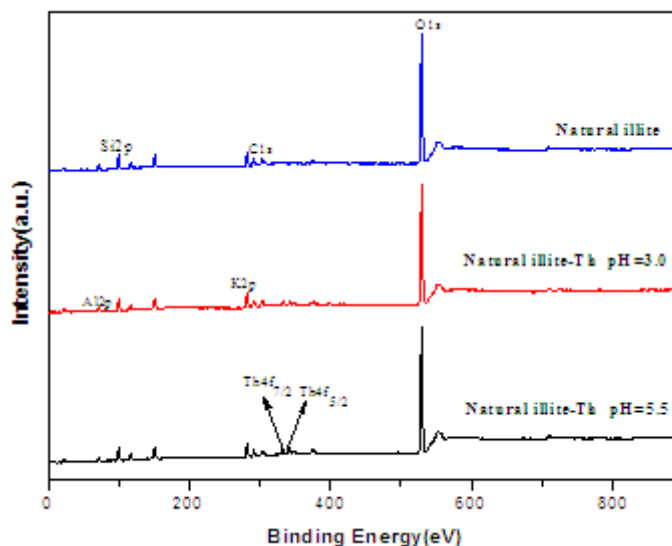
Fig 12. The total scans of XPS spectrum of natural illite before and after Th(IV) sorption.
T=25±2℃,C$_{Th(IV)}$=2.0×10^{-4}mol/L, m/V=5g/L ,t=20h

The high resolution of Th peaks is provided in Fig.13. Table 6 lists a summary of peak position of the XPS spectra. Th4f spectra before and after sorption could be characterized with two doublet-peaks Th $4f_{7/2}$ and Th $4f_{5/2}$ for Th 4f. As showed in Fig.13 (e), the peaks of binding energy for $Th(NO_3)_4$ are centered at 334.0 eV for Th $4f_{7/2}$ and 342.3 eV for Th $4f_{5/2}$, respectively. The peaks of binding energy for $Th(OH)_4$ are higher energy (334.5 eV for Th $4f_{7/2}$ and 343.8 eV for Th $4f_{5/2}$) in Fig.13(d). As can be seen in Fig.13 (b) and (c), The adsorbed Th(IV) of the binding energies of the Th4f are shifted to lower values (in Table 6) for $Th(NO_3)_4$. The main peaks position of Th4f in Fig.13 (b) (c) is different with (d) (e), indicating that Th(IV) adsorbed on natural illite is not the existing forms of $Th(NO_3)_4$ or $Th(OH)_4$. It shows Th(IV) adsorbed on natural illite is attributed to cation exchange or surface complexation, and Th strongly adsorbed on the natural illite inhibits the $Th(OH)_4$ precipitate generated on the natural illite. At the same time, the binding energy of Th $4f_{5/2}$ and Th $4f_{7/2}$ sorption of Th(IV) is lower in pH at 5.5 than pH 3, which indicates the existing forms of Th(IV) sorbed on illite are different under the two different experimental conditions.
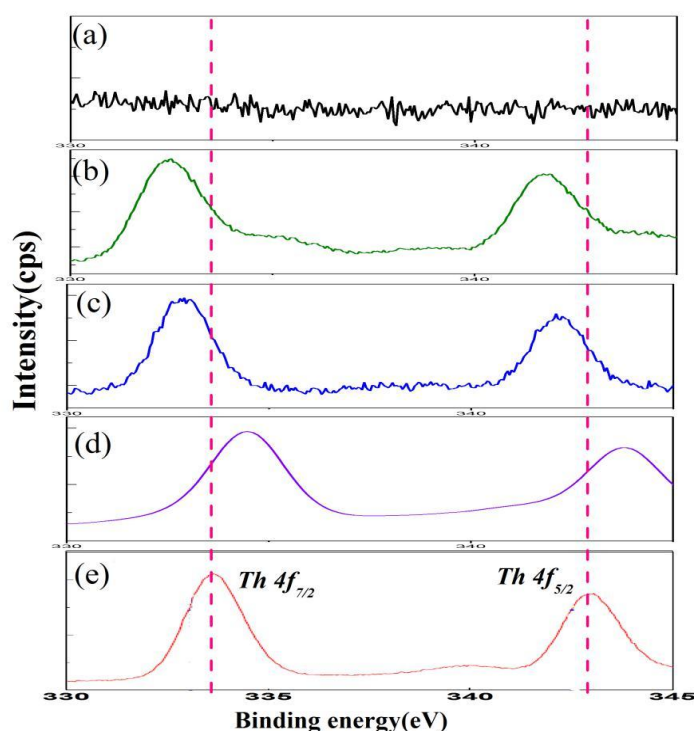
Fig 13. The high-resolution Th 4f spectra and XPS spectrum of the natural illite
(a) Natural illite; (b) pH=5.5; (c) pH=3.0; (d) $Th(OH)_4(s)$; (e) $Th(NO_3)_4$;
T=25$\pm$2℃, $C_{Th(IV)}$=2.0$\times$10^{-4}mol/L, m/V=5g/L, t=20h.

Table 6. *Th4f of binding energy*

	Th4f$_{7/2}$ (eV)	Th4f$_{5/2}$ (eV)
pH 5.5	332.4	341.1
pH 3.0	332.9	341.7
Th(OH)$_4$	334.5	343.8
Th(NO$_3$)$_4$	334.0	342.3

4. CONCLUSIONS

The results of Th(IV) sorption on natural illite at various experimental conditions, the conclusions can be drawn as follows: The sorption of Th(IV) can be described by a pseudo-second-order rate equation well. The sorption of Th(IV) is influenced by temperature obviously. Sorption of Th(IV) on natural illite is a spontaneous endothermic process, and can be described by Langmuir model. The sorption of Th(IV) on natural illite is also influenced by solid-to-liquid ratio and foreign ions obviously. Sorption of Th(IV) on natural illite is mainly dominated by outer-sphere complexation on the hydroxyl groups on the edge of natural illite sheet and ion exchange on the permanent negative charge of natural illite. Compared with pure illite, the sorption of Th(IV) on natural illite is much better under the same conditions.

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