Research paper

Adsorption behavior of Th(IV) onto illite: Effect of contact time, pH value, ionic strength, humic acid and temperature

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ABSTRACT

The adsorption experiments of Th(IV) on illite as a function of time, pH, ionic strength, temperature and humic acid (HA) were investigated using batch experiments. The results showed that adsorption of Th(IV) on illite was strongly dependent on contact time, pH, and temperature and independent on humic acid(HA). The Th(IV) adsorption on illite increases with increasing pH (pH < 4.5) and temperature, but decreases with increasing ionic strength at pH < 4.5. Th(IV) adsorption data were successfully described by the pseudo second-order kinetic model and the intraparticle diffusion equation. Langmuir adsorption isotherm model simulated the adsorption process better than Freundlich model. The thermodynamic parameters of enthalpy, entropy and free energy change were calculated and thermodynamic parameters revealed the spontaneity and exothermic nature of adsorption Th(IV) on illite. Th(IV) of adsorption mechanism on illite is outer-sphere surface complexation and ion exchange with Na^+/H^+ on illite at low pH, whereas inner-sphere surface complexation was the main adsorption mechanism at high pH.

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1. Introduction

With the deepening of the world energy crisis, nuclear power has been strongly developed. As a potential nuclear fuel, Thorium has been widely developed. The resulting in radioactive thorium pollutants, especially thorium and uranium smelting plant discharge of waste water and ore mining process in the tailings, the radioactive thorium may enter the biosphere with the water cycle. Once it enters the living bodies provoke the inner irradiation, and results in appearance of cancer (Humelnicu et al., 2006). Many approaches have been applied to remove Th(IV), such as precipitation, electrochemical treatment, chemical oxidation or reduction, ion exchange, and adsorption. Among these techniques, adsorption method is a cost-effective and widely used.

Clay minerals are among the most important natural sorbents for metal cations in soils and sediments due to their large specific surface area, negative surface charge, and reactive surface site hydroxyl groups (Smain and Aicha, 2009). Among natural mineral sorbents we mention bentonite, vermiculite, clinoptilolite, rectorite, zeolitic volcanic tuff, palygorskite, kaolin, illite, which act as a natural scavenger of pollutants by taking up cations or anions and no affecting the clay mineral structure (Humelnicu et al., 2006).

In last decades, adsorption of Th(IV) on different clay minerals as a function of pH, ionic strength, sorbate and humic substances have

been studied extensively (Chang et al., 2007; Xu et al., 2007; Fan et al., 2008a,b; Pan et al., 2011a,b). Many mechanisms have been postulated for Th(IV) adsorption, such as surface complexation (out-sphere and inner-sphere), cation exchange, physical sorption, chemisorption, precipitation. The result of the previous studies showed that adsorption of Th(IV) is strongly pH dependent and weakly(strongly) ionic strength dependent. Humic acid (HA), as natural organic material, is a chemically heterogeneous compound with lots of functional groups, such as carboxyl, phenol, amino, hydroxyl. HA can strong complexation ability with radionuclides in natural water. Previous works demonstrated that the functional groups of HA play the most important role to bind with both dissolved metal ions and clay surfaces (Xu et al., 2007; Fan et al., 2008a,b). However, the effect of HA on Th(IV) adsorption on clay illite as well as Th(IV) on HA-clay hydrids is scare.

Illite is 2:1 layer type typical clays: its structure consists of two tetrahedral sheets that sandwich an octahedral sheet and it is not expanding. Tetrahedral silicon is substituted by trivalent aluminum in tetrahedral layer of the illite sheet, and generated a negative charge, hydrated potassium ions is adsorbed in the interlayer region to maintain electro neutrality. But potassium ions in the interlayer are not available for exchange with other cations in solution, so only cations at the external surfaces are exchangeable (Kim et al., 2006; Missana et al., 2008; Cuevas et al., 2009). The structure is schematically represented in Fig. 1a (Konan et al., 2012). The cation exchange capacity of illite is smaller than that of smectite but higher than that of kaolinite, about 20–30 meq/100 g. Some researchers study the adsorption of As(V),

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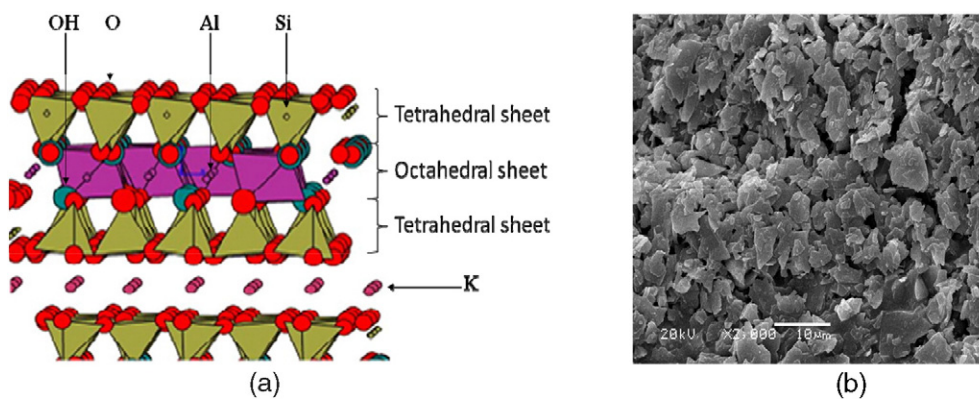E-mail address: hxzhang@lzu.edu.cn (Z. Hongxia).

Fig. 1. (a) Illite space structure as 3 layers 2:1 type (Konan et al., 2012) and (b) scanning electron microscope image of the illite.

U(VI), Ni(II), Cu(II), Zn(II), Pb(II), Sr(II) and Cs(I) on illite (Elzinga and Sparks, 2001; Echeverría et al., 2005; Turan et al., 2011; Wainipee et al., 2013; Hong et al., 2014; Cui et al., 2015).

Although illite has been studied extensively in the adsorption of metal ions and radionuclides, the detailed characterization of illite is still scare. There are large reserves of illite in South China. The specific property and large distribution of illite make it to be of great value, which has a quite important reference value in appraising uptake and diffusion of Th(IV) on illite. The main objective of the work is to investigate the effects of time, pH, ionic strength, temperature, and HA on Th(IV) adsorption and to investigate the sorption-desorption of thorium(IV) on illite. At the same time, the illite samples were characterized in detail using XRD, FTIR, EDS and acid-based titration. The experimental data are tested with adsorption model. Finally, the adsorption mechanism of Th(IV) on illite is discussed.

2. Experimental

2.1. Materials

All chemicals used were A.R. reagents and without further treatment. The illite sample was purchased from Henan Yongli Industry Group Co., Ltd. Henan, PR China. The sample was immersed with 0.1 mol/L HCl, then rinsed with distilled water until no chloride was detected, then was dried at 45 °C, and was ground to 200 mesh. The specific surface area of illite was determined to be 15.42 m^2/g using BET-N$_2$ adsorption method. Analysis of the illite by X-ray fluorescence is showed in Table SI-1. pHpzc (point of zero charge) value of the illite is 4.14. XRD and FTIR spectrum (in Supporting Information) illustrate the sample is illite. SEM of illite (Fig. 1b) show that the illite appeared as irregular lamellar crystals.

A stock solution of Th(NO$_3$)$_4$ was prepared by dissolving Th(NO$_3$)$_4$.5H$_2$O (A.R. grade) in distilled-deionized water. HA was bought from sigma-Aldrich. The main elements were: C 38.69%, H 3.34%, N 0.66% and O 57.84%. The stock solution of HA was prepared by dissolving HA in NaOH solution. pHpzc value of the HA is 4.16.

Acid and base titration and spectroscopic measurements about illite and HA sample are in Supporting Information.

2.2. Adsorption experiments

The stock suspension of illite(5 g/L or 10 g/L), NaNO$_3$, and Th(IV) stock solution were added in the polyethylene tubes sealed with screw-caps (8 ml capacity). The solution pH(2–8) was adjusted by adding negligible volumes of 0.01 M HNO$_3$ or 0.01 M NaOH to achieve the desired pH, then the mixture was shaken and centrifuged.

The concentration of Th(IV) was analyzed by spectrophotometry at wavelength 664 nm by using Th(IV) arsenazo(III) complex (Zhang et al., 2015). The detection limit of spectrophotometry to Th(IV)

solution is 1.64×10^{-6} mol/L. The adsorption of Th(IV) on the test tube wall was negligible. All the experimental data were the average of duplicate experiments. The relative errors of data were about 5%.

The sorption percent (ad$sorption\% = (C_0 − C_e) / C_0 \times 100\%$) and sorption amount ($q_e = (C_0 − C_e) \cdot V / m$) were then calculated from the initial Th(IV) concentration (C_0), the final Th(IV) concentration (C_e), the illite mass (m) and the suspension volume (V).

For desorption experiment, after centrifugation at the end of adsorption experiments, half of the supernatant was pipetted and the equal volume of electrolyte solution with same pH was added. The mixture was shaken and centrifuged at the same conditions as in adsorption experiments. (Zhang et al., 2015).

For FT-IR, XRD and EDS spectroscopy, the samples were filtered and washed three times with ethanol, then dried at 50 °C for 24 h.

3. Results and discussion

3.1. Adsorption kinetics

When pH = 3.00 ± 0.05, the adsorption kinetics of Th(IV) on illite at different solid-liquid, reaction temperatures and initial concentrations were investigated (Fig. 2), respectively. Solid–liquid (m/V) is an important parameter because it determines the capacity of an adsorbent for a given concentration of adsorbate. As shown in Fig. 2(a), (b), the adsorption percentage of Th(IV) onto illite increased with m/V increasing, while adsorption capacity of Th(IV) decreased with m/V increasing. The adsorption percentage of Th(IV) was 51% for 10 g/L and 29% for 5 g/L while the adsorption capacity of Th(IV) was 9.00×10^{-6} mol/g for 10 g/L and 1.12×10^{-5} mol/g for 5 g/L at equilibrium. This can explain the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions.

The effect of temperature on Th(IV) adsorption kinetics onto illite showed in Fig. 2(c), (d). The adsorption equilibrium time was about 30 min at 318 K, about 70 min at 308 K and about 100 min at 298 K. This was due to the higher rate of diffusion of Th(IV) onto illite surface at higher temperature. The adsorption percentage and capacity of Th(IV) onto illite increased with temperature rising. The adsorption percentage was 51% at 298 K, 59% at 308 K, 64% at 318 K, and adsorption capacity 9.00×10^{-6} mol/g at 298 K, 1.02×10^{-6} mol/g at 308 K, 1.21×10^{-5} mol/g at 318 K. This was due to the easier diffusion of Th(IV) onto illite surface at higher temperature.

The initial Th(IV) concentration has a pronounced effect on the kinetics of Th(IV) adsorption onto illite. The adsorptive equilibrium time increased with increasing initial concentrations of Th(IV) (30 min, 90 min). Additionally, an increase in the initial Th(IV) concentration leaded to an increase(3.76×10^{-6} mol/g–9.00×10^{-6} mol/g) in the adsorption capacity of Th(IV) on illite while the adsorption percentage (85%–51%) decrease. This was due to the adsorbent of adsorption site is not saturated at low concentration. Additionally, this was due to the