Research paper

Competitive adsorption of U(VI) and Co(II) on montmorillonite: A batch and spectroscopic approach

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ABSTRACT

The competitive adsorption of U(VI) and Co(II) on montmorillonite (Mt) was investigated by batch and spectroscopic techniques. The batch experiments indicated that competitive adsorption of U(VI) and Co(II) on Mt decreased with increasing ionic strength at low pH conditions, whereas no effect of ionic strength was observed at high pH, indicating that the outer-sphere and inner-sphere surface complexation dominated the competitive adsorption of U(VI) and Co(II) at low and high pH, respectively. In the binary-solute systems, Co(II) slightly inhibited U(VI) adsorption at low pH, whereas no effect of Co(II) on U(VI) adsorption was observed at high pH. The adsorption kinetics of U(VI) and Co(II) on Mt at single-solute systems were both well described by pseudo-second-order kinetic model due to the higher correlation coefficient ($R^2 > 0.9999$). The adsorption isotherms of U(VI) on Mt can be satisfactorily fitted by Freundlich model, while Langmuir model gave the better fits for Co(II) adsorption. The maximum adsorption capacities of U(VI) and Co(II) on Mt calculated from Langmuir model were 4.57 and 6.92 mg·g^{-1} at pH 5.0 and 323 K, respectively. According to XPS analysis, hydroxyl groups of Mt were responsible for the competitive adsorption of U(VI) and Co(II). The thermodynamic parameters suggested that both the adsorption of U(VI) and Co(II) on Mt were spontaneous and endothermic processes. These observations are crucial for understanding the fate and transport of radionuclides on the clay mineral in the natural environment.

1. Introduction

The plenty of radioactive wastes are generated with the rapid development of the safe production of nuclear energy, which may severely influence the environment diversity and human health (Sun et al., 2011). Uranium as a common radionuclide contaminant has been extensively employed on nuclear material production sites and nuclear industry, which primarily exists in the oxidized (U(VI)) and reduced (U(IV)) states in (sub)-surface environments(Sun et al., 2012). Meanwhile, ^{60}Co as a typical radionuclide was derived from pressurized water nuclear power reactors, radiotherapy of cancer and tumor (H et al., 2007). It is demonstrated that U(VI) can directly damage biological organization or produce reactive species (free radicals) that can subsequently react with bio-molecular result in mangy diseases, whereas radioactive ^{60}Co can seriously damage human blood cells and result in hematological diseases such as aplastic anemia, leukemia, and even death (Zou

et al., 2017). Therefore, the adsorption of long-lived radioactive U (VI) and Co(II) from nuclear waste solutions are becoming increasingly urgent issues in the world. In recent years, the adsorption of U (VI) and Co (II) on a variety of adsorbents in single-solute system had been extensively studied such as metal (hydr)oxides (Ding et al., 2015a, 2015b; Li et al., 2017; Liu et al., 2017), carbon-based nanoparticles (Ding et al., 2014; Sun et al., 2017; Sun et al., 2016a) and clay minerals (Karaa et al., 2003; Misaelides et al., 1995; Sun et al., 2014a). In these studies, the effect of water chemistries on radionuclide adsorption was elucidated by batch techniques. Sun et al. demonstrated that the adsorption of U(VI) on sericite in the presence of *Bacillus subtilis* increased with increasing CO_2 contents at pH < 6.0 due to the electrostatic attraction between positively charged U(VI) species and negative charged surface of adsorbents (Sun et al., 2016b). Lu et al. based on surface complexation modeling investigated that the adsorption of U(VI) on a novel magnesium silicate/diatomiteat pH < 4.0 and pH > 4.5 was

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attributed to cation exchange and inner-sphere surface complexation (Lu et al., 2017b). Jin et al. found that theadsorption of Co(II) on graphene oxide was outer-sphere surface complexation/ion exchange at pH < 7, whereas the inner-sphere surface complexation was observed at pH 7–9 (Jin et al., 2014). However, multiple radionuclides co-exist and may mutual affect radionuclide adsorption behavior in real wastewater systems (Ding et al., 2016). Therefore, it is imperative to investigate the competitive adsorption of radionuclides under multi-solute systems. Šljivić-Ivanović et al. found the significant decrease of Sr(II) adsorption on oxides and aluminosilite in the presence of co-exisiting Co(II) (Šljivić-Ivanović et al., 2015). Cheng et al. also found that decreased adsorption of Sr(II) on graphene oxides was observed at U(VI) concentration < 0.2 mmol·L^{-1}, whereas the Sr(II) adsorption significantly increased with increasing U(VI) concentration due to the formation of new available adsorption sites provided by U(VI) co-precipitates according to EXAFS analysis (Cheng et al., 2017). However, few studies has been paid to the competitive adsorption mechanism of U(VI) and Co(II) on montmorillonite by batch and spectroscopic techniques.

Owing to the high cation exchange capacities, low-cost and ubiquitous availability, montmorillonite has also been extensively investigated as adsorbent (He et al., 2006; Yuan et al., 2009), including the adsorption of radionuclides. Ma et al. demonstrated competitive adsorption of Co(II), Sr(II) and Cs(I) on phosphate-modified montmorillonite by surface complexation (Ma et al., 2011). Mahmoud et al. reported the competitive adsorption of ^{134}Cs(I), ^{60}Co(II) and $^{152+154}$Eu(III) on sepiolite and demonstrated that ^{134}Cs(I) and $^{152+154}$Eu(III) were mainly removed by outer-sphere complexation while the main adsorption mechanism of ^{60}Co(II) was inner-sphere surface complexation (Mahmoud et al., 2017). Recently, it is demonstrated that the adsorption of U(VI) at high pH conditions were strongly influenced by Ca(II) ions (Dong and Brooks, 2006; Fox et al., 2006; Richter et al., 2016; Zhang et al., 2015). Meleshyn et al. investigated that the adsorption of U(VI) on Ca-bentonites was significantly lower (a factor of 2–3 in comparison) than that of Na-bentonites (Meleshyn et al., 2009). Therefore, more studies regarding the effect of Ca(II) on U(VI) adsorption at water-mineral interface are needed to accurately predict the fate and transport of radionuclides in natural environments.

The intentions of this study were (1) to characterize morphology and the oxygenated functional groups of Ca-montmorillonite (Mt) using Powder X-ray diffraction (XRD), scanning electron microscopy (SEM), zeta potentials and X-ray photoelectron spectroscopy (XPS) techniques; (2) to investigate the effect of reaction time, pH, ionic strength and initial concentration on the competitive adsorption of U(VI) and Co(II) onto Mt in binary systems; (3) to explore the interaction of U(VI) and Co(II) onto Mt using XPS and FT-IR techniques. The competitive adsorption of radionuclides on clay minerals changes the physical-chemical behaviors of radionuclides and controls the migration, mobility and bioavailability of radionuclides in the environment. Therefore, the highlight of this study is to evaluate the fate and transport of radionuclides in the natural environment.

2. Experimental section

2.1. Preparation and characterization

Mt used in this study was collected from in Inner Mongolia, China. Mt was purified using a conventional sedimentation method and then dried at 60 °C overnight. The stock U(VI) solution (0.1 mmol·L^{-1}) was prepared by dissolving uranium nitrate (UO$_2$(NO$_3$)$_2$·6H$_2$O, spectrographic purity, Sigma-Aldrich) with Milli-Q water. Co(II) stock solution at 60.0 mg·L^{-1} was prepared by the dissolution and then dilution of Co(NO$_3$)$_2$(purity 99.99%, Sigma-Aldrich) with Milli-Q water. All chemicals using in this study were analytical-grade, and all the solutions were prepared with Milli-Q water. The surface morphology and chemical composition of Mt were characterized by SEM (2100F microscope) with

an energy dispersive X-ray facility and XRF (Shimadzu-1800), respectively. The identification and surface functional groups of Mt were recorded by XRD (D/max-RD diffractometer) and FT-IR (VERTEX-70Perkin-Elmer 100 spectrometer, USA) in KBr pellet method (0.2% to 1% of the sample in KBr), respectively. The XRD patterns were obtained with a Cu Kα radiation at scan rate of 5 min^{-1} with 0.2° divergence slit size generated at 40 kV and 30 mA. Phase identification was carried out and compared with the Joint Committee of Powder Diffraction Standards (JCPDS) database. The specific surface area of Mt was measured by 13-point BET-nitrogen isotherms with a Novawin 3000e Surface area and Pore size Analyzer. Briefly, 0.15 g Mt was out-gassed at 300 °C for 24 h before N$_2$ adsorption-desorption. XPS analysis was performed using a Thermo Scientific K-Alpha instrument equipped with an Al Kα source (10 mA, 14 kV). Zeta potentials of Mt were determined by the Nano-ZS Zeta sizer in electrophoretic light scattering mode (Malvern Instruments Ltd., Worcestershire, UK) for dilute particle dispersions.

2.2. Batch adsorption experiments

Batch adsorption experiments were carried out with 1 g·L^{-1} Mt and 10 mg·L^{-1} radionuclide under ambient condition in the presence of 0.001 mol·L^{-1} NaCl solutions. For competitive adsorption, the initial concentration of each radionuclide in multi-solute systems was the same as that in single-solute systems. For pH-dependent experiments, the pH values were adjusted to be in the range of 2.0–10.0 ± 0.1 for single- and binary-solute systems by adding the negligible volume of 0.01–1.00 mol·L^{-1} NaOH and HNO$_3$ solution. In order to close the pH values of natural environment and to avoid the precipitation at alkaline pH, all the experiments were conducted at pH 5.0 ± 0.1 unless specified. The adsorption isotherms of U(VI) and Co(II) were investigated at concentration ranging from 0.1 to 10.0 mg·L^{-1}. Then dispersions were shaken for 24 h to reach adsorption equilibrium. Based on adsorption kinetics, 24 h was determined to be adequate time for equilibration. After equilibrium, the solid phases were separated from liquid phases by centrifugation at 9500 rpm for 15 min, and then the supernatant was poured into a syringe and was filtered through a 0.22-μm membrane. The Mt-free experiments were also conducted under the same experimental conditions to eliminate the effect of tube walls. The concentration of U(VI) and Co(II) in supernatant was analyzed by liquid scintillation counting on a Packard 3100 TR/AB liquid scintillation analyzer (Perkin-Elmer) with the scintillation cocktail (Ultima Gold AB, Packard) and flame atomic absorption spectrometry(AAS6300C, Shimadu), respectively. The adsorption percentage (%) and adsorption capacity (q$_e$) can be expressed as Eqs. (1) and (2), respectively:

$$Adsorption(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

$$q_e = \frac{C_0 - C_e}{C_0} \times V \tag{2}$$

where C$_0$ (mg·L^{-1}) and C$_e$ (mg·L^{-1}) were initial concentration and the equilibrium concentration, respectively. m (g) and V (mL) were the mass of Mt and the volume of the dispersions, respectively. All experimental data were obtained by the averaging triplicate determinations and the relative errors were within 5% (Sun et al., 2016b).

3. Results and discussion

3.1. Characterization

The mineralogy of Mt was identified by XRD (Fig. 1A). The main diffraction peaks at 2θ = 5.84, 17.18, 19.86, 29.5, 34.84, 54.38, 61.94° corresponded to (001), (003), (100), (005), (006), (210), (0010) planes of montmorillonite, respectively (Schlautman and Morgan, 1994). However, the peaks at 2θ = 26.70° could be attributed to the (011)