Research paper

Adsorption of uranyl ions on kaolinite, montmorillonite, humic acid and composite clay material

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ABSTRACT

Adsorption of uranyl ions onto kaolinite, montmorillonite, humic acid and composite clay material (both clays and humic acid) was studied by measuring the system response to clay suspensions (pre-equilibrated with or without uranyl) and to perturbations of the solution chemistry. Adsorption behavior of selected materials under the frame of batch experiments was tested at high uranyl concentrations (6–1170 μg/mL; 2.5×10^{-2} to 4.9 μM), whereas that under flow through continuous stirred reactor experiments was tested at low concentrations (1.00×10^{-4} to 1.18×10^{-4} M). Both experiments were developed at pH 4.5 and ionic strength 0.2 mM. The adsorption experiments follow a Langmuir isotherm model with a good correlation coefficient ($R^2 > 0.97$). The calculated amount of adsorbed and desorbed uranyl was carried out by numeric integration of the experimental data, whereas the desorption rates were determined from the breakthrough curve experiments. Kaolinite with highly disordered structure adsorbed less uranyl (3.86×10^{-6} mol/g) than well-ordered kaolinite (1.76×10^{-5} mol/g). Higher amount of uranyl was adsorbed by montmorillonite (3.60×10^{-5} mol/g) and only half of adsorbed amount was desorbed (1.85×10^{-5} mol/g). The molecular interactions between kaolinite, montmorillonite, humic acid, composite material and saturated uranyl ion solutions were studied by molecular fluorescence, infrared and X-ray photoelectron spectroscopy. The Stern–Volmer constant obtained for montmorillonite (2.6×10^3 M^{-1}) is higher than for kaolinite (0.3×10^3 M^{-1}). Molecular vibrations of Si–O stretching and Al–OH bending related to hydroxylated groups ($\equiv$SiOH or $\equiv$AlOH) of kaolinite and montmorillonite show structural changes when uranyl ions are adsorbed. X-ray photoelectron spectroscopy shows that the U $4f_{7/2}$ core level signals occur at 380.5 eV in either kaolinite or montmorillonite that resulted from the interaction of aluminol surface sites with the $(UO_2)_3(OH)_5^+$.

1. Introduction

Clay minerals have been used for a plethora of applications due to their large adsorption capacity and swelling characteristics in aqueous suspensions (van Olphen, 1977). Also, their cation exchange capacity and adsorptive affinity for organic and inorganic ions make them candidates for use in decontamination and disposal of high-level heavy metal wastes. Among the actinides, uranium (U) is of special concern due to its radiotoxicity, migration and exposure paths in the environment.

The most stable valence of U under oxidizing geochemical conditions and acidic aqueous solutions is U(VI), where it occurs as uranyl (UO_2^{2+}) ions and at higher pH hydrolyzes to form monomers, dimers, and trimers (Grenthe et al., 1992). The pH dependent adsorption behavior is similar to other metal oxides with a cationic adsorption edge

at pH 5 to 6 and an additional anionic adsorption edge around pH 8 in systems equilibrated with atmospheric CO_2 (Chisholm-Brause et al., 2001). Despite the importance of this mechanism, there is a limited knowledge about the interactions between UO_2^{2+} ions and clay mineral surfaces (Hudson et al., 1999).

The mobility of UO_2^{2+} ions in environmental soils is determined by their interactions with minerals (i.e. clay minerals, Al-, Fe-oxyhydroxides). Many experimental clay adsorption studies focused on the interaction of actinides (i.e. UO_2^{2+} ions) with high surface area materials proposed as potential adsorbent materials either in the pure clay minerals such as kaolinite (Guerra et al., 2010; Křepelová et al., 2006; Payne et al., 2004; Samadfam et al., 2000), montmorillonite (Catalano and Brown, 2005; Chisholm-Brause et al., 2001; Hyun et al., 2001; Kowal-Fouchard et al., 2004; McKinley et al., 1995; Pabalan and Turner, 1997; Schlegel and Descontes, 2009; Tsunashima et al., 1981), di-tri-smectite (Bauer et al., 2001; Giaquinta et al., 1997; Korichi and Bensmaili, 2009), beidellite (Greathouse and Cygan, 2006), biotite

(Lee et al., 2009), halloysite (Kilislioglu and Bilgin, 2002), or clay rocks such as bentonite (Olguin et al., 1997) and opalinus clay (Joseph et al., 2011; Pekala et al., 2009).

Several experimental studies reported the UO_2^{2+} ions' (beyond 10^{-7} M) adsorption onto clay minerals in the presence of humic acid, which favors the increases of the sorption of the UO_2^{2+} onto clay minerals (Ivanov et al., 2012; Kepelov et al., 2007; Křepelová et al., 2006, 2008; Monsallier and Choppin, 2003; Sachs and Bernhard, 2008).

Kaolinite, montmorillonite, humic acid and a composite material (kaolinite, montmorillonite and humic acid) were selected in this work for the UO_2^{2+} ion adsorption experiments as a means of effecting the removal of U from surface waters. Both clays are widely employed as a reference for clay minerals due to their relative abundance in many soils, low cost, relative high surface area, negative surface charge, surface interaction with cations and, an additional uptake mechanism by interlayer adsorption or fixation in smectite structure. Thus, clay materials act as main sorbents for tri- and hexavalent actinides and may also serve as environmental protection of a nuclear waste repository.

The main goal of this work is to evaluate the UO_2^{2+} sorption onto kaolinite, montmorillonite, humic acid, and a composite material (clays and humic acid) under different experimental conditions and to improve the understanding of the UO_2^{2+} sorption mechanism. Experiments were carried out with UO_2^{2+} solutions whose concentrations for batch experiments ranged from 6 to 1170 µg/L (2.5×10^{-2} to 4.9 µM) and for the flow-through continuous reactor experiments from 1.00×10^{-4} to 1.18×10^{-4} M. A continuously stirred flow-through reactor was used to facilitate the intensive pre-washing and good preconditioning of clays for the appropriate control of the chemical conditions imposed during our experiments (Grolimund et al., 1995). Sorption experiments were also coupled with spectroscopic experiments, in order to identify the molecular vibration changes of silanol and aluminol sites in the presence of UO_2^{2+} and the possible UO_2^{2+} species adsorbed onto clays or precipitated phases as well.

2. Materials and analytic techniques

2.1. Materials

Kaolinite, montmorillonite and sapropel from Portuguese occurrences (Ovar district, Porto Santo Island, Madeira Arq., estuarine of Sado River), and a composite material constituted by a mixture of kaolinite (60%), smectite (30%) and humic acid (10%) were used as selected materials for the adsorption experiments.

The <2 µm clay fractions were extracted by sedimentation from raw kaolin and bentonite rocks and then, used for adsorption experiments. Both kaolinite samples (SVP 7 and SVP 44) previously characterized (Bobos and Gomes, 1998; Bobos et al., 2001) were selected for adsorption experiments to verify whether the order–disorder or defect structure may influence the adsorption capacity. The sample PS 1 corresponds to Ca-montmorillonite. Humic acid extracted from sapropel (unconsolidated sedimentary rock rich in bituminous substance and poor in cellulosic material) was isolated by a procedure recommended by the International Humic Substances Society (IHSS) as described in literature (Esteves da Silva et al., 1996).

2.2. Experimental

2.2.1. Batch and kinetic adsorption experiments

Continental surface waters may contain 0.1 to 500 µg/L U (4.2×10^{-4}–2.1 µM) (Kim, 1986), whereas the groundwaters in the vicinity of U mill tailings may reach 707 µg/L U (2.97 µM) (Junghans and Helling, 1998). To test the maximum adsorption capacity of the selected clay minerals and composite material, the UO_2^{2+} concentrations used for batch experiments ranged from 6 to 1170 µg/mL (2.5×10^{-2} to 4.9 µM) (Table 1). Uranyl acetate of analytical grade was used as source of U(VI). Equilibrium adsorption isotherms were carried out by adding 10 µL of 0.25, 0.50, 0,75, 1, 2, 3 and 5 mM of UO_2^{2+} ions solutions to 0.25 g clay samples (in triplicate) in 50 mL polypropylene centrifuge tubes at a pH 4.5. Suspensions were shaken for 48 h, centrifuged, and vacuum filtered through 0.45 µm cellulose nitrate filters. The filtrates were preserved by adding HNO_3 (65%) and stored at 4 °C prior to chemical analysis by inductively coupled plasma-mass spectrometry (ICP-MS). The UO_2^{2+} ions retained by the solid phase were obtained by difference between the initial and remaining concentration in the supernatant.

The equilibrium adsorption isotherm data of UO_2^{2+} were analyzed using the linear Langmuir expression (Eq. 1):

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C}{Q_O} \qquad (1)$$

where q_e is the amount of UO_2^{2+} taken up when the equilibrium concentration of UO_2^{2+} ions in solution is C_e. The Q_o is the saturated adsorption capacity (monolayer capacity) or maximum adsorption capacity determined by the number of reactive surface adsorption sites ($Q_o = 1/m$; m = slope), and b is the Langmuir constant, the affinity of the adsorbate for the surface, related to free energy adsorption. The Q_o of composite material was calculated taking into account the percentual participation of each clay mineral and humic acid [$Q_{o(composite)} = 0.6 \times Q_{o(Kaolinite)} + 0.3 \times Q_{o(Smectite)} + 0.1 \times Q_{o(HA)}$].

The essential feature of Langmuir isotherm is also expressed in terms of a dimension-less factor called separation factor or equilibrium parameter (R_L), defined by Eq. (2) of Weber and Chakkravorti (1974):

$$R_L = 1/(1 + b\, C_i) \qquad (2)$$

where C_i is the initial concentration of UO_2^{2+} and b is the Langmuir constant.

Sorption kinetic studies of UO_2^{2+} ions (0.1 mM) onto kaolinite, montmorillonite, humic acid and composite material were carried out using a continuously stirred flow-through reactor loaded with 0.58 g of clays (13 g/L) in the size range of 0.4–20 µm. Input solution flows through 0.2 µm membranes at room temperature with a flow rate of 0.8 mL/min using a peristaltic pump for 18–20 h from a reservoir into the reactor. Outflow solutions were collected at different times for ICP-MS analysis.

The system was previously preconditioned with $NaCH_3COO$ (pH 4.7) until reaching an approximately constant pH in the outflow solution. The UO_2^{2+} solution was pumped into the reactor afterwards, ideally until the clayey system reaches saturation (inflow and outflow solutions with the same UO_2^{2+} concentration). After this step, the original $NaCH_3COO$

Table 1
Chemical compositions, cation exchange capacity, surface area and Langmuir relationships of clay minerals and composite material used for adsorption experiments.

Samples	SiO_2 (%)	Al_2O_3 (%)	FeO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	S_{BET} (m²/g)	CEC (mmol/g)	Q_o (µg/mg)	b (µL/µg)	R_L	$[UO_2^{2+}]$ (µg/mL)	R^2
Kaolinite (SVP 7)[‡]	54.44	45.66	–	–	–	–	–	17	0.027	1.41 ± 0.03	0.052 ± 0.008	0.15 ± 0.07	68–203	0.999
Kaolinite (SVP 44)[‡]	53.94	48.75	–	–	–	–	–	16	0.032	1.40 ± 0.03	0.052 ± 0.008	0.15 ± 0.07	68–203	0.999
Ca-montmorillonite	49.80	17.14	10.32	3.87	3.89	2.71	0.36	85	1.15	90 ± 1.2	0.0031 ± 0.0006	0.50 ± 0.21	162–1350	0.981
Composite material	51.28	26.93	2.85	1.62	16.94	0.34	–	51	0.076	30.7 ± 0.7	0.018 ± 0.003	0.18 ± 0.14	694–1369	0.995

- [‡] Chemical compositions from Bobos et al. (2001)