

Effect of silicate on the sorption properties of kaolinite: removal of U(VI) and mechanism

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Abstract The surface and sorption properties of kaolinite were analyzed as a function of silicate. Batch experiments indicate that the U(VI) sorption is promoted by the addition of silicate at low pH while is depressed at high pH. The sorption was acceptably predicted by the formation of a ternary silicate surface complex under the experimental conditions. The pseudo-second order kinetic model fit the sorption kinetics better. The sorption isotherms are more in accordance with Langmuir model and the thermodynamic parameters indicate a spontaneous and endothermic sorption process.

Keywords Kaolinite · U(VI) · Silicate · Sorption · Surface complexes

Introduction

The highly radioactive nuclides connected with nuclear fuels processing and nuclear wastes disposal are known to possess extremely long half-lives and high mobility in the environment [1–3]. They may leak into natural aquatic

systems through refining of nuclear fuel, medical diagnosis, deep geological disposal of high-level nuclear wastes and underground nuclear tests. Previous reports indicate that minerals are the key factors controlling the fate and the migration of radionuclides in natural systems [4–7].

Uranium (U) is an important and representative radionuclide both in the environment and in the processing of nuclear waste management. The dominant U species in oxidizing environments is in the form of an oxo-cation, uranyl (UO_2^{2+}), which is highly mobile and prone to complex with organic and inorganic matter [8]. In addition, U(VI) can be taken as an analogue of hexavalent actinides with high specific activity, namely, Pu(VI) and Np(VI) [9]. Since uranyl sorption onto mineral/water interface plays a significant role in radionuclides transport properties, this sorption process has been widely studied by diverse methods like batch experiments [10, 11], and techniques such as X-ray adsorption fine structure (XAFS) [12, 13] and fluorescence spectroscopy [14]. Many researchers mainly investigated the system of the sole uranyl sorbed on minerals [15, 16]. However, natural aquatic environments are generally systems containing many components or phases, while the effects of other solutes on the sorption of uranyl on minerals could not be easily neglected [6, 17]. The uranyl sorption on γ -alumina was promoted in the presence of phosphate, which could be interpreted by the formation of phosphate ternary surface complexes or surface precipitates of uranyl phosphate at relatively high phosphate concentration [18]. The presence of Ca^{2+} decreased uranyl sorption on quartz where calcium–uranyl–carbonate complexes was the dominant U species [19]. In addition, as important components as well as inorganic ions in natural aquatic environments, the influence of humic acids (HA) was investigated by Křepelová et al. [13], who reported that HA enhanced the sorption of

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uranyl in the acidic pH and reduced it in the near-neutral pH range.

As the second most abundant element and a major species exists in nature, silicon is easy to enter the aqueous system by the dissolution of clays as well as the degradation of glass containers [20]. In spite of its ubiquitous existence in the natural environment, the effect of silicate on radionuclides sorption has not been investigated extensively [17]. Soluble silicates have apparent influences on radionuclides sorption on clays due to the competition with the sorbates for sorption sites. The formation of chemical bonds between silicate and surface reactive groups could also alter the surface affinity to the sorbates [17, 21, 22]. The inhibition effect of silicate on arsenite sorption onto Fe-oxides was observed with the mechanism of anion displacement [23, 24]. The competing effect of silicate on the sorption of Se(IV) onto magnetite was also confirmed [25]. The sorption of Cs(I) onto magnetite surface as a function of silicate was studied by Marmier and Fromage [21], who found that the presence of silicate in solution increased Cs(I) sorption by acting as a “bridge”.

Consequently, in the present work, we investigated the sorption mechanism of U(VI) on clays as a function of soluble silicate. As is well-crystallized and ubiquitous in nature, kaolinite, a typical 1:1 aluminosilicate, was selected as a representative of many clay minerals [26]. Batch experiments were conducted to explore the interactions of U(VI) and soluble silicate on the kaolinite–water interface. In addition, zeta potential (ZP) and particle size analysis were also employed to help interpreting the sorption mechanisms.

Materials and methods

Materials

The chemicals NaNO_3 , HNO_3 , $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and NaOH in analytical grade (Sinopharm Chemical Reagent Co., Ltd) were used in the experiments. The kaolinite powders were obtained from Jingde county, Jiangxi province, China, and were used directly without further purification. The sample has been characterized in previous reports [27], which indicated typical kaolinite structure. The Milli-Q water was obtained from Direct-Q3 system (Milli-pore) with resistivity of 18.2 $\text{M}\Omega \text{ cm}$. The uranyl stock solution (1.0 mmol L^{-1}) was prepared by dissolving analytical-grade uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (99.99% purity, Sigma-Aldrich) in Milli-Q water, which was further diluted to the experimental concentration. $0.1 \text{ mmol L}^{-1} \text{ NaNO}_3$ and $0.01 \text{ mmol L}^{-1} \text{ Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ stock solutions were prepared for further dilution. The

stock suspension of kaolinite (6.0 g L^{-1}) was prepared by dispersing kaolinite in Milli-Q water.

Methods

The sorption experiments of U(VI) on kaolinite with and without the addition of silicate were carried out in polyethylene tubes (10 mL, sealed caps, Lebus) at room temperature. Pipet the stock suspensions of kaolinite and stock solutions of NaNO_3 , U(VI) and silicate into polyethylene tubes to obtain the required concentration of each component. Then the pH values of the suspensions were quickly adjusted with $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ or NaOH . After the tubes were shaken for 24 h, the separation of solid phase was conducted by centrifugation (LG-10, Lab) at 9000 rpm for 30 min [17]. The sorption isotherm experiments were conducted in the vapour-bathing constant temperature vibrator to obtain the desired reaction temperature.

The U(VI) concentrations of the supernatant were determined by the kinetic phosphorescence analyzer (KPA-11, Richland), while the silicate concentrations were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Atomscan Advantage, Thermo Jarrell-ASH). The amounts of U(VI) sorbed on kaolinite (q_e) were calculated from the difference between the initial (C_0 , mmol L^{-1}) and the equilibrium concentration (C_e , mmol L^{-1}) (sorption percentage (%) = $(C_0 - C_e)/C_0 \times 100\%$, and $q_e = (C_0 - C_e)/m \times V$, where V (L) represents the volume of the total suspension, and m (g) represents the mass of the sorbents). The zeta potential and particle size of the kaolinite were measured using a Zeta-sizer Nano ZS Instrument (Malvern Co., UK) at $25 \text{ }^\circ\text{C}$. Triplicate experiments were conducted to obtain the experimental data and the relative errors were less than $\pm 5\%$.

Results and discussion

Zeta potential of kaolinite suspensions

Understanding the surface charge characteristics of kaolinite suspensions is favorable for the study of the mechanism of the sorption of radionuclides. The zeta potential, reflecting relative movement of clay particles and water, could provide information for electrical potentials of clay surfaces [26]. The ZP values of kaolinite before and after silicate and/or U(VI) sorption are presented in Fig. 1. The pH_{PZC} is defined as the pH value where there is a neutral net electrical charge at the mineral surface. For pH below pH_{PZC} , the surface exhibits positively charged; while above this pH, the surface of the mineral displays a negative charge. The results show that kaolinite has a

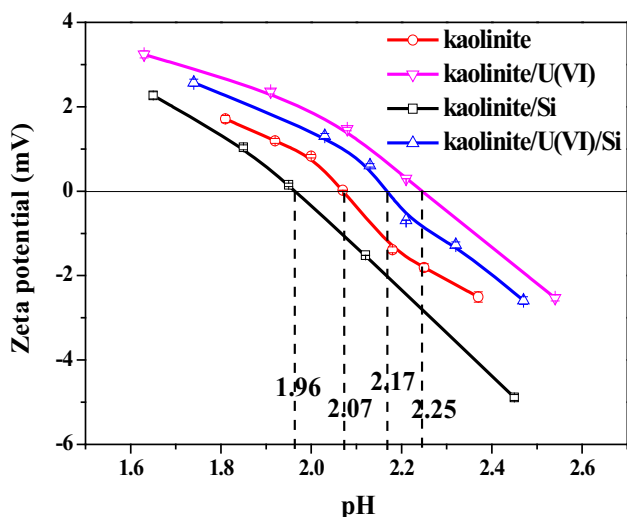


Fig. 1 The zeta potentials of kaolinite before and after U(VI)/silicate sorption versus pH. $C(U(VI)) = 4.17 \times 10^{-2} \text{ mmol L}^{-1}$, $m/V = 1.0 \text{ g(kaolinite) L}^{-1}$, $I = 0.01 \text{ mol L}^{-1} \text{ NaNO}_3$, $C(\text{silicate})_{\text{added}} = 1.0 \text{ mmol L}^{-1}$, $T = 298 \text{ K}$

pH_{PZC} value of ~ 2.07 , which is comparable to the published values for kaolinite [28]. The surface charge of kaolinite in aqueous solutions is negative in the pH range of our sorption study 3.0–11.0), arising directly from Al^{3+} substitution for Si^{4+} in the tetrahedral sheet of the mineral [29]. The protonation or deprotonation of surface hydroxyl groups will lead to a pH dependent variable charge for the alumina faces and edges [26]. The pH_{PZC} value decreases to ~ 1.96 when only the addition of silicate, which could be interpreted by that silicate makes hydrated kaolinite surface more negative. However, the addition of UO_2^{2+} ions makes the pH_{PZC} value of kaolinite higher due to that the thickness of diffuse electrical double layer decreases correspondingly [26]. As for the addition of both silicate and uranyl ions, the pH_{PZC} value of kaolinite increases slightly relative to primary kaolinite. The possible interpretation is that uranyl may display larger influence on the zeta potential of clays compared with silicate concerning the concentrations of silicate and uranyl ions used in our experiment.

The effect of silicate on the aggregation of kaolinite

Clay and mineral particles are the main inorganic colloid particles in natural aquatic systems, where the aggregation of colloids takes place spontaneously under changing solution conditions. The presence of specifically adsorbed ions could be considered as the main variable factor influencing the property of the solid/liquid interface [30]. Thus, the particle size of kaolinite as a function of silicate concentrations at different pH was measured and the size distribution is shown in Fig. 2. The initial average diameter

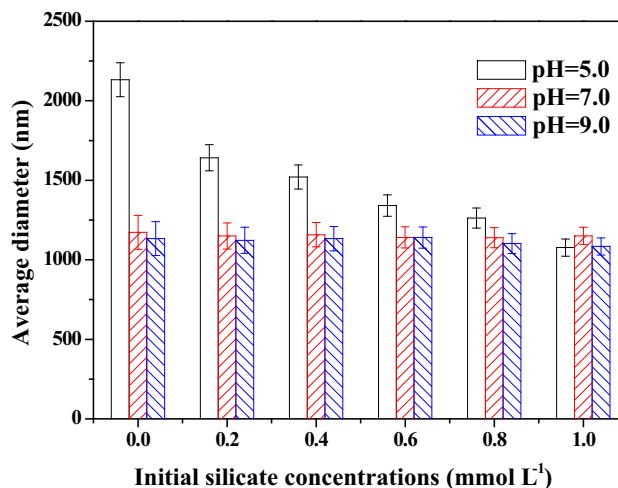


Fig. 2 The particle size distribution of kaolinite as a function of added silicate concentrations and pH. $m/V = 1.0 \text{ g(kaolinite) L}^{-1}$, $I = 0.01 \text{ mol L}^{-1} \text{ NaNO}_3$, $T = 298 \text{ K}$, $\text{pH} = 5.0, 7.0 \text{ and } 9.0 \pm 0.1$, respectively

of kaolinite at pH 5.0 is about 2100 nm. It could be easy to observe that the presence of silicate promotes the particle aggregation in acidic conditions. While the particle size of kaolinite decreases distinctly with the addition of the increasing silicate amount. When the addition of silicate reaches up to 1.0 mmol L^{-1} , the average diameter decreases to 1100 nm, which indicates the inhibition effect of silicate on the aggregation of kaolinite at acidic conditions. It is important to emphasize that the surface of kaolinite is negatively charged at the specific pH we discussed, which is opposite to that of hematite. The silicate specifically sorbed on kaolinite adds negative charge to the particle surface, leading to stronger repulsion between negative particles, thus inhibits the aggregation of particles. However, the destabilization effect of sulfate on hematite which enhances aggregation of the hematite particles was reported by Xu et al. [30]. They attributed it to specific sorption and then the neutralization process with the positive surface charges of hematite. Our experiments were slightly similar to the research system of hematite with sulfate. However, hematite has quite high pH_{pzc} , which is opposite to kaolinite at the pH we discussed. Thus, the effect of inorganic anions on materials with opposite pH_{pzc} might be opposite. The inhibition effect of silicate may be part of the reason increasing U(VI) sorption on kaolinite at acidic condition discussed in the latter part. As for neutral to alkaline conditions, the initial average diameter of kaolinite without silicate is $\sim 1200 \text{ nm}$. Furthermore, the addition of silicate seems to have little effect on the aggregation of kaolinite at high pH, which indicates particle aggregation might not be the dominant reason affecting U(VI) sorption at high pH.

The effects of silicate and pH on the sorption of U(VI)

pH is an important parameters for the sorption of radionuclides from aqueous solutions and presents great impact on the surface properties of sorbents as well as the species distribution of sorbates [31]. pH sorption edge that usually acquired at fixed sorbate concentration could provide information about the sorption dependence of aqueous pH values [32]. The pH sorption edge of U(VI) on kaolinite is shown in Fig. 3a. The U(VI) sorption increases with pH up to 7.0, which is in consistent with previous studies [32, 33]. The species distribution of U(VI) in our experiment conditions was calculated by Visual MINTEQ version 3.1 [34] and is depicted in Fig. 4a. The predominant

species at pH 3.0–7.0 are UO_2^{2+} , $\text{UO}_2(\text{OH})^+$ and $(\text{UO}_2)_3(\text{OH})_5^+$, which are all positive. Concerning the more negative zeta potential of kaolinite with higher pH, the electrostatic attraction between U(VI) and kaolinite becomes stronger, causing more U(VI) sorption with increasing pH. At pH 7.0–11.0, U(VI) sorption decreases with increasing pH, where U(VI) exists mainly in the form of $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2\text{CO}_3(\text{aq})$. The decrease of U(VI) sorption is ascribed to the formation of aqueous U(VI)–carbonate complexes where carbonate competed with kaolinite for combining U(VI) as our experiments were carried out at atmospheric CO_2 conditions, which could be demonstrated by the no appearance of sorption plateau at neutral pH range [32]. U(VI) sorption increases relatively in pH 4.0–6.5 in the presence of silicate. The addition of silicate could decrease the electrostatic potential of the sorbent surface, which has been shown in Fig. 1. Moreover, the addition of silicate can alter the species distribution of U(VI) and the result is shown in

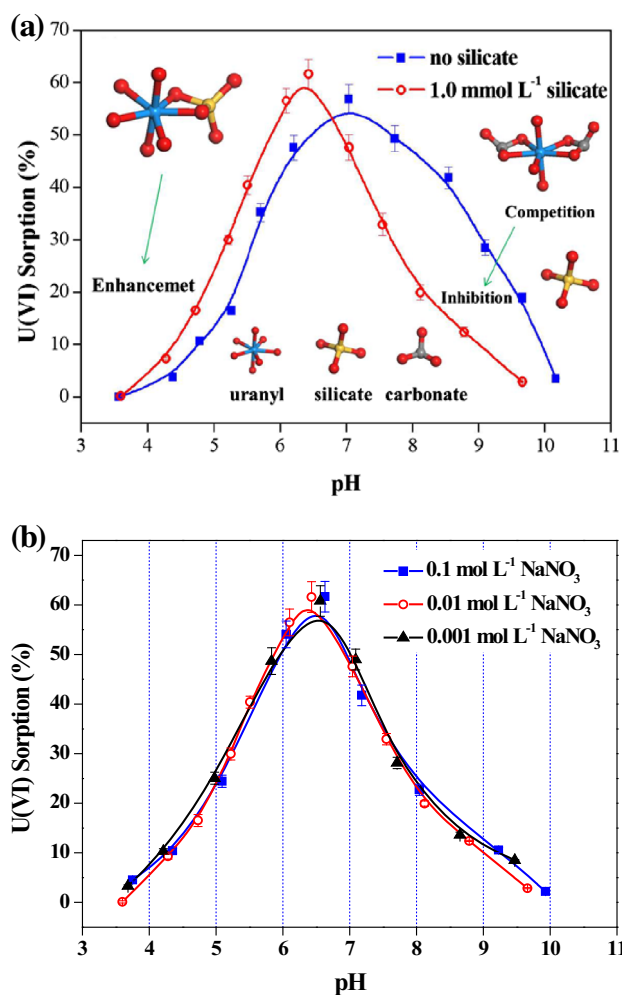


Fig. 3 a Influence of pH on U(VI) sorption on kaolinite with and without the addition of silicate. $I = 0.01 \text{ mol L}^{-1} \text{ NaNO}_3$; Blue balls, uranium atoms. Yellow balls, silicon atoms. Gray balls, carbon atoms. Red balls, oxygen atoms. b Influence of ionic strength on U(VI) sorption on kaolinite with the addition of silicate. $C(\text{U(VI)}) = 4.17 \times 10^{-2} \text{ mmol L}^{-1}$, $m/V = 1.0 \text{ g(kaolinite) L}^{-1}$, $C(\text{silicate})_{\text{add}} = 1.0 \text{ mmol L}^{-1}$, $T = 298 \text{ K}$. (Color figure online)

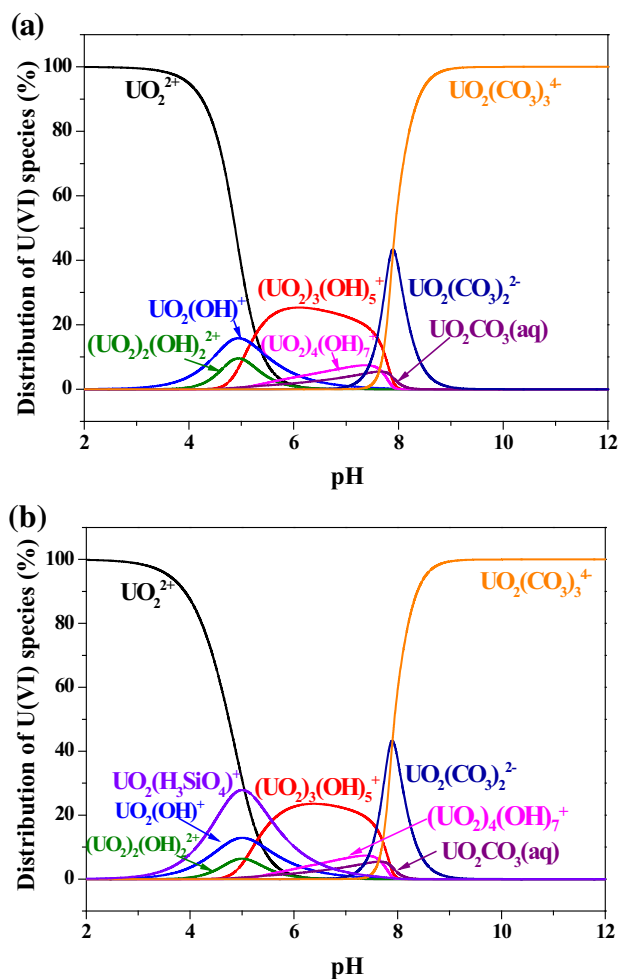


Fig. 4 Species of U(VI) in NaNO_3 solutions in the absence (a) and presence (b) of silicate. $C(\text{U(VI)}) = 4.17 \times 10^{-2} \text{ mmol L}^{-1}$, $C(\text{silicate})_{\text{add}} = 1.0 \text{ mmol L}^{-1}$, $I = 0.01 \text{ mol L}^{-1} \text{ NaNO}_3$, $T = 298 \text{ K}$

Fig. 4b. It could be seen that $\text{UO}_2(\text{H}_3\text{SiO}_4)^+$ takes up a large proportion in pH 4.0–6.5, indicating that silicate could form complex with U(VI) [35]. While at high pH, the species of U(VI) is mainly anionic. The anionic silicate in solution will compete with anionic U(VI) species for sorption sites, which leads to further decrease of U(VI) sorption in the presence of silicate. In order to confirm the type of uranyl surface complex containing silicate, three pH sorption edges at different ionic strengths in the presence of silicate were conducted and the result is shown in Fig. 3b. Results indicated that the sorption edges are independent of ionic strength, which suggests that the sorption is mainly dominated by inner-sphere surface complexation [36, 37].

To examine the affinity of silicate towards kaolinite, the silicate concentration in supernatant of kaolinite/silicate

system was measured, taking the single kaolinite as a comparison. As is depicted in Fig. 5a, the solubility of kaolinite varies with pH. The silicate concentration is high in strong acidic/alkaline conditions, suggesting the occurrence of obvious dissolution of kaolinite [38]. When at nearly neutral pH conditions that is relatively moderate, the dissolution is not that drastic since the concentration of silicate in solution becomes lower. While it is important to emphasize that the silicate dissolved from kaolinite is not that much in the whole pH range as the maximum concentration in solution is less than 0.1 mmol L^{-1} . Concerning the kaolinite system with 1.0 mmol L^{-1} silicate, there was no pronounced changing trend of silicate concentration with pH except that the silicate concentration are all around 0.97 mmol L^{-1} ($<1.0 \text{ mmol L}^{-1}$), indicating that the kaolinite surface could adsorb silicate slightly. Moreover, the silicate concentrations of kaolinite/U(VI)/silicate system at three ionic strengths were also measured (Fig. 5b). There is little discrepancy among the three sets of data and they are similar to that of kaolinite/silicate system, suggesting that the mechanism of silicate sorption on kaolinite may be inner-sphere complexation [37].

In addition, the inhibiting effect of silicate for particle aggregation may also contribute to the increasing U(VI) sorption on kaolinite. The positive effect is similar to that of silicate on Cs(I) sorption on magnetite reported by Marmier and Fromage [21]. However, U(VI) sorption decreases more sharply when $\text{pH} > 6.5$ in the presence of silicate (Fig. 3a). In spite of the repulsion between anionic U(VI) species and kaolinite, the competition of negative silicate for sorption active sites may play an important role for the sorption decrease.

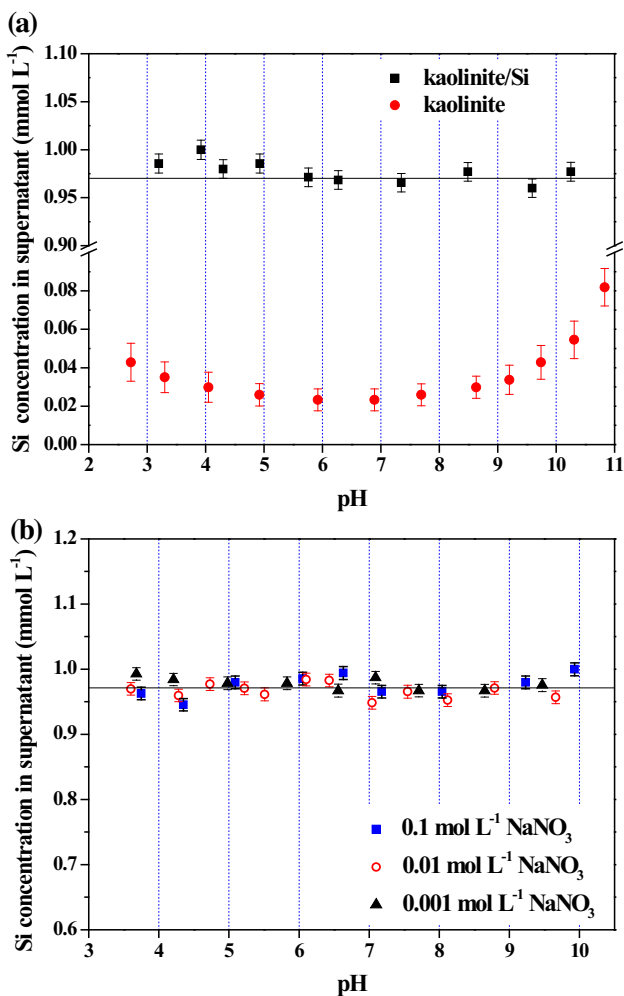


Fig. 5 **a** Silicate concentration in supernatant of kaolinite with and without the addition of silicate as a function of pH. **b** Silicate concentration in supernatant of kaolinite/U(VI)/silicate system at three ionic strengths as a function of pH. $C(\text{silicate})_{\text{add}} = 1.0 \text{ mmol L}^{-1}$, $C(\text{U(VI)}) = 4.17 \times 10^{-2} \text{ mmol L}^{-1}$, $m/V = 1.0 \text{ g(kaolinite) L}^{-1}$, $I = 0.01 \text{ mol L}^{-1} \text{ NaNO}_3$, $T = 298 \text{ K}$

Influence of silicate on U(VI) sorption kinetics

To investigate the sorption of U(VI) on kaolinite from another view, kinetic experiments have been carried out with and without the addition of silicate. The corresponding results at three pH values are presented in Fig. 6, which indicate the undeniable influence of silicate on U(VI) sorption. Similar tendency could be found that the sorption of U(VI) on kaolinite increases rapidly in the first 4 h while reaches steady state later on according to the kinetic curves. The fast velocity reveals that strong chemical sorption plays a major role in the sorption of U(VI) on kaolinite, which is in accordance with the results of Gao et al. [32] and Yang et al. [3]. Although there was similar trend of sorption kinetics, U(VI) sorption as a function of silicate differs at various pH. A sorption promoting effect of silicate could be observed from Fig. 6 at pH 5.0, while the sorption inhibiting ones were found at pH 7.0 and 9.0. It is worth mentioning that the relevant data of kinetics in

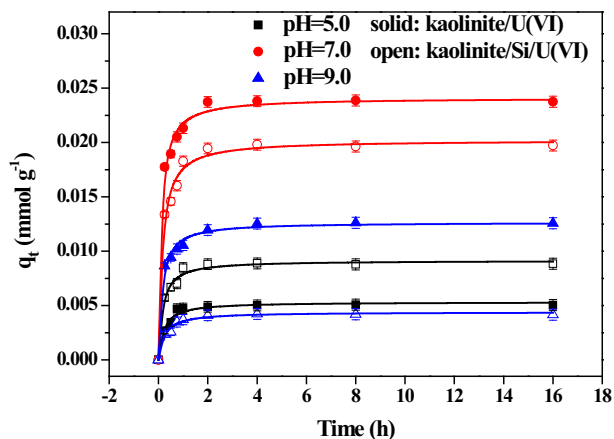


Fig. 6 U(VI) sorption on kaolinite with and without the addition of silicate as a function of reaction time. The solid lines represent the pseudo-second-order model simulation. $C(\text{U(VI)}) = 4.17 \times 10^{-2} \text{ mmol L}^{-1}$, $m/V = 1.0 \text{ g(kaolinite) L}^{-1}$, $I = 0.01 \text{ mol L}^{-1} \text{ NaNO}_3$, $C(\text{silicate})_{\text{add}} = 1.0 \text{ mmol L}^{-1}$, $T = 298 \text{ K}$, $\text{pH} = 5.0, 7.0$ and 9.0 ± 0.1 , respectively

Fig. 6 are consistent with those in Fig. 3, which helps to verify the sorption law as a function of pH.

To confirm the essential mechanism of the sorption process, the experimental kinetic data are fitted by pseudo-first order as well as pseudo-second order kinetic models, whose linear forms are expressed as Eqs. (1) and (2) [17, 39], respectively:

$$\ln(q_e - q_t) = \ln q_e - k_f t \quad (1)$$

$$t/q_t = 1/(k_s \times q_e^2) + t/q_e \quad (2)$$

where q_e and q_t (mmol g^{-1} of dry weight) are the amount of U(VI) sorbed on kaolinite at equilibrium and at time t , respectively. k_f (h^{-1}) and k_s (g (mmol h)^{-1}) represent the rate constant of pseudo-first order and pseudo-second order kinetics, respectively. The relevant simulation parameters of both models are presented in Table 1. The sorption is better fitted by the pseudo-second order kinetic model ($R^2 > 0.99$) compared with pseudo-first order one ($R^2 < 0.99$), which denotes that the chemisorption of U(VI) on kaolinite is the rate-limiting step [39].

Table 1 Kinetic parameters of U(VI) sorption on kaolinite with and without the addition of silicate

System	pH	Pseudo-first-order model			Pseudo-second-order model		
		q_e (mmol g^{-1})	k_f (h^{-1})	R^2	q_e (mmol g^{-1})	k_s (g (mmol h)^{-1})	R^2
kaolinite/U(VI)	5.0	5.03×10^{-3}	2.80	0.987	5.11×10^{-3}	1571.38	0.999
kaolinite/Si/U(VI)	5.0	8.69×10^{-3}	3.33	0.969	8.92×10^{-3}	1055.79	0.999
kaolinite/U(VI)	7.0	22.90×10^{-3}	4.80	0.963	23.94×10^{-3}	503.64	0.999
kaolinite/Si/U(VI)	7.0	19.19×10^{-3}	3.53	0.962	19.89×10^{-3}	457.51	0.999
kaolinite/U(VI)	9.0	11.93×10^{-3}	3.84	0.946	12.72×10^{-3}	554.75	0.999
kaolinite/Si/U(VI)	9.0	4.15×10^{-3}	2.47	0.973	4.23×10^{-3}	1644.69	0.999

Sorption isotherms

The sorption isotherms of U(VI) on kaolinite with and without the addition of silicate at pH 5.5 are shown in Fig. 7a. It is easy to find that the isotherm of U(VI) with silicate is much higher than that without silicate, i.e., the addition of silicate facilitates U(VI) sorption on kaolinite. The potential mechanism of the significant positive effect of silicate may be ascribed to that the silicate bridges the sorbent surface and U(VI) and hence promotes the formation of ternary complexes. To quantify the sorption data specifically, Langmuir and Freundlich models were utilized to simulate the sorption of U(VI) on kaolinite. The Langmuir and Freundlich isotherm are expressed as Eqs. (3) and (4) [40], respectively:

$$q_e = \frac{bq_{\text{max}}C_e}{1 + bC_e} \quad (3)$$

$$q_e = k_F C_e^{1/n} \quad (4)$$

where q_{max} (mmol g^{-1}) denotes the maximum sorption capacity of sorbent with monolayer coverage. b (L mmol^{-1}) is the Langmuir constant related to the free energy of sorption. $1/n$ denotes the heterogeneity of the sorption sites and the indicator of isotherm nonlinearity while k_F ($\text{mmol}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$) denotes the Freundlich equilibrium coefficient related to the distribution of the sorbate on the solid and liquid phases.

Simulation curves of both models are shown in Fig. 7a, where the solid and dashed lines denote Langmuir and Freundlich model, respectively. The relevant fitting parameters calculated from the two models are listed in Table 2. The sorption isotherm of U(VI) on kaolinite, regardless of the addition of silicate or not, can be better fitted by the Langmuir model compared to the Freundlich model, which indicates that the whole surface of kaolinite has homogeneous sorption activity and the sorbed U(VI) will not compete with each other consequently. This result also demonstrates the dominant mechanism of monolayer sorption and chemisorption [39, 41].

The sorption isotherms for U(VI) with silicate at 298, 313 and 328 K are also shown in Fig. 7a. The sorption

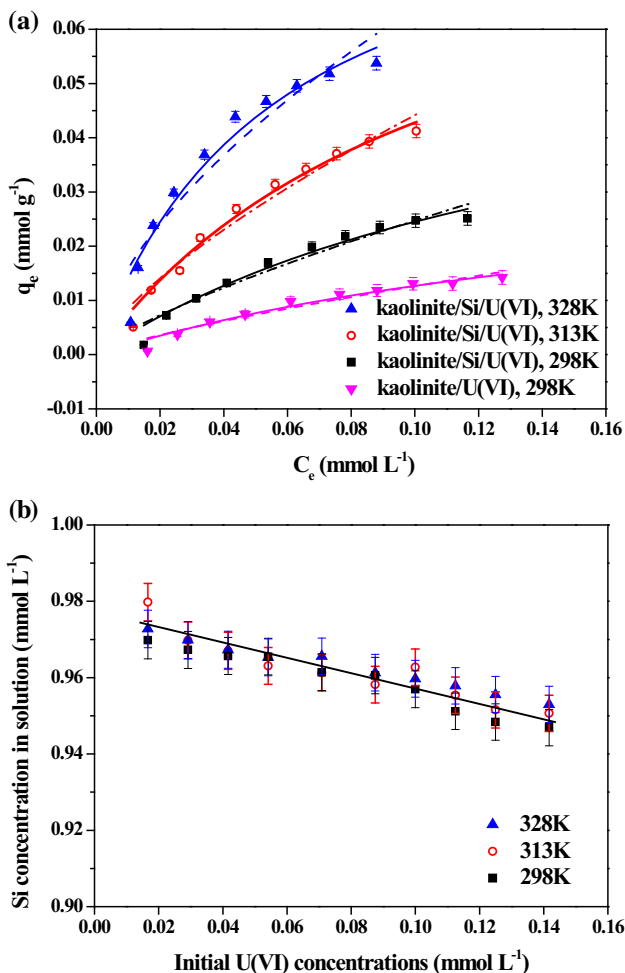


Fig. 7 **a** Sorption isotherms of U(VI) on kaolinite with and without the addition of silicate. **b** Silicate concentration in supernatant of kaolinite/U(VI)/silicate system at three temperatures. pH = 5.5 ± 0.1, C(U(VI)) = 4.17 × 10⁻² mmol L⁻¹, m/V = 1.0 g(kaolinite) L⁻¹, I = 0.01 mol L⁻¹ NaNO₃, C(silicate)_{add} = 1.0 mmol L⁻¹. Solid line Langmuir model, dashed line Freundlich model

isotherm becomes higher with higher temperature, which reveals that high temperature is favorable for U(VI) sorption on kaolinite. The thermodynamic parameters (ΔG° , ΔS° , and ΔH°) can be obtained by the temperature-

dependent equations. Free energy change (ΔG°) is calculated from Eq. (5):

$$\Delta G^\circ = -RT \ln K^\circ \tag{5}$$

where K° represents the sorption equilibrium constant, T is the reaction temperature and R is the universal constant (8.314 J (mol K)⁻¹). $\ln K^\circ$ can be determined by plotting $\ln K_d$ versus C_e of U(VI) and extrapolating C_e to zero. The corresponding values of $\ln K^\circ$ at 298, 313 and 328 K are 5.94, 6.63 and 7.33, respectively. Standard entropy change (ΔS°) can be obtained using Eq (6):

$$\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_p = -\Delta S^\circ \tag{6}$$

While the standard enthalpy change (ΔH°) is calculated from Eq. (7):

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ \tag{7}$$

The thermodynamic parameters of U(VI) sorption on kaolinite with the addition of silicate are presented in Table 3. The negative free energy change (ΔG°) indicates a spontaneous process under the experimental conditions. More negative values of ΔG° are obtained with increasing temperatures, elucidating that the sorption is more favorable at higher temperature. The positive value of entropy change (ΔS°) denotes some structural changes in the process of U(VI) sorption on kaolinite with silicate, causing an increasing disorderness of the solid–liquid system [41]. A positive value of ΔH° indicates that U(VI) sorption on kaolinite is an endothermic process, which is in accordance with the previous reports [11, 42]. U(VI) dissolves well in water, and its hydration sheath needs to be destroyed before sorption, the process of which consumes energy and is preferred at high temperature [40]. The energy needed exceeds the exothermicity of U(VI) attached to the kaolinite surface, that is to say, the endothermicity of the desolvation procedure goes beyond that of the enthalpy of sorption to a great extent.

Moreover, the silicate concentrations in supernatant of kaolinite/U(VI)/silicate system at different temperatures were also measured and shown in Fig. 7b. The silicate concentration decreases gradually with increasing U(VI)

Table 2 Parameters of Langmuir and Freundlich models for simulation of U(VI) sorption isotherm

System	T (K)	Langmuir model			Freundlich model		
		q_{max} (mmol g ⁻¹)	b (L mmol ⁻¹)	R^2	k_F (mmol ^{1-1/n} L ^{1/n} g ⁻¹)	1/n	R^2
kaolinite/U(VI)	298	0.037	5.19	0.955	0.075	0.777	0.934
kaolinite/Si/U(VI)	298	0.064	6.18	0.962	0.141	0.759	0.940
	313	0.090	8.93	0.982	0.227	0.711	0.962
	328	0.092	17.97	0.946	0.257	0.604	0.902

Table 3 Thermodynamic parameters for U(VI) sorption on kaolinite with the addition of silicate

T (K)	ΔG° (kJ mol ⁻¹)	ΔS° (J (mol K) ⁻¹)	ΔH° (kJ mol ⁻¹)
298	-14.71		37.64
313	-17.25	175.7	37.74
328	-19.98		37.64

concentration at specific temperature, which means that more silicate participating in the sorption process leads to more U(VI) sorption on kaolinite, indicating that silicate takes part in the interaction of U(VI) and kaolinite indeed. However, there is little discrepancy among the changing trends of silicate concentration at three temperatures, indicating the weak influence of temperature on the affinity of silicate to kaolinite.

Conclusions

The addition of silicates decreases the zeta potential of kaolinite and inhibits the aggregation of kaolinite particles. In addition, the adsorbed silicate on kaolinite provides more potential sorption sites for U(VI), which results in the increased sorption of U(VI) at acidic conditions. The sorption can be explained by the formation of ternary surface complexes and silicate acts as a “bridge” between U(VI) and kaolinite. While at alkaline conditions, the sorption is decreased due to the competition between silicate and anionic U(VI) species at the sorption sites. The sorption isotherms of U(VI) with and without silicates are more in accordance with Langmuir model than Freundlich model, demonstrating the dominant mechanism of monolayer sorption and chemisorption. The thermodynamic parameters indicate that U(VI) sorption with silicates is spontaneous and endothermic, which could supplement the thermodynamic databases predicting radionuclide migration in the subsurface. To better understand the sorption and uptake behavior of radionuclides in natural aquatic environments, molecular-level spectroscopic technique is needed in the following work.

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