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Adsorption of antimony(V) on kaolinite as a function of pH, ionic strength and humic acid

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Abstract The present work investigated the adsorption and mobility (desorption) of Sb(V) on kaolinite using batch experiments. The adsorption of Sb(V) on kaolinite was studied as a function of contact time, pH, ionic strength, humic acid (HA), initial Sb(V) concentration and temperature. Kinetic studies suggest that the equilibrium is achieved within 24 h. The adsorption of Sb(V) was strongly affected by changes in I at low ionic strength and unaffected at high ionic strength. The adsorption is weakly dependent on the presence of humic acid, but is strongly dependent on pH. Within the range tested, the optimal pH for Sb(V) adsorption is 3.6, and close to 75% removal can be achieved. Desorption is dependent on the original suspension pH. The addition sequence of Sb(V)/HA do not influence the adsorption of Sb(V) on kaolinite. The adsorption data fit both the Freundlich and Langmuir isotherm. The thermodynamic parameters (ΔH^0 , ΔS^0 and ΔG^0) were calculated from the temperature dependence, and the results suggest the endothermic and spontaneous nature of the process.

Keywords Adsorption · Desorption · Antimony(V) · Kaolinite

Introduction

Antimony (Sb) is a toxic element widely distributed in the lithosphere and is of increasing environmental concern due to increased awareness of its risk to plants, animal and human health (Shotyk et al. 2005). The toxicity of antimony is assumed to be similar to that of arsenic with respect to effects and mechanism (Gebel 1997). It has been used in a variety of industrial products such as lead-acid batteries, small arms bullets, flame retardants and glass products although Sb and its compounds are considered as pollutants of priority interest (Filella et al. 2002a).

Concentrations of Sb in nonpolluted waters and soils are typically <1 µg/L and 1 mg/kg, respectively (Takayanagi et al. 1996; Filella et al. 2002a; Mitsunobu et al. 2006). However, elevated concentrations of Sb in airborne particulate matter, soils and waters were observed near Sb mining areas and in the areas contaminated by human activities (He and Yang 1999; Zheng et al. 2000; Flynn et al. 2003; Wilson et al. 2004; He 2007; Ning and Xiao 2007; Steely et al. 2007). On the other hand, the availability and mobility of Sb can be affected by geochemical and biological processes such as adsorption/desorption. Thus, a clear understanding of adsorption/desorption processes is critical in determining the transformation and fate of antimony in the aquatic system, such as sediments, soils, and ground water.

Antimony exists primarily as Sb(V) in oxic systems and Sb(III) in anoxic systems. Some studies showed that Sb(V) is the most stable form in environment (Mitsunobu et al.

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2006; Nakamaru et al. 2006; Scheinost et al. 2006; Steely et al. 2007). This observation may be due to the oxidation of Sb(III) to Sb(V) by humic acids existing naturally (Buschmann and Sigg 2004; Buschmann et al. 2005; Steely et al. 2007). Sb(V) ion hydrolyse easily in aqueous solution, thus making it difficult for Sb(V) ion to exist in free Sb^{5+} cation. In the pH range of 2–11, Sb(V) should exist as a negatively charged complex, $\text{Sb}(\text{OH})_6^-$ (Filella et al. 2002a).

Only very few adsorption studies of Sb on natural sorbents have been reported to date (Filella et al. 2002b). Previous work by Thanabalasingam and Pickering (1990) indicated that the adsorption capacity of Mn, Fe and Al hydroxides for Sb(III) decreases in the sequence $\text{MnOOH} > \text{Al}(\text{OH})_3 > \text{FeOOH}$. Some studies demonstrated that both Sb(III) and Sb(V) can strongly bind to Fe hydroxides, and pH had a strong influence on Sb(III) and Sb(V) adsorption (Ambe 1987; Tighe et al. 2005; Leuz et al. 2006; Scheinost et al. 2006; Watkins et al. 2006). These studies have focused on Sb adsorption on Fe oxides. However, very few studies addressed the adsorption of Sb on clay minerals such as kaolinite, montmorillonite and illite, whereas clay minerals are found in almost every type of sediments and soils (Xi et al. 2009). Kaolinite occurs commonly in soils and sediments. It is known that some oxyanions such as arsenite (Lin and Puls 2000) and arsenate (Saada et al. 2003) can adsorb on kaolinite. However, very few studies reported the adsorption of Sb on kaolinite (Xi et al. 2009).

Several factors may affect the adsorption of Sb including pH, ionic strength (I), foreign ions, temperature and dissolved natural organic compounds. Humic acid (HA), naturally occurring organic polyacid and having a high affinity for mineral surfaces, has been recognized as an important factor controlling the behavior of various elements in the natural environments (Takahashi et al. 1997; Tugulea 2004; Chen and Wang 2007).

China is rich in Sb mineral resources. The Xikuangshan Sb mine, located near Lengshuijiang City, Hunan Province, China, is one of the largest Sb mines in the world. It is believed that Sb pollution from this particular mine and from Sb mining activities in China in general is very severe, resulting in significant environmental problems in China (He and Yang 1999; He 2007). The distribution, speciation, fate and bioavailability of antimony in environment are less understood. The objective of this study was to determine whether kaolinite can immobilize Sb(V) by adsorption from antimony-contaminant water or soil and to examine the effect of pH, ionic strength, temperature and humic acid on the adsorption of Sb(V) on kaolinite surface.

Materials and methods

Reagents and materials

All the chemicals used were of analytical grade or higher and used without further purification. Double distilled water was used throughout. All samples were analyzed within 2 days of completing each test. All experiments were performed in duplicate.

The kaolinite used in this study was obtained from Sigma-Aldrich and consists of about 85% kaolinite, with the main accessory phase of muscovite and quartz. The specific surface area of the kaolinite was $15.8 \text{ m}^2/\text{g}$ determined by BET method using N_2 . The point of zero charge (pH_{zpc}) was 3.5 by using acidic–basic titration method at different ionic strength. The humic acid (HA) used was Fluka humic acid with technical grade, and used without further purification. The main elemental components of HA are: C 48.95%, H 4.34%, O 30.64% and N 0.72%. A known amount of HA were dissolved in a minimum volume of 0.1 M NaOH to make 1 g/L HA solution after adjusting pH to neutral with 0.1 M NaOH and HCl. The solution was allowed to store in the dark at 277 K in amber glass bottles.

Kinetic studies

Stock solution of 1,000 mg/L Sb(V) in double distilled water was prepared from potassium pyroantimonate. The kinetic studies were conducted to examine the influence of time on the adsorption of Sb(V) on kaolinite in 0.02 M $\text{Ca}(\text{NO}_3)_2$ at pH 6. Batch method was used to examine the effect of time on the adsorption by shaking kaolinite suspensions in a series of 50 mL polythene centrifuge tubes containing 500 mg of kaolinite in 20 mL of 1 mg/L Sb(V) for 0.5, 1, 2, 4, 8, 12, 24, 36 and 48 h. At the designed time, the tubes were centrifuged at 4,000 rpm for 20 min to separate the solid from liquid phases followed by filtering with $0.22 \mu\text{m}$ cellulose nitrate membranes.

Adsorption of Sb(V) as a function of pH and ionic strength

Batch adsorption of Sb(V) at different pH and ionic strength was examined by shaking kaolinite suspensions in 50 mL polythene centrifuge tubes containing 500 mg of kaolinite in 20 mL of 1 mg/L Sb(V) for 24 h. Suspension pH was adjusted with 0.1 M NaOH/ HNO_3 after addition of the 1 mg/L Sb(V) solution. Ionic strength was maintained by adding $\text{Ca}(\text{NO}_3)_2$. After the 24 h reaction period, the tubes were centrifuged and filtered.

Desorption of Sb(V)

Desorption was conducted for kaolinite which were treated with Sb(V) solutions between pH 3 and 10. The Sb(V) treated kaolinite was resuspended in 20 mL of 0.1 M MgSO_4 . The 0.1 M MgSO_4 /kaolinite suspension was shaken for 12 h followed by centrifugation and filtration.

Adsorption isotherms

The influence of the initial Sb(V) concentration was determined in 0.02 M $\text{Ca}(\text{NO}_3)_2$ at pH 6. The tests were run with initial Sb(V) concentration ranging from 0.05 to 3 mg/L at 278, 298 and 323 K respectively in order to calculate the thermodynamic parameters of the absorption reaction.

Sb(V) adsorption in the presence of humic acid

The influence of humic acid on Sb(V) adsorption was investigated by simultaneously adding Sb(V) and humic acid stock solutions to sorbent suspension, then adjusting suspension pH to a given value. In addition, the effect of addition sequences on Sb(V) adsorption was studied by adding humic acid to the kaolinite suspension and then adding Sb(V) 1 day later.

Analytical methods

The pH of the solutions was measured using a basic PB-10 pH meter (Sartorius, Germany), calibrated using commercial pH 4.0, 7.0 and 10.0 buffers. Mixed reducing reagent (5% ascorbic acid + 5% thiourea) and 4 M HCl was added to the filtered supernatants from adsorption and desorption experiments. The mixture was left to stand at room temperature for 30 min to ensure complete reduction of Sb(V) to Sb(III) before the stibine generation. Then the concentration of Sb in the supernatants was measured with a hydride generation atomic fluorescence spectrometer (AFS-230, Beijing Haiguang Instrument Co., China) (Zhang et al. 2005). For hydride generation, 2% KBH_4 (prepared in 0.5% KOH) and 5% HCl reacted with the samples. Calibration was achieved using dilutions prepared from a commercially available 100 mg/L Sb standard solution.

Results and discussion

Effect of time

The equilibrium time for Sb(V) was determined by taking samples at different time intervals for 48 h and the results are shown in Fig. 1. The kinetic profile showed adsorption

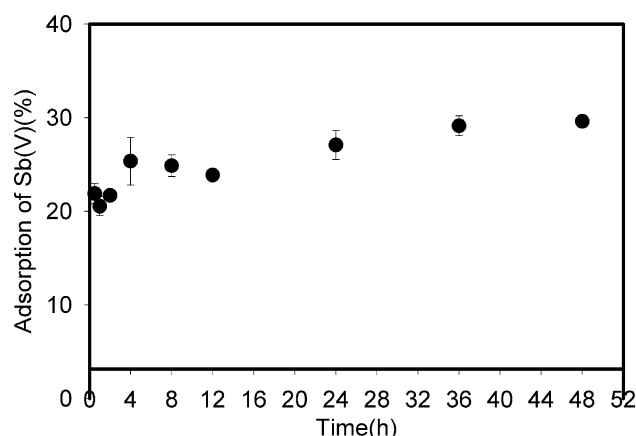


Fig. 1 Adsorption of Sb(V) on kaolinite as a function of contact time, with reaction conditions: ionic strength (I) = 0.02 M $\text{Ca}(\text{NO}_3)_2$, pH = 6.0 ± 0.1 , $T = 298 \pm 1$ K, initial Sb(V) concentration (C_0) = 1 mg/L, $m/v = 0.5$ g/20 ml

reaction is rapid initially and becoming slow after 8 h. The slight decrease in adsorption between 4 and 12 h can be observed. The adsorption amount was 25.3, 24.9, 23.8, and 27.1% at 4, 8, 12, and 24 h, respectively. This slight decrease may be due to the desorption of Sb(V) that weakly bound to the surface of kaolinite, or may be due to the experimental errors. Researchers often interpret the rapid reaction as adsorption by high affinity sites and the slow reaction as either adsorption by lower reactive sites, solid-state diffusion into the mineral defects, or the precipitation of ion on mineral surface (Axe and Anderson 1997). Similar fast adsorption were found for Sb(V) adsorption onto hematite (Ambe 1987). Adsorption reaction may approach equilibrium after 20 h. Thus, the following experiments used the equilibrium time of 24 h.

Sorption isotherms

The adsorption isotherms were obtained with initial Sb(V) concentration range from 50 to 3,000 $\mu\text{g/L}$ at pH 6 and at 278, 298 and 323 K (Fig. 2). The results indicated that the adsorption isotherms is higher at high temperature than at low temperature, i.e., adsorption of Sb(V) on kaolinite increases with rise in temperature. The experimental adsorption data were fitted by the Langmuir isotherm model and Freundlich isotherm model. Langmuir and Freundlich equations are the simplest and most commonly used isotherms to represent adsorption of components from a liquid phase on to a solid.

$$q_e = KC_e^{1/n} \quad (1)$$

Here C_e is the equilibrium concentration of adsorbate in solution ($\mu\text{g Sb/L}$), q_e is the equilibrium sorption amount ($\mu\text{g Sb/g sorbent}$), K is a Freundlich's constant related to the sorption capacity, and $1/n$ is the other Freundlich's

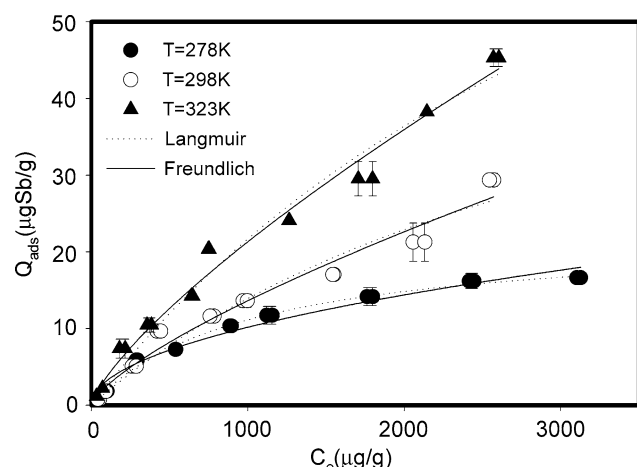


Fig. 2 Adsorption isotherms for antimonate on kaolinite at different temperature with reaction conditions: ionic strength = 0.02 M $\text{Ca}(\text{NO}_3)_2$, pH = 6 ± 0.1 , initial Sb(V) concentration from 0.5 to 3 mg/L, m/v 0.5 g/20 ml, reaction time = 24 h

constant that is considered relative indicator of adsorption intensity. The Langmuir adsorption equation can be expressed as

$$q_e = \frac{Q_0 b C_e}{(1 + b C_e)} \quad (2)$$

where q_e and C_e were defined previously, b is a constant related to the binding strength, and Q_0 is the maximum adsorption capacity ($\mu\text{g Sb/g sorbent}$). Both Langmuir and Freundlich adsorption equation can be linearized to obtain the parameters from experimental data.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K \quad (4)$$

Relevant data are listed in Table 1. Correlation coefficients (r^2) at 278 K, 298 K and 323 K were 0.987, 0.956 and 0.977, respectively, for the Langmuir model, 0.965, 0.966 and 0.984, respectively, for the Freundlich model, indicating a well fit with both the Freundlich model and Langmuir model. Under the experimental conditions, the largest sorption capacities were 16, 29 and 45 $\mu\text{g/g}$ at three temperature. The maximum adsorption capacity

Table 1 Freundlich's and Langmuir's constants for adsorption of Sb(V) by kaolinite

Temperature (K)	Langmuir constants			Freundlich constants		
	Q_0 ($\mu\text{g/g}$)	b (L/ μg)	r^2	K ($\mu\text{g/g}$)	$1/n$	r^2
278	22.2	1×10^{-3}	0.987	0.3204	0.5005	0.965
298	59	3×10^{-4}	0.956	0.0877	0.7305	0.966
323	133.5	2×10^{-4}	0.977	0.1157	0.755	0.984

calculated from the Langmuir equation is 22, 59 and 133 $\mu\text{g/g}$ at 278, 298 and 323 K. According to acidic–basic titration data, the total hydroxyl groups (SOH) per one gram for kaolinite is 58 μmol (Saada et al. 2003). The specific surface area of the kaolinite used in this study is similar to that of the kaolinite used by Saada. So we can assume that the SOH sites on the surface of the two kind of kaolinite are similar. Under our experimental conditions (500 mg kaolinite for 20 mL solution), the total number of SOH sites can be estimated at about 49 μmol per one gram kaolinite if the 85% purity of kaolinite was considered. The value is much higher than the maximum Sb(V) adsorption of 29 $\mu\text{g/g}$ for kaolinite at 298 K, i.e. 0.24 μmol of Sb(V) adsorbed on 500 mg kaolinite. Our results demonstrated that the kaolinite sorption sites were not saturated for the studied Sb(V) concentration range. The maximum adsorption capacity for Sb(V) agree with experimentally determined values from adsorption experiments on kaolinite for As(V) (Saada et al. 2003).

Effect of pH

The adsorption of Sb(V) on kaolinite as a function of pH from 3 to 10 is shown in Fig. 3. The adsorption of Sb(V) on kaolinite is strongly dependent on pH and decreased rapidly from pH 3.6 to 6.8 and slowly from 6.8 to 9.2. At pH 3.6, the amount of adsorbed Sb(V) on kaolinite remained close to 75%, while the amount of adsorbed Sb(V) on kaolinite reduced to less than 20% at pH 9.2. The similar pH-dependence curve of Sb(V) adsorption on iron oxide has been reported (McComb et al. 2007). The amount of adsorbed Sb(V) on goethite was near 100% in both 0.1 M

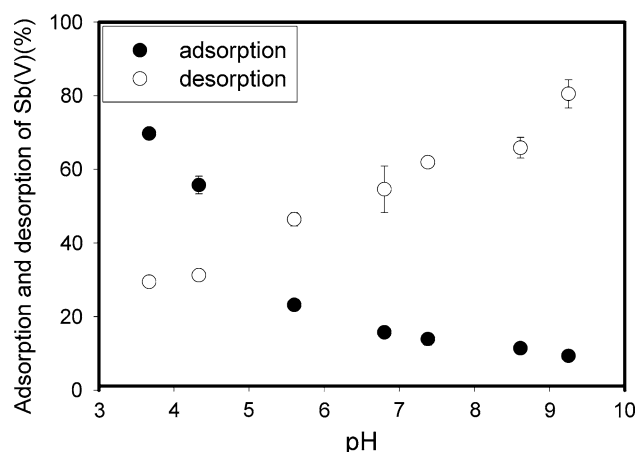


Fig. 3 Adsorption and desorption of Sb(V) from Sb(V) treated kaolinite. Adsorption reaction conditions: ionic strength (I) = 0.02 M $\text{Ca}(\text{NO}_3)_2$, $T = 298 \pm 1$ K, initial Sb(V) concentration (C_0) = 1 mg/L, $m/v = 0.5$ g/20 mL, reaction time = 24 h. Desorption reaction conditions: $T = 298 \pm 1$ K, $m/v = 0.5$ g/20 ml, 0.1 M MgSO_4 extraction solution, reaction time = 12 h

and 0.01 M KClO_4 solution between pH 3 and 6 at 298 K, and then drastically decreased above pH 6 (Leuz et al. 2006). Between pH 2 and 6, the adsorption of Sb(V) on hematite was above 90% at 323 K in 0.25 M LiCl solution and steeply decreased above pH 6. Tighe et al. (2005) measured the adsorption of Sb(V) onto amorphous $\text{Fe}(\text{OH})_3$ and found that the amount adsorbed was high at pH 3.5 but declined at higher pH. The pH-dependence of the adsorption of Sb(V) on kaolinite is similar to that of arsenate and phosphate on kaolinite (Violante and Pigna 2002). Filella et al. (2002b) addressed aspect of the solution chemistry of Sb(V) and thought that $[\text{Sb}(\text{OH})_6]^-$ is the main species of Sb(V) present in the pH range of 2–11. Kaolinite is a non-swelling 1:1 layer phyllosilicate. The PZC values for the phyllosilicate are typically below pH 3 due to permanent structural negative charge (Manning and Goldberg 1997). The PZC value of kaolinite used in the study is 3.5. This maximum adsorption phenomenon of Sb(V) on kaolinite is a consequence of the increase of positive surface charge of kaolinite with decreasing pH, resulting in greater attraction for anions. Moreover, the formation of oligomers such as $\text{Sb}_{12}(\text{OH})_{64}^{4-}$ is favored for Sb(V) on aqueous solutions at pH values below 7 according to McComb et al. (2007). Thus under acidic conditions, across-surface antimonite oligomerization likely stabilize the adsorbed Sb(V). The present study indicates that the mobility and bioavailability of Sb(V) is lower when the value of pH of environment is low.

Desorption

The desorption of adsorbed Sb(V) from Sb(V)-treated kaolinite was studied by adding 0.1 M MgSO_4 . Results was presented in Fig. 3, showing that the magnitude of Sb(V) recovery was strongly dependent on the original suspension pH. A maximum of 80% desorption was observed at pH 9.2. McComb et al. (2007) studied the desorption kinetic of Sb(V) from iron oxide and an enhanced rate of desorption at higher pH was observed. The observed easily desorption of Sb(V) at high pH is partly due to the reduced positive charge on the kaolinite but might also be influenced by the increased tendency of under alkaline conditions of adsorbed Sb(V) oxyanion oligomers to be hydrolyzed to more readily desorbed monomers.

Effect of ionic strength

Adsorption of Sb(V) on kaolinite as a function of $\text{Ca}(\text{NO}_3)_2$ concentration is shown in Fig. 4. The influence of ionic strength on the adsorption of Sb(V) was strong at the ionic strength range of 0.01–0.05 M and resulted in a lower adsorption of Sb(V) at higher ionic strength. While Sb(V) adsorption was relatively unaffected by changes in ionic

strength at the ionic strength range of 0.05–0.1 M. The studies on the adsorption of selenite and selenate on iron oxides indicated that it is possible to distinguish between inner-sphere and outer-sphere anion surface complexes by studying the effects of ionic strength on anion partitioning (Hayes et al. 1988). Adsorption behavior that is unaffected by changes in ionic strength is macroscopic evidence for inner-sphere complexation. This observation of Sb(V) adsorption may suggest that Sb(V) form both inner-sphere and outer-sphere complex on kaolinite. The inner-sphere complex is stronger than the outer-sphere complex and was not dependent on the ionic strength. Since the NO_3^- ions present in the background electrolyte can compete sorption site with Sb(V) binding outer-spherically to the kaolinite surface, the adsorption of Sb(V) experienced a significant reduction when the ionic strength (and therefore the NO_3^- concentration) raises from 0.01–0.05 M. However, when the NO_3^- concentration increased beyond 0.05 M, the Sb(V) might only form strong bond (inner-sphere complex) with kaolinite and the adsorption of Sb(V) on kaolinite was not affected by the changes in ionic strength. However spectroscopic methods such as EXAFS, FTIR and XPS are the direct method to prove the binding forms between the ions and minerals (Fendorf et al. 1994). It is well known that some anions such as arsenite and arsenate can be absorbed on minerals by a specific adsorption mechanism (Arai et al. 2001). Recent studies of Sb adsorption mechanisms on minerals have focused primarily on iron oxides. Investigations using ATR-IR spectroscopy showed that Sb(V) adsorbed on iron oxide surface forms an inner-sphere surface interaction with the formation of Sb–O–Fe bonds as well as some outer-sphere adsorption (McComb et al. 2007). Recent work by Scheinost and others (Scheinost et al. 2006) using EXAFS spectroscopy showed that Sb(III) forms a bidentate, corner-sharing inner-sphere complex at the goethite surface. The studies on the binding mechanisms between Sb and kaolinite have not been reported to date.

Effect of humic acid and addition sequences of Sb(V)/HA

The effects of humic acid and addition sequences of Sb(V)/HA are shown in Fig. 5. The addition of HA slightly reduces Sb(V) adsorption compared with the adsorption system without HA between pH 3 and 10. The influence of humic acid on the adsorption of Sb(V) on kaolinite depends on the complex behavior of Sb(V) with HA in solution, the complex behavior of Sb(V) with surface adsorbed HA on kaolinite and the complex behavior of Sb(V) with the functional groups of kaolinite. Humic acid had very limited affinity to Sb(V) (Pilarski et al. 1995), but can strongly adsorb on the kaolinite (Saada et al. 2003; Wan and Liu

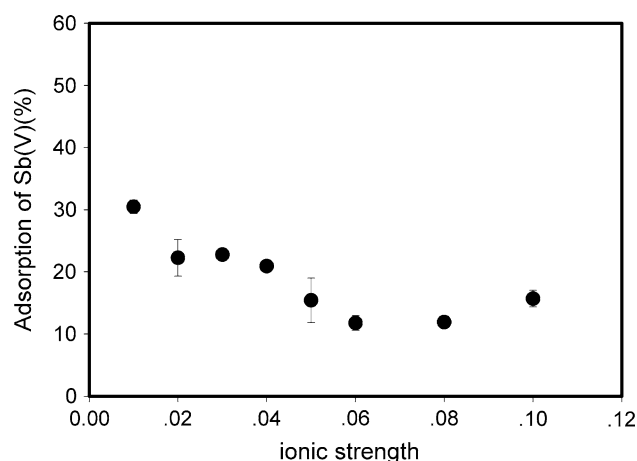


Fig. 4 The effect of ionic strength on the adsorption of antimonate on kaolinite with reaction conditions: $T = 298 \pm 1$ K, $\text{pH} = 6 \pm 0.1$, initial Sb(V) concentration (C_0) = 1 mg/L, $m/v = 0.5$ g/20 mL, reaction time = 24 h

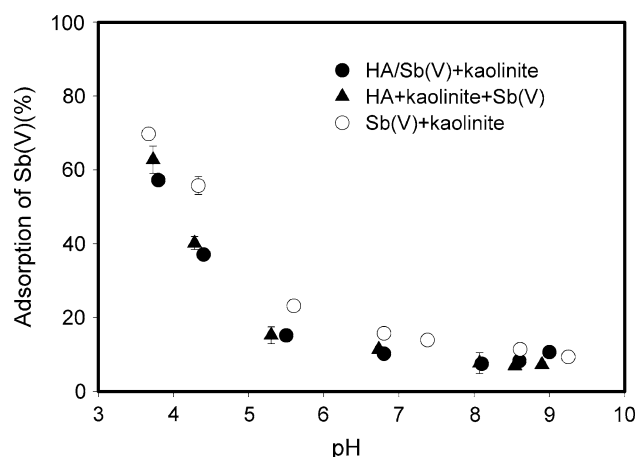


Fig. 5 Effect of humic acid and the addition sequences of Sb(V) and HA on the adsorption of Sb(V) with reaction conditions: ionic strength (I) = 0.02 M $\text{Ca(NO}_3)_2$, $T = 298 \pm 1$ K, initial concentration (C_0) = 1 mg/L for Sb(V) and 50 mg/L for HA, $m/v = 0.5$ g/20 mL, reaction time = 24 h

2006). The weakly reduce of adsorption in ternary Sb(V) –HA–kaolinite system compared with binary Sb(V) –kaolinite system may partly due to the fact that HA is competing for the available adsorption sites. The variation of the order of Sb(V) and HA addition to the kaolinite suspension did not result in significant differences of Sb(V) adsorption. The observation well agree with the experimental result of As(V) adsorption on goethite (Grafe et al. 2001). Many authors interpreted that humic substances (HS) are homogeneous in solution and no difference in the surface adsorbed HS and solution soluble HS, and thereby no effect of addition sequences on metal ions' adsorption on solid surface (Strathmann and Myneni 2005).

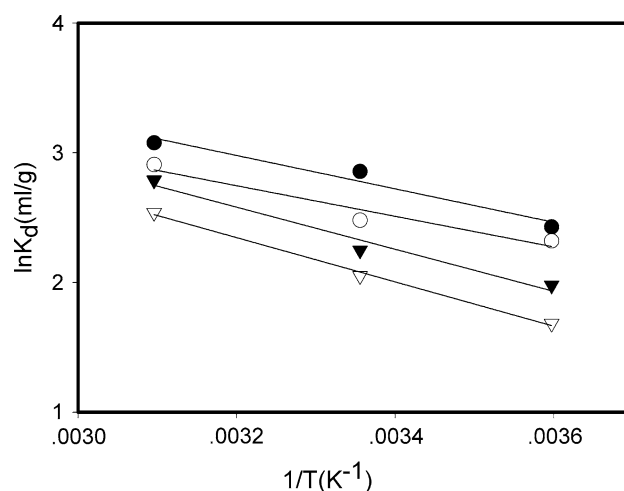


Fig. 6 Plot of distribution coefficient K_d versus temperature for antimonate adsorption

Table 2 Values of thermodynamic parameters for the adsorption of antimonate on kaolinite

C_0 ($\mu\text{g/L}$)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)	ΔG^0 (kJ/mol)		
			278 K	298 K	323 K
500	10.71	59.04	−5.7	−6.88	−8.36
800	9.8	54.19	−5.26	−6.35	−7.7
1,500	13.49	64.62	−4.47	−5.77	−7.38
2,000	14.19	64.92	−3.86	−5.16	−6.78

Thermodynamic Parameters

The adsorption of Sb(V) on kaolinite as a function of temperature was investigated at three different temperatures. The standard enthalpy (ΔH^0) and standard entropy changes (ΔS^0) can be calculated from the slope and intercept of the plot of $\ln K_d$ versus $1/T$ (Fig. 6) by using the equation:

$$\ln K_d = \Delta S^0/R - \Delta H^0/RT \quad (5)$$

The Gibbs free energy (ΔG^0) of adsorption can be calculated from the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

where R (8.3145 J/mol K) is the ideal gas constant, and T (K) is the temperature. Detailed data calculated from Eqs. 4 and 5 are listed in Table 2. The values of ΔG^0 calculated are negative, that is to say that the adsorption of Sb(V) on kaolinite is a spontaneous process and the adsorptive forces are strong enough to break the potential barrier. The decrease in ΔG^0 with increasing temperature implies more efficient adsorption at higher temperatures. Results showed that the values of ΔH^0 are positive under the experimental conditions. This indicated that the

adsorption reaction of Sb(V) on kaolinite is endothermic process. The positive value for entropy changes (ΔS^0) reflects the affinity of kaolinite toward Sb(V) anion in aqueous solutions (Genc-Fuhrman et al. 2004). The increase in adsorption with increasing temperature may also indicate that chemisorption might take place in the system and possibly that there is some tunneling of adsorbed ions into mineral phases in the kaolinite (Axe and Anderson 1997). The values of ΔG^0 , ΔH^0 and ΔS^0 in the adsorption experiment are not only dependent on the mineral composition but also dependent on the experimental conditions. Moreover, estimation of thermodynamic parameters using linear plots of thermodynamic models could introduce some errors that could shift values from the border of one extreme to another. When this occurs, adsorption reactions that have small but negative ΔG^0 could shift to small but positive ΔG^0 (Unuabonah et al. 2008). So, the calculations of thermodynamic parameters can not be considered as very accurate considering the limited measurements and the lack of purity of kaolinite.

Conclusions

In this study, the adsorption of Sb(V) on kaolinite was discussed for the first time and the effect of pH, ionic strength, temperature and humic acid was examined. The adsorption of Sb(V) on kaolinite reached equilibration within 24 h. The adsorption isotherms can be described with both Freundlich equation and Langmuir equation. The adsorption of Sb(V) was markedly reduced by increasing ionic strength at ionic strength range of 0.01–0.05 M and was unaffected by the changes at the ionic strength in the range of 0.05–0.1 M. It was found that adsorption of Sb(V) on kaolinite was strongly dependent on pH and decreased with increasing of pH. Desorption of Sb(V) from kaolinite was dependent on the original suspension pH. With the increasing of pH, desorption of Sb(V) increased. It is suggested that Sb(V) may form mainly outer-sphere complex at high pH and inner-sphere complex at low pH on kaolinite surface. No significant effects of humic acid and the addition sequence of Sb(V)/humic acid was observed. The thermodynamic data of the process was calculated according to the adsorption isotherms at different temperature. A positive value of the standard enthalpy change and a negative value of the free energy changes indicate that the adsorption is endothermic and spontaneous. The results clearly show that the adsorption of Sb(V) on kaolinite play an important role in determining the fate and transformation in natural environments. Spectroscopic study on the microstructure of Sb(V) may be necessary to identify the species of Sb(V) on kaolinite surface in future.

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