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Adsorption of antimony(III) and antimony(V) on bentonite: Kinetics, thermodynamics and anion competition

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ABSTRACT

This research attempted to study the adsorption of Sb(III) and Sb(V) on bentonite using batch experiments. The effects of reaction time, temperature, initial Sb concentration, and competitive anions at different concentrations on the adsorption of Sb(III) and Sb(V) were investigated. Kinetic studies suggested that the adsorption equilibriums for both Sb(III) and Sb(V) were reached within 24 h. The desorption of Sb adsorbate on the bentonite was observed following Sb(III) adsorption, probably due to the oxidation of Sb(III) on the bentonite surface and subsequent desorption of Sb(V). In addition, oxidation of Sb(III) can occur in the solution medium also, which decreases the concentration of Sb(III) in the solution thereby driving the equilibrium in the direction of desorption from the surface. The adsorption data at three temperatures were successfully modeled using Langmuir ($r^2>0.82$) and Freundlich ($r^2>0.99$) isotherms. The thermodynamic parameters (ΔG^0, ΔH^0, and ΔS^0) were calculated from the temperature dependence, suggesting that the adsorption process of Sb(III) is spontaneously exothermic, while the adsorption process of Sb(V) is spontaneously endothermic. Competitive anions such as NO_3^-, SO_4^{2-}, and PO_4^{3-} hardly affected the Sb(III) adsorption on bentonite, while $SO_4^{2-}$and PO_4^{3-} could compete with $Sb(OH)_6^-$ for adsorption sites. The competition between PO_4^{3-} and $Sb(OH)_6^-$ on adsorption sites was presumably due to the formation of surface complexes and the surface accumulation or precipitation of PO_4^{3-} on bentonite surface.

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1. Introduction

Antimony (Sb) is a hazardous substance widely distributed in the lithosphere and has been widely applied in various industrial products such as increasing the hardness of alloys in lead–acid batteries and in small arms bullets, functioning as a flame retardant, and being used in the clarification of glass products [1,2]. So antimony is ubiquitously present in the environment as a result of natural processes such as rock weathering and soil runoff, and human activities [3]. In recent years, Sb has attracted increasing attention, primarily due to its industrial applications and its toxicity to humans.

The antimony concentration is less than 1 μg/L and within the lower mg/kg range in uncontaminated waters and soils, respectively [1,2,4,5]. Anthropogenic sources of Sb, however, greatly increase Sb concentration in soils and waters and thus pose the greatest threat to the environment. The important sources of Sb are emissions from vehicles, smelters and municipal wastes [6–9]. As a result, elevated concentrations of Sb in both soils and waters have been detected near Sb mining areas as well as other areas contaminated by human activities [6,9–15]. However, very little is known about the mobility of Sb in the environment. The availability and mobility of Sb is supposed to be affected by geochemical 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. Both Sb(III) and Sb(V) ions hydrolyse easily in aqueous solution, thus making it difficult to keep antimony ions stable in solution except in highly acidic media. In the pH range of 2 to 11, Sb (III) should form a neutral complex, $Sb(OH)_3$, whereas Sb(V) should exist as a negatively charged complex, $Sb(OH)_6^-$ [2,16,17].

Few adsorption studies of Sb on natural sorbents have been reported to date [2]. Previous work by Thanabalasingam and Pickering indicated that the adsorption capacity of Fe, Mn and Al hydroxides for Sb(III) decreases in the sequence $MnOOH>Al(OH)_3>FeOOH$ [18]. Some studies demonstrated that both Sb(III) and Sb(V) can strongly bind to Fe hydroxides, however, the binding mechanism is still unclear [17,19–22]. Previous studies focused on Sb adsorption on metal oxides. However, only sporadic studies addressed the adsorption of Sb with clay minerals, although one or more of clay minerals are found in almost every type of sediments and soils [23,24]. Bentonite as a major type of silicate clay mineral is mainly composed of montmorillonite, a 2:1 type of aluminosilicate clay. A number of papers were published on adsorption behavior of heavy metal on the bentonite [25,26]. However, the adsorption of Sb on bentonite has not been studied previously.

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China is rich in Sb mineral resources. The Sb mine of Xikuangshan, located near Lengshuijiang City, Hunan Province, China, is one of the largest Sb mines in the world. It is believed that Sb pollution from Sb mining and smelting in China is generally very severe, resulting in significant environmental problems [9,10].

The objective of the present study was to determine whether bentonite could immobilize Sb by sorption and to examine the effect of the reaction time, initial Sb concentration, competitive anions, and temperature on the sorption of Sb on bentonite.

2. Materials and methods

2.1. Reagents and materials

All chemicals in this study were reagent-grade or better and were used without further purification. Double distilled water was used throughout. All samples were analyzed within 2 days after completing each sorption test. All experiments were performed in duplicate.

The Ca bentonite (Sigma-Aldrich, USA) was used in the adsorption experiments. X-ray diffraction analysis of the bentonite showed that it contains 85% of montmorillonite, 3.5% of illite, and 11% of quartz. The specific surface area of the bentonite was 99 m^2/g determined by BET method using N_2. The point of zero charge (pH_{zpc}) was 2.6 measured by acidic-basic titration method at different ionic strengths.

2.2. Kinetic experiment of adsorption

Stock solution of 1000 mg/L Sb(III) or Sb(V) in double distilled water were prepared from potassium antimonyl tartrate or potassium pyroantimonate, respectively. The kinetic studies were conducted to examine the influence of reaction time on the adsorption of Sb(III) and Sb(V) on bentonite in 0.02 M $Ca(NO_3)_2$ at pH 6. Batch method was used to examine the effect of reaction time on the adsorption by shaking bentonite suspensions in a series of 50 mL polythene centrifuge tubes containing 500 mg of bentonite in 20 mL of 1 mg/L Sb(III) or Sb(V) for 0.5, 1, 2, 4, 8, 12, 24, 36 and 48 h. Then, the suspensions were centrifuged at 4000 rpm for 20 min and the supernatants were filtered through 0.22 μm cellulose nitrate membranes.

2.3. Isotherm adsorption experiments

Batch isotherm adsorption experiments were conducted with fixed amount of bentonite but varying initial adsorbate concentrations by adding various volumes of stock solutions of Sb(III) and Sb (V). The initial antimony concentration in solution ranged from 0.05 to 4 mg/L. Ionic strength was maintained by electrolyte ($Ca(NO_3)_2$) addition. The pH of the suspension was adjusted to 6 with 0.1 M $NaOH/HNO_3$. The suspension was shaken for 24 h at 278, 298 and 323 K separately in order to calculate the thermodynamic parameters of the adsorption reaction.

2.4. Adsorption models

Freundlich and Langmuir models are the simplest and most commonly used isotherms to simulate adsorption of components from a liquid phase on to a solid. The Langmuir model is a valid monolayer sorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration sorbate in the plane of the surface. The Langmuir equation is written as

$$q_e = \frac{Q_0 bC_e}{(1 + bC_e)} \text{ (nonlinearform)} \quad (1)$$

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

where C_e is the equilibrium concentration of absorbate in the bulk solution (μg/L), q_e is the equilibrium content in solid phase (μg/g), Q_0 (μg/g) and b (L/g) are sorption capacity and sorption energy, respectively. Maximum sorption capacity (Q_0) represents complete monolayer coverage of sorbent with sorbate and b represents enthalpy of sorption and varies with temperature. The constants are calculated from slope and intercept of the linear plots of C_e/q_e versus C_e, respectively. The dimensionless parameters of the equilibrium or adsorption intensity, R_L, based on the further analysis of Langmuir equation can be expressed as [27,28]:

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

where C_0 (μg/L) is the initial concentration of Sb. There are four probabilities for the R_L value: (i) for favorable adsorption, $0 < R_L < 1$, (ii) for unfavorable adsorption, $R_L > 1$, (iii) for linear adsorption, $R_L = 1$, and (iv) for irreversible adsorption, $R_L = 0$.

The Freundlich equation is an empirical adsorption model that can be expressed as

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

where q_e and C_e are defined previously, K is a Freundlich's constant related to the sorption capacity, and 1/n is considered to be relative indicator of adsorption intensity. Linear form of Freundlich equation is:

$$\log q_e = \frac{1}{n}\log C_e + \log K. \quad (5)$$

2.5. Competitive adsorption experiment

The competitive anions in this study included SO_4^{2-}, PO_4^{3-} and NO_3^-. The effect of these competitive anions on adsorption was investigated by determining the amount of the Sb(III) or Sb(V) adsorption at different concentrations of SO_4^{2-}, PO_4^{3-} and NO_3^- ranging from 0.005 to 0.1 M at pH 6 and 298 K with the initial Sb concentration of 1 mg/L. After 24 h of equilibration, the suspensions were centrifuged and filtered as before.

2.6. 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 experiments. Then the concentration of Sb in the supernatants was measured with a hydride generation atomic fluorescence spectrometer (AFS-230, Beijing Haiguang Instrument Co., China) [29]. For hydride generation, 2% KBH_4 (prepared in 0.5% KOH) and 5% HCl reacted with the samples. Calibration was done with commercial standard solution of Sb.

3. Results and discussions

3.1. Effect of reaction time on the adsorption of Sb(III) and Sb(V)

Fig. 1 shows the adsorption of Sb(III) and Sb(V) on bentonite as a function of reaction time. The kinetic profile for the adsorption of Sb (III) showed a fast initially adsorption and the maximum adsorption was reached within 30 min. However, as reaction time increased, desorption of Sb(III) was observed and up to 6% of the initially adsorbed amount of Sb(III) was desorbed from bentonite. Similar fast equilibrium time was found for Sb(III) adsorption on to goethite and desorption of Sb(III) from goethite can occur after 60 min [17]. It is possible that trace iron oxides or humic acid associated with bentonite

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