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# Adsorption and desorption characteristics of arsenic on soils: kinetics, equilibrium, and effect of $\text{Fe}(\text{OH})_3$ colloid, $\text{H}_2\text{SiO}_3$ colloid and phosphate

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## Abstract

Adsorption and desorption of arsenic on different soils may affect the mobility, toxicity and bioavailability of arsenic in soil media. In this study, laboratory batch experiments were carried out to study the adsorption and desorption of arsenic in three soils in China with different physicochemical properties. The results show that the adsorption was relatively fast for Beijing soil and Hainan soil, the reactions almost completed within the first few hours, while it was relatively slow for Jilin soil. The adsorption isotherms for three soils fitted very well to both the Langmuir and Freundlich models. The content of organic matter in the soils was the major factor to determine the adsorption capacity. The thermodynamic parameters for the adsorption of arsenic were determined at three different temperatures of 283 K, 303 K and 323 K. The adsorption reactions were endothermic and the process of adsorption was favored at high temperature. The adsorption behavior of arsenic on soils was strongly dependent on the concentrations of  $\text{Fe}(\text{OH})_3$  and  $\text{H}_2\text{SiO}_3$  colloid. Phosphate suppressed the adsorption of arsenite and arsenate, especially for BJ soil. The desorption data showed that desorption hysteresis occurred at the concentration studied. These findings improve our knowledge in modeling arsenic adsorption to common soil minerals.

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*Keywords:* Adsorption; Desorption; Arsenic; Soil

## 1. Introduction

Arsenic has become an important topic in environmental research because of its toxicity, geological

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abundance and human use [1,2]. Total arsenic content in natural soils is usually below 10 mg·kg<sup>-1</sup>[3], however, it can be greatly increased in polluted mine soils[4], substantially exceeding the guideline limit of 50 mg kg<sup>-1</sup> for agricultural soils. The toxicity of arsenic species depends on its chemical forms[5,6]: inorganic arsenic are more toxic than methylated arsenic, and in particular, As(III) is more toxic than As(V)[7,8]. The mobility, toxicity and bioavailability of arsenic in soil are largely depended upon the adsorption/desorption of arsenic by the soil. Hence, in order to elucidate the behavior of arsenic in soil, it is important to study the adsorption/desorption process[9,10].

Previous researchers have shown that Fe and Al oxides and hydroxides have a high affinity to arsenic[6,11,12]. Studies such as extended X-ray adsorption fine structure spectroscopy[13,14] and Fourier transform infrared[15,16] showed that both As(V) and As(III) could form mono- or bidentate inner-sphere surface complexes with iron oxides via a ligand exchange mechanism. Recently, some investigations focused on the arsenic adsorption characteristics in soils. Zhang et al. [17] observed that adsorption of arsenate was strongly kinetic by Olivier loam, Sharkey clay, and Windsor sand. Jiang et al. [18,19] also studied the adsorption of arsenate on 16 soils and found the Jiangxi and Hubei soils were more effective adsorbents for arsenate than other soils. Although much work has been devoted to examining the adsorption characteristic, such studies have generally used either adsorption kinetic in soil or only for adsorption capacity. There is a lack of knowledge, however, on the thermodynamic adsorption behavior of arsenic on soil. Temperature might play an important role in controlling the distribution of arsenic in soil environment. Therefore, understanding of the thermodynamic adsorption behavior of arsenic on soil is also an important issue.

Several factors may affect the adsorption/desorption of arsenic, including the complexes of the soils. Soils are heterogeneous complexes of organic matter, metal oxides, clay minerals and microorganisms, with diverse structures[20]. Some of the common exchangeable cations and anions, such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and NO<sub>3</sub><sup>-</sup>, all exist. Therefore, soil has the high ability to adsorb metals or metalloids. Moreover, the chemical behavior of AsO<sub>4</sub><sup>3-</sup> is similar to that of PO<sub>4</sub><sup>3-</sup> in soils, competitive adsorption of arsenate and phosphate on soils may happen. Furthermore, there are many kinds of soil colloids with different charges in soils, for example, in general, H<sub>2</sub>SiO<sub>3</sub> colloid surface has negative charge and Fe(OH)<sub>3</sub> colloid surface has positive charge, which may affect the adsorption of arsenic on soils. However, little investigation had been conducted on the adsorption of arsenic by soils and rare reports had been developed to the study of arsenic adsorption on individual soil minerals with different pH, ionic strength, and humic acid[21,22]. Detailed information on the adsorption of arsenic on soils with different mineralogical and chemical properties is still not available. Therefore, it is of paramount important to study the effects of soil properties on arsenic adsorption.

Furthermore, only a limited number of studies have investigated release or desorption of arsenic from minerals and soils[17,23]. Helle et al. [24] suggested that desorption of arsenate from calcite was fast and complete within hours, indicating that arsenate was not readily incorporated into the calcite crystal lattice. In contrast, Zhang et al. [17] reported that desorption of As(V) was hysteresis in nature and was an indication of lack of equilibrium retention and/or irreversible or slowly reversible processes. O'Reilly et al. [25] concluded that a significant amount of As(V) bound to goethite (>60%) was not readily dissociated through exposure to 6 mM phosphate solution after 5 months of exposure. These contradictory results indicate that further studies should be carried out to investigate desorption of arsenic from soil and consequent migration to the environment.

The objectives of this research were to investigate the kinetics and equilibrium of the adsorption and desorption of arsenic on three different soils in China with different physicochemical properties. The adsorption isotherms and experimental data regressive analysis were investigated with Langmuir and Freundlich models. In addition, the adsorption data of arsenic at different temperatures were studied and adsorption thermodynamic parameters (i.e.  $\Delta H^0$ ,  $\Delta S^0$ ,  $\Delta G^0$ ) were measured. The effect of several

environmental parameters, such as  $\text{H}_2\text{SiO}_3$  colloid,  $\text{Fe}(\text{OH})_3$  colloid and phosphate on arsenic adsorption were examined. To better understand the adsorption/desorption behavior, desorption of arsenic at soil surface using batch adsorption experiments were also investigated.

## 2. Materials and methods

### 2.1. Materials

All chemicals used were of analytical reagent grade. Stock solutions of arsenic were purchased from National Institute of Metrology (Beijing, China). These stock solutions were kept at 4 °C in darkness. The working solutions of arsenic ( $0.4\text{--}40.0 \mu\text{g}\cdot\text{L}^{-1}$ ) were prepared daily by dilution of the stock solution with dilute HCl. Working solutions of 20 % (w/v) potassium tetrahydroborate were prepared daily by dilution of the  $\text{KBH}_4$  stock solution in 5 % NaOH. Pre-reducing solutions containing 10 % (w/v) thiourea (Beijing Chemical Works, China) and 10 % (w/v) ascorbic acid (Sigma, USA) were prepared fresh daily in water. Glassware used was soaked in a 10% (v/v) nitric acid solution and rinsed with Milli-Q water (18.2 M $\Omega$  cm).

### 2.2. Soils

Three surface soil samples (0–20 cm) were collected from cultivated land in Beijing, Jilin and Hainan provinces of China, in areas away from industrial site. Each sample consisted of a homogenate of four sub-samples located in an imaginary circle about 2 m diameter around the sampling point without apparent anthropogenic influence. The soils represent typical Chinese soils with different physical and chemical properties. Soil samples were air-dried, homogenized and ground to pass through 1 mm nylon fibre sieve, and stored for subsequent analysis and experiments.

Soil pH was measured in 0.01 M  $\text{CaCl}_2$  at 1:2.5 (w:v) soil solution ratio. Cation exchange capacity (CEC) was determined by the method of ammonium acetate centrifugal exchange. Zeta potential was determined by dynamic light scattering (DLS), using a Coulter Nicomp™ 380 ZLS Particle Size Analyzer (Santa Barbara, CA, USA). Organic matter (OM) content was determined by the Walkley-Black's procedure. Concentrations of Fe, Al, Mn and P were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, OPTIMA2000DV, Perkin Elmer) after digestion of soils with  $\text{HF-HNO}_3\text{-HClO}_4$ . Soil texture was obtained by hydrometer method. All measurements were repeated in triplicate. The soil properties are summarized in Table 1.

### 2.3. Kinetic batch experiments

Kinetic batch experiments were conducted to determine the adsorption rate for arsenic on three soils at constant room temperature of  $25 \pm 1$  °C. Initial arsenic solution ( $40 \mu\text{g}\cdot\text{L}^{-1}$ ) was prepared from stock solutions in 0.01 M  $\text{NaNO}_3$  background solution to maintain constant ionic strength. Batch experiments were initiated by mixing 20 mg of air-dry soil with 5.0 mL of arsenic solution. The mixtures were shaken at 200 rpm on a reciprocal shaker and subsequently centrifuged for 10 min at 5000 rpm after each specified reaction time. One milliliter aliquot was sampled from the supernatant at reaction times of 10 min, 30 min, 1 h, 2 h, 6 h, 10 h, 24 h, 2 d, 6 d, 10 d, 16 d, 22 d, 29 d, and 36 d, respectively.

The AFS-9800 atomic fluorescence spectrometer (Beijing Kechuang Haiguang Instrument Company, China) was used for arsenic determination. The arsine was generated by adding precise known volumes of sample, a reducing potassium tetrahydroborate solution (20 %), hydrochloric acid (10 %) using an autosampler. And a pre-reducing solution (thiourea 10 % and ascorbic acid 10 %) was used to pre-reduce

As(V) to As(III), when the task was to speciate As(III) and As(V). As(V) was determined by the difference between total inorganic arsenic and As(III). The amount of arsenic adsorbed was calculated by the difference between the initial and final concentrations of arsenic in the equilibrium solution. Adsorption determinations were performed in triplicate.

Table 1. Selected physical and chemical properties of the studied soils.

	unit	BJ soil	JL soil	HN soil
pH		7.3	6.38	8.17
Conductivity	$\mu\text{s}\cdot\text{cm}^{-1}$	14.44	316	26.7
Zeta potential	mV	-17.48	-63.55	37.14
	1-0.05	59.01	45.18	37.06
Soil texture	0.05-0.01	24.49	36.55	16.24
	0.01-0.001	9.16	6.09	25.38
	<0.001	8.44	12.18	21.32
CEC	$\text{mmol}\cdot(100\text{g})^{-1}$	6.83	40.80	11.47
Organic matter	$\text{g kg}^{-1}$	79.16	149.68	3.36
P	$\text{mg}\cdot\text{kg}^{-1}$	959.73	1352.67	1486.73
As	$\text{mg}\cdot\text{kg}^{-1}$	6.56	13.91	1.14
Ca	$\text{mg}\cdot\text{kg}^{-1}$	10777.32	49595.39	632.32
Mg	$\text{mg}\cdot\text{kg}^{-1}$	6998.58	17126.26	3484.00
Fe	$\text{mg}\cdot\text{kg}^{-1}$	39025.27	39090.51	33012.77
Al	$\text{mg}\cdot\text{kg}^{-1}$	36495.95	75520.19	67231.68
Mn	$\text{mg}\cdot\text{kg}^{-1}$	444.58	933.55	107.41
BET specific surface area	$\text{m}^2\cdot\text{g}$	11.97	5.165	27.20

#### 2.4. Adsorption experiments

A batch equilibration method was used for adsorption of arsenic. In all adsorption experiments, 20 mg of soil and 5.0 ml of  $0.01 \text{ mol L}^{-1}$   $\text{NaNO}_3$  containing different initial arsenic concentrations were used. After shaking for 48 h (15 d for JL soil) at room temperature ( $25 \pm 1^\circ\text{C}$ ) except for the thermodynamic experiments, in which temperatures of 283, 303 and 323 K were adjusted, the mixtures were centrifuging at 5000 rpm for 10 min. One milliliter aliquot was sampled and determined with AFS-9800 atomic fluorescence spectrometer.

The effect of  $\text{H}_2\text{SiO}_3$  colloid and  $\text{Fe}(\text{OH})_3$  colloid on As(III) and As(V) adsorption on soils were examined with the concentration from  $2 \times 10^{-5}$  to  $1.0 \text{ mmol}\cdot\text{L}^{-1}$  and from  $1 \times 10^{-6}$  to  $0.5 \text{ mmol}\cdot\text{L}^{-1}$  for  $\text{H}_2\text{SiO}_3$  colloid and  $\text{Fe}(\text{OH})_3$  colloid, respectively. In these adsorption experiments, 20 mg of soils were added into 5.0 ml of different concentrations of  $\text{H}_2\text{SiO}_3$  colloid or  $\text{Fe}(\text{OH})_3$  colloid containing  $10.0 \mu\text{g}\cdot\text{L}^{-1}$  initial As(III) or As(V) concentrations. After shaking for 48 h (15 d for JL soil) at room temperature ( $25 \pm 1^\circ\text{C}$ ), the mixtures were then centrifuging and determined with AFS-9800 atomic fluorescence spectrometer.

Competition adsorption between arsenic and  $\text{PO}_4^{3-}$  on these soils was studied with increasing concentration of arsenic while keeping  $\text{PO}_4^{3-}$  concentration. Fifteen milligram of soil was added into 4.9 mL different concentration of arsenic solution (As(III) or As(V),  $1.5\text{-}12.0 \mu\text{g}\cdot\text{L}^{-1}$ ), and then 0.1 mL  $0.5 \text{ g}\cdot\text{L}^{-1}$   $\text{Na}_3\text{PO}_4$  solution was added into the above solution. After shaking and centrifugation, supernatant

was sampled and analyzed by atomic fluorescence spectrometry. Experiments without  $\text{Na}_3\text{PO}_4$  were also carried out by the same procedure used as control. All measures were repeated at least in triplicate.

### 2.5. Desorption experiments

Desorption experiments of arsenic were conducted in sequential decant-refill steps immediately following the completion of the adsorption experiments. Supernatant was removed and immediately replaced by the same volume of background solution ( $\text{NaNO}_3$ :  $0.01\text{mol}\cdot\text{L}^{-1}$ ), the vials resealed and shaken for an additional 24 h for Beijing (BJ) soil and Hainan (HN) soil, for an additional 48 h for Jilin (JL) soil. After equilibration, the vials were centrifuged, arsenic in the supernatant was determined, and the amount of arsenic desorbed was calculated from mass differences. The above process was repeated for eight complete cycles. All samples were performed at least in triplicate.

## 3. Results

### 3.1. Soil properties

The physical and chemical properties of three Chinese soils varied widely (Table 1). The zeta potential, pH, OM, and conductivity ranged greatly among three soils. Extractable P, Fe, Al, Ca and Mn also differed greatly. Total arsenic concentrations in the soils ranged from  $1.14$  to  $13.91\text{ mg}\cdot\text{kg}^{-1}$ . All of these soils could be considered as uncontaminated soils (Jiang et al. 2005). On the basis of the particle size distribution, these soils were all sandy-loam, however, BJ soil was cinnamon soil, HN soil was latosol in red, JL soil was meadow soil in black and possessed low pH, high conductivity, and the extractable P, Fe, Al, Ca and Mn were all higher than the other two soils.

### 3.2. Kinetic batch experiments

Results from kinetic batch experiments are presented in Fig. 1 in order to illustrate the changes in adsorbed of arsenic versus time by the soils. For all soils, the rate of arsenic retention was rapid during the initial stages of reaction and was then followed by gradual or somewhat slow reactions that were best characterized by continued arsenic retention, which could clearly depicted by steady increase of arsenic adsorption with reaction time. However, there was obvious difference among these soils. For example, after 2 h of reaction, arsenic adsorption was 99.0 and 98.7 % for BJ soil and HN soil, while it was only 34.0 % for JL soil. The results also indicated that it took longer time for JL soil to adsorb arsenic (about 15 d). The different relative reaction rates could relate to the different physical and chemical properties of these soils. For examples, JL soil possesses very high conductivity ( $316\ \mu\text{s}\cdot\text{cm}^{-1}$ ) and cation exchange capacity ( $40.80\text{ mmol}\cdot(100\text{g})^{-1}$ ), which implies that the exchangeable ions are abundant in JL soil which can interact with arsenic and prolong the reaction time.

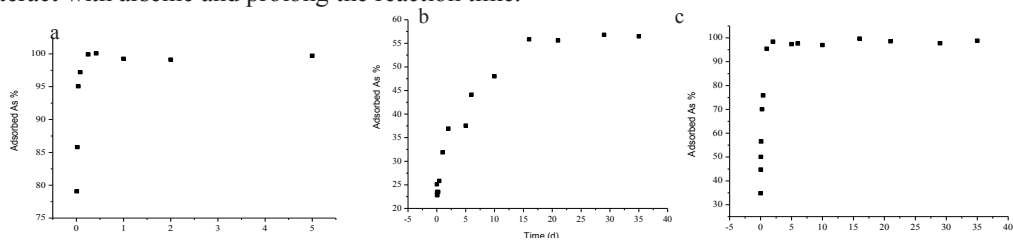


Fig. 1. Adsorbed of arsenic versus time during adsorption on different soils (a: BJ soil, b: JL soil, c: HN soil).

In addition, the kinetic results presented in Fig. 1 concurred with the nonlinear forms which also illustrated the time dependence of arsenic adsorption. These findings were in agreement with the biphasic arsenic adsorption behavior observed on several soil minerals[12] as well as whole soils[17] over different time scales (minutes to months). In heterogeneous soil systems, nonequilibrium conditions of arsenate adsorption may due to several mechanisms which were proposed by Zhang[17]: (1) heterogeneity of sorption sites, (2) slow precipitation at the mineral surface, and (3) slow diffusion to sites within the soil matrix.

### 3.3. Adsorption isotherms

Langmuir and Freundlich isotherms were employed to describe the adsorption of arsenic on soils at 283, 303 and 323 K. Langmuir isotherm is mainly applied to monolayer adsorption on perfectly smooth and homogeneous surface within the adsorbent.

The adsorption capacity  $q_{max}$  and adsorption constant  $K_L$  can be determined from the slope and intercept of a linearized plot of  $C_e/q_e$  against  $C_e$ .

The Freundlich isotherm is derived by assuming a heterogeneous surface with a nonuniform distribution of the heat of sorption over the surface.

The experimental data were correlated by Freundlich and Langmuir models. Based on those model equations, the adsorption parameters  $q_{max}$ ,  $K_L$ ,  $K_F$ ,  $n$ , and the correlation coefficient values ( $R$ ) of arsenic by these soils were obtained (Table 2). As seen in Table 2, the adsorption of arsenic on these soils was well fitted both to the Langmuir isotherm model and to the Freundlich isotherm model with high  $R$  values 0.9585-0.9980, 0.9621-0.9852 for Langmuir and Freundlich isotherm model, respectively. Furthermore, the values of  $K_L$  for the Langmuir isotherm were between 0 and 1, and the Freundlich constant  $1/n$  was smaller than 1 (0.56-0.88), indicating a favorable process. The results indicated that adsorption parameters - Langmuir  $q_{max}$ ,  $K_L$ , and Freundlich  $K_F$  - exhibited a linear relationship with the organic matter (Fig. 2), however, the total amount of Fe and Al contents were no found to be correlated with arsenic adsorption parameter.

Table 2. Isotherm model constants of two isotherm models for arsenic adsorption on soils.

Sample	283 K			303 K			323 K		
	Langmuir model								
Soil	$q_{max}$	$K_L$	R	$q_{max}$	$K_L$	R	$q_{max}$	$K_L$	R
BJ	13.22	0.037	0.9585	14.65	0.055	0.9615	16.37	0.20	0.9752
JL	9.96	0.064	0.9742	10.55	0.070	0.9794	19.46	0.13	0.9980
HN	23.27	0.21	0.9877	26.06	0.23	0.9928	27.08	0.26	0.9964
Freundlich model									
	$K_f$	n	R	$K_f$	n	R	$K_f$	n	R
BJ	1.94	1.13	0.9852	3.10	1.32	0.9654	4.71	1.35	0.9842
JL	0.58	1.41	0.9657	0.66	1.26	0.9662	0.77	1.37	0.9708
HN	3.59	1.77	0.9793	4.82	1.76	0.9689	5.38	1.79	0.9621

\*The unit of  $K_f$  is  $(\text{mg kg}^{-1}) (\text{L mg}^{-1})^{1/n}$ ,  $K_L$  is  $(\text{L mg}^{-1})$  and  $q_{max}$  is  $(\text{mg kg}^{-1})$ .

The adsorption of arsenic ( $q_{max}$  and  $K_f$  in Langmuir model and Freundlich model, respectively) increased with the rise in temperature, illuminating an endothermic process for arsenic adsorption on these soils. The results indicated that the adsorption of arsenic in these soils was favored at high



temperature and was blocked at low temperature. However, the existing information on the arsenic adsorption characteristic depending on temperature is limited and somewhat contradictory. Attundogan et al. [26] reported that the adsorption of arsenite was exothermic, and arsenate adsorption was endothermic when arsenic adsorption from aqueous solutions by activated red mud, while Mohapatra et al. [20] concluded arsenate adsorption on clay minerals was exothermic. The difference of these adsorption results may result from the adsorbents with different physical and chemical properties.

### 3.4. Thermodynamic parameters associated with the adsorption processes

The thermodynamic functions of the adsorbed phase can be calculated from the variation of the thermodynamic equilibrium constant  $K_0$  under different temperatures. The standard molar free energy of adsorption,  $\Delta G^0$ , is calculated from the relationship.

The thermodynamic parameters values obtained are given in Table 3.  $\Delta G^0$  values were in the range of  $-1.78$  to  $-2.34$   $\text{kJ}\cdot\text{mol}^{-1}$  and  $-3.87$  to  $-5.60$   $\text{kJ}\cdot\text{mol}^{-1}$  when adsorption temperature was from 283 to 323 K for BJ soil and HN soil, while  $\Delta G^0$  values were from 4.89 to 3.14  $\text{kJ}\cdot\text{mol}^{-1}$  for JL soil. It indicated that adsorption process was spontaneous for BJ soil and HN soil and non-spontaneous for JL soil. The positive adsorption entropy indicated that the degrees of the freedom increase at the solid-liquid interface during the adsorption of arsenic on these soils. The adsorption enthalpy of arsenic was 2.13, 16.06, 8.28  $\text{kJ}\cdot\text{mol}^{-1}$  for BJ soil, JL soil and HN soil respectively, and the positive values of  $\Delta H^0$  indicated that the arsenic adsorption process was endothermic, which was consistent with the adsorption isotherm. Generally, the enthalpy of physisorption was smaller than 20  $\text{kJ}\cdot\text{mol}^{-1}$ [27]. Based on the above  $\Delta H^0$ , it suggests that the adsorption of arsenic is a physisorption process.

Table 3. Thermodynamic parameters for arsenic adsorption on soils.

Sample	283 K				303 K				323 K			
	$\text{Ln}(K_0)$	$\Delta G^0$	$\Delta H^0$	$\Delta S^0$	$\text{Ln}(K_0)$	$\Delta G^0$	$\Delta H^0$	$\Delta S^0$	$\text{Ln}(K_0)$	$\Delta G^0$	$\Delta H^0$	$\Delta S^0$
BJ soil	0.76	-1.78	2.13	14.31	0.81	-2.04	2.13	15.27	0.87	-2.34	2.13	16.36
JL soil	-2.08	4.89	16.06	40.90	-1.48	3.74	16.06	40.64	-1.17	3.14	16.06	39.90
HN soil	1.64	-3.87	8.28	42.91	1.83	-4.62	8.28	42.55	2.08	-5.60	8.28	42.95

\*The unit of  $\Delta G^0$  is ( $\text{kJ}\cdot\text{mol}^{-1}$ ),  $\Delta H^0$  is ( $\text{kJ}\cdot\text{mol}^{-1}$ ),  $\Delta S^0$  is ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ).

### 3.5. Adsorption and desorption

Fig. 2 is a plot of the adsorption and the desorption isotherms of arsenic on these soils. The desorption times were either 8 days (for BJ soil) or 16 days (for JL soil and HN soil). Under the nearly identical experimental conditions, hysteresis during arsenic desorption was significant for both JL soil and HN soil but not significant for BJ soil. There would also be a corresponding concentration-dependent effect in this study: at low input arsenic concentrations, only small proportions were desorbed. In contrast, the percentage of desorption increased at high input arsenic concentrations, which meant the amounts adsorbed increased.

Distinct discrepancies between adsorption and successive desorption isotherms indicated that that arsenic is incorporated into the soils under our experimental conditions. At lower initial concentrations of arsenic, there were only a limited number of high-energy sites available on the solid surface that could be initially occupied[28]. Thus, preferential adsorption at the high-energy sites of these soil particles made sequential desorption more difficult. In contrast, at high concentrations of arsenic, the limited high energy

sites became saturated and adsorption of arsenic occurred at lower energy sites as well, which consequently made the overall desorption easier. In this work, high adsorption capacity and irreversible adsorption of arsenic on soils suggest that arsenic has high healthy and environmental risks.

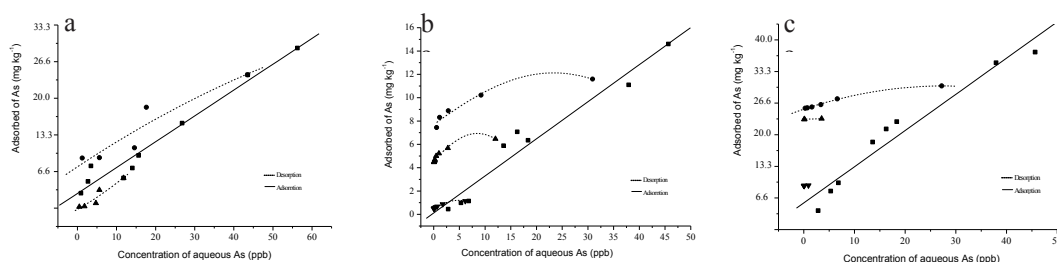


Fig. 2. Adsorption and desorption isotherms of arsenic on soils (a: BJ soil, b: JL soil, c: HN soil. For BJ soil, ■: adsorption data, ●: 80  $\mu\text{g}\cdot\text{L}^{-1}$  of initial arsenic with desorption, ▲: 20  $\mu\text{g}\cdot\text{L}^{-1}$  of initial arsenic with desorption. For JL soil and HN soil, ■: adsorption data, ●: 45.65  $\mu\text{g}\cdot\text{L}^{-1}$  of initial arsenic with desorption, ▼: 16.25  $\mu\text{g}\cdot\text{L}^{-1}$  of initial arsenic with desorption, ▼: 6.82  $\mu\text{g}\cdot\text{L}^{-1}$  of initial arsenic with desorption. T=298 k).

### 3.6. Adsorption characteristics of As(III) and As(V): Effect of $\text{Na}_3\text{PO}_4$ , $\text{Fe}(\text{OH})_3$ and $\text{H}_2\text{SiO}_3$ colloid solution

Inorganic arsenic has four oxidation states: +5, +3, 0, and -3. In the soil/water environment, it is mainly present in the +3 and +5 oxidation states. In reduced environments, arsenious acid is a common As(III) aqueous species, whereas oxidized environments contain more As(V) aqueous species. These two aqueous species may be adsorbed onto inorganic and organic soil components and precipitate in a variety of forms. The environmental fate of arsenic in subsurface environments is highly dependent on the arsenic speciation, some coexisting ions, such as  $\text{PO}_4^{3-}$  and  $\text{Fe}(\text{OH})_3$  and  $\text{H}_2\text{SiO}_3$  colloidal solution. The experiments below were performed to investigate the adsorption characteristics of As(III) and As(V) on soils at these conditions.

$\text{H}_2\text{SiO}_3$  colloid was homemade with the particle size of 50 nm. Fig. 3 reveals that arsenic adsorption on soils increased significantly with the decreasing of  $\text{H}_2\text{SiO}_3$  colloid concentration. Especially for HN soil, the max adsorption percents for As(III) and As(V) reached 98% and 74% when the concentrations of  $\text{H}_2\text{SiO}_3$  colloid were lower than  $1 \times 10^{-5} \text{ mol L}^{-1}$ , which were higher than that of BJ soil and JL soil (lower than 30%). The high adsorption capacity of HN soil consisted with the result of  $q_{\text{max}}$  in adsorption isotherm experiment.

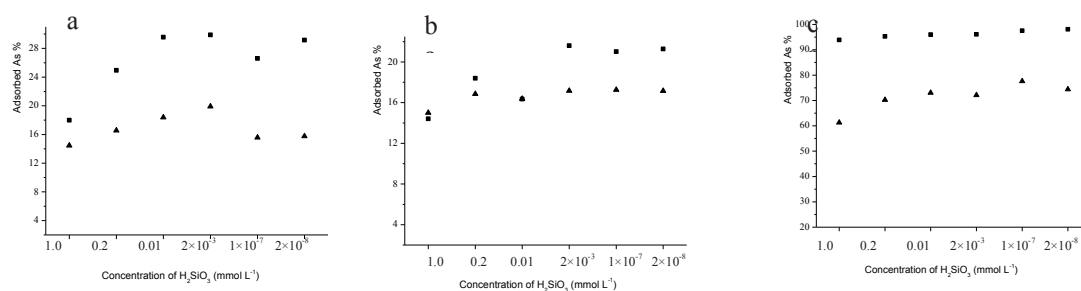


Fig. 3. Effect of  $\text{H}_2\text{SiO}_3$  colloid on the adsorption of As(III) and As(V) on three soils (a: BJ soil, b: JL soil, c: HN soil).for arsenate. ■ for arsenate, ▲ for arsenite)



Meanwhile, the soils had lower adsorption capacity for As(III) than that for As(V) with the existence of  $\text{H}_2\text{SiO}_3$  colloidal solution. The possible reason may be the different pH in these solutions. When the concentrations of  $\text{H}_2\text{SiO}_3$  were lower than  $0.001 \text{ mol}\cdot\text{L}^{-1}$ , the pH values were from 5.35 to 5.91.  $\text{pK}_a$  values for arsenious acid are as follow:  $\text{pK}_a^1 = 9.2$  and  $\text{pK}_a^2 = 12.1$ , while  $\text{pK}_a$  values for arsenic acid are  $\text{pK}_a^1 = 2.3$ ,  $\text{pK}_a^2 = 6.8$ , and  $\text{pK}_a^3 = 11.6$ . Therefore, at pH 5.35 to 5.91, the surface has a net positive charge, As(III) exists in neutral  $\text{H}_3\text{AsO}_3^0$  which has less influence than the adsorption for negatively charged As(V) species which exists in  $\text{H}_2\text{AsO}_4^-$ . The inflections or maxima in the adsorption of arsenic at pH values close their  $\text{pK}_a$  are well documented phenomenon [12,26].

$\text{Fe}(\text{OH})_3$  colloidal solution was synthesized in our laboratory and TEM showed that  $\text{Fe}(\text{OH})_3$  particle was nanorod with 3-70 nm in long diameter. Nanoparticles with high specific surface area tend to adsorb a large variety of toxic chemicals, which may enhance the toxicity of toxic chemicals. It was found from Fig. 4 that As(V) was adsorbed in larger amounts than As(III) when the concentrations of  $\text{Fe}(\text{OH})_3$  colloid were lower than  $0.01 \text{ mmol}\cdot\text{L}^{-1}$ . Interestingly, the maximum As(V) adsorption percents were 95% and 53% for BJ soil and JL soil, the maximum As(III) adsorption percents were 64% and 36% for BJ soil and JL soil when the concentrations of  $\text{Fe}(\text{OH})_3$  colloidal were about  $0.5 \text{ mmol}\cdot\text{L}^{-1}$ . However, the maximal adsorption percents for arsenate and arsenite reached 98% and 76% for HN soil when the concentrations of  $\text{Fe}(\text{OH})_3$  colloidal were lower than  $0.01 \text{ mmol}\cdot\text{L}^{-1}$ . Furthermore, the soils had lower As(III) adsorption than As(V) adsorption under this conditions. Such a difference in As(III) and As(V) sorption efficiency on soils could be related to possible differences between arsenic surface complexes on these different adsorbents. Interestingly, a recent study by Wang et al. [29] proposed that arsenate is absorbed more efficiently than arsenite on the green rusts, for arsenate, the presence of binuclear bidentate double-corner complexes and monodentate mononuclear corner-sharing complexes at the surface of green rusts. And for arsenite, the presence of dimers of As(III) pyramids binding to the edges of the GR1C1 layers by corner sharing with  $\text{FeO}_6$  octahedra. While Raven et al. [12] observed that arsenite adsorption was higher than arsenate adsorption on ferrihydrite throughout the pH range of 3-11. These findings indicate that different ferrous-base compounds have the different adsorption capacity for arsenic, which in turn complicates the adsorption behavior of arsenic in soils.

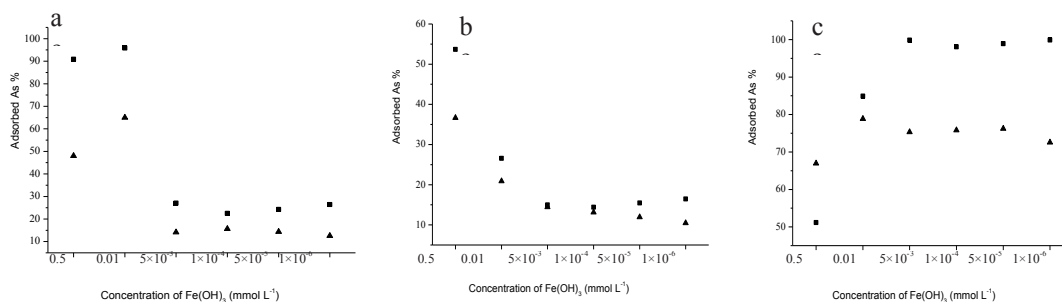


Fig. 4. Effect of  $\text{Fe}(\text{OH})_3$  colloid on the adsorption of As(III) and As(V) on three soils (a: BJ soil, b: JL soil, c: HN soil. ■ for arsenate, ▲ for arsenite)

A variation in competitiveness between arsenic and  $\text{PO}_4^{3-}$  is shown in Fig. 5. Phosphate suppressed the adsorption of As(V) more severely than that of As(III) on BJ soil. For example, at the arsenic concentration of  $12.0 \mu\text{g}\cdot\text{L}^{-1}$ , the As(V) adsorbed on BJ soil was  $1.75 \text{ mg}\cdot\text{kg}^{-1}$  in the absence of phosphate, while it was only  $0.75 \text{ mg}\cdot\text{kg}^{-1}$  in the presence of phosphate, the same results for As(III) were  $1.16$  and  $0.33 \text{ mg}\cdot\text{kg}^{-1}$ , respectively.

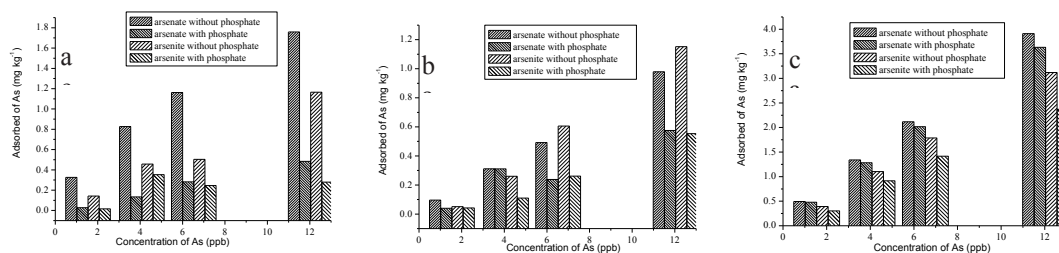


Fig. 5. Effect of phosphate on the adsorption of As(III) and As(V) on three soils (a: BJ soil, b: JL soil, c: HN soil).

The significant competitive adsorption of phosphate with arsenic by BJ soil indicated that the solid adsorbent surfaces had affinity for both solute molecules at the same sites. In this case, surface adsorption was proposed as the dominant mechanism for adsorption of arsenic, whereas adsorption is only one monolayer thick for single-solute systems; multilayers could be adsorbed in bisolute systems. The surface adsorption process would be confined to the available surface area. The greater competition of phosphate for the adsorbent was simply because the high-energy sites were largely occupied by phosphate, which was present in a large excess concentration ( $10 \text{ mg}\cdot\text{L}^{-1}$ ) according to the laws of thermodynamics. As for the JL soil, phosphate suppressed the adsorption of As(III) more severely than that of As(V). Interestingly, there was less effect for  $\text{PO}_4^{3-}$  on As(III) or As(V) adsorption on HN soil. The results show that the competition in adsorption phosphate and arsenic (arsenite and arsenate) may vary greatly on soils characterized by different mineralogy and chemical properties. These findings were supported by Violante and Pigna[21] who demonstrated that the Fe, Mn, and Ti oxides were more effective in sorbing  $\text{AsO}_4^{3-}$  than  $\text{PO}_4^{3-}$ . In contrast, minerals richer in Al were much more effective in retaining  $\text{PO}_4^{3-}$  than  $\text{AsO}_4^{3-}$ . In this study, the amounts of Fe and Al varied widely which may result in the difference in competitiveness between arsenic and  $\text{PO}_4^{3-}$  on these soils.

#### 4. Conclusions

Our results indicate that arsenic adsorption onto soils varied greatly with the soil properties, among which soil organic matter content exhibited the most important influence on arsenic adsorption. Temperature, concentrations of  $\text{Fe}(\text{OH})_3$ ,  $\text{H}_2\text{SiO}_3$ , and phosphate also affected the absorption. The desorption data showed that hysteresis occurred at the concentration studied.

The information reported in this work will benefit to a better understanding of the role of soil components on the mobility and potential toxicity of arsenic in natural soil environments. In further studies, soil column leaching tests must be carefully investigated because soil column leaching tests may indicate a high potential risk in regard to water pollution, and its entry into the food chain. Spectroscopic studies are also needed to elucidate the specific complexes formed between the various arsenic compounds and soil mineral surfaces.

#### Acknowledgements

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