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Mechanism of arsenic sorption onto laterite iron concretions

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ABSTRACT

We investigated arsenic sorption mechanisms onto laterite iron concretions (LIC) using electrophoretic mobility (EM) measurements, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and surface complexation modeling. Competitive sorption experiments were also conducted in the presence of phosphate and sulfate, as these compounds may interfere with arsenic sorption in waters from sulfide mining waste and ore stock piles.

Electrophoretic mobility measurement results indicate that arsenic sorption lowered the point of zero charge of the LIC at pH 3–10. This observation implies both As (III) and As (V) form inner-sphere complexes on the LIC. The FTIR studies suggest that both As (III) and As (V) also form inner-sphere complexes with LIC.

Arsenic sorption onto LIC was modeled by surface complexation modeling using the generalized composite approach. The model assumes that all mineral phases contributing to sorption are represented by one type of surface group. Adsorption edge experimental data was used to verify model performance. Arsenic (III) sorption onto LIC, which is markedly reduced by increasing ionic strength, was modeled using the triple-layer model, while As (V) sorption onto LIC was modeled using both the diffuse and the triple-layer models. The presence of phosphate reduces the amount of both As (V) and As (III) sorbed, while sulfate only reduces adsorption of As (III).

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1. Introduction

Arsenic is a toxic trace element introduced into the environment through weathering of arsenic bearing minerals, agricultural use of arsenical pesticide, industrial waste discharges, and geothermal discharge [1]. Arsenic (III) occurs naturally as arsenite (H_3AsO_3) and predominates under reducing conditions, while As (V) occurs predominantly under oxidizing conditions and mainly exists as arsenate ($H_2AsO_4^-$ and $HAsO_4^{2-}$) over the pH range of 2–9 [1]. As (III) is inherently more toxic than As (V) and poses a greater threat to society due to its higher solubility [2,3]. The detrimental health effects of arsenic prompted the World Health Organization (WHO) to change the drinking water arsenic standards from 0.05 to 0.01 mg/L [4]. Consequently, there is growing interest in using low-cost materials to remove arsenic from drinking water. One promising method appears to be sorption of inorganic arsenic compounds from solution using natural sorbents. Low-cost natural materials such as activated red mud [5] and nat-

ural zeolites [6] have been tested as potential sorbents of arsenic species.

Arsenic (III) and As (V) are adsorbed onto laterite iron concretions (LIC) surfaces but have different sorption behaviors. Arsenic (V) sorption onto LIC is characterized by an apparent sorption maximum at a pH value of 4 [7]. On the contrary, As (III) sorption is characterized by a sorption maximum occurring in the pH range of 7–8. Earlier work by Partey et al. [7] shows that ionic strength effects are more prominent in As (III) sorption than As (V), due to the different nature of bonding mechanism exhibited by the two species.

Fourier transform infrared (FTIR), Raman and extended X-ray absorption fine structure (EXAFS) spectroscopy have been used to determine the mechanism of ion attachment to metal oxides surfaces. Previous spectroscopic studies indicate As (V) adsorbs on iron and aluminum oxides as inner-sphere bidentate and monodentate complexes [8–11], while As (III) adsorbs as inner-sphere and outer-sphere complexes [8,10,11].

Electrophoretic mobility (EM), which is a measure of the movement of charged particles in response to an applied electric field, can be used to distinguish between inner-sphere and outer-sphere complexes [8]. If a water molecule is present between the surface functional groups and the adsorbing ion, an outer-sphere complex

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is formed; if there is no water of hydration present and there is direct sorption, then an inner-sphere complex is formed [12]. The presence of an inner-sphere complex may alter the EM of the suspended solids in the presence of the sorbed species because the sorbed species resides in the shear plane (compact layer) [13]. However, with outer-sphere complexes the sorbed species will reside inside the outer plane and will not alter the EM of the suspended solid [13]. The point of zero-charge (PZC) indicates a condition of zero surface charge. Changes in PZC of minerals and reversals of EM as ion concentration increases are indications of inner-sphere surface complex formation [13].

Advancement on surface complexation models has greatly enhanced the understanding of adsorption processes, and an extension of this approach to natural systems is now occurring [14]. Vithanage et al. [15] used the diffuse-layer model to describe As (III) and As (V) adsorption on natural red earth. Others have shown that the diffuse and triple-layer models can simulate experimental data of arsenic adsorption on pure metal hydroxide solids [8,15–17].

The scope of this study is to: (1) determine the point of zero-charge and electrophoretic mobility of the LIC surface with and without bound arsenic; (2) use Fourier transform infrared spectroscopy to investigate the form and structure of adsorbed ions on LIC; (3) use surface complexation models to describe arsenic sorption onto LIC; and (4) evaluate the effects of competing ions such as phosphate and sulfate on arsenic sorption onto LIC. A combination of these results will elucidate the mechanism(s) of arsenic sorption onto LIC. Parameters obtained will be used to optimize LIC applications, and design an appropriate and effective arsenic filtering device.

2. Materials and methods

2.1. Laterite iron concretion

The LIC used for this study was obtained from Prestea, Ghana (5° 28′ 15.06″ N and 2° 11′ 27.17″ W). A full description of LIC can be found in Partey et al. [7]. X-ray fluorescence and BET (Brunauer, Emmett and Teller) analyses were previously [7] preformed to aid in characterizing the LIC. The surface area of the ground LIC was determined as 32 m^2/g.

2.2. Competitive sorption

The interference of phosphate and sulfate on arsenic sorption was investigated in batch experiments. The methods used are similar to the batch experiments described in Partey et al. [7]. The difference is arsenic concentration of 1.0 mg/L was added to the 10.0 mg/L phosphate solution, and in a separate experiment 1.0 mg/L of arsenic solution was added to a 500.0 mg/L sulfate solution. These experiments were performed in a N$_2$ atmosphere to prevent As (III) oxidation to As (V). All experiments were accompanied by stock arsenic solutions to serve as controls. Though the concentration of phosphate and sulfate used in this study exceed that of most drinking water, higher concentrations were needed to examine how LIC will perform in the presence of competing ions.

2.3. Electrophoretic mobility

The electrophoretic mobility for the LIC was determined by microelectrophoresis using a Zeta-Meter 3.0 system. In an attempt to eliminate CO$_2$ from the system, all the EM experiments were performed under a N$_2$ atmosphere. Electrophoretic mobility measurements were taken at various pH values using LIC suspensions containing 0.2 g/L of solid particles less than 5 μm in size in a 0.01 M NaCl solution. Electrophoretic mobility measurements were also determined using 0.035 and 3.5 mM arsenic solutions in 0.01 M

NaCl to match the zero arsenic reference. The final suspension was adjusted to the desired pH (4–10) with 0.1 M HCl or NaOH, which caused less than 1% change in the ionic strength. The suspension was shaken for 2 and 1 h for As (III) and As (V), respectively at 22 °C. In general, an average EM value was obtained after 20 particles were counted. The point of zero charge was obtained by interpolating the data to zero EM.

2.4. ATR-FTIR spectroscopy

Samples for spectroscopic analysis were prepared by reacting 2.0 g of LIC with 20 mL of a 0.1 M NaCl solution containing 0.1 M of either As (III) at pH 5 and 10.5 or As (V) at pH 5 and 9. All experiments were conducted in a N$_2$ atmosphere to avoid oxidation of As (III) to As (V). Following the procedure of Goldberg and Johnston [8], samples were rinsed with 20 mL of doubly deionized water and air dried. Reference samples were reacted with a solution containing 0.1 M NaCl. Fourier transform infrared spectra were obtained with an Avatar 370 Model spectrometer and a horizontal thermo Nicolet attenuated total reflectance (ATR) attachment that has a ZnSe crystal set at 40° angle of incidence.

Spectra were obtained at a resolution of 4 cm^{-1} with each spectrum corresponding to the co-addition of 64 scans using a medium-band liquid nitrogen cooled mercury cadmium telluride (MCT) detector. Infrared spectra of As (V) and As (III) sorbed on LIC were obtained as dry samples in KBr pellets prepared by adding 3 mg of ground LIC to 250 mg of spectral grade KBr. Attenuated total reflectance of 1 mL of 0.1 M NaCl and 0.1 M arsenic solutions as well as a reference solution were recorded.

2.5. Surface complexation models

We modeled the surface complexation of LIC using the generalized composite approach (GC) [18]. This approach assumes that all mineral phases contribute to sorption and the sorption sites are represented by one type of surface group. One major caveat with the GC approach is the derived constants for surface complexation are valid only for the system under study and cannot be transferred to other systems. However, the method has fewer equations hence the degrees of freedom are likely to be very small. The computer program FITEQL [19] was used to determine the surface acidity and arsenic binding constants. The stoichiometries of the surface complexes used to fit sorption data are listed in Tables 1 and 2. The surface site densities were set at a value of 2.31 sites/nm^2 after Davis and Kent [14] for natural materials. Surface complexation constants were optimized with fixed site densities using MINTEQA2 [20]. The activity coefficients of aqueous species were calculated using the Davies equation for both model fitting and predictions. The con-

Table 1
Reactions used in the diffuse double-layer modeling and equilibrium constants.

Diffuse layer model			
Site density (sites nm^{-2})			2.31
Surface area (32 m^2/g)			

Surface hydrolysis reactions	Intrinsic acidity constants		
	0.1 M	0.01 M	0.001 M
SOH$_{(s)}$ + H$^+_{(aq)}$ ⇔ SOH$_2^+_{(s)}$	7.30	7.30	7.30
SOH$_{(s)}$ ⇔ SO$^-_{(s)}$ + H$^+_{(aq)}$	−9.10	−9.10	−9.10

As (V) sorption reaction	Intrinsic acidity constants		
	0.1 M	0.01 M	0.001 M
SOH$_{(s)}$ + H$_3$AsO$_{4(aq)}$ ⇔ SH$_2$AsO$_{4(s)}$ + H$_2$O	12.35	12.35	12.35
SOH$_{(s)}$ + H$_3$AsO$_{4(aq)}$ ⇔ SHAsO$_4^-_{(s)}$ + H$_{(aq)}^+$ + H$_2$O	5.62	5.62	5.62
SOH$_{(s)}$ + H$_3$AsO$_{4(aq)}$ ⇔ SAsO$_4^{2-}_{(s)}$ + 2H$_{(aq)}^+$ + H$_2$O	−1.40	−1.40	−1.40