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# Arsenic retention and transport behavior in the presence of typical anionic and nonionic surfactants

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## ABSTRACT

The massive production and wide use of surfactants have resulted in a large amount of surfactant residuals being discharged into the environment, which could have an impact on arsenic behavior. In the present study, the influence of the anionic surfactant sodium dodecyl benzene sulfonate (SDBS) and nonionic surfactant polyethylene glycol octylphenyl ether (Triton X-100) on arsenic behavior was investigated in batch and column tests. The presence of SDBS and Triton X-100 reduced arsenic retention onto ferrihydrite (FH), enhanced arsenic transport through FH coated sand (FH-sand) columns and promoted arsenic release from the FH surface. With coexisting surfactants in solution, the equilibrium adsorbed amount of arsenic on FH decreased by up to 29.7% and the adsorption rate decreased by up to 52.3%. Pre-coating with surfactants caused a decrease in the adsorbed amount and adsorption rate of arsenic by up to 15.1% and 58.3%, respectively. Because of the adsorption attenuation caused by surfactants, breakthrough of As(V) and As(III) with SDBS in columns packed with FH-sand was 23.8% and 14.3% faster than that in those without SDBS, respectively. In columns packed with SDBS-coated FH-sand, transport of arsenic was enhanced to a greater extent. Breakthrough of As(V) and As(III) was 52.4% and 43.8% faster and the cumulative retention amount was 44.5% and 57.3% less than that in pure FH-sand column systems, respectively. Mobilization of arsenic by surfactants increased with the increase of the initial adsorbed amount of arsenic. The cumulative release amount of As(V) and As(III) from the packed column reached 10.8% and 36.0%, respectively.

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## Introduction

Surfactants are generally a group of chemicals consisting of both polar and nonpolar groups. Due to their solubilization and cleaning properties, surfactants are widely used in household detergents, the textile industry, and in smelting

and mining activities. The world production of surfactants has been up to 18.2 million tons annually (Céspedes et al., 2008; Ying, 2006). According to the properties of their polar groups, surfactants are mainly divided into anionic type, cationic type and nonionic type, among which anionic and nonionic surfactants are most widely used. After being used,

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surfactant residuals are discharged into sewage treatment plants or directly to environmental media such as water, soil and sediment. This leads to different levels of surfactants being detected in environmental compartments (Lara-Martin et al., 2006, 2008; Marcomini et al., 2000; Shalaby, 2007; Ying et al., 2002; Ying, 2006). The distribution and behavior of surfactants in the environment have been widely studied to assess the environmental risks. When entering the environment, surfactants tend to be adsorbed onto particles and sediments, thus altering the physicochemical characteristics of particle surfaces and influencing the environmental behavior of other pollutants. It is suggested that surfactants could exert significant effects on the adsorption and release of organic matters and heavy metals (Pan et al., 2009; Song et al., 2008; Tripathi and Brown, 2008; Turner and Xu, 2008). The mechanisms mainly include adsorption competition, complexation reactions, solubilization and electrostatic repulsion (Clara et al., 2007; de Wolf and Feijtel, 1998; Fu et al., 2007; Kloepper-Sams et al., 1996; Lara-Martin et al., 2008; Shalaby, 2007). Considering the widespread use of surfactants and conspicuous toxicity of arsenic, this study investigated the potential effects of surfactants on the behavior of arsenic in the environment.

Arsenic retention on particles and transport in sediments are two main factors controlling its bioavailability and toxicity. Both processes are to a great extent influenced by coexisting substances such as natural organic matters (NOM) and anions. It has been well documented that such substances may reduce arsenic adsorption and enhance arsenic transport through adsorption competition, complexation reactions, anion exchange and electrostatic repulsion (Barringer et al., 2011; Dias et al., 2009; Garcia-Sanchez et al., 2010; Garcia et al., 2007; Guo et al., 2014; He et al., 2010; Radloff et al., 2007; Reza et al., 2010; Serfes et al., 2003; Zheng et al., 2004). Thus, through such mechanisms, surfactant molecules may potentially influence arsenic adsorption and transport behavior in the environment.

In natural environments, there could be three scenarios in which surfactants influence arsenic adsorption and mobilization (Sharma et al., 2011). The first scenario represents water environments where surfactants coexist with arsenic. There could be adsorption competition, as both substances are likely to be adsorbed by particulate matters. The second scenario indicates that wastewater containing arsenic could be discharged into water and sediments that are coated with surfactants. As known under circumstances such as mining sites and wastewater discharge locations, large amounts of surfactants could be adsorbed onto sediments. The occupation of adsorption sites on particle surfaces by surfactants may result in a reduction of arsenic adsorption. In the third scenario, opposite to the second, arsenic-contaminated sediments may be exposed to surfactants, leading to the mobilization of arsenic.

Based on the situations described above, a typical anionic surfactant, sodium dodecyl benzene sulfonate (SDBS), and nonionic surfactant, polyethylene glycol octylphenyl ether (Triton X-100), were employed to investigate the influence of surfactants on arsenic adsorption and mobilization. Synthetic ferrihydrite (FH) was chosen as a representative model mineral that has great affinity with arsenic in the environment. Specifically, both batch and column experiments were conducted to examine: (1) adsorption of arsenic onto FH in the presence

of surfactants; (2) arsenic transport through FH-coated sand (FH-sand) columns in the presence of surfactants and arsenic transport through columns packed with surfactant-coated FH-sand; and (3) mobilization of adsorbed arsenic from FH and FH-sand by surfactants.

## 1. Materials and methods

### 1.1. Materials

Chemicals used in the experiments were of analytical grade and used without further purification. Stock solutions of 1000 mg/L As(V) and As(III) were prepared by dissolving 4.160 g  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  and 1.732 g  $\text{NaAsO}_2$  into 1.0 L de-ionized water, respectively. Stock solutions of SDBS and Triton X-100 were both prepared by dissolving 1.000 g surfactant in 1.0 L de-ionized water. Characteristics of surfactants are shown in Table 1. De-ionized water used for all As(III) experiments was deoxygenated by boiling for 10 min and cooling down to room temperature before use.

### 1.2. Synthesis of FH and FH-sand

FH used in this study was synthesized according to Schwertmann's method (Sharma et al., 2011). Under continuous stirring, a solution of 1.0 mol/L KOH was added to a 500 mL solution of 0.2 mol/L  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  at a rate of approximately 50 mL/min, till the pH of the solution reached 7.5. The mixture was aged for 2 hr, then the supernatant was removed and the suspension was washed three times with de-ionized water. Then the suspension was centrifuged at 5000 r/min for 10 min, and the precipitate was resuspended in 1.0 L de-ionized water. The FH concentration of the resulting suspension was approximately 10 g/L. The specific surface area of the freeze-dried FH particles was  $81.9 \pm 2.1 \text{ m}^2/\text{g}$ , measured using the BET- $\text{N}_2$  adsorption method. The FH-sand was prepared by mixing 100.0 g washed quartz sand with an average particle diameter of 2.0 mm with the FH suspension and aging for 24 hr. The particles were dried at  $50.0^\circ\text{C}$  for 24 hr and the residual was removed using a 2-mm sieve. The iron content of FH-sand was 120 mg/kg, tested by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Agilent 7500a, USA) after extraction with 0.1 mol/L HCl.

### 1.3. Adsorption isotherm of surfactants on FH

Experimental details and results regarding the adsorption isotherm of SDBS and Triton X-100 onto FH are given in Appendix A Fig. S1.

**Table 1 – Characteristics of surfactants.**

Surfactant	Type	MW (g/mol)	Molecular formation	CMC (mg/L)
SDBS	Anionic	348.48	$\text{C}_{18}\text{H}_{29}\text{SO}_3\text{Na}$	522
Triton X-100	Nonionic	646.86	$\text{C}_{14}\text{HO}_{22}(\text{C}_2\text{H}_4\text{O})_{10}$	150
SDBS: sodium dodecyl benzene sulfonate. CMC: critical micelle concentration.				

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