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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-Martín 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; Klopper-Sams et al., 1996; Lara-Martín 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 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- 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°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	$\text{C}_{18}\text{H}_{29}\text{SO}_2\text{Na}$	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.

1.4. Influence of surfactants on arsenic adsorption isotherm onto FH

The adsorption isotherm of arsenic in the presence of surfactants was investigated. In a batch of 50-mL centrifuge tubes, 40 mL mixtures containing 0.1 g/L FH, 0 or 50 mg/L surfactant, and different concentrations of As(V) or As(III) were shaken at 150 r/min and 25°C for 16 hr. During the adsorption, the pH of all solutions was adjusted to 7.0 ± 0.1 at prescribed time intervals using HCl and NaOH solutions. Then the mixtures were centrifuged at 8000 r/min for 15 min. The supernatants were taken and passed through a 0.22- μ m membrane filter. The concentrations of As(V) and As(III) were analyzed using ICP-MS.

In order to determine the adsorption isotherm of arsenic onto surfactant-coated FH, before the arsenic adsorption experiment, surfactants were adsorbed onto FH by shaking 40 mL mixtures containing 0.1 g/L FH and 50 mg/L SDBS or Triton X-100 for 16 hr. Then the mixtures were centrifuged at 8000 r/min for 15 min and the supernatant was removed. A series of arsenic solutions with different concentrations were added into the tubes, and shaken at 150 r/min and 25°C for 16 hr. The pH of the suspensions was adjusted and maintained at 7.0 ± 0.1 during the adsorption experiments using HCl and NaOH solutions. Then the mixtures were centrifuged at 8000 r/min for 15 min and the arsenic concentration was measured using ICP-MS with proper dilution.

1.5. Influence of surfactants on arsenic adsorption kinetics onto FH

To study the effects of surfactants at different concentrations on arsenic adsorption kinetics onto FH, 500 μ g/L As(V) or As(III) was mixed with SDBS or Triton X-100 of prescribed concentrations in 500-mL bottles, respectively. The dosage of FH was 0.01 g/L. All solutions were uniformly stirred with magnetic stirrers. The pH of all solutions was maintained at 7.0 ± 0.1 with HCl or NaOH solutions during the adsorption experiments. For As(III), the adsorption experiments were conducted in the dark under N₂ atmosphere to avoid oxidation and photolysis. During the experiments, 1.0 mL aliquots were taken from each bottle at prescribed time intervals and centrifuged at 10,000 r/min for 5 min, then the supernatant was taken and filtered through a 0.22- μ m membrane filter and stored at 4°C in the dark for arsenic concentration analysis.

The adsorption kinetics of arsenic onto surfactant-coated FH was also investigated. In 50-mL centrifuge tubes, 0.5 mL FH suspension was first incubated with 49.5 mL 50 mg/L SDBS or Triton X-100 for 16 hr under 150 r/min. Then the suspension was transferred into a 500-mL bottle containing 450 mL As(V) or As(III) solution, achieving an arsenic concentration of 500 μ g/L. Thus the concentration of surfactant was less than 5 mg/L. The pH of all solutions was maintained at 7.0 ± 0.1 during the experiment. At each prescribed time interval, 1.0 mL of solution was taken from each bottle and centrifuged at 10,000 r/min for 5 min, then the supernatant was taken and filtered through a 0.22- μ m membrane filter and stored at 4°C in the dark for arsenic concentration analysis.

1.6. Breakthrough of arsenic in the presence and pre-adsorption of SDBS

Columns used in this study were of 3.0 cm internal diameter and 12.0 cm length. Each column was uniformly packed with 110.0 g FH-sand and equilibrated by an upward flow of de-ionized water for 48 hr before the column investigation. The density of FH-sand was 2.5 g/cm³ and the porosity of the packed columns was 0.48. The influent rate was maintained at 0.12 cm/min throughout the experiments. All As(III) flow-through experiments were conducted in the dark and under N₂ atmosphere.

To study the transport of arsenic in the presence of SDBS in flow-through columns, comparison of arsenic breakthrough from columns with influx of 500 μ g/L arsenic and of 500 μ g/L arsenic with the coexistence of 30 mg/L SDBS was made. These solutions were pumped into the columns in an up-flow mode. The column adsorption experiments were carried out for 500 hr (corresponding to 568.2 pore volumes (PV)) until the arsenic concentration in the effluent achieved a stable value. About 2.5 mL effluent was periodically taken from each column and centrifuged at 10,000 r/min for 5 min, then the supernatant was filtered through a 0.22- μ m membrane filter and stored at 4°C in the dark for analysis. The breakthrough curves were acquired by recording the concentrations as a function of time.

To investigate arsenic transport through FH-sand coated with SDBS, a solution of 500 mg/L SDBS was constantly introduced into the FH-sand column for 96 hr. Then a solution of 500 μ g/L As(V) or As(III) was introduced into the column to achieve a stable arsenic concentration in the effluent. At prescribed time intervals, 2.5 mL effluent was taken and centrifuged at 10,000 r/min for 5 min, then the supernatant was filtered through a 0.22- μ m membrane filter and stored at 4°C in the dark for analysis.

1.7. Mobilization of arsenic from FH by surfactants

FH samples with different loading amounts of arsenic were acquired from the batch experiments. Then mobilization of arsenic from FH by surfactants was investigated in 40 mL 50 mg/L SDBS or Triton X-100 solutions. In such an experimental system, a relatively high surfactant concentration was chosen based on the great retention amount of arsenic onto FH compared to that on natural sediments. After shaking at 150 r/min for 16 hr and centrifuging at 8000 r/min for 15 min, the equilibrium concentration of arsenic in the supernatant was measured using ICP-MS.

1.8. Mobilization of arsenic from columns by SDBS

To study arsenic release from arsenic-loaded FH-sand, 500 μ g/L As(V) and As(III) solutions were individually introduced to FH-sand columns until the arsenic concentration in the effluent reached 95% of the influx concentration. Then a solution of 30 mg/L SDBS was continuously pumped into the columns for 144 hr. The effluent from the column was collected and samples were periodically taken from the collected solution. The ratio of the cumulative released amount of arsenic to the sorption amount was calculated and plotted as a function of time.

1.9. Zeta potential measurement

The Zeta potential of the FH particles in suspensions was determined using a ZetaSizer 3000 instrument (Malvern, UK). Suspensions of 0.1 g/L FH, 0.1 g/L FH with 30 mg/L SDBS or Triton X-100 were prepared. The pH of each batch of suspensions was adjusted to values ranging from 4 to 9. After shaking for 16 hr, the final pH and Zeta potential values of all suspensions were measured.

2. Results and discussion

2.1. Zeta potential measurement

Zeta potential has been widely applied to characterize potential effects between particle surfaces and water. In this study, the adsorption of surfactants on FH significantly affected arsenic adsorption and transport behavior. As shown in Fig. 1, the isoelectric point was 7.2. The adsorption of SDBS significantly increased the negative charge on the FH surface. When the pH was 7.0, the adsorption of SDBS caused the surface charge to decrease from -1.49 to -39.6 mV. This was an important factor contributing to the inhibition of arsenic adsorption, especially the adsorption of As(V), which mainly existed as anionic HAsO_4^{2-} and H_2AsO_4^- under the experimental pH condition of 7.0. For the nonionic Triton X-100, its adsorption onto FH had little effect on the surface charge, which indicated that there should be no significant electrostatic repulsion between Triton X-100 and arsenic species.

2.2. Influence of surfactants on arsenic adsorption isotherm onto FH

2.2.1. Adsorption isotherm of arsenic in the presence of surfactants

As shown in Fig. 2a and b, adsorption isotherms of As(V) and As(III) were notably influenced by the coexistence of 50 mg/L SDBS or Triton X-100 compared to the systems without surfactants. The effects on the adsorption isotherms were mainly reflected in decreases in the equilibrium adsorbed amounts of As(V) and As(III) under the influence of SDBS or

Triton X-100. In addition, the experimental data was best fitted with the Langmuir model, presented as:

$$q_e = q_{\max} \frac{k_L C_e}{1 + k_L C_e} \quad (1)$$

where q_e (mg/g) is the equilibrium adsorbed amount, q_{\max} (mg/g) is the maximum adsorbed amount, and k_L (L/mg) is the Langmuir equilibrium constant.

Details of the fitting results are given in Appendix Fig. S2. Specifically, as shown in Table 2, without the effects of surfactants, the calculated maximum adsorbed amount of As(V) and As(III) on FH was 40.5 and 83.3 mg/g, respectively. In the presence of 50 mg/L SDBS and Triton X-100, the maximum adsorbed amount of As(V) decreased to 38.3 and 38.5 mg/g, while that of As(III) decreased to 77.5 and 75.8 mg/g. In addition, according to the fitting results, the influence of SDBS on As(V) adsorption was greater, while Triton X-100 showed greater effects on the adsorption of As(III) onto FH. Under the experimental pH conditions, As(V) existed mainly as anionic HAsO_4^{2-} , while As(III) existed as neutral H_3AsO_3 (Smedley et al., 2005). According to the Zeta potential analysis, when the pH was approximately 7.0, the adsorption of SDBS caused a FH surface charge decrease from -1.49 mV to -39.6 mV, indicating that there could be electrostatic repulsion between SDBS and the negatively charged As(V). The influence of SDBS on As(III) retention and the effects of Triton X-100 on As(V) and As(III) retention were mainly due to the occupation of adsorption sites on FH particles.

2.2.2. Adsorption isotherm of arsenic onto surfactant-coated FH

Adsorption isotherms of arsenic onto surfactant-coated FH are shown in Fig. 2c and d. It was found that the pre-coating of SDBS and Triton X-100 slightly reduced the adsorbed amount of As(V), but had less effect on the amount of adsorbed As(III). Similarly, Langmuir fitting of the experimental data is also given in Table 2. According to the fitting results, the adsorbed amounts of As(V) and As(III) onto SDBS-coated FH decreased to 36.8 and 75.8 mg/g, respectively. For Triton X-100-coated FH, the adsorbed amounts of As(V) and As(III) decreased to 37.7 and 77.5 mg/g, respectively. Compared to the coexisting condition, pre-coating of surfactants onto FH had greater effects on arsenic adsorption isotherms.

2.3. Influence of surfactants on arsenic adsorption kinetics

2.3.1. Adsorption kinetics of arsenic coexisting with SDBS or Triton X-100

Studies have shown that the adsorption kinetics of arsenic onto FH mainly includes three processes: external diffusion, internal diffusion and surface adsorption (Radu et al., 2005; Zhang and Selim, 2005; Zhao et al., 2011). Therefore, the presence of surfactants could affect arsenic adsorption behavior by affecting these three processes. As shown in Fig. 3a and b, adsorption kinetics of As(V) and As(III) were slightly affected in the presence of SDBS and Triton X-100, and the extent of the effects increased with the increase of surfactant concentrations. The kinetics represented a two-stage process, in which adsorption equilibrium of As(V) and As(III) was achieved at 60 and 150 min, respectively. This indicated that the presence of SDBS and Triton X-100 had little effect on the

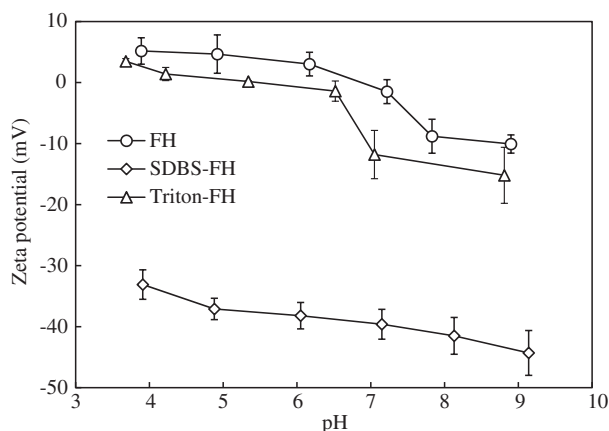


Fig. 1 – Zeta potential of FH (ferrihydrite) with or without coating by surfactants.

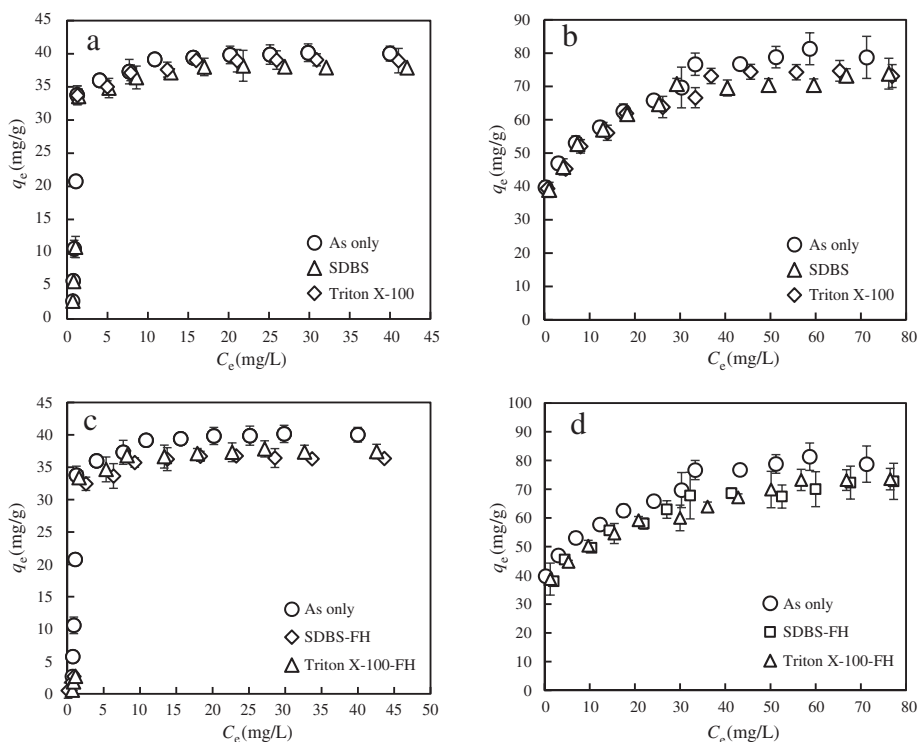


Fig. 2 – Adsorption isotherm of As(V) (a) and As(III) (b) onto FH in the presence of SDBS or Triton X-100 at pH 7.0. Adsorption isotherm of As(V) (c) and As(III) (d) onto FH coated with SDBS or Triton X-100 at pH 7.0.

time for achieving equilibrium. Thus, to further compare arsenic adsorption kinetics with or without the presence of surfactants, the adsorption kinetics was fitted to the Pseudo-second order kinetic model, presented as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

q_t (mg/g) is the adsorbed amount of arsenic at time t , presented as:

$$q_t = \frac{C_0 - C_t}{m} V \quad (3)$$

where q_e (mg/g) is the equilibrium adsorption amount, k_2 (g/(mg·min)) is the second order adsorption kinetic constant, m (g) is the dosage of FH, and C_0 (mg/L) and C_t (mg/L) represent the initial arsenic concentration and concentration at time t , respectively.

Details of the adsorption kinetic fitting are given in Appendix A Fig. S3. According to the fitting results given in Table 3, the presence of SDBS and Triton X-100 mainly affected arsenic adsorption kinetics in two aspects: equilibrium adsorbed amount and adsorption rate. The presence of SDBS, at 10 and 50 mg/L, reduced the equilibrium adsorbed amount of both As(V) and As(III) on FH. This could mainly be attributed to the occupation of adsorption sites on the FH surface by the adsorption of SDBS. The effects on the adsorption rate of arsenic varied with the concentration of SDBS. Specifically, when the suspensions contained 10 mg/L SDBS, the second-order adsorption kinetic constants k_2 of As(V) and As(III) increased from 7.4 and 2.6 to 9.9 and 3.0, respectively, which indicated that SDBS at 10 mg/L could to some extent promote the adsorption rate. When the concentration of SDBS increased to 50 mg/L, the adsorption kinetic

Table 2 – Langmuir fitting for As adsorption onto FH coexisting with surfactant and As adsorption onto surfactant-coated FH.

Adsorption of As coexisting with surfactants					Adsorption of As on surfactant coated FH			
	Surfactant	k_L (L/mg)	q_{max} (mg/g)	R^2	FH	k_L (L/mg)	q_{max} (mg/g)	R^2
As(V)	Without surfactant	2.3	40.5	0.999	Bare FH	2.3	40.5	0.999
	SDBS	3.2	38.3	0.999	SDBS-FH	3.7	36.8	0.999
	Triton X-100	2.7	38.5	0.998	Triton X-100-FH	3.4	37.7	0.999
As(III)	Without surfactant	0.3	83.3	0.993	Bare FH	0.3	83.3	0.993
	SDBS	0.3	77.5	0.995	SDBS-FH	0.2	75.8	0.997
	Triton X-100	0.3	75.8	0.998	Triton X-100-FH	0.2	77.5	0.998

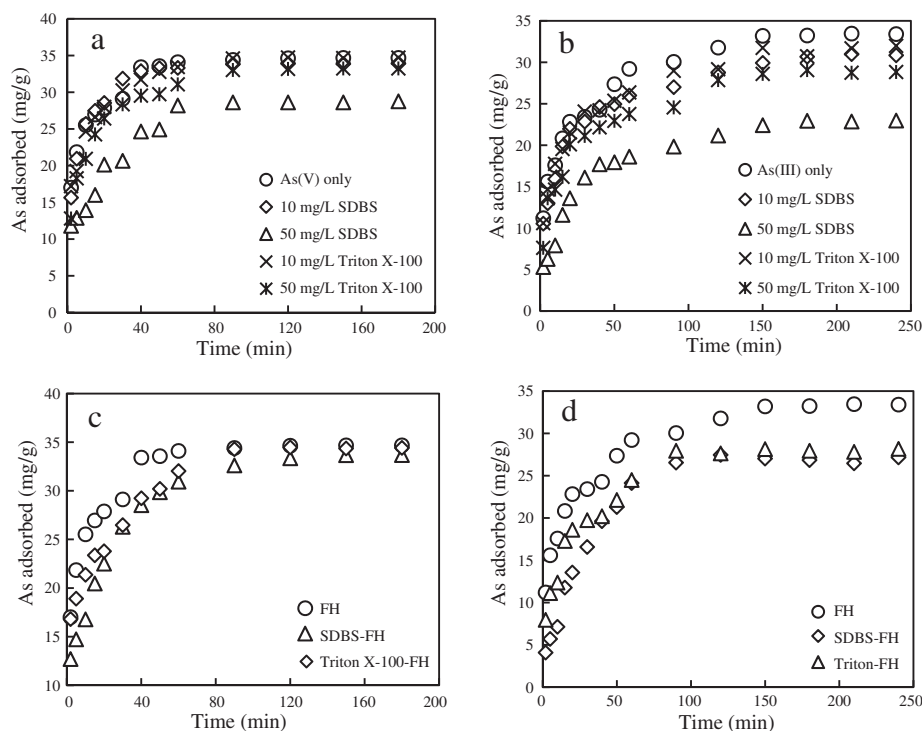


Fig. 3 – Adsorption kinetics of As(V) (a) and As(III) (b) on FH in the presence of SDBS or Triton X-100 at different concentrations at pH 7.0. Adsorption kinetics of As(V) (c) and As(III) (d) on FH coated with SDBS and Triton X-100 at pH 7.0.

constants of As(V) and As(III) decreased to 3.6 and 2.5, respectively. The adsorption of SDBS could reduce the interfacial tension between FH and water as well as enhance the wettability of the FH surface, promoting the external diffusion of arsenic to the FH surface (Sastry and Dave, 1999; Thibaut et al., 2000; Wang and Kwak, 1999; Yang et al., 2007, 2010). The nonionic surfactant Triton X-100 exerted different impacts on the adsorption kinetics of As(V) and As(III). At both 10 and 50 mg/L, Triton X-100 caused a decrease of both equilibrium adsorption amount and second-order adsorption kinetic constant of As(V). As for As(III), the coexistence of 10 and 50 mg/L Triton X-100 reduced its equilibrium adsorbed amounts while enhancing the adsorption rate.

2.3.2. Adsorption kinetics of arsenic onto surfactant-coated FH

In the natural environment, wastewater containing arsenic could be discharged into surfactant-loaded soil and sediment. Thus, the pre-coating of surfactants could potentially have impacts on arsenic retention, enhancing its mobility in the environment. Similarly, the experimental data was also fitted to the Pseudo-second order kinetic model. According to Fig. 3c and d and Table 3, the adsorption kinetics of As(V) and As(III) on surfactant-coated FH changed compared to that on bare FH. The adsorption of As(V) was able to reach equilibrium at 60 min and the equilibrium adsorption amount did not obviously decrease. The pre-coating of SDBS and Triton X-100 caused a decrease of the adsorption kinetic constant of As(V) from 7.4 to 3.1 and 3.9, respectively. This was attributed to the electrostatic repulsion between adsorbed SDBS and As(V) anions. As for As(III), adsorption equilibrium on surfactant-coated FH was achieved at 90 min, which was

60 min faster than that on bare FH. In addition, with pre-coating of SDBS and Triton X-100, the adsorption kinetics of As(III) increased from 2.6 to 2.8 and 2.9, respectively. However, the equilibrium adsorption amount of As(III) decreased from 35.0 mg/g to 29.9 and 29.7 mg/g, respectively.

Table 3 – Pseudo-second order kinetic fitting of As adsorption in the presence of surfactant and onto surfactant-coated FH.

Batch	k_2 (g/(mg·min))	q_e (mg/g)	R^2
As adsorption in the presence of SDBS or Triton X-100			
As(V)	7.4	35.6	0.999
10 mg/L SDBS	9.9	34.6	0.999
50 mg/L SDBS	3.6	30.5	0.997
10 mg/L Triton X-100	6.5	35.7	0.999
50 mg/L Triton X-100	5.1	34.5	0.999
As(III)	2.6	35.0	0.998
10 mg/L SDBS	3.0	32.05	0.998
50 mg/L SDBS	2.5	24.6	0.998
10 mg/L Triton X-100	2.8	33.0	0.997
50 mg/L Triton X-100	2.8	30.3	0.997
As adsorption on FH coated with SDBS and Triton X-100			
As(V) FH	7.4	35.6	0.999
SDBS-FH	3.1	35.6	0.998
Triton X-100-FH	3.9	36.0	0.991
As(III) FH	2.6	35.0	0.998
SDBS-FH	2.8	29.9	0.994
Triton X-100-FH	2.9	29.7	0.997

FH: ferrihydrite; SDBS: sodium dodecyl benzene sulfonate.

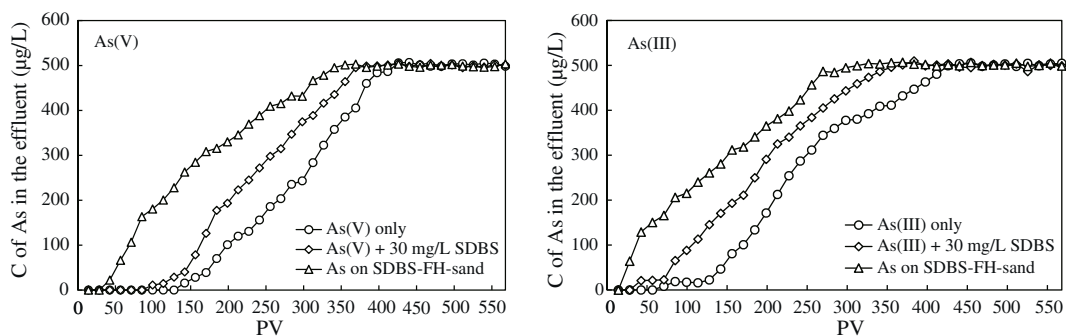


Fig. 4 – Breakthrough curves of As(V) and As(III) in the presence of SDBS at pH 7.0.

2.4. Transport behavior of arsenic in the presence of SDBS

Transport of arsenic through sediment is an important process governing arsenic concentrations in groundwater (Sharma et al., 2011). Based on the batch tests discussed above, surfactants had the potential to affect arsenic adsorption onto FH by competing for adsorption sites and electrostatic repulsion. Thus, surfactants could also influence the transport behavior in flow-through systems. The column experiments were conducted concerning two aspects: (1) transport of arsenic through FH-sand column with the coexistence of SDBS; and (2) arsenic transport through SDBS coated FH-sand. Comparison between the breakthrough of arsenic with and without the presence of SDBS was made to quantify the transport behavior of arsenic under the effect of SDBS. The flow-through experiment was run for 568 PV. As shown in Fig. 4, As(V) and As(III) had similar transport behavior in FH-sand columns. The PV when the concentration of arsenic in the effluent reached 50% of the influx concentration was employed to compare the breakthrough of arsenic in the absence or presence of SDBS (Sharma et al., 2011). Thus, breakthrough of As(III) occurred at 227.2 PV, more rapidly than As(V) breakthrough, which occurred at 298.2 PV, indicating the greater mobility of As(III). In the presence of SDBS, breakthrough of As(V) and As(III) occurred at 227.2 and 184.6 PV, 23.8 and 14.3% faster than that in SDBS-free systems, respectively. Since the concentration of arsenic (C) in the effluent could be represented as a function of time (t), the cumulative adsorption amount of arsenic (Q) throughout the process of breakthrough could be calculated from the start of influx to the achievement of stable concentration in the effluent, presented as the following formulation:

$$Q = C_0 \cdot t_e \cdot v - \int_{t_0}^{t_e} C(T) \cdot v \cdot dt \quad (8)$$

where t_0 (hr), and t_e (hr) are the times when arsenic concentration in the effluent became larger than zero and reached stability, which could be acquired from the breakthrough curves; C_0 is the influx concentration of arsenic (500 µg/L in this study); and v is the influent rate (50 mL/hr in this study).

The integral was calculated using Origin software. The maximum cumulative retention amount of As(V) and As(III) on FH-sand during the flow-through process was 56.8 and

49.8 mg/kg. Under the influence of SDBS, the cumulative adsorbed amount of As(V) and As(III) was 47.0 and 36.8 mg/kg, which was 17.2% and 26.0% less than that in the corresponding SDBS-free columns, respectively. In summary, the presence of SDBS had great potential to enhance arsenic breakthrough and reduce arsenic retention, promoting its transport through sediment.

Similarly, this study also investigated arsenic transport through FH-sand coated with SDBS. It was indicated that compared to the systems with coexisting SDBS, the pre-coating of SDBS caused more significant impacts on arsenic transport. The breakthrough of As(V) and As(III) occurred at 142.0 and 127.8 PV, which was 52.4% and 43.8% more rapid than in columns packed with bare FH-sand. In addition, the calculated cumulative adsorbed amount of As(V) and As(III) on SDBS-coated FH-sand was 31.5 and 21.2 mg/kg, respectively, which was 44.5% and 57.3% less than the amount of arsenic retained by the bare FH-sand. The pre-coating of SDBS on FH-sand resulted in an obvious inhibition of arsenic retention, indicating that when passing through sediment coated with SDBS in the environment, arsenic mobility would be greatly enhanced.

2.5. Mobilization of arsenic from FH and FH-sand by surfactants

Surfactants have been widely used in the enhanced remediation of pollution caused by organic matters and heavy metals (Edwards et al., 1991; Mulligan et al., 2001; Nivas et al., 1996; Tripathi and Brown, 2008; Zhao et al., 2006). Previous studies have shown that surfactants with a concentration higher than 10 CMC (critical micelle concentration) had great potential in eluting arsenic from mine tailings. The eluting process was essentially a process of release of arsenic by surfactants (Mukhopadhyay et al., 2013; Wang and Mulligan, 2009a, 2009b). Thus, the present study investigated the possibility and efficiency of arsenic mobilization from FH and FH-sand by surfactants in both batch tests and column experiments. In addition, the effect of the initial loading amount of arsenic on its mobilization by surfactants was also studied. As shown in Fig. 5, the release rate of As(V) by SDBS and Triton X-100 was 2.9% and 2.3%, respectively. The concentrations of As(V) in SDBS and Triton X-100 system reached 1.2 and 0.9 mg/L, respectively. Because of its greater mobility, the maximum release rate of As(III) by SDBS and Triton X-100 was 7.3% and 5.9%, respectively. Meanwhile, the equilibrium concentrations in SDBS and

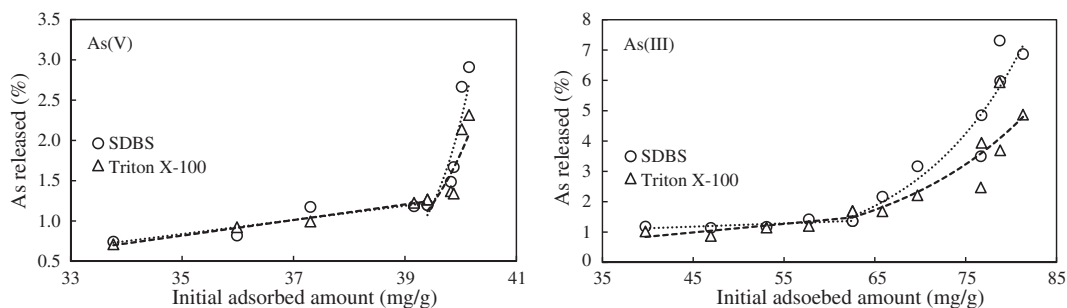


Fig. 5 – Influence of initial adsorbed amount of As on its mobilization by SDBS and Triton X-100.

Triton X-100 solution reached 5.8 and 4.7 mg/L. The relatively low mobilization rates indicated that the fraction of arsenic mobilized from the FH surface was mainly the weakly associated fractions, and the mobilization could be mainly attributed to adsorption exchange by surfactants. In addition, the mobilization of arsenic by 50 mg/L SDBS and Triton X-100 increased with the increase of initial arsenic loading amount. To be specific, the release rate increased linearly with initial adsorbed amount when the initial adsorbed amount of As(V) and As(III) was lower than 38.9 and 57.7 mg/g, corresponding to 97.0% and 79.5% of the maximum adsorption amount, respectively. As the initial adsorption amount increased, the release rate sharply increased. This indicated that the more serious arsenic pollution was, the more arsenic could be replaced by surfactants.

In the column experiments, 50 mg/L SDBS solution was continuously pumped into a column packed with arsenic-loaded FH-sand. The effluents were collected and the cumulative released amounts of arsenic were calculated and recorded as a function of flushing time. As shown in Fig. 6, the amount of As(V) and As(III) mobilized by SDBS was significantly larger than that mobilized by water. During the mobilization process, more As(III) was replaced by the flow through of SDBS than As(V), which was consistent with the batch experiments indicating the greater mobility of As(III). There was up to 10.8% of As(V) and 36.0% of adsorbed As(III) cumulatively mobilized by the continuous influx of 30 mg/L SDBS for 144 hr. Compared to the slight release in batch experiments, continuous influx of SDBS solution showed greater efficiency in mobilizing arsenic.

3. Conclusions

The present study investigated arsenic retention, transport and release behavior in the presence of the anionic surfactant SDBS and nonionic surfactant Triton X-100. The results of this study showed that the presence of anionic SDBS and nonionic Triton X-100 could enhance the mobility of arsenic by reducing arsenic retention onto FH, enhancing arsenic transport through FH-sand columns and promoting arsenic mobilization from FH. Mechanisms by which surfactants influence arsenic behavior include electrostatic repulsion and occupation of adsorption sites.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2015.12.007>.

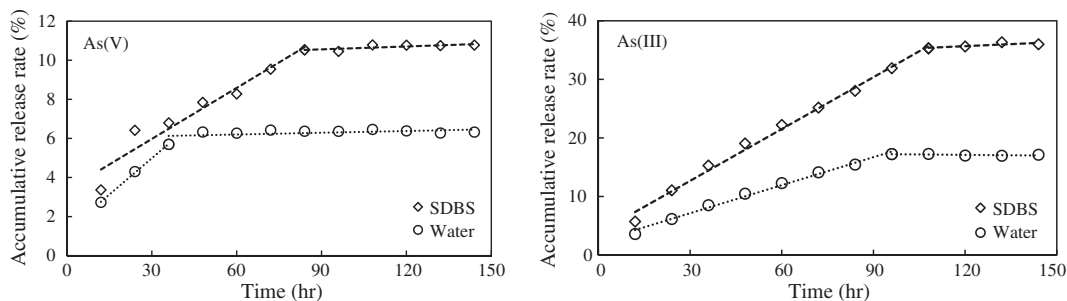


Fig. 6 – Release of As(V) and As(III) from columns by the influx of 50 mg/L SDBS.

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