Reusability of Al-F Hydroxide Precipitates Generated in Adsorption and Coagulation Treatment of Fluoride for Adsorptive Removal of Arsenic

Jiawei Ju,^{1,2} Zan He,^{1,2} Ruiping Liu,^{1,*} Huijuan Liu,¹ Xiwang Zhang,³ and Jiuhui Qu¹

¹Key Laboratory of Aquatic Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China.

²College of Resources and Environment, University of Chinese Academy of Sciences, Beijing, China.

³Department of Chemical Engineering, Monash University, Clayton, Australia.

Received: June 10, 2014

Accepted in revised form: April 14, 2015

Abstract

This study aims to investigate the feasibility of utilizing Al-F hydroxide precipitates generated in Al hydroxide [Al(OH)₃] adsorption [Al(OH)₃-F_{ads}] and aluminum (Al) coagulation [Al(OH)₃-F_{coag}] for adsorptive removal of As(III) and As(V). Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and pristine Al(OH)₃ were characterized by nitrogen sorption, X-ray photoelectron spectroscopy, and fourier transform infrared spectroscopy (FTIR) before and after arsenic adsorption. The kinetic study indicated that As(III) and As(V) adsorption on these Al-based solid wastes followed the pseudo-second-order model. The calculated adsorption capacity of Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag} for As(III) was 48.0 and 31.0 mg/g, while it was 84.0 and 56.3 mg/g for As(V), respectively. These adsorption capacities were 25–50% lower compared with pristine Al(OH)₃. Anion exchange of fluoride by H₂AsO₄[−] and HAsO₄^{2−} dominated in As(V) removal by Al(OH)₃-F_{ads}, while formation of an As-O complex played a more important role in As(V) removal by Al(OH)₃-F_{coag}. The maximum concentration of released fluoride after the adsorption of As(III) and As(V) by Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag} was below the Chinese Class-II industrial discharge standard for fluoride (<20 mg/L). Results from this study indicated that the aluminum hydroxides generated in the fluoride removal process could be reclaimed as an adsorbent for As(III)/As(V) removal from industrial wastewater.

Key words: adsorption; Al(OH)₃; arsenic; fluoride; reclamation

Introduction

THE CONTAMINATION OF toxic arsenic (As) due to geochemical reactions and anthropic activities is a worldwide challenge to ecological safety and human health. Inorganic arsenic in water primarily exists in two oxidation states, neutral arsenite [As(III)] and negatively charged arsenate [As(V)]. Many technologies have been tested and applied for arsenic removal, including oxidation/precipitation (Borho and Wilderer, 1996; Leupin and Hug, 2005), coagulation/coprecipitation (Cheng *et al.*, 1994; Hering *et al.*, 1997; Wickramasinghe *et al.*, 2004), adsorption (Guo *et al.*, 2007; Maiti *et al.*, 2012), ion exchange (Kim and Benjamin, 2004; Baciocchi *et al.*, 2005), reverse osmosis (Kang *et al.*, 2000; Ning, 2002), electrodialysis (Weng *et al.*, 2005), and bioremediation (Katsoyiannis *et al.*, 2002). Among them, adsorption is one of the most widely used technologies due to its easy operation and maintenance, high efficiency, and low cost.

In the past decade, much effort has been focused on the development of novel adsorbents with high removal capacity, such as nanocrystalline TiO₂ (Xu and Meng, 2009), treated laterite (Guo *et al.*, 2007; Maiti *et al.*, 2012), iron and manganese binary oxide (Wu *et al.*, 2011), and magnetite Fe₃O₄-reduced graphite oxide (Luo *et al.*, 2012). However, their high fabrication cost limits their wide application in practice. Most recently, some low-cost adsorbents such as agricultural and industrial by-products have been investigated for arsenic removal (Soner Altundoğan *et al.*, 2000; Mandal *et al.*, 2012). For instance, Mandal *et al.* (2012) studied the adsorption of As(III) and As(V) by the mangrove sediment, and results showed that ligand exchange and adsorption reactions occurred in both organic matter and the hydroxide phase (Mandal *et al.*, 2012). Industrial waste such as red mud and iron oxide-loaded melted municipal solid waste incinerator slag was also tested, and the calculated maximum adsorption capacity for As(III) and As(V) was 8.86 and 10.80 μmol/g, respectively. Besides, the adsorption of As(III) onto red mud was exothermic, whereas that of As(V) was endothermic (Soner Altundoğan *et al.*, 2000).

Fluorosis due to the long-term exposure to fluoride through drinking water is another global health concern. Aluminum (Al) coagulation and Al (hydro) oxide adsorption have been

*Corresponding author: Key Laboratory of Aquatic Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. Phone: +86 10 62849128; Fax: +86 10 62849160; E-mail: liuruiping@rcees.ac.cn

well studied and widely used for fluoride removal. However, the large amounts of aluminum hydroxide solid wastes generated in both processes have created a high demand for more environmentally benign and cost-effective alternatives. One option that exhibits a promising future is the conversion of the solid wastes into adsorbents. With our knowledge of the solid wastes having a high porosity and an affinity for arsenic, we aim to investigate the feasibility of using the solid wastes as sorbents for arsenic removal in this study. Furthermore, the fluoride removal mechanisms and the speciation of fluoride involved in these two systems are different. In Al (hydro) oxide adsorption, fluoride is mostly adsorbed on the surface of adsorbents. By contrast, in coagulation, fluoride participates in the formation of aluminum hydroxide $[\text{Al}(\text{OH})_3]$ precipitates, and hence, it is captured inside the particles besides attaching to the surfaces. In addition, the different states of fluoride may affect the interfacial characteristics of these two wastes which, in turn, affect their performance in arsenic removal.

In this study, we aim to investigate the feasibility of reusing two kinds of solid wastes generated in the adsorption and coagulation treatment of fluoride as adsorbents for arsenic removal. The solid wastes obtained from the adsorption process were mainly $\text{Al}(\text{OH})_3$ flocs with adsorbed fluoride, which were named as $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$. However, the solid wastes obtained from the coagulation process were mainly Al-F-OH precipitates, which were named as $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$. The adsorption performance of $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$, and pristine $\text{Al}(\text{OH})_3$ for As(III) and As(V) removal was evaluated in terms of adsorption isotherms and adsorption kinetics. These adsorbents before and after arsenic adsorption were characterized by X-ray photoelectron spectroscopy (XPS), fourier transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) surface area analyzer, and sequential extraction procedures to illustrate the adsorption mechanism.

Chemicals and Methods

Chemicals

All chemicals used in this study were of analytical grade. The stock solutions of As(III), As(V), fluoride, and Al salt were prepared by dissolving NaAsO_2 , Na_3AsO_4 , NaF, and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in deionized water, respectively.

Preparation of $\text{Al}(\text{OH})_3\text{-F}$ solid wastes

A plexiglass beaker on a conventional Jar test apparatus was used to fabricate the three adsorbents, $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$, and pristine $\text{Al}(\text{OH})_3$. First, NaOH solution (1.25 M) was slowly added into 500 mL $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution (20 mmol/L) under stirring at 100 rpm until the pH of the solution reached 7.0 ± 0.2 . After settling for 30 min, the resultant solids were separated from the solution by filtration with a 0.45- μm membrane and washed with distilled water several times. After freeze-drying, pristine $\text{Al}(\text{OH})_3$ was obtained. The procedure of fabricating $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ was similar with that of pristine $\text{Al}(\text{OH})_3$, only with a slight modification. For preparing $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, 500 mL fluoride solution (178 mM) was added into the beaker after the formation of $\text{Al}(\text{OH})_3$ solids under slow stirring at 50 rpm for 20 min; meanwhile, pH was maintained at 7.0 ± 0.2 . For fabricating $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$, 500 mL fluoride solution (178 mM) was added

into 500 mL $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ solution (20 mM) instead of NaOH solution. Then, pH was adjusted to 7.0 ± 0.2 with NaOH or HNO_3 . The two kinds of obtained fluoride-containing solid wastes were washed with distilled water for several times, freeze-dried, and then kept in an air-tight container for use.

Batch adsorption experiments

Equilibrium isotherm experiments were performed in 50-mL polypropylene tubes with As(III) or As(V) solutions at an initial concentration in the range of 5–80 mg/L at room temperature and an adsorbent dosage of 0.02 g/L. During the adsorption, the pH of the solutions was maintained at 7 with HNO_3 or NaOH. The tubes were shaken at 30 rpm on a utility rotary shaker for 24 h. The liquid phase was then filtered by a 0.45- μm membrane to analyze the concentrations of fluoride, As(III), As(V), and Al. The used adsorbents were freeze-dried for subsequent characterization.

The experiments of adsorption kinetics were conducted in 1,000 mL As(III) or As(V) solution with an initial concentration of 10 mg/L and an adsorbent dosage of 0.02 g/L. Samples were taken at specified time intervals. The pH effect on the adsorption performance of the adsorbents was studied by the solution pH that varied in the range of 4–9 at an As(III) or As(V) initial concentration of 80 mg/L.

Extraction procedure

Sequential extraction experiments were carried out to clarify the species distribution of As(III) or As(V) in different binding phases on used adsorbents. A three-step extraction was conducted to investigate the following three binding phases of arsenic (Shiowatana *et al.*, 2001): (1) water-soluble As; (2) surface-adsorbed As; and (3) AlO-associated As. First, the extraction was carried out in sequence with ultra-pure water, 0.5 M NaHCO_3 , and 0.1 M NaOH in polypropylene centrifuge tubes. These tubes were shaken for 24 h at 30 rpm. After each step of extraction, the samples were centrifuged at 3,000 rpm for 2 min. The obtained liquid phase was filtered through a 0.45- μm membrane for As analysis. The three target phases of arsenic after each step of extraction corresponded to water-soluble As (Species-I), surface-adsorbed As (Species-II), and AlO-associated As (Species-III).

Analysis and characterization

The concentrations of Al and As were analyzed by inductively coupled plasma–optical emission spectroscopy (OPTIMA 2000DA; PerkinElmer), and the detection limits were 0.8 $\mu\text{g/L}$ for Al and 4 $\mu\text{g/L}$ for As. The concentrations of fluoride were measured by a fluoride ion selective electrode (PF-1; Kangyi Instrument Ltd.) with the detection limit of 0.05 mg/L. BET surface area (S_{BET}) was determined by standard multipoint techniques of N_2 adsorption with a BET analyzer (ASAP2000; Micromeritics). The ζ -potential of samples was measured by a ζ -potential analyzer (Zetasizer 2000; Malvern). XPS results were obtained by an ESCA-lab-220i-XL spectrometer (Shimadzu) with monochromatic Al K α radiation (225 W, 15 mA, 15 kV).

Adsorption models

Adsorption kinetic models. The following two kinetic models were used to clarify the adsorption process pseudo-

first-order (Yuh-Shan, 2004) and pseudo-second-order (Ho and McKay, 1999) as described in Equations (1) and (2), respectively.

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \quad (2)$$

where q and q_e are the mass of metal adsorbed (mg/g) at time t and at equilibrium, respectively; k_1 and k_2 are the pseudo-first-order and pseudo-second-order kinetic rate constants.

Adsorption isotherm models. The Langmuir (Mckay *et al.*, 1982) and Freundlich (Mckay *et al.*, 1982) isotherms were used to analyze the adsorption of As(III)/As(V) on $\text{Al}(\text{OH})_3$ -F solid wastes and pristine $\text{Al}(\text{OH})_3$ as represented by the equations below.

$$q_e = \frac{q_m L C_e}{1 + L C_e} \quad (3)$$

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

where C_e and q_e are the As(III) or As(V) concentration and the amount of As(III) or As(V) adsorbed at equilibrium; q_m and L are Langmuir constants related to adsorption capacity and energy of adsorption; K_F is the Freundlich constant; and n is an indication of surface heterogeneity and surface affinity of adsorption.

Results and Discussion

Adsorbent characterization

Table 1 illustrates S_{BET} , pore size, and pH_{PZC} of pristine $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_3$ -F_{ads}, and $\text{Al}(\text{OH})_3$ -F_{coag}. $\text{Al}(\text{OH})_3$ showed the highest S_{BET} of 195.6 m²/g, which is slightly higher compared with $\text{Al}(\text{OH})_3$ -F_{ads} and $\text{Al}(\text{OH})_3$ -F_{coag}, 150.2 and 123.7 m²/g, respectively. This indicates that some pores of the pristine $\text{Al}(\text{OH})_3$ might be filled by fluoride. The average pore size of $\text{Al}(\text{OH})_3$ -F_{ads} and $\text{Al}(\text{OH})_3$ -F_{coag} also slightly declined compared with $\text{Al}(\text{OH})_3$, which provides further

evidence. The ratios of F to Al ($R_{\text{F:Al}}$) on the surfaces of these adsorbents, as indicated by XPS analysis, were observed to be 2.2:1 and 0.8:1 for $\text{Al}(\text{OH})_3$ -F_{ads} and $\text{Al}(\text{OH})_3$ -F_{coag}, respectively. However, the corresponding $R_{\text{F:Al}}$ values in the bulk phases were both determined to be 1.0:1. This indicates that fluoride mainly exists on the surface of $\text{Al}(\text{OH})_3$ -F_{ads}, whereas it is included within $\text{Al}(\text{OH})_3$ -F_{coag}.

Adsorption kinetics

Figure 1 illustrates the variation of adsorption density of As(III) and As(V) (q_t) onto pristine $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_3$ -F_{ads}, and $\text{Al}(\text{OH})_3$ -F_{coag} as a function of adsorption time. It is clear that the incorporation of fluoride into $\text{Al}(\text{OH})_3$ inhibited the adsorption of both As(III) and As(V). The maximum q_t value of $\text{Al}(\text{OH})_3$ is 8.4 mg/g for As(III) and 58.7 mg/g for As(V), respectively. By contrast, the maximum $q_{t,\text{As(III)}}$ values of $\text{Al}(\text{OH})_3$ -F_{ads} and $\text{Al}(\text{OH})_3$ -F_{coag} are 4.3 and 6.5 mg/g, respectively, being 49.3% and 22.9% lower compared with $\text{Al}(\text{OH})_3$. The adsorption of As(V) onto $\text{Al}(\text{OH})_3$ -F_{ads} and $\text{Al}(\text{OH})_3$ -F_{coag} is also lower compared with onto $\text{Al}(\text{OH})_3$. The maximum $q_{t,\text{As(V)}}$ value is 30.6 mg/g for $\text{Al}(\text{OH})_3$ -F_{ads} and 43.5 mg/g for $\text{Al}(\text{OH})_3$ -F_{coag}, which are 47.9% and 25.9% lower compared with $\text{Al}(\text{OH})_3$, respectively. Moreover, the incorporation of fluoride in $\text{Al}(\text{OH})_3$ -F_{ads} and

FIG. 1. The variation of adsorption density of As(III) and As(V) onto the three adsorbents with prolonged contact time (experimental conditions: initial concentration = 10 mg/L, contact time = 24 h, pH = 7, ionic strength = 0.01 M NaNO₃, adsorbent dose = 0.02 g/L).

TABLE 1. THE MAIN CHARACTERISTICS OF THE THREE ADSORBENTS

	$\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$	$\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$	$\text{Al}(\text{OH})_3$
Specific surface area (m ² /g)	150.2	123.7	195.6
Pore size (nm)	16.6	16.6	18.0
pH _{PZC}	7.4	8.0	8.0
Ratio of F to Al			
Surface ^a	2.2:1	0.84:1	f ^c
Bulk phase ^b	1.0:1	1.0:1	f ^c

^aThe ratio of F to Al on surface was obtained from the results of X-ray photoelectron spectroscopy.

^bThe ratio of F to Al in the bulk phase was obtained from the analysis of the concentration of Al and F before and after the fabrication of $\text{Al}(\text{OH})_3$ -F_{ads} and $\text{Al}(\text{OH})_3$ -F_{coag}.

^cThere is no F on $\text{Al}(\text{OH})_3$ surfaces, and the ratio of F to Al is meaningless.

TABLE 2. KINETICS PARAMETERS OF PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER FOR AS(III) AND AS(V) ADSORPTION

Model	Parameter	$Al(OH)_3\text{-}F_{ads}$		$Al(OH)_3\text{-}F_{coag}$		$Al(OH)_3$	
		As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
Pseudo-first-order kinetic model	$q_{e,exp}$ (mg/g)	4.3	30.6	6.5	43.5	8.4	58.7
	k_1 (h^{-1})	1.0	3.0	1.6	1.7	20.5	24.5
	$q_{e,cal}$ (mg/g)	3.9	28.2	6.1	39.8	7.9	56.2
	R^2	0.98	0.96	0.97	0.95	0.85	0.95
Pseudo-second-order kinetic model	k_2 (mg/[g·h])	0.1	0.05	0.1	0.02	1.8	0.3
	$q_{e,cal}$ (mg/g)	4.6	31.3	7.0	45.5	8.3	58.9
	R^2	0.99	0.99	0.99	0.99	0.98	0.99

$Al(OH)_3\text{-}F_{coag}$ slowed down the adsorption of As(III) and As(V) to some extent. Adsorption of As(III) and As(V) on $Al(OH)_3$ was very fast and $q_{e,As(III)}$ and $q_{e,As(V)}$ almost reached equilibrium within 2 h. However, it took about 12 h for $Al(OH)_3\text{-}F_{ads}$ and $Al(OH)_3\text{-}F_{coag}$ to reach the adsorption equilibrium of As(III) and As(V).

To further illustrate the effect of fluoride on the adsorption of arsenic, the experimental data were respectively fitted by pseudo-first-order and pseudo-second-order kinetic models. Table 2 summarizes the obtained parameters and regression coefficient (R^2). The fitted curves using these kinetic equations are plotted in Fig. 1. As indicated by higher R^2 , the pseudo-second-order model better fits the adsorption of arsenic onto these adsorbents than the pseudo-first-order model. The value of k_2q_e in the pseudo-second-order model is an indicator of the adsorption rate. The calculated k_2q_e values of As(III) adsorption onto $Al(OH)_3\text{-}F_{ads}$, $Al(OH)_3\text{-}F_{coag}$, and $Al(OH)_3$ are 0.5, 0.7, and 15.0/h, respectively. The adsorption of As(V) on the adsorbents yields higher k_2q_e values, being 1.6, 0.9, and 17.7/h, respectively, which is related to the faster adsorption rate of As(V) compared with As(III) adsorption. The different adsorption rate between As(III) and As(V) is attributed to the difference of the electrostatic interactions between them and these adsorbents. The pH_{PZC} values of $Al(OH)_3\text{-}F_{ads}$, $Al(OH)_3\text{-}F_{coag}$, and $Al(OH)_3$ were determined to be 7.4, 8.0, and 8.0, respectively. Hence, the three adsorbents have positive surfaces at pH 7 in this study. As(III) exists as the neutral species H_3AsO_3 at pH 7, whereas As(V) is predominantly in the negatively charged species $H_2AsO_4^-$ and $HAAsO_4^{2-}$. Hence, the stronger electrostatic attraction between As(V) and the adsorbent surfaces leads to the faster and more significant adsorption of As(V) on these adsorbents.

Adsorption isotherm

Figure 2 illustrates the adsorption isotherm of As(III) and As(V) onto $Al(OH)_3$, $Al(OH)_3\text{-}F_{ads}$, and $Al(OH)_3\text{-}F_{coag}$. The maximum adsorption capacities ($q_{e,exp}$) of As(III) and As(V) onto these three adsorbents are listed in Table 3. The results also show that the incorporation of fluoride into $Al(OH)_3$ through either adsorption or coagulation greatly decreased its adsorption capacity toward As(III) and As(V). Compared with $Al(OH)_3\text{-}F_{coag}$, $Al(OH)_3\text{-}F_{ads}$ has a higher $q_{e,exp}$, which indicates that more adsorption sites are available on the $Al(OH)_3\text{-}F_{ads}$ surface than on the $Al(OH)_3\text{-}F_{coag}$ surface. This

was confirmed by S_{BET} analysis. The S_{BET} of $Al(OH)_3\text{-}F_{ads}$ and $Al(OH)_3\text{-}F_{coag}$ are 150.2 and 123.7 m^2/g , respectively.

Table 3 illustrates the fitted parameters for the Langmuir and Freundlich models. The Langmuir model has a higher R^2 value, which means that it is more suitable to describe the adsorption of As(III) and As(V) than the Freundlich model. The Langmuir isotherm is based on the assumption that monolayer surface coverage limits the adsorption due to surface saturation (Guo *et al.*, 2007). The maximum adsorption capacity calculated by the Langmuir model ($Q_{max,cal}$) of As(III) and As(V) on both $Al(OH)_3\text{-}F_{ads}$ and $Al(OH)_3\text{-}F_{coag}$ is lower than those on $Al(OH)_3$. The introduction of negatively charged

FIG. 2. Adsorption isotherms of As(III) and As(V) onto the three adsorbents (experimental conditions: contact time = 24 h, pH = 7, ionic strength = 0.01 M $NaNO_3$, adsorbent dose = 0.02 g/L).

TABLE 3. LANGMUIR AND FREUNDLICH PARAMETERS FOR THE ADSORPTION OF As(III) AND As(V) ONTO THE THREE ADSORBENTS

Model	Parameter	$Al(OH)_3\text{-}F_{ads}$		$Al(OH)_3\text{-}F_{coag}$		$Al(OH)_3$	
		As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
Langmuir model	$q_{e,exp}$ (mg/g)	33.0	74.1	25.7	55.9	45.0	111.0
	$Q_{max,cal}$ (mg/g)	47.9	84.0	31.0	56.3	65.1	113.0
	L (L/mg)	0.01	1.3	0.06	1.5	0.03	1.6
	R^2	0.99	0.99	0.99	0.98	0.99	0.99
Freundlich model	F	1.7	21.5	4.2	39.5	5.4	85.8
	N	1.4	3.1	2.4	10.6	2.0	13.6
	R^2	0.97	0.93	0.91	0.92	0.95	0.94

fluoride into $Al(OH)_3$ not only occupies the surface sites but also inhibits the adsorption of As(III) and As(V). In addition, the L values of $Al(OH)_3\text{-}F_{ads}$, $Al(OH)_3\text{-}F_{coag}$, and $Al(OH)_3$ were calculated to be 1.3, 1.5, and 1.6 L/mg for As(V) and 0.01, 0.06, and 0.03 L/mg for As(III), and this indicated the stronger affinity of these adsorbents toward As(V) than that toward As(III).

Effect of pH on the adsorption of As(III) and As(V)

Figure 3 illustrates the adsorption density of As(III) and As(V) onto these adsorbents over a wide pH range from 4 to 9. The adsorption of As(III) onto $Al(OH)_3\text{-}F_{ads}$, $Al(OH)_3\text{-}F_{coag}$, and $Al(OH)_3$ declines with increasing pH in pH ranges from 4 to 6 and from 7 to 9. At pH below 8, nonionic H_3AsO_3 is the dominant As(III) species, and the adsorption of As(III)

was mainly attributed to the Van der Waal force (Lin and Wu, 2001) and the formation of an inner sphere surface complex (Ona-Nguema *et al.*, 2005). At elevated pH above 7, the dissociation of H_3AsO_3 to anionic $H_2AsO_3^-$ occurred, and the adsorption of As(III) onto the positive surfaces was improved due to specific bonding and electrostatic interaction. At pH above 8, these adsorbents showed negatively charged surfaces, and the adsorption of negative As(III) was inhibited accordingly.

The uptake of As(V) on these adsorbents also declines with increasing pH. Results of MINTEQ modeling indicate that As(V) mainly exists in the form of $H_2AsO_4^-$ in the pH range from 3 to 7 and $HAsO_4^{2-}$ is the dominant species at pH >7. On the other hand, the point of zero charge (pH_{pzc}) was determined to be 7.4, 8.0, and 8.0 for $Al(OH)_3\text{-}F_{ads}$, $Al(OH)_3\text{-}F_{coag}$, and $Al(OH)_3$. At pH below these pH_{pzc} , these adsorbents showed positive surfaces as described in Equation (5). The electrostatic attraction between the positively charged sites and As(V), $H_2AsO_4^-$ and $HAsO_4^{2-}$ is stronger at a lower pH which, in turn, results in a higher As(V) uptake. At pH above pH_{pzc} , these adsorbents exhibited negative surfaces as described in Equation (6) and the repulsive forces inhibited the adsorption of negative As(V) species thereafter.

Proposed mechanisms involved in the adsorption of As(III) and As(V)

The variation of solution pH during the adsorption of As(III) and As(V) onto these three adsorbents was monitored and the results are shown in Fig. 4. A significant decrease in solution pH during As(III) and As(V) adsorption as a function of adsorption time was observed. The pH of the solution remained unchanged after 50 min for As(III) and 5 h for As(V). To make the variation of pH with contact time more obvious, the results were only shown up to 50 min for As(III) and 5 h for As(V).

The decrease of pH during As(III) and As(V) adsorption can be explained by the deprotonation of the $H_nAsO_4^{(3-n)-}$ or $H_nAsO_3^{(3-n)-}$ ($n = 1, 2, 3$). During the adsorption process, the protonated sites on the surface will adsorb negatively charged As(III) and As(V) species. This will shift the

FIG. 3. Uptake of As(III) and As(V) onto the three adsorbents in the pH range 4–9 (experimental conditions: initial concentration = 80 mg/L, contact time = 24 h, ionic strength = 0.01 M NaNO₃, adsorbent doses = 0.02 g/L).

FIG. 4. Solution pH variation during the adsorption of As(III)/As(V) by the three adsorbents with prolonged time (experimental conditions: initial concentration = 80 mg/L, contact time = 24 h, ionic strength = 0.01 M NaNO₃, adsorbent dose = 0.02 g/L).

equilibrium of deprotonation and release more hydrogen ions, thus leading to the reduction of pH. A longer time is required to achieve equilibrium for As(V), and the equilibrium pH is also lower compared with As(III). This further suggests that the adsorption of As(III) and As(V) may be dominated by different mechanisms. Sequential extraction experiments were conducted to provide quantitative information on the distribution of arsenic [i.e., As(III) and As(V)] in three different binding phases on the three adsorbents, and the ratios of the arsenic species are shown in Fig. 5. The water-soluble fraction (Species-I) is the dominant As(III) species on Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and Al(OH)₃ and its ratios are 51.3%, 42.2%, and 47.3%, respectively. By contrast, the ratios of As(III) species binding to -OAl (Species-III) are much lower, being 7.8%, 20.0%, and 14.6% for Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and Al(OH)₃, respectively. This indicates that the incorporation of As(III) onto Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and Al(OH)₃ mainly exists in a soluble form.

However, the smaller variation of pH values for Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag} indicated that other processes apart from complexation may take place in the adsorption of As(V), such as ion exchange (Liu *et al.*, 2012), as described in Equations (7) and (8).

FIG. 5. The content and ratios of As(III)/As(V) in different binding species within the three adsorbents.

For the binding phases of As(V), Al(OH)₃-F_{coag} has the highest percentage of 34.7% for the soluble form (Species-I). Its percentage of Species-II and Species-III is 26.9% and 38.4%, respectively. The As(V) species binding to -OAl, expressed as Species-III, bond strongly with the solid phase and hardly released into the solution. A slight difference is observed between Species-I and Species-III for As(V) loaded on Al(OH)₃-F_{coag}, which indicates that both complexation and electrostatic attraction play important roles in As(V) removal by Al(OH)₃-F_{coag}. Compared with Al(OH)₃-F_{coag}, the ratios of Species-III on Al(OH)₃-F_{ads} and Al(OH)₃ are much lower, being 23.9% and 28.2%, respectively. This means that the formation of an As-O complex is of more importance for As(V) removal by Al(OH)₃-F_{coag} than by the other two adsorbents. As(V) on Al(OH)₃-F_{ads} and Al(OH)₃ is mainly extracted in the surface-adsorbed fraction (Species-II) at 58.7% and 42.6%, respectively. Fluoride is mostly adsorbed on the surface of the adsorbent Al(OH)₃-F_{ads} in the removal of fluoride by adsorption. Thus, more F⁻ on the surface of Al(OH)₃-F_{ads} could exchange with the negatively charged anions H₂AsO₄⁻ and HAsO₄²⁻ compared with Al(OH)₃-F_{coag} in the adsorption of As(V).

After discussing the adsorptive properties of Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag}, it is necessary to address whether fluoride and Al are leached during the adsorption process. The concentration of leached fluoride in the solution was measured during adsorption of As(III) and As(V), and the results are illustrated in Fig. 6a. The maximum concentration of released

FIG. 6. The release of fluoride and Al from Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag} during adsorption of As(III)/As(V). (a) The concentrations of leaching fluoride; (b) the ratios of released fluoride to Al.

fluoride is 11.3 mg/L in the adsorption of As(III) by Al(OH)₃-F_{ads}, 11.8 mg/L in the adsorption of As(III) by Al(OH)₃-F_{coag}, 14.6 mg/L in the adsorption of As(V) by Al(OH)₃-F_{ads}, and 14.0 mg/L in the adsorption of As(V) by Al(OH)₃-F_{coag}. These are all below the Chinese Class-II industrial discharge standard for fluoride (<20 mg/L). The ratio of released fluoride to Al ($R_{F:Al}$) in molar terms during As(V) adsorption is higher than that during As(III) adsorption, as shown in Fig.

6b. Due to the hard-hard combination, in agreement with the soft-hard acid base concept, the presence of fluoride ion can produce changes in the concentration of Al in water. For Al(OH)₃-F_{ads}, the value of $R_{F:Al}$ first increases and then decreases with the increasing equilibrium concentration of As(III)/As(V). This suggests that the fluoride ions compete for the active sites with negatively charged anions, H₂AsO₄⁻ and HAsO₄²⁻. The variation of $R_{F:Al}$ for Al(OH)₃-F_{coag} is small compared with Al(OH)₃-F_{ads}. This indicates that the fluoride mainly exists on the surface of Al(OH)₃-F_{ads}, whereas it is solidified within Al(OH)₃-F_{coag}.

The XPS binding energy and the ratios of main elements on the surfaces of different adsorbents before and after adsorbing arsenic were obtained from XPS analysis. As shown in Fig. 7a, the adsorption of As(III) and As(V) shows little influence on the binding energy of O 1s within Al(OH)₃-F_{ads} and Al(OH)₃, and the interaction between O atoms and arsenic is assumed to be weak. Interestingly, the binding energy of O 1s within Al(OH)₃-F_{coag} slightly shifts from 531.3 to 531.7 eV after adsorbing As(III) and to 531.8 eV after adsorbing As(V). This might be attributed to the decreased electron density in the O 1s shell owing to the combination of As(III) and As(V) with the interfacial -OH groups (Mohan and Pittman, 2007). Hence, it is further proven that the formation of surface complexes plays a more dominant role in the adsorption of arsenic by Al(OH)₃-F_{coag} than that by Al(OH)₃-F_{ads} and Al(OH)₃.

XPS spectra in Fig. 7b shows little variation in the binding energy of F 1s after the adsorption of As(III) for both Al(OH)₃-F_{ads} and Al(OH)₃-F_{coag}, and it is suggested that elemental F rarely participates in the removal of As(III). The adsorption of As(V) onto Al(OH)₃-F_{ads} contributes to the shift of the binding energy of F 1s from 685.0 to 685.4 eV, and this is attributed to the stronger binding between fluoride and Al(OH)₃-F_{ads} surfaces. On the other hand, the content of F1s on surfaces also shows different trends after the adsorption of As(III) and As(V). After adsorbing As(III), the content of F1s slightly decreases from 12.9% to 10.4% for Al(OH)₃-F_{coag}, whereas it significantly decreases from 28.7% to 14.5% for Al(OH)₃-F_{ads}. The adsorption of As(V) also contributes to a sharp decrease of F 1s content from 28.7% to 7.2% for Al(OH)₃-F_{ads} and to an insignificant change from 12.9% to 10% for Al(OH)₃-F_{coag}. This further demonstrates that fluoride mainly exists on the surface of Al(OH)₃-F_{ads}, whereas it is solidified within Al(OH)₃-F_{coag} through the formation of inner-sphere Al-F complexes. Moreover, it can be concluded that more F⁻ on the surface of Al(OH)₃-F_{ads} exchanges with the negatively charged anions H₂AsO₄⁻ and HAsO₄²⁻ compared with Al(OH)₃-F_{coag}, as indicated in Equations (7) and (8).

The adsorption of arsenic onto aluminum (hydro) oxides is highly dependent on the interfacial hydroxyl groups (-OH), and the formation of surface complexes plays an important role. Figure 8 illustrates the FTIR spectra of Al(OH)₃-F_{ads}, Al(OH)₃-F_{coag}, and Al(OH)₃ before and after the adsorption of As(III) and As(V). These three adsorbents show a broad band centered at 960 cm⁻¹, which corresponds to the bending vibration of the -OH groups on their surfaces (Sun and Donner, 1996). Moreover, the intensity of the hydroxyl band on Al(OH)₃-F_{coag} is stronger than on Al(OH)₃-F_{ads} and Al(OH)₃, indicating more -OH sites on the surface. As mentioned above, coprecipitation and adsorption are involved in the removal of fluoride by coagulation and Al-F-OH participates formed thereafter (Gong *et al.*, 2012). These peaks reduce

FIG. 7. X-ray photoelectron spectroscopy spectra of (a) O 1s and (b) F 1s on the surfaces of the three adsorbents.

remarkably after the adsorption of As(III) and As(V), owing to the participation and the consumption of $-\text{OH}$ groups by arsenic species. In addition, new peaks at 997 and 870 cm^{-1} appear that are assigned to the O-As(III) and O-As(V) stretching vibrations (Sun and Doner, 1996). Only a slight difference is observed in the intensity of O-As(III) on the three adsorbents. By contrast, the intensity of O-As(V) on $\text{Al(OH)}_3\text{-F}_{\text{ads}}$ is much weaker than that on $\text{Al(OH)}_3\text{-F}_{\text{coag}}$ and Al(OH)_3 . This indicates that the surface complexation is less

FIG. 8. Fourier transform infrared spectroscopy (FTIR) spectra of adsorbents before and after adsorption of As(III) and As(V).

dominant in $\text{Al(OH)}_3\text{-F}_{\text{ads}}$ than $\text{Al(OH)}_3\text{-F}_{\text{coag}}$ and Al(OH)_3 , in agreement with the XPS results.

Conclusions

The Al-based solid wastes generated from fluoride removal by adsorption and coagulation, $\text{Al(OH)}_3\text{-F}_{\text{coag}}$ and $\text{Al(OH)}_3\text{-F}_{\text{ads}}$, were characterized and applied for adsorptive removal of As(III) and As(V) from the aqueous solution. Kinetic study results indicate that As(III) and As(V) adsorption on these Al-based solid wastes followed the pseudo-second-order model. The calculated adsorption capacity of $\text{Al(OH)}_3\text{-F}_{\text{ads}}$ and $\text{Al(OH)}_3\text{-F}_{\text{coag}}$ for As(III) was 48.0 and 31.0 mg/g , while for As(V) it was 84.0 and 56.3 mg/g , respectively. These adsorption capacities were 25–50% lower

than those of pristine $\text{Al}(\text{OH})_3$. Anion exchange of fluoride by H_2AsO_4^- and HAsO_4^{2-} dominated in As(V) removal by $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$, while formation of an As-O complex played a more important role in As(V) removal by $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$. The maximum concentration of released fluoride after the adsorption of As(III) and As(V) by $\text{Al}(\text{OH})_3\text{-F}_{\text{ads}}$ and $\text{Al}(\text{OH})_3\text{-F}_{\text{coag}}$ was below the Chinese Class-II industrial discharge standard for fluoride (<20 mg/L). The solid wastes generated in fluoride removal processes could be potentially utilized as adsorbents for As(III)/As(V) removal from industrial wastewater. It is noted that the arsenic content in the obtained solid wastes exceeds the *Identification Standards for Hazardous Wastes* of China and should be carefully and safely handled and disposed. The strategy for the stabilization and safe disposal of these solid wastes is to be studied in the future.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant no. 21177143 and 21177144) and the key project of the National “863” High-tech R&D Program of China (2012AA062604). Appreciation is also extended to the Outstanding Youngster Fund (51422813) and Joint Research Fund for Overseas Chinese Scholars and Scholars in Hong Kong and Macao (51328803).

Author Disclosure Statement

No competing financial interests exist.

References

- Baciacchi, R., Chiavola, A., and Gavasci, R. (2005). Ion exchange equilibria of arsenic in the presence of high sulphate and nitrate concentrations. *Water Supply* 5, 67.
- Borho, M., and Wilderer, P. (1996). Optimized removal of arsenate (III) by adaptation of oxidation and precipitation processes to the filtration step. *Water Sci. Technol.* 34, 25.
- Cheng, R.C., Liang, S., Wang, H.-C., and Beuhler, M.D. (1994). Enhanced coagulation for arsenic removal. *J. Am. Water Works Assoc.* 86, 79.
- Gong, W.X., Qu, J.H., Liu, R.P., and Lan, H.C. (2012). Effect of aluminum fluoride complexation on fluoride removal by coagulation. *Colloid. Surface. A* 395, 88.
- Guo, H., Stüben, D., and Berner, Z. (2007). Adsorption of arsenic (III) and arsenic (V) from groundwater using natural siderite as the adsorbent. *J. Colloid. Interface Sci.* 315, 47.
- Hering, J.G., Chen, P.-Y., Wilkie, J.A., and Elimelech, M. (1997). Arsenic removal from drinking water during coagulation. *J. Environ. Eng.* 123, 800.
- Ho, Y.S., and McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochem.* 34, 451.
- Kang, M., Kawasaki, M., Tamada, S., Kamei, T., and Magara, Y. (2000). Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes. *Desalination* 131, 293.
- Katsoyiannis, I., Zouboulis, A., Althoff, H., and Bartel, H. (2002). As (III) removal from groundwaters using fixed-bed upflow bioreactors. *Chemosphere* 47, 325.
- Kim, J., and Benjamin, M.M. (2004). Modeling a novel ion exchange process for arsenic and nitrate removal. *Water Res.* 38, 2053.
- Leupin, O.X., and Hug, S.J. (2005). Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron. *Water Res.* 39, 1729.
- Lin, T.F., and Wu, J.K. (2001). Adsorption of arsenite and arsenate within activated alumina grains: Equilibrium and kinetics. *Water Res.* 35, 2049.
- Liu, R., Gong, W., Lan, H., Yang, T., Liu, H., and Qu, J. (2012). Simultaneous removal of arsenate and fluoride by iron and aluminum binary oxide: Competitive adsorption effects. *Sep. Purif. Technol.* 92, 100.
- Luo, X., Wang, C., Luo, S., Dong, R., Tu, X., and Zeng, G. (2012). Adsorption of As (III) and As (V) from water using magnetite Fe_3O_4 -reduced graphite oxide-MnO₂ nanocomposites. *Chem. Eng. J.* 187, 45.
- Maiti, A., Basu, J.K., and De, S. (2012). Experimental and kinetic modeling of As (V) and As (III) adsorption on treated laterite using synthetic and contaminated groundwater: Effects of phosphate, silicate and carbonate ions. *Chem. Eng. J.* 191, 1.
- Mandal, S., Majumder, N., Chowdhury, C., Ganguly, D., Dey, M., and Jana, T. (2012). Adsorption kinetic control of As (III and V) mobilization and sequestration by Mangrove sediment. *Environ. Earth Sci.* 65, 2027.
- McKay, G., Blair, H., and Gardner, J. (1982). Adsorption of dyes on chitin. I. Equilibrium studies. *J. Appl. Polym. Sci.* 27, 3043.
- Mohan, D., and Pittman, C.U., Jr. (2007). Arsenic removal from water/wastewater using adsorbents—a critical review. *J. Hazard. Mater.* 142, 1.
- Ning, R.Y. (2002). Arsenic removal by reverse osmosis. *Desalination* 143, 237.
- Ona-Nguema, G., Morin, G., Juillot, F., Calas, G., and Brown, G.E. (2005). EXAFS analysis of arsenite adsorption onto two-line ferrihydrite, hematite, goethite, and lepidocrocite. *Environ. Sci. Technol.* 39, 9147.
- Shiowatana, J., McLaren, R.G., Chanmekha, N., and Samphao, A. (2001). Fractionation of arsenic in soil by a continuous-flow sequential extraction method. *J. Environ. Qual.* 30, 1940.
- Soner Altundoğan, H., Altundoğan, S., Tümen, F., and Bildik, M. (2000). Arsenic removal from aqueous solutions by adsorption on red mud. *Waste Manage.* 20, 761.
- Sun, X., and Doner, H.E. (1996). An investigation of arsenate and arsenite bonding structures on goethite by FTIR. *Soil Sci.* 161, 865.
- Weng, Y.-H., Chaung-Hsieh, L.H., Lee, H.-H., Li, K.-C., and Huang, C. (2005). Removal of arsenic and humic substances (HSs) by electro-ultrafiltration (EUF). *J. Hazard. Mater.* 122, 171.
- Wickramasinghe, S., Han, B., Zimbron, J., Shen, Z., and Karim, M. (2004). Arsenic removal by coagulation and filtration: Comparison of groundwaters from the United States and Bangladesh. *Desalination* 169, 231.
- Wu, K., Liu, R., Liu, H., Chang, F., Lan, H., and Qu, J. (2011). Arsenic species transformation and transportation in arsenic removal by Fe-Mn binary oxide-coated diatomite: Pilot-scale field study. *J. Environ. Eng.* 137, 1122.
- Xu, Z., and Meng, X. (2009). Size effects of nanocrystalline TiO₂ on As (V) and As (III) adsorption and As (III) photo-oxidation. *J. Hazard. Mater.* 168, 747.
- Yuh-Shan, H. (2004). Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics* 59, 171.