Arsenic(V) removal with a Ce(IV)-doped iron oxide adsorbent

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Abstract

The removal of arsenic(V) by a new Ce–Fe adsorbent was evaluated under various conditions. Under an initial As(V) of 1.0 mg l^{-1} , the adsorption capacity of the Ce–Fe adsorbent was constant around a value of 16 mg g^{-1} over a wide pH range (3–7), while a maximum adsorption capacity of 8.3 mg g^{-1} was obtained over a narrow pH range around 5.5 for activated alumina, a conventional adsorbent. Kinetics of adsorption obeys a pseudo-first-order rate equation with the rate constant K_{ad} as $1.84 \times 10^{-3} \text{ min}^{-1}$. The pattern of adsorption of As(V) by the adsorbent fitted well both the Langmuir and Freundlich models. A Langmuir Q_0 of 70.4 mg g^{-1} was obtained at an initial pH of 5.0 and temperature of 20°C , significantly higher than those of other adsorbents reported. Phosphate seriously inhibited the removal of As(V) while fluoride did not compete with As(V) even at an F/As molar ratio as high as 30, suggesting that the adsorption sites for As(V) and fluoride were different. Salinity, hardness, and other inorganic anions such as Cl^- , NO_3^- , and SO_4^{2-} had no apparent effect on As(V) adsorption. Fourier transform infrared spectra of Ce–Fe adsorbent before and after As(V) adsorption demonstrated that M–OH groups plays an important role for As(V) ions removal in the adsorption mechanisms of Ce–Fe adsorbent.

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1. Introduction

Human poisoning and death from arsenic have occurred as a result of drinking water contaminated with arsenic in Taiwan (Tseng et al., 1968), Chile (Borgono et al., 1977), Bangladesh, and Bengal, India (Jiang, 2001), Vietnam (Berg et al., 2001) and other parts of the world. Chronic arsenism poses a serious health problem in China also. About 14.6 million people, who are mainly distributed in the northwest China including Inner Mongolia, Xinjiang, and Guizhuo, are exposed to

drinking water containing arsenic with a concentration of 0.03 mg l^{-1} or higher (Zhang and Chen, 1997). If China lowers its current drinking water standard of As from 0.05 to 0.01 mg l^{-1} , a level adopted by WHO (1996) and some industrialized countries (EPA, 2001), the population affected will increase significantly. The problem is that such a lowering of the standard will demand a level of treatment not ordinarily available in the small community water systems. It is of great importance to develop alternative technologies for treating drinking water contaminated with arsenic effectively at a reasonable cost.

Various technologies such as coagulation (Gregor, 2001), ion exchange and adsorption (Ghurye et al., 1999) have been employed for arsenic removal from water. Compared with aluminum coagulants, iron(III) salts have been found to be more effective for arsenic

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removal (Jekel, 1994; Jiang, 2001). Although the coagulation process is a simple and economically sound one, it produces a wet bulky sludge, and furthermore, could not satisfy the stringent standard of WHO. Because of the ease of handling, sludge-free operation, and possibility of regeneration, the adsorption process appears to be the most promising one. Activated alumina has long been the most often used adsorbent for arsenic removal (EPA, 2000). However, the problems including the need for pH adjustment, the relatively low adsorption capacity, and aluminum dissolution have prevented activated alumina from wider applications.

It has been reported that the hydrous oxides of rare earth elements have a high affinity for such hazardous anions as arsenate, fluoride and phosphate (Hideaki et al., 1987; Tokunaga et al., 1995, 1997). Tokunaga et al. (1995) compared the removal of fluoride by multivalent metals such as Al(III), Y(III), La(III), Ce(III/IV), and Zr(IV) in the form of oxides, hydrous oxides and basic carbonates, and found that hydrous Ce(IV) oxide was the most effective one for removing fluoride without significant dissolution even at pH 2. The problem for the use of Ce compounds might be mainly the cost. La- and Y-impregnated alumina as well as La-impregnated silica gel (Wasay et al., 1996a,b) has been developed for the removal of the above hazardous ions. The endurance of such an adsorbent has always been a challenging problem.

On the other hand, iron oxides, especially amorphous iron oxides, have also been reported to be effective for arsenic removal (Pierce and Moore, 1982; Cornell and Schwertmann, 1996; Reed et al., 2000), but the endurance and stability of the adsorbent should be improved. While the crystalline oxides of iron are stable in aquatic environment, the efficiency for arsenic removal is poor. If the adsorption capacity and the endurance of the iron compounds for arsenic could be improved further, the application of an iron oxide based adsorbent might possibly be of a sound foreground. The objective of this study was to investigate a possible strategy for the removal of arsenic employing the iron oxide doped with cerium ions. An iron based inorganic adsorbent (Ce-Fe adsorbent) was obtained by doping a small part of cerium salt into iron salt solutions, and the adsorption performance of Ce-Fe adsorbent for arsenic removal was evaluated on synthetic arsenic-bearing water under various conditions. The adsorbent was also applied for the removal of arsenic from groundwater in Inner Mongolia, China. The dominating species (70%) of arsenic is As(III) (arsenite) in groundwater in Inner Mongolia of China (Cao, 1996), however, it could be easily transformed to As(V) (arsenate) using oxidants like chlorine or hydrogen peroxide. So, As(V) was selected as the removal target in this study.

2. Materials and methods

2.1. Materials

All the chemicals used were of analytical reagent grade. A 1000 mg l⁻¹ As(V) stock solution was prepared by dissolving 4.1653 g Na₂AsO₄ · 7H₂O in 1 l of distilled water. As(V)-bearing water was prepared by diluting As(V) stock solution to given As concentrations with tap water.

The groundwater sample was taken from a well in Zhijiliang Village located in Inner Mongolia, China, and the characteristics of the sample are shown in Table 1. Arsenate (As(V)) and arsenite (As(III)) co-existed in the groundwater (BGS, 2000). The drinking water sample was analyzed and used for experiment several days after sampling. In this case, it is considered that only As(V) remained in the sample (Cao, 1996). High concentrations of arsenic ions (1.10 mg l⁻¹) as well as total organic carbon (TOC) (10 mg l⁻¹) were detected. The high concentration of TOC was possibly attributed to the high concentration of humic acids in groundwater of this area (BGS, 2000).

2.2. Preparation and characterization

The iron based adsorbent Ce-Fe adsorbent was prepared by mixing Fe³⁺, Fe²⁺, and Ce⁴⁺ in a molar ratio of 2:1:0.8 for 1 h at pH 9.5 under gentle stirring (60 rpm). A precipitate was obtained by adding 1 M NaOH solution, and used as an adsorbent after drying. Powdered activated alumina was supplied by Mizusawa Industrial Chemical, Japan. Hydrous cerium oxide and iron oxide (Fe³⁺:Fe²⁺ = 2:1) were prepared by referring to the method of Hideaki et al. (1987).

Table 1
Characteristics of groundwater samples

Parameters	Value
pH (spot)	7.57
Turbidity, NTU	311
Temperature, °C (spot)	13
Arsenic, mg l ⁻¹	1.10
Fluoride, mg l ⁻¹	1.59
Total hardness, mg l ⁻¹	51.5
Iron, mg l ⁻¹	4.22
Chloride, mg l ⁻¹	178
Sulfate, mg l ⁻¹	331
Total organic carbon, mg l ⁻¹	10
NH ₃ -N, mg l ⁻¹	0.40
Manganese, mg l ⁻¹	0.92
Sodium, mg l ⁻¹	119
Potassium, mg l ⁻¹	3.0
Aluminum, mg l ⁻¹	1.11

Fourier transform infrared (FTIR) spectra of Ce–Fe adsorbent before and after adsorption were recorded on Perkin Elmer (USA) system 2000 spectrophotometer with a resolution of 2 cm^{-1} . All IR measurements were carried out at room temperature. The specific surface areas of Ce–Fe adsorbent, the hydrous cerium oxide and iron oxide were determined using the BET gas adsorption method (ASAP2000V3.01A; Micromeritics, Norcross, USA).

The surface charge of Ce–Fe, Ce oxide and Fe oxide adsorbent was calculated by the acid–base titration method (Park and Huang, 1986). The adsorbent (2.5 g) was added into 1 l of CO_2 -free 0.5, 0.05, and 0.005 M sodium perchlorate solutions. The resulting mixture was shaken at 20°C for five days in a sealed bottle. An automatic acid–base titration (665-Dosimat682; Merohm; Swiss) was conducted respectively on 80 ml of filtrate and suspension while being bubbled with nitrogen gas. The acid titration was made with 50 mM HClO_4 solution up to pH 4.00. The base titration was made with 50 mM NaOH solution up to pH 10.00. The net titration curve was obtained by taking the difference in the titration volumes (ΔV) for the suspension and the filtrate at given pH values. The surface charge was calculated from the net titration curve using the following equation:

$$\sigma_0 = \Delta VMF / SAV, \quad (1)$$

where σ_0 is the surface charge (C cm^{-2}), ΔV the difference in the titration volume for the suspension and the filtrate at a given pH value (ml), M the molarity of acid and base (mM), F the Faraday's constant (C mol^{-1}), S the surface area of adsorbent ($\text{m}^2\text{ g}^{-1}$), A the amount of adsorbent used for titration (g l^{-1}), and V the volume of filtrate and suspension used for titration (ml).

2.3. Adsorption experiment

A given volume of As(V) stock solution was added separately to a conical flask, and the volume was made up to 100 ml with tap water. After pH adjustment, the flasks were shaken at 120 rpm and 20°C for approximately 24 h following the addition of the adsorbent (normally 60 mg l^{-1}). Then the solution was filtered with a $0.45\text{ }\mu\text{m}$ -membrane filter for analysis. pH was measured with a pH meter (model 828, ORION, USA), As was analyzed on ICP-AES (model 9000, ULTIM, France), F^- on ion meter (IM-40m, TOA, Japan), PO_4^{3-} (ascorbic acid method), and hardness (EDTA titrimetric method) (APHA, 1995).

The effects of equilibrium pH on As(V) adsorption with Ce–Fe adsorbent and activated alumina were investigated respectively under an adsorbent dose of 60 mg l^{-1} and As(V) concentration of 1.0 mg l^{-1} . A kinetic

study on the adsorption of As(V) with Ce–Fe adsorbent was carried out at different time intervals under a pH of 5.0. The adsorption isotherms were studied by varying doses of adsorbent under a fixed As(V) concentration (40 mg l^{-1}). The agitation time used for isotherm studies was 76 h. Isotherms were modeled using both the Langmuir and Freundlich equations. Container adsorption tests were also carried out in order to find blank adsorption.

The effects of salinity, hardness, fluoride and phosphate on adsorption were conducted under different doses of NaCl, CaCO_3 , NaF, and NaH_2PO_4 , respectively. The As(V) concentration was fixed at 1.0 mg l^{-1} , and adsorption was conducted at a pH 5.0 for 24 h.

A groundwater sample was collected from a wasted well in the home yard of Zhijiliang Village, a typical chronic arsenism area in Inner Mongolia of China, and analyzed according to standard methods for the examination of water and wastewater (APHA, 1995). Then the adsorption of arsenic to Ce–Fe adsorbent in the groundwater sample was compared with that in synthetic groundwater under a pH of 8 (natural pH).

3. Results and discussion

3.1. Batch experiment for adsorption

3.1.1. Effect of pH on As(V) removal

Fig. 1 compares the effects of equilibrium pH on As(V) removal by Ce–Fe adsorbent and activated alumina. The optimum pH for As(V) removal by activated alumina was in a narrow range between 5.5 and 6.0, and As removal sharply decreased beyond the range. In comparison, As(V) removal by Ce–Fe adsorbent was

Fig. 1. The pH dependence for As(V) adsorption by Ce–Fe adsorbent and activated alumina. Adsorbent amount was 60 mg l^{-1} ; initial As(V) concentrations, 1.0 mg l^{-1} ; shaking time, 24 h; and temperature, 20°C .

almost a constant value in a pH range between 3 and 7, and the adsorption capacity of Ce–Fe adsorbent was much higher than that of activated alumina. The significant difference between the optimum pH ranges of Ce–Fe adsorbent and alumina might be due to different adsorption mechanisms, which require further studies. However, it is a great advantage that Ce–Fe adsorbent could be operated at a neutral pH without sacrificing the adsorption capacity.

3.1.2. Kinetic study

The removal of As(V) is time dependent and the equilibrium time required for maximum removal of As(V) was 24 h. The adsorption follows pseudo-first-order reaction as shown in Fig. 2. The adsorption rate constant for As(V) was calculated by using the following equation (Lagergren, 1898):

$$\log(q_e - q) = \log q_e - k_{ad}t/2.303, \quad (2)$$

where q_e and q are the amount of As(V) adsorbed (both in mg g^{-1}) at the equilibrium time and time t (min), respectively, and k_{ad} is the rate constant of adsorption (min^{-1}). The value of k_{ad} for As(V) was found to be as $1.84 \times 10^{-3} \text{ min}^{-1}$, calculated from the slope of the linear plot of $\log(q_e - q)$ vs t in Fig. 2.

3.1.3. Adsorption isotherm

Two adsorption isotherms, namely the Langmuir and Freundlich isotherm models, were used to analyze adsorption data. The Langmuir equation was applied for adsorption equilibrium as follows:

$$1/Q_e = 1/(Q_0 b C_e) + (1/Q_0), \quad (3)$$

Fig. 2. Lagergren plot for As(V) adsorption. Correction coefficient of the linear plot = 0.98; adsorbent amount was 60 mg l^{-1} ; initial As(V) concentrations, 1.0 mg g^{-1} ; pH, 5.0; and temperature, 20°C .

where C_e is equilibrium concentration (mg l^{-1}), Q_e is the amount adsorbed under equilibrium (mg g^{-1}), Q_0 (mg g^{-1}) is the theoretical maximum adsorption capacity, and b (l mg^{-1}) is a Langmuir constant related to energy of adsorption. A linear plot of $1/Q_e$ vs $1/C_e$ was obtained with a $R^2 = 0.95$, indicating that adsorption of As(V) onto Ce–Fe adsorbent obeys the Langmuir isotherm model. Q_0 and b were determined from the slope and intercept of the plot as 70.4 mg g^{-1} and 10.9 l mg^{-1} , respectively. It has been reported that the Langmuir Q_0 values of activated carbon at pH 5, activated alumina at pH 6–7, and La-impregnated silica gel at pH 7 were less than 4.0 mg g^{-1} , 5.0 mg g^{-1} , and 8.8 mg g^{-1} (Gupta and Chen, 1978; Huang and Fu, 1984; Wasay et al., 1996b), respectively. In comparison, it is clear that the Q_0 obtained in this study (70.4 mg g^{-1}) was very high.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined by $R_L = 1/(1 + bC_0)$, where C_0 is the initial concentration of As(V). The R_L value in this study (0.0023) was in the range between 0 and 1, which belongs to the type of favorable adsorption according to McKay et al. (1982).

On the other hand, the Freundlich isotherm model could be expressed as follows:

$$\ln Q_e = \ln k_f + 1/n \ln C_e, \quad (4)$$

where k_f and n are empirical constants incorporating all factors affecting the adsorption process. A linear plot of $\ln Q_e$ vs $\ln C_e$ was also obtained with a $R^2 = 0.99$, showing that the adsorption follows the Freundlich isotherm model as well. k_f and n values calculated from the intercept and slope of the plot were 60.4 and 16.1, respectively.

3.1.4. Effects of competing ions on As(V) removal

Groundwater in northwest China is usually accompanied with a high salinity and hardness. And co-occurring inorganic anions such as fluoride and phosphate may directly compete with As(V) for binding sites of the adsorbent and affect As(V) removal (Wasay et al., 1996b). Fig. 3 indicates that the relatively high level of salinity and hardness in water did not affect As(V) removal performance of the adsorbent.

Fig. 4(a) shows the effect of phosphate on As(V) removal. With the increase of molar ratio of P to As, the As(V) adsorption capacity (mmol g^{-1}) of the adsorbent decreased significantly, indicating that competition for the binding sites of the adsorbent occurred between arsenate and phosphate. Similar adsorption behaviors of phosphate and arsenate on Ce–Fe adsorbent could perhaps be attributed to the fact that arsenic acid and phosphoric acid are both triprotic acid with similar ionization constants (Goldberg, 1986). The adsorption

Fig. 3. Effects of salinity and hardness on As(V) removal. Adsorbent amount was 60 mg l^{-1} ; initial As(V) concentrations, 1.0 mg g^{-1} ; shaking time, 24 h; pH, 5.0; and temperature, 20°C .

(a)

(b)

Fig. 4. Effects of PO_4^{3-} and F^- on As(V) removal. (a) Effects of PO_4^{3-} on As(V) removal, (b) effects of F^- on As(V) removal; adsorbent amount was 60 mg l^{-1} ; initial As(V) concentrations, 1.0 mg g^{-1} ; shaking time, 24 h; pH, 5.0; and temperature, 20°C .

capacity of arsenate in terms of mole was almost the same with that of phosphate when the P/As molar ratio was 1.0, indicating that the affinity of the two anions to the adsorbent was about the same.

The adsorption capacity (mmol g^{-1}) of As(V) and that of fluoride are plotted against F/As molar ratio at pH = 5.0 (Fig. 4(b)). The adsorption capacity of fluoride increased with the increase of F/As mole ratio, since fluoride concentration increased with the increase of the ratio. It is interesting that the adsorption capacity of As(V) was almost a constant value in spite of the increase of the F/As molar ratio. The most possible reason for this phenomenon is that the active binding sites of Ce–Fe adsorbent for fluoride ions were different from those for arsenate ions. The mechanisms for this, however, require further study. Other anions such as Cl^- , NO_3^- , and SO_4^{2-} did not interfere with the removal of As(V).

3.1.5. Removal of arsenic from groundwater of Inner Mongolia

The adsorption equilibrium tests in tap water and Zhijiliang groundwater sample were carried out respectively under the natural condition (pH = 8), and the results are shown in Fig. 5. It was found that the adsorption capacity of the adsorbent for As(V) removal in Zhijiliang groundwater sample was lower than that in tap water. Normal co-existing ions such as Na^+ , Ca^{2+} , Mg^{2+} , F^- , Cl^- , NO_3^- , and SO_4^{2-} do not interfere with the adsorption of As(V). The possible reason for the low adsorption capacity of the adsorbent in the groundwater sample was the presence of a high concentration humic acids. Humic acids in groundwater might compete with

Fig. 5. Adsorption of As on Ce–Fe adsorbent in tap water and groundwater. Adsorbent amount was 60 mg l^{-1} ; initial As(V) concentrations of tap water sample, 1.0 mg g^{-1} ; shaking time, 24 h; pH, 5.0; and temperature, 20°C .

As(V) for the adsorption sites of the adsorbent. So, proper measures should be taken to prevent the interference from humic acids in groundwater if a high concentration of TOC exists.

3.2. Adsorption mechanisms

Anions can be adsorbed on adsorbents through nonspecific and/or specific adsorption. Nonspecific adsorption involves the coulombic forces, and is mainly limited to pH-dependent sites below pH_{ZPC} (the pH value at which surface charge is zero) of the adsorbent (Hingston et al., 1967). The specific adsorption, however, involves ligand exchange reactions where the anions displace OH^- and/or H_2O from the surface (Prasad, 1994).

As an adsorbent based on hydrous metal oxides, Ce-Fe adsorbent possibly contains the hydroxyl group (M-OH; M represents surface metal ions of Ce and Fe) in aqueous environment. IR spectroscopy has been considered as a kind of direct means for investigating mechanisms of arsenic adsorption on amorphous oxides and goethite (Sun and Doner, 1996; Goldberg and Johnston, 2001). The FTIR spectra of Ce-Fe adsorbent before and after As(V) binding adsorption at pH 5 are shown in Fig. 6. According to Russell (1979), the band at wave number around $3550\text{--}3200\text{ cm}^{-1}$ represents OH stretching vibration, and that at 1641 cm^{-1} represents HOH bending vibration of water ((1) and (2) in Fig. 6). A strong band at 1122 cm^{-1} , which corresponds to the bending vibration of hydroxyl group (M-OH) (Nakamoto, 1978), was observed from the sample before adsorption (line 1, Fig. 6). After adsorption, the M-OH bending band almost disappeared, while the features assigned to H_2O remained unchanged. On the other

Fig. 6. FTIR spectra of (1) Ce-Fe adsorbent; (2) Ce-Fe adsorbent after As(V) adsorption.

hand, a new band at 828 cm^{-1} , which corresponds to As-O stretching vibration (Nakamoto, 1978) appeared as shown in line 2. There is an overlap between O-As-O bending vibration and substrate surface vibration at 470 cm^{-1} , but the increase in intensity of this band after adsorption gives support to our conclusion. In fact, the

Fig. 7. Surface charge of Ce-Fe adsorbent (a), hydrous cerium oxide (b) and iron oxide (c) as a function of pH at different ionic strengths. Adsorbent amount was 2.5 g l^{-1} ; shaking time, five days; and temperature, $20\text{ }^{\circ}\text{C}$.

effluent pH rose from the initial value of 5.0–6.2 following adsorption for 24 h in most of our experiments. The FTIR data and pH increase in the effluent indicate that substitution of M–OH groups by As(V) ions plays a very important role in the adsorption mechanisms of Ce–Fe adsorbent (Tokunaga et al., 1995). In an article reported by Goldberg and Johnston (2001), the positions of the As–O bands of a 0.1 M As(V) solution in the IR spectrum occurred at 878 and 907 cm^{-1} under pH 5. Shift of the As–O bands occurred following adsorption of As(V) to the amorphous Fe oxide sample at pH 5, and two new bands 824 and 861 cm^{-1} were obtained. They speculated from this result that the As–O groups possibly were involved in surface complexation, and assigned the 824 cm^{-1} band to the Fe–O–As groups. It is possible that the 828 cm^{-1} band obtained in this study also corresponded to a metal–O–As group.

According to the above description, the Ce–Fe adsorbent surface can be considered as an amphoteric surface site with surface hydroxyl groups (M–OH). The surface acid–base characteristics of Ce–Fe adsorbent, Fe oxide, and Ce oxide were investigated. The surface area of Ce–Fe adsorbent was 90 $\text{m}^2 \text{g}^{-1}$, which was lower than those of hydrous cerium oxide (122 $\text{m}^2 \text{g}^{-1}$) and iron oxide (98 $\text{m}^2 \text{g}^{-1}$). The surface charge was measured at different pH and ionic strengths by the titration method and the results are shown in Fig. 7. The pH_{ZPC} for hydrous cerium oxide (Fig. 7(b)) and iron oxide (Fig. 7(c)) are 6.7 and 6.2, respectively. According to Stumm (1992), the point of zero charge of a composite oxide is approximately the weighted average of the values of its components. The pH_{ZPC} of Ce–Fe adsorbent, however, was 5.8 (Fig. 7(a)), significantly lower than the weighted average (6.4) of the values of hydrous cerium oxide and iron oxide. The surface of Ce–Fe adsorbent was positively charged at $\text{pH} < 5.8$, which was favorable for nonspecific adsorption of As(V) through coulombic attraction between anions and the adsorbent (Wasay et al., 1996a). Since high As(V) removal could be obtained at $\text{pH} > 5.8$, it is speculated that specific adsorption dominates in the adsorption of As(V) onto Ce–Fe adsorbent.

4. Conclusions

An iron based inorganic adsorbent, developed by doping cerium ions into iron ions, was used for As(V) removal. In terms of adsorption pH range and adsorption capacity, the new adsorbent demonstrated a much better performance than activated alumina. The pattern of adsorption of As(V) by the adsorbent fitted well to both of the Langmuir and Freundlich models. The Langmuir Q_0 of 70.4 mg g^{-1} was significantly higher than those of other conventional As adsorbents. FTIR spectra of Ce–Fe adsorbent before and after As(V) adsorption demonstrated that M–OH groups plays an

important role for As(V) ion removal in the adsorption mechanisms of Ce–Fe adsorbent. The adsorption mechanism, however, requires further studies.

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