

Short communication

Treatment of groundwater polluted by arsenic compounds by zero valent iron

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Abstract

Batch experiments were carried out to study the kinetics and efficiency of inorganic arsenic removal by zero valent iron (ZVI) powder, and as well as the effects of pH, anions, and humic material (HM) on this process. Moreover, column experiment was conducted for 31 days to treat arsenate solution of 500 $\mu\text{g As/L}$ using waste iron chippings as filling. Batch experiments showed that both arsenate and arsenite compounds could be removed efficiently from simulated groundwater by ZVI under aerobic and relative anaerobic conditions. Aerobic condition was favorable to arsenic removal especially for arsenate, while arsenite could be removed more rapidly than arsenate in relative anaerobic condition. Oxidation of arsenite to arsenate by iron species in aerobic environment was observed, which is thought to be an important pathway of arsenite removal. In an unsealed system, the removal efficiency of both arsenate and arsenite decreased at higher pH value. In a sealed system, acidic and alkaline condition seemed to be favorable for arsenate and arsenite removal, respectively. Phosphate and low concentration sulfate caused a decrease in arsenate removal, while high concentration sulfate as well as nitrate caused slight increase in arsenate removal. Presence of HM in solution slightly inhibited arsenic removal. Arsenic removal efficiency in column study was influenced by flow rate and work period of the column. More than 98% of arsenate could be removed stably with a hydraulic resident time of 2 h at last, and the effluent meet the drinking water standard.

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1. Introduction

Arsenic compounds are often found in contaminated groundwater [1], which can come from both natural processes, such as weathering of arsenic minerals, and anthropogenic activities including mining, industrial waste discharge, and application of arsenic herbicides and pesticides [2]. Arsenic exists in groundwater predominantly as inorganic arsenite, As(III) (H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-}), and arsenate, As(V) (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-}) [3]. Arsenate is predominantly anionic at circum-neutral pH, while arsenite is uncharged.

Zero valent iron (ZVI) has been successfully used as a filter medium to remove different contaminants in groundwater, including halogenated organic compounds, nitrate and nitrite, and heavy metals [4–8]. Recently, ZVI has been found to have ability to remove arsenic compounds in water [9–12]. Compared with other methods, ZVI can simultaneously remove As(V) and As(III) without pre-oxidation. This will aggrandize the applica-

tion of ZVI in treatment of industrial wastewater treatment or as constitute of permeable reactive barrier (PRB) in remediation of contaminated groundwater.

Though there are lots of studies published about the process of arsenic compounds removal by ZVI, some aspects are still not very clear. Several studies have found that arsenate can be removed more easily than arsenite [9,13], while it has been reported by Su and Plus that arsenite shows greater removal rates than arsenate in their experiment [11]. Moreover, both reductions of arsenate to arsenite [9] and oxidation of arsenite to arsenate [11,13] have been reported in different papers focused on ZVI systems. Anions, including phosphate, silicate, carbonate, sulfate, and nitrate, etc., are usually regarded as inhibitors in arsenic removal by iron species. The inhibiting effect has been explained primarily as competition [14,15]. But arsenic removal was also found to be enhanced when sulfate presented in anaerobic condition in another study, which was attributed to the formation of arsenopyrite (FeAsS) precipitate [16].

The purpose of this study was to demonstrate the efficiency of ZVI technology for inorganic arsenic removal from aqueous solution under aerobic and relative anaerobic conditions, and to investigate the potential influencing factors such as pH,

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anions, and humic substance. Moreover, efficiency and feasibility of application of one industrial waste iron chippings to arsenic removal were evaluated using column experiment.

2. Materials and methods

2.1. Materials

Two types of metal iron were used in this study. Pure ZVI powder (Fe% >99%, <200 mesh) was purchased from Tianjin Fuchen Chemical Reagent Co., Inc., China. Iron chippings were obtained as industrial waste and screened to less than 20 mesh. The iron content in chippings was larger than 95%, which was composed of ZVI (78%), FeO (7%), Fe₃O₄ (15%), as the result of X-ray fluorescence and X-ray diffraction analysis, provided by Center Lab of Nankai University. Arsenic trioxide and sodium arsenate hydrate were of analytic purity (>99%, purchased from Whenzhou Chemical Reagent Co., Inc., China), which were directly dissolved into distilled water as stock solutions for As(III) and As(V), respectively. Reagents used in this paper were analytically pure except for sodium humate, which was chemically pure.

2.2. Batch experiment design

Batch experiment was designed to investigate the kinetics and efficiency of arsenic removal by ZVI in 100 mL Erlenmeyer flasks containing 0.25 g iron powder and 100 mL simulated groundwater with certain level of arsenic (arsenate or arsenite). Chemical compositions of the simulated groundwater are provided in Table 1, which was chosen on the base of Lien's work [17]. Two arsenic concentrations, 100 and 500 µg As/L, were prepared, and experiments were carried out in sealed or unsealed systems. For sealed system, flasks were capped and wrapped with polytetrafluoroethylene tape to simulate relative anaerobic condition. And for unsealed system, flasks were uncapped to simulate aerobic condition. Sampling was performed at certain intervals, and then analysis was carried out.

Speciation of arsenic was measured for unsealed system with 500 µg As/L arsenite initially, in order to evaluate the change of speciation during removal process by ZVI. The effect of Fe²⁺ on oxidation of arsenite to arsenate was also studied subsequently by replacing ZVI with FeSO₄ (1 mM).

Effects on arsenic removal of some environmental factors, involving pH, anions (sulfate, nitrate, phosphate), and HM, were studied in the above batch systems. Initial pH value of experimental system was modified using 0.1 mol/L hydrochloric acid

and sodium hydroxide, and no buffer was made during the reaction. Sodium sulfate, sodium nitrate, and sodium dihydrogen phosphate were used to alter the anion concentration in systems. Commercial sodium humate was used to study the effect of HM. All batch experiments above were ducipately repeated.

2.3. Column experiment design

Column experiment was carried out to investigate the removal efficiency of arsenate by industrial iron chippings. The column was divided into two sections, A and B, in order to sample different effluents and illustrate the efficiency in different section. Each section was of 20 cm length and 11.50 mm i.d., as shown in Fig. 1, and each was packed with 1.1 g iron chippings. Influent containing arsenate (500 µg As/L) was pumped into the device, flowed through column A then to column B.

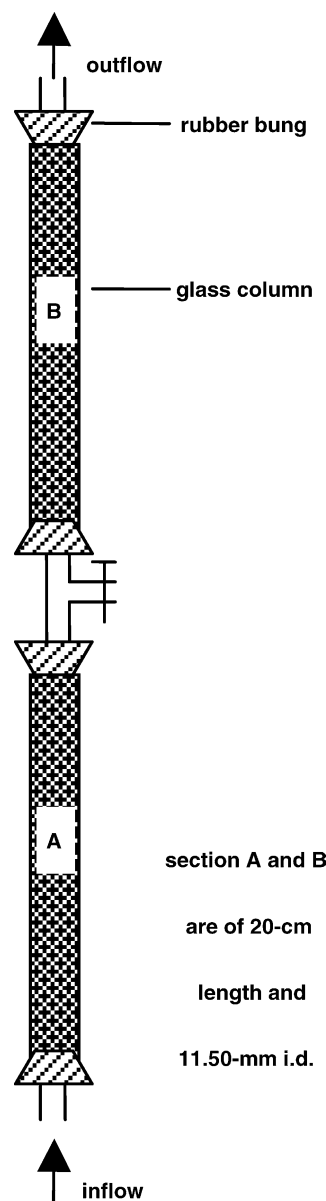


Fig. 1. Sketch of the column system.

Table 1
The chemical compositions of simulated groundwater^a

Chemicals	Amount (mg/L)
CaCl ₂ ·2H ₂ O	230
Na ₂ SO ₄	1200
NaHCO ₃	370
MgCl ₂ ·6H ₂ O	135

^a Reagents were directly dissolved into deionized water.

Flow rate was controlled by a constant flow pump. During 31 days performance period, the influent flow rate was increased from 3.75 to 15.0 mL/h stage by stage, while the HRT in the whole device decreased from 8 to 2 h accordingly. The effluents from the columns A and B were sampled and analyzed, respectively, every day.

2.4. Analysis for As

The arsenic compounds in aqueous samples were determined using New Silver Salt Spectrophotometry, which is a standard method recommended by State Environmental Protection Administration of China [18,19]. Arsenic was first reduced into arsine by KBH_4 in a sulfuric–tartaric acid medium with pH value of 1.1 for total arsenic, or in an acetic acid medium with pH value of 3.2 for arsenite only. And then the generated arsine was absorbed by an absorbing solution containing silver nitrate, polyvinyl alcohol, and ethanol. The color developed due to the reaction between arsine and silver nitrate was photometrically measured at 410 nm. The molar absorptivity of the reaction solution is $6.5 \times 10^5 \text{ L}/(\text{mol cm})$, and the detection limit is 0.0004 mg As/L. When arsenate and arsenite exist simultaneously, concentration of the arsenate was calculated by subtraction of that of the arsenite from the total arsenic concentration.

3. Results and discussion

3.1. Efficiency and kinetics of arsenic removal by ZVI powder

The removal of arsenic compounds at two concentration levels (100 and 500 $\mu\text{g As/L}$) by ZVI is shown in Fig. 2. Controls without ZVI showed no loss of arsenic over the typical experimental period in either sealed or unsealed system. For the two arsenic concentration levels of our study, removal process of both arsenate and arsenite conformed to the first-order kinetics, in either sealed or unsealed system (Table 2).

In unsealed system, arsenate was removed more efficiently from water than arsenite. Over 95% of arsenate was removed from water in 4 h for both 100 and 500 $\mu\text{g As/L}$, while only about 60% of arsenite was removed in the same period. The reaction rate constants (k) of arsenate removal (500 $\mu\text{g As/L}$: 0.348, 100 $\mu\text{g As/L}$: 0.367) were obviously greater than those of arsenite (500 $\mu\text{g As/L}$: 0.223, 100 $\mu\text{g As/L}$: 0.243) (Table 2). However, arsenite could also be removed to high extent when time is enough, with 95% removal efficiency in 16 h for two levels.

Arsenate removal efficiency in sealed system was significantly reduced compared to that in unsealed system, while the change of oxidation condition had fewer effects on arsenite removal. Hence, arsenite was removed more rapidly than arsenate in this relative anaerobic condition, especially for the lower arsenic concentration. However, more than 80% of arsenate still could be removed in 16 h.

The different results of both arsenite and arsenate removal in unsealed (aerobic) and sealed (relative anaerobic) system indicates that different mechanisms might predominate. Previous studies have shown that surface precipitation and adsorption appears to be the predominant mechanisms for arsenic removal by ZVI, while precipitation seems to be more important in anaerobic environment [9,11]. In our experiment, arsenic could be removed more efficiently in aerobic environment, especially for arsenate. This might be attributed to adsorption of arsenic to iron and its corrosion products because of the interaction between arsenic compounds and iron (oxyhydr)oxides [13,20,21].

3.2. Oxidation of arsenite in ZVI–water system

Oxidation of arsenite to arsenate when ZVI exists has been reported in several works [11,13], and the authors attributed this to the effect of birnessite and iron (oxyhydro)oxides synthesized from Fe(II), which is minutely formed in ZVI–water system. In our study, a reduction in ratio of aqueous As(III)/total aqueous As with reaction time in aerobic condition was observed in ZVI–water system, when only As(III) was added initially.

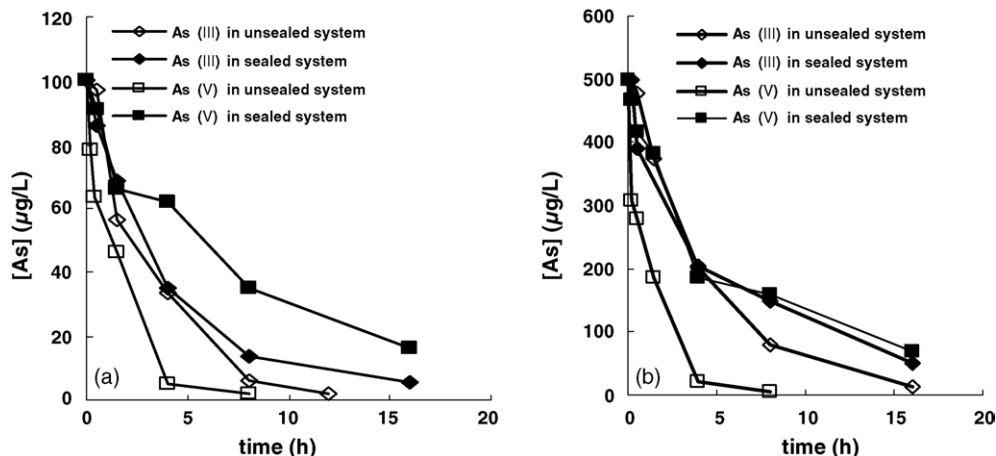


Fig. 2. Removal of arsenic compounds by ZVI as a function of time. Reactors contained 2.5 g/L ZVI with $[\text{As}] = 100 \mu\text{g/L}$ (a) or $[\text{As}] = 500 \mu\text{g/L}$ (b) at initial pH of 8.28 initially, in unsealed/sealed systems.

Table 2
First-order kinetic parameter of arsenic removal

	Arsenate				Arsenite			
	100 µg As/L		500 µg As/L		100 µg As/L		500 µg As/L	
	Sealed	Unsealed	Sealed	Unsealed	Sealed	Unsealed	Sealed	Unsealed
k	0.112	0.367	0.122	0.348	0.205	0.243	0.142	0.223
R^2	0.9805	0.8775	0.9456	0.9403	0.9888	0.9992	0.9783	0.9990

Sealed or unsealed reactors contained 2.5 g/L ZVI with [As] = 100 or 500 µg/L, at pH of 8.28 initially.

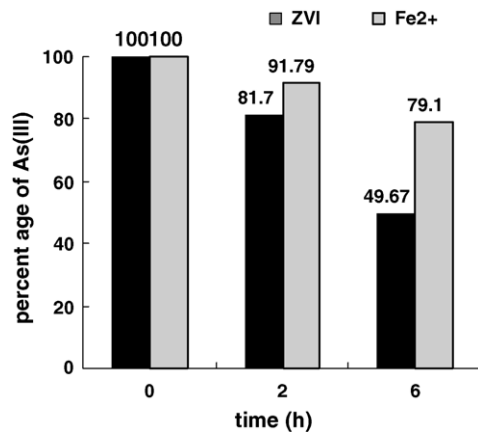
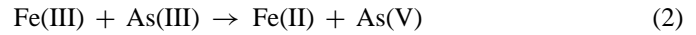
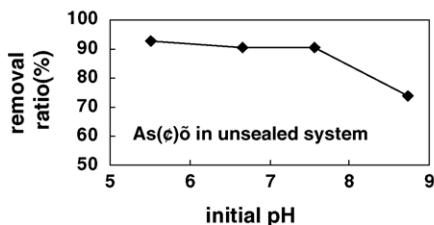
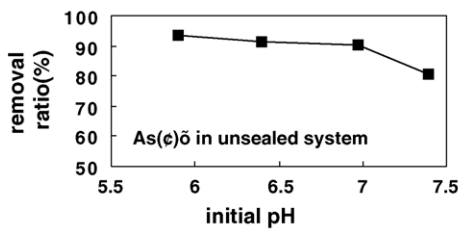


Fig. 3. Percentage of As(III) in total arsenic in aqueous phase as a function of reaction time. Reactors contained ZVI (2.5 g/L) or Fe²⁺ (1 mM) with [As(III)] = 500 µg/L at pH 7.0 initially, in unsealed system.

And this phenomenon also existed when ZVI was replaced with Fe²⁺ (Fig. 3), while controls without iron showed no proportion variety over the experimental period. It might be an evidence that oxidation of arsenite to arsenate by iron species takes place not only on the surface of iron particles. A hypothetical oxidation process is demonstrated as Eqs. (1) and (2). This oxidation of As(III) to As(V) might be the reason for the high removal rate of As(III) in unsealed system:



3.3. Effect of pH

Removal efficiency of arsenic was studied as a function of initial pH in both sealed and unsealed systems in a period of 4 h (Fig. 4). In unsealed system, the removal ratio of both arsenate and arsenite become to decrease above neutral pH value. This is because that lower pH value is propitious for the formation of iron hydroxide, which is thought to be the main active component for the removal of arsenic compounds under aerobic condition [22,23].

In sealed system, the removal efficiency of arsenic went through a minimum at pH around 6.5. As a whole, arsenate was removed more efficiently at low pH value while alkaline condition was propitious to arsenite removal when system was sealed. Lower pH value favors ZVI corrosion which is very significant to arsenate adsorption. pH near the PZC of iron oxide minerals is favorable for decreasing the disturbance of other anions on the surface area of powders [24–26], which might be used to explain why arsenite was removed more efficiently at an initial pH of 8.73 in sealed system.

3.4. Effect of anions

The effects of different level of sulfate, nitrate, and phosphate on arsenate removal in sealed system at pH of 8.28 initially, were also investigated. At lower sulfate concentra-

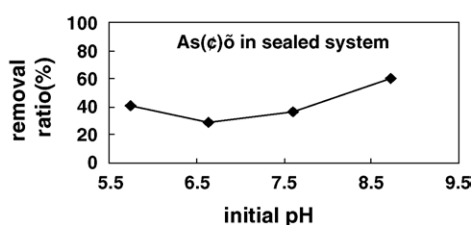
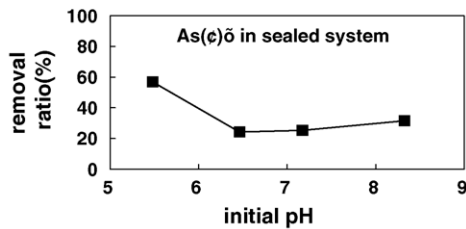


Fig. 4. Removal ratio of arsenic compounds in 4 h as a function of initial pH value in unsealed and sealed systems. Reactors contained 2.5 g/L ZVI with [As] = 500 µg/L initially.

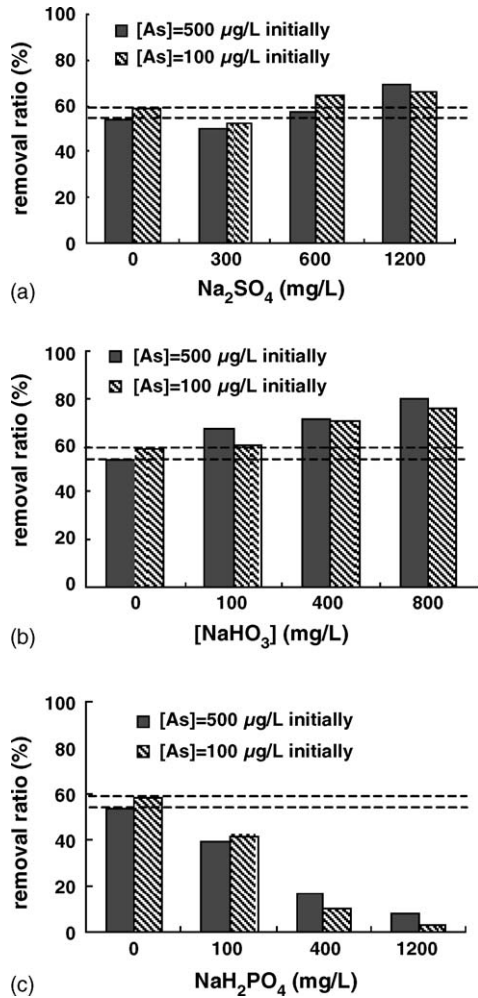
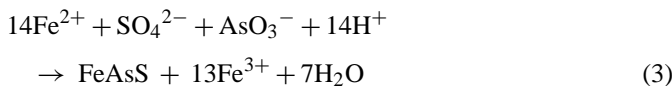


Fig. 5. Removal ratio of arsenate in 6 h as a function of sulfate, nitrate and phosphate concentration. Unsealed reactor contained 2.5 g/L ZVI with [As(V)] = 500 or 100 µg/L initially.

tions (300 mg Na₂SO₄/L), the removal was slightly slackened because of the electrical repulsion between SO₄²⁻ and AsO₃⁻, which resembled the former result of others [14]. Whereas, when the sulfate concentration increased to higher level (600 and 1200 mg Na₂SO₄/L), arsenate removal was increased (Fig. 5(a)). This result might be due to the acceleration of precipitation which accords with Eq. (3) [16].



An increase of arsenate removal efficiency was observed when more sodium nitrate presented (Fig. 5(b)). This result was different from the former study [14]. We attribute it to the higher nitrate level used in our system. The standard electrode potential (E^0) of NO₃⁻/NO₂⁻ (0.01 V) is higher than that of Fe(OH)₂/Fe (-0.877 V) in alkaline solution, which indicates that nitrate possesses the capacity for accelerating the corrosion of ZVI.

Phosphate evidently inhibited arsenate removal (Fig. 5(c)), which was identical with other researches [14,15,26]. This is due to the competitive between arsenate and phosphate species. This effect became more distinct when concentration ratio of

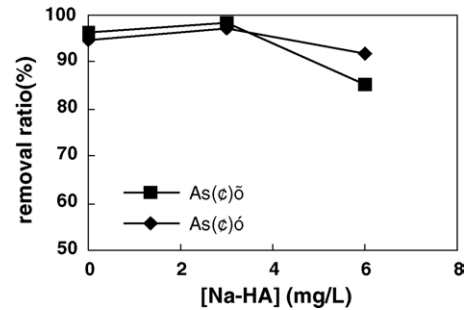


Fig. 6. Removal ratio of arsenate as a function of sodium humate concentration. Unsealed reactor contained 500 µg As/L arsenate initially, with a reaction time of 4 h.

phosphate to arsenate was elevated. Furthermore, visible deceleration of iron corrosion was observed when orthophosphate existed. This might also contribute to the reduction of arsenate removal efficiency.

3.5. Effect of humic material

Natural organic material (NOM) is widespread in natural water, and might affect the removal efficiency of arsenic compounds through different ways, such as speciation of arsenic in aqueous phase and their interaction with the surface of iron and its corrosion products [27]. In our experiment, sodium humate was chosen as a representative NOM to assess its influence on arsenic removal in unsealed system. As Fig. 6 shows, sodium humate inhibits arsenic removal at high concentration (6 mg/L). The inhibition might be due to the metal-bridge combination occurring between humic acid and arsenic compound [28], which could diminish the tendencies of dissolved anions to form surface complexes. Competition between arsenate anions and electronegative humate was likely to contribute the further reduction in the removal efficiency of arsenate.

3.6. Removal efficiency of arsenate in column

During the 31-day performance, 204 pore volumes of simulated groundwater containing 500 µg As/L arsenate were entered to column. The flow rate was increased during the experimental period to reach an acceptable efficiency with a shorter HRT. As Fig. 7 shows, majority of arsenate was removed in column A, and the arsenic concentration in the effluent of column B is usually less than 10 µg As/L, which meet the drinking water standard issued by World Health Organization [29]. In column A, the removal efficiency of effluent was affected by flow rate and the running days: In the first 16 days, the arsenate removal efficiency of effluent A decreased from about 90 to 54% gradually when the HRT was shortened from 8 to 4 h. After that, the removal efficiency increased even if the HRT was further shortened to 2 h finally. At the last days of experiment, arsenate removal efficiency of effluent A was around 93%, while that of effluent B was above 98%. The increase in removal efficiency with running days can be explained by the formation of corrosion products of iron in the column, which aggrandizes the adsorption of arsenate [13].

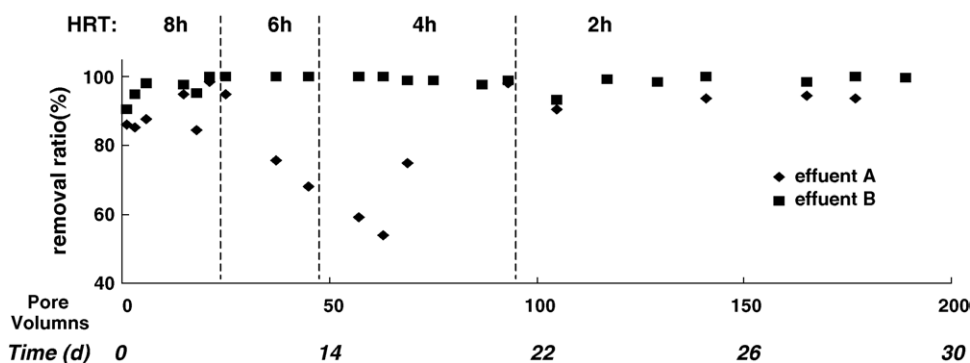


Fig. 7. Arsenate removal efficiency in the effluent of columns A and B as a function of pore volumes. Influent water contained 500 $\mu\text{g As/L}$ arsenate and the flow rate was increased with days.

4. Conclusions

Batch experiments demonstrated that arsenic compounds can be removed efficiently by ZVI powder. Arsenite can be removed more rapidly than arsenate in relative anaerobic condition, while results are contrary in aerobic condition. Different mechanisms are believed to predominate in aerobic and anaerobic environment. Arsenic appears to be removed mainly by precipitation in anaerobic condition, while the adsorption of arsenic to iron and iron corrosion products is very important in aerobic condition. Oxidation of arsenite to arsenate can be promoted by iron species in aerobic environment. Low pH is propitious to remove arsenic compounds in aerobic condition, while in relative anaerobic condition, acidic and alkaline condition seems to be favorable for arsenate and arsenite removal, respectively. Low concentration of sulfate inhibits arsenate removal, but opposite effect presents when sulfate concentration increased above 600 mg $\text{Na}_2\text{SO}_4/\text{L}$. Presence of high-level nitrate anion can accelerate arsenate removal while phosphate provides a competitive effect. Arsenic removal efficiency slightly decreases when 6 mg/L sodium humate was added, which might be attributed to complexation of arsenic and HM in aqueous phase. Result of column experiment proves that a high removal efficiency (>98%) can be achieved using industrial waste iron chippings as filling with a HRT of 2 h, which suggests a potential application of this material in PRB or other ZVI technology.

Acknowledgments

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References

- [1] D.K. Nordstrom, Worldwide occurrences of arsenic in groundwater, *Science* 296 (2002) 2143–2145.
- [2] ATSDR (Agency for Toxic Substances and Disease Registry), Toxicological Profile for Arsenic, U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA, 2000.
- [3] J.F. Ferguson, J. Garvis, Review of arsenic cycle in natural waters, *Water Res.* 6 (1972) 1259–1274.
- [4] L.J. Matheson, P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron metal, *Environ. Sci. Technol.* 28 (1994) 2045–2053.
- [5] L. Gui, R.W. Gillham, M.S. Odziemkowski, Reduction of *N*-nitrosodimethylamine with granular iron and nickel-enhanced iron. 1. Pathways and kinetics, *Environ. Sci. Technol.* 34 (2000) 3489–3494.
- [6] A. Agrawal, W.J. Ferguson, B.O. Gardner, et al., Effect of carbonate species on the kinetics of dechlorination of 1,1,1-trichloroethane by zero-valent iron, *Environ. Sci. Technol.* 36 (2002) 4326–4333.
- [7] M.J. Alowitz, M.M. Scherer, Kinetics of nitrate, nitrite, and Cr(VI) reduction by iron metal, *Environ. Sci. Technol.* 36 (2002) 299–306.
- [8] S.Y. Oh, D.K. Cha, P.C. Chiu, Graphite-mediated reduction of 2,4-dinitrotoluene with elemental iron, *Environ. Sci. Technol.* 36 (2002) 2178–2184.
- [9] J.A. Lackovic, N.P. Nikolaidis, G.M. Dobbs, Inorganic arsenic removal by zero-valent iron, *Environ. Eng. Sci.* 17 (2000) 29–39.
- [10] J. Farrell, J.P. Wang, P. O'Day, et al., Electrochemical and spectroscopic study of arsenate removal from water using zero-valent iron media, *Environ. Sci. Technol.* 35 (2001) 2026–2032.
- [11] C.M. Su, R.W. Puls, Arsenate and arsenite removal by zerovalent iron: kinetics, redox transformation, and implications for in situ groundwater remediation, *Environ. Sci. Technol.* 35 (2001) 1487–1492.
- [12] N. Melitas, J.P. Wang, M. Conklin, et al., Understanding soluble arsenate removal kinetics by zerovalent iron media, *Environ. Sci. Technol.* 36 (2002) 2074–2081.
- [13] B.A. Manning, M.L. Hunt, C. Amrhein, Arsenic(III) and arsenic(V) reactions with zerovalent iron corrosion products, *Environ. Sci. Technol.* 36 (2002) 5455–5461.
- [14] C.M. Su, R.W. Puls, Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride, *Environ. Sci. Technol.* 35 (2001) 4562–4568.
- [15] L.C. Roberts, S.J. Hug, T. Ruettimann, et al., Arsenic removal with iron(II) and iron(III) in waters with high silicate and phosphate concentrations, *Environ. Sci. Technol.* 38 (2004) 307–315.
- [16] A. Ramaswami, S. Tawachsupa, M. Isleyen, Batch-mixed iron treatment of high arsenic waters, *Water Res.* 35 (2001) 4474–4479.
- [17] H.L. Lien, R. Wilkin, High-level arsenite removal from groundwater by zero-valent iron, *Chemosphere* 59 (2005) 377–386.
- [18] State Environmental Protection Administration of China, Supervision and Determination of Water and Waste Water, fourth ed., China Environmental Science Press, Beijing, 2002.
- [19] J.B. Shi, Z.Y. Tang, Z.X. Jin, et al., Determination of As(III) and As(V) in soils using sequential extraction combined with flow injection hydride generation atomic fluorescence detection, *Anal. Chim. Acta* 477 (2003) 139–147.
- [20] A. Jain, K.P. Raven, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH-release stoichiometry, *Environ. Sci. Technol.* 33 (1999) 1179–1184.

- [21] M.L. Farquhar, J.M. Charnock, F.R. Livens, et al., Mechanisms of arsenic uptake from aqueous solution by interaction with goethite, lepidocrocite, mackinawite, and pyrite: an X-ray absorption spectroscopy study, *Environ. Sci. Technol.* 36 (2002) 1757–1762.
- [22] X.G. Meng, S. Bang, G.P. Korfiatis, Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride, *Water Res.* 34 (2000) 1255–1261.
- [23] O. Sracek, P. Bhattacharya, G. Jacks, Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments, *Appl. Geochem.* 19 (2004) 169–180.
- [24] G.A. Parks, P.L. De Bruyn, The zero point of charge of oxides, *J. Phys. Chem.* 66 (1) (1962) 967–973.
- [25] D.O. Lumsdon, L.J. Evans, Surface complexation model parameters for goethite (α -FeOOH), *J. Colloid Interface Sci.* 164 (1) (1994) 119–125.
- [26] B.A. Manning, S. Goldberg, Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals, *Soil Sci. Am.* 60 (1996) 121–131.
- [27] A.D. Redman, D.L. Macalady, D. Ahmann, Natural organic matter affects arsenic speciation and sorption onto hematite, *Environ. Sci. Technol.* 36 (2002) 2889–2896.
- [28] J. Rau, H.J. Knackmuss, A. Stolzn, Effects of different quinoid redox mediators on the anaerobic reduction of azo dyes by bacteria, *Environ. Sci. Technol.* 36 (2002) 1497–1504.
- [29] World Health Organization, Guidelines for drinking water during coagulation, *J. Environ. Eng.* 123 (1997) 800–807.