

Removal of Arsenate from Aqueous Solution Using Nanoscale Iron Particles

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Removal of As(V) using nanoscale iron particles was examined in batch reactors. Nanoscale iron particles, utilizing zero-valent iron with a diameter less than 100 nm as reactive materials, have been demonstrated to effectively remediate a wide variety of common environmental contaminants. In this study, characterization of nanoscale iron particles and their corrosion products was conducted using SEM-EDX, XRD, BET surface area analyzer and Laser Zee Meter. SEM-EDX results indicated adsorption of arsenic onto the iron surface, and XRD analysis found the formation of iron corrosion products including lepidocrocite, magnetite and/or maghemite at a reaction period of 7 d. Measurements of zeta potential revealed that the nanoscale iron particles have a zero point of charge at pH 4.4. Increasing adsorption amounts of arsenic with decreasing pH can therefore be attributed to the positive surface charge of the particles at lower pH. The maximum adsorption capacity of nanoscale iron particles determined by the Langmuir equation was about 38.2 mg/g. Normalization of the adsorption capacity to specific surface areas provides insight into the importance of iron types and the contact time of reactions in influencing arsenic uptake.

Key words: arsenic, nanoscale iron, groundwater remediation, adsorption

Introduction

Groundwater resources contaminated by elevated levels of arsenic either through natural or anthropogenic sources have been reported in many countries including Bangladesh, West Bengal, Chile, Mexico, Taiwan and parts of the United States (Welch et al. 1988; Nickson et al. 1998; Smedley and Kinniburgh 2002; Nordstrom 2002). Arsenic has been classified as a Group A carcinogen by the United States Environmental Protection Agency and has been associated with a multitude of other non-cancer health effects such as black-foot diseases (Borum et al. 1994). In Taiwan, arsenic hazard is a significant public concern, partially because of past black-foot diseases. The WHO guideline value for arsenic in drinking water was lowered to 10 µg/L in 1993. To reduce public health risks from arsenic uptake, the Taiwanese limit for drinking water was also set at 10 µg/L.

Arsenic occurrence in natural water is mostly found in inorganic forms as trivalent arsenite [As(III)] and pentavalent arsenate [As(V)] (Cullen and Reimer 1989; Korte and Fernando 1991). Arsenic speciation is highly dependent on redox potential and pH. Under oxidizing conditions, As(V) is predominant and is in the form of oxyanions (H_2AsO_4^- , HAsO_4^{2-}) in wide pH conditions. Under reducing conditions, arsenic occurs mostly as As(III) and the uncharged arsenite species H_3AsO_3^0 predominates at pH less than about 9.2.

Many technologies have been developed for arsenic

removal from drinking water supplies including chemical precipitation, ion exchange and adsorption techniques using various adsorbents such as activated alumina (Kuriakose et al. 2004), iron oxide (e.g., Dixit and Hering 2003) and zero-valent iron (e.g., Lackovic et al. 2000; Nikolaidis et al. 2003; Lien and Wilkin 2005). The use of zero-valent iron for effective removal of arsenic has recently received attention. Studies have shown that zero-valent iron may serve as reactive media for permeable reactive barriers to remove arsenic in the subsurface (e.g., Blowes et al. 2000; Su and Puls 2001a,b, 2004) and may be used in small-scale drinking water systems for rural areas (Lackovic et al. 2000). It has been found that the removal of arsenic in zero-valent iron systems involves complicated processes including surface adsorption, precipitation, co-precipitation and redox reactions (Lackovic et al. 2000; Lien and Wilkin 2005). The formation of corrosion products of iron is believed to play an important role in arsenic removal mechanisms (Manning et al. 2002; Su and Puls 2004).

Nanoscale iron particles, an innovative extension of conventional zero-valent iron technology, have shown excellent performance in remediation of a wide array of contaminants (Zhang 2003). Interest in nanoscale iron particles has grown rapidly over the last 3 to 4 years and has mostly been focused on the degradation of chlorinated organic solvents. Studies on the use of nanoscale iron particles for arsenic removal are, however, still limited (Kanel et al. 2005). Because of their small particle size (<100 nm) and high reactivity, they could be directly injected into the subsurface to remediate arsenic contam-

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ination. Recent field tests have demonstrated promising prospects for in situ remediation (Elliot and Zhang 2001; Zhang 2003).

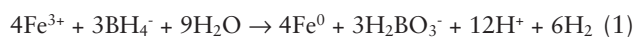
The objectives of this study were aimed at: (i) assessing the effectiveness of nanoscale iron particles for removal of arsenate, (ii) characterizing nanoscale iron particles and identifying their corrosion products in arsenic solutions, (iii) investigating effects of pH and initial arsenic concentrations on arsenic removal, and (iv) determining the maximum arsenic adsorption capacity of nanoscale iron particles.

Experimental Section

Materials and Chemicals

All chemicals were reagent grade or above and used without further purification. Deionized water was used for preparation of all reagent solutions. Sodium arsenate 7-hydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, 99%) was purchased from J.T. Baker. Sodium borohydride (NaBH_4 , 98%) and ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 98%) were obtained from Aldrich.

Synthesis of nanoscale iron particles was achieved by adding a 1:1 volume ratio of NaBH_4 (0.25 M) into $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.045 M) solution at $22 \pm 1^\circ\text{C}$ with vigorous mixing as describing by Lien and Zhang (2005). Ferric iron was reduced by borohydride according to the following reaction:



After the mixture was stirred for 20 min or until visible hydrogen evolution had ceased, the iron particles were then washed with a large volume (>100 mL/g iron) of Milli-Q water at least three times. The iron was used without further treatment.

Solid-Phase Characterization

Characterization of nanoscale iron particles was conducted using x-ray diffraction (XRD), scanning electron microscopy (SEM), a surface area analyzer and a zeta potential instrument. XRD measurements were performed using a MultiFlex Rigaku x-ray diffractometer (Rigaku Co.) at 40 kV and 40 mA with a copper target tube radiation ($\text{Cu K}\alpha_1$) producing x-rays with a wavelength of 1.54056 Å. Samples were placed on a quartz plate and were scanned from 20 to 80° (2θ) at a rate of 2° $2\theta/\text{min}$. Morphological analysis of nanoscale iron particles was performed by SEM using a Hitachi S-4300 microscope (Hitachi Science Systems, Ltd.) with energy-dispersive x-ray (EDX) analysis (at 10 kV). The specific surface area of nanoscale iron particles was measured by Brunauer-Emmett-Teller (BET) N_2 method using a COULTER SA 3100 surface area analyzer (Coulter Co.).

Zeta potential of nanoscale iron particles in aqueous solutions was measured by a Laser Zee Meter (Pen Kem

Inc., model 3.0). The solution contained 0.2 g/L nanoscale iron particles and 10^{-2} M NaClO_4 . Prior to analysis, the solution pH was adjusted to desired values by adding 1.0 M HNO_3 or KOH , and was shaken for 24 h.

Batch Tests

Stock solutions of 1000 mg/L As(V) were prepared from reagent-grade $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in deionized water. For the study of pH effects on arsenic removal, the experiments were carried out in plastic reaction vessels containing 0.1 g/L nanoscale iron particles in 100 mL of arsenic solution at $22 \pm 1^\circ\text{C}$. Two initial arsenic concentrations (5.2 and 11.1 mg/L) were used in the study and the solution pH was adjusted by 1 M HCl or NaOH . For the study of adsorption isotherms, plastic reaction vessels containing 0.25 g nanoscale iron particles in 200 mL of arsenic solution were performed at pH 7.0. The initial arsenic concentration varied between 1 and 100 mg/L. Adsorption isotherms on nanoscale iron particles were conducted to evaluate the maximum adsorption capacity at $22 \pm 1^\circ\text{C}$. The solution pH was controlled only at the beginning of the reaction using 1 M HCl or NaOH . For both studies, reaction vessels were placed on a rotary shaker (100 rpm) and the contact time of reactions was set at 120 h based on preliminary tests that confirmed attainment of equilibrium under these conditions within this time period.

Arsenic Analysis

Chemical analysis for arsenic was carried out using an inductively coupled plasma-optical emission spectrometry (ICP-OES, PerkinElmer Optima 2000DV, PerkinElmer Inc.). The wavelength of arsenic was set at 193.696 and 188.979 nm. Prior to analysis, samples were filtered through 0.2- μm filters and acidified with 3% HNO_3 . The detection limit of arsenic was 10 $\mu\text{g/L}$ and analyses of duplicate samples indicated an analytical error of less than 5% for arsenic concentration analyzed in the laboratory.

Results and Discussion

Characterization of Nanoscale Iron Particles and their Corrosion Products

The SEM image of nanoscale iron particles shows that they are comprised of spherical particles assembled in chains (Fig. 1). The nanoscale iron particles had an average size diameter in the range of 50 to 100 nm. The size of particles is consistent with previous studies (Kanel et al. 2005; Lien and Zhang 2005) and the observation of chain structure of nanoscale iron particles is in agreement with the study conducted by Nurmi et al. (2005). A specific surface area of nanoscale iron particles was in an average of 33.5 m^2/g as measured by a BET surface analyzer.



Fig. 1. SEM image of the fresh nanoscale iron particles.

The results of XRD analysis of fresh and As(V)-treated nanoscale iron particles are shown in Fig. 2. The XRD pattern of fresh nanoscale iron particles showed a major characteristic peak at 44.7 degrees 2θ , indicating the presence of elemental iron (Fig. 2A). After reactions with arsenic for 7 d, corrosion products including lepidocrocite, magnetite and/or maghemite were found at the surface of As(V)-treated nanoscale iron particles according to the XRD analysis (Fig. 2B). Though arsenic removal in zero-valent iron systems may involve many complicated processes, it is well agreed that arsenic removal mechanisms are largely related to these corrosion products of iron through adsorption and co-precipitation (Farrell et al. 2001; Manning et al. 2002; Melitas et al. 2002a,b). Adsorption of arsenic onto the particle surface was further confirmed by SEM-EDX analysis. Samples were taken

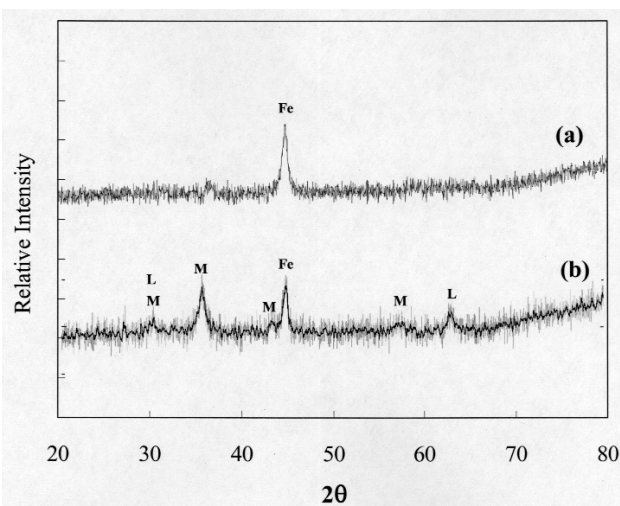


Fig. 2. XRD patterns of: (A) fresh, and (B) As(V)-treated nanoscale iron particles. Peaks are due to zero-valent iron (Fe), lepidocrocite (γ -FeOOH) (L) and magnetite/maghemite ($\text{Fe}_3\text{O}_4/\gamma$ - Fe_2O_3) (M).

when nanoscale iron particles reacted with 100 mg/L of arsenic at 7 d. As shown in Fig. 3, the EDX spectrum indicated the presence of arsenic at the surface of As(V)-treated nanoscale iron particles. The elemental composition by weight percent of the As(V)-treated samples was determined by a quantitative analysis of EDX. The ratio of Fe:O:As was 87.1:11.5:1.4.

In order to investigate the surface charge of the solids, the zeta potentials of nanoscale iron particles were measured as a function of pH in 10^{-2} M NaClO_4 solutions as shown in Fig. 4. The nanoscale iron particles were positively charged up to around pH 4 and then became negatively charged. Hence, the zero point of charge was determined to be at pH 4.4. In other words, the nanoscale iron particles possess a positive surface charge at lower pH (<4.4) and a negative surface charge when the solution pH is greater than 4.4.

Effect of pH on Arsenic Removal

Adsorption of As(V) onto nanoscale iron particles as a function of pH from 2 to 12 is illustrated in Fig. 5. Arsenate adsorption on the solids decreased with increasing pH. Similar trends have been found in several previous studies using various iron oxides (Dixit and Hering 2003). At pH 2.2, nanoscale iron particles adsorbed maximum amounts of arsenic. However, only approximately 40 and 50% removal efficiencies were achieved when initial arsenic concentrations were 5.2 and 11.1 mg/L, respectively. Nevertheless, the increase of removal efficiency at higher initial concentration suggests the adsorption of arsenic onto the iron surface is dependent on arsenic concentrations.

The nanoscale iron particles that have a high affinity for arsenate at lower pH can be attributed to the positive surface charge of the solids as measured by zeta potential (Fig. 4). As(V) species exist as oxyanions (H_2AsO_4^- , HAsO_4^{2-}) at a wide pH range in water. H_2AsO_4^- is dominant at low pH ($2.2 < \text{pH} < 6.9$) while at higher pH, HAsO_4^{2-} becomes dominant ($6.9 < \text{pH} < 11.5$). As a result, the electrostatic attraction between H_2AsO_4^- and the positively charged particle surface occurred at lower

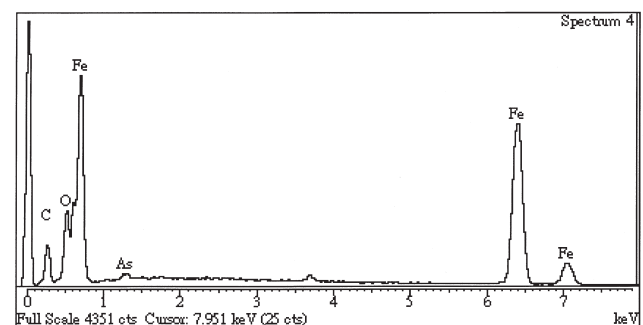


Fig. 3. SEM-EDX spectrum of As(V)-treated nanoscale iron particles.

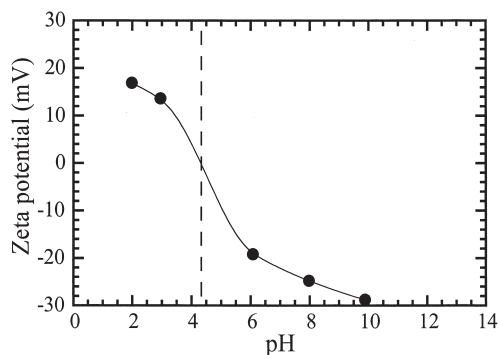


Fig. 4. Zeta potential of nanoscale iron particles as a function of pH.

pH whereas the electrostatic repulsion between HAsO_4^{2-} and the negatively charged particle surface took place as increased pH.

Arsenic Adsorption Capacity

Adsorption isotherms on the nanoscale iron particles were conducted to estimate the maximum adsorption capacity. The adsorption of arsenic onto the nanoscale iron particles showed nonlinear behaviour (Fig. 6) and can be described by the Langmuir equation:

$$\frac{x}{m} = \frac{q_m K C_e}{1 + K C_e} \quad (2)$$

where x/m (mg/g) is the amount of arsenic adsorbed, q_m (mg/g) is the maximum adsorption capacity, K (L/mg) is the adsorption constant and C_e (mg/L) is the equilibrium concentration of arsenic in the solution. Plots of $1/(x/m)$ versus $1/C_e$ through linear regression analysis gave straight line results. The maximum adsorption and the adsorption constant can then be calculated by linear regression analyses. The equation ($r^2 = 0.98$) gives a value of the maximum adsorption capacity (38.2 mg/g) and the sorption constant (1.06 L/mg). Because adsorption is a surface phenomenon in which a chemical species adheres to an interface, the adsorption capacity can further be

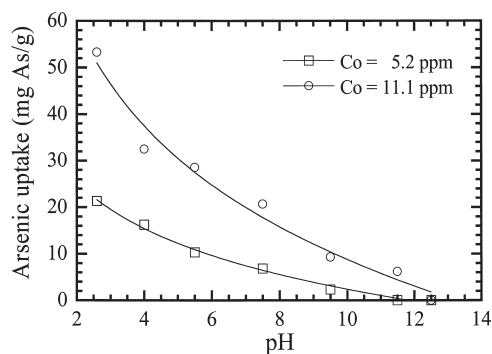


Fig. 5. Arsenic adsorption onto nanoscale iron particles at various pH and initial arsenic concentrations.

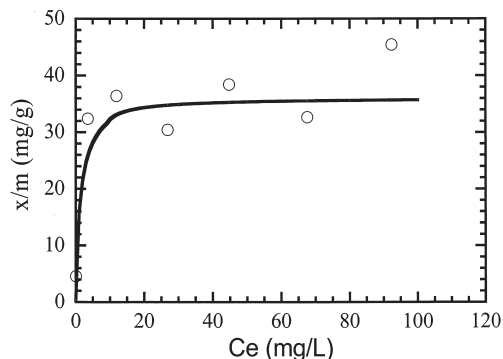


Fig. 6. Adsorption isotherm for arsenate by nanoscale iron particles at pH 7.0.

expressed as a unit area basis by normalizing to specific surface areas of adsorbents. Accordingly, the arsenic adsorption capacity per unit area of nanoscale iron particles was determined to be 1.14 mg/m^2 .

Compared with other studies as listed in Table 1, it was found that the surface-area normalized adsorption capacity of nanoscale iron particles is higher than that of Peerless iron. The adsorption isotherms on both iron particles were examined by batch tests (Su and Puls 2001b). Because the arsenic removal by iron involved complicated surface interaction, many variables may influence the arsenic adsorption capacity such as iron types, pretreated procedures and the contact time during experiments. The effect of iron filing type that caused a different adsorption capacity has been reported (Lackovic et al. 2000). Furthermore, the surface-area normalized adsorption capacity obtained from column tests is generally greater than that estimated from batch tests. This may imply the importance of contact time between iron and arsenic in obtaining the maximum adsorption capacity. In general, the contact time for arsenic and iron to reach equilibrium is in the range of a few hours to a few days in batch experiments. However, column tests allow a longer period of time for iron corrosion products to be better generated. The iron corrosion products such as iron oxide are believed to be responsible for the arsenic removal through adsorption and/or precipitation. The iron oxide with porous and incoherent nature on iron leading to increase of the surface area may allow continued adsorption of arsenic. Nikolaidis et al. (2003) reported an increase of surface area for reactive media containing iron filings and sand from $1 \text{ m}^2/\text{g}$ at initial conditions to $37.8 \text{ m}^2/\text{g}$ after reactions.

Conclusions

The present study on the removal of arsenate suggests that nanoscale iron particles can serve as an effective remedial reagent with high arsenic removal capacity. In particular, the following conclusions can be drawn:

TABLE 1. Comparison of arsenate removal capacity with different studies

Iron type	Adsorption capacity (mg/g)	BET surface area (m ² /g)	Surface area normalized adsorption capacity (mg/m ²)	Experiment conditions	References
Synthesized nanoscale iron	38.2	33.5	1.14	Batch	This study
Peerless iron	0.73	2.53	0.29	Batch	Su and Puls (2001b)
Master Builders iron	0.93 ^a	1	0.93	Column with a barite column in series	Lackovic et al. (2000)
J.T. Baker iron	0.22 ^a	0.1	2.2	Column with a barite column in series	Lackovic et al. (2000)
J.T. Baker iron	0.67	0.1	6.7	Column	Lackovic et al. (2000)
Connelly iron	4.4 ^b	1	4.4	Column	Nikolaidis et al. (2003)

^aThe presence of SO₄²⁻ may decrease the adsorption capacity.

^bCapacity was expressed as mg As per g of media containing both iron and sand.

- 1 Nanoscale iron particles are comprised of spherical particles assembled in chains. The nanoscale iron particles have an average size diameter in the range of 50 to 100 nm and a specific surface area in an average of 33.5 m²/g.
- 2 The XRD analysis revealed that iron corrosion products including lepidocrocite, magnetite and/or maghemite were formed at the surface of As(V)-treated nanoscale iron particles after reactions with arsenic for 7 d. The presence of arsenic on the iron surface was also indicated by SEM-EDX analysis.
- 3 Adsorption of arsenic is dependent on pH and initial arsenic concentrations. Arsenic adsorption on the surface of nanoscale iron particles decreased with increasing pH. A higher amount of arsenic adsorbed was observed when experiments were conducted with a higher initial arsenic concentration.
- 4 The adsorption of arsenic onto the nanoscale iron particles can be described by the Langmuir equation. The maximum adsorption capacity was determined to be about 38.2 mg/g. The surface-area normalized adsorption capacity of nanoscale iron particles is higher than that of commercial-grade iron conducted in batch tests.

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