

Ca–alginate-entrapped nanoscale iron: arsenic treatability and mechanism studies

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Abstract The use of nanoscale zero-valent iron (NZVI, diameter 10–90 nm with an average value of 35 nm) entrapped in calcium (Ca)–alginate beads shows great promise for aqueous arsenic treatment. This research evaluated Ca–alginate-entrapped NZVI as an advanced treatment technique for aqueous arsenic removal. Arsenic is a serious threat to human health and millions of people are affected by arsenic contamination in various parts of the world including the USA. In bench scale batch studies with initial As(V) concentrations of 1–10 mg L⁻¹, ~85–100 % arsenic removal was achieved within 2 h. While the

reaction kinetics differ between bare and entrapped NZVI, the overall reductions of arsenic are comparable. Surface area-normalized arsenic reduction reaction rate constants (k_{sa}) for bare and entrapped NZVI were $3.40\text{--}5.96 \times 10^{-3}$ and $3.92\text{--}4.43 \times 10^{-3}$ L m⁻² min⁻¹, respectively. The entrapped NZVI removed ~100 µg L⁻¹ As(V) to below detection limit within 2 h and groundwater with 53 µg L⁻¹ As(V) was remediated to below instrument detection limit (10 µg L⁻¹) within 1 h. The presence of Na⁺, Ca²⁺, Cl⁻, and HCO₃⁻ did not affect arsenic removal by entrapped NZVI and there was no leaching of iron from the beads. X-ray diffraction and Fourier

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transform infrared spectroscopic techniques have been used to understand the mechanism of arsenic removal by the entrapped NZVI. Ca–alginate polymer is an excellent choice as an entrapment medium as it is non-toxic and has little solubility in water.

Keywords Iron nanoparticles · Alginate beads · Entrapment · Arsenic · Groundwater remediation · Environmental effects

Introduction

As our ability to provide safe potable water to an increasing world population has become more challenging, the demands for advanced water treatment techniques have intensified. One of these challenges is to reduce arsenic concentrations to an acceptable level in finished water. Long-term ingestion of arsenic has been linked to a number of debilitating health problems in humans including cancer (Marshall et al. 2007). More recently arsenic exposure has been linked with uterine function damage (Akram et al. 2010) as well as higher heart stroke rates (Lisabeth et al. 2010). Water with $\sim 150 \mu\text{g L}^{-1}$ arsenic caused cancer in 1 % of men over the age of 30 in Chile which increased to 3 % with $\sim 450 \mu\text{g L}^{-1}$ arsenic and increased bladder cancer occurrences (Marshall et al. 2007). Similar incidences have been reported from countries like Argentina, Bangladesh, India, Japan, the USA, and Vietnam that have arsenic contamination (Mandal and Suzuki 2002). Long-term ingestion of water containing arsenic, even at significantly lower concentrations, may result in unacceptable adverse chronic health risks (Shiber 2005).

In 2006, the United States Environmental Protection Agency, USEPA (2001) reduced the maximum contaminant level (MCL) for arsenic in drinking water from 50 to $10 \mu\text{g L}^{-1}$. The stringent new MCL has challenged many water utilities particularly the small facilities as they do not have the resources needed to achieve the new treatment goal (USEPA 2013). As many as 3,000 community water systems serving 11 million people in the USA are reported to be not in compliance with the present MCL (USEPA 2013).

The most commonly used treatment techniques for arsenic remediation in drinking water include chemical precipitation (using iron or aluminum salts), coagulation/filtration, and ion exchange (USEPA 2004). Chemical

precipitation (Jain et al. 2009; Farrell et al. 2001) works well but needs pre-filtration. Coagulation calls for increased infrastructure as it needs to be followed by sedimentation and filtration, and it is not very effective in arsenic removal (Mohan and Pittman 2007). Ion exchange is very effective in arsenic removal but oftentimes results in a high operational and maintenance cost as well as produces toxic concentrates and solid wastes (Mohan and Pittman 2007).

Laboratory studies indicate that nanoscale zero-valent iron (NZVI) particles are very versatile material for aqueous contaminant remediation including chlorinated compounds (Bezbaruah et al. 2011; Krajangpan et al. 2012), explosives (Kim et al. 2007), heavy metals (Moraci and Calabro 2010), pesticides (Thompson et al. 2010), and inorganics (Almeelbi and Bezbaruah 2012; Bezbaruah et al. 2009) to name a few. NZVI is characterized by smaller particle size ($<100 \text{ nm}$) and higher surface area ($22\text{--}54 \text{ m}^2 \text{ g}^{-1}$; Bezbaruah et al. 2009; Liu et al. 2005) as compared to micro ZVI (MZVI) which has a size in the μm range and surface area of $1\text{--}2 \text{ m}^2 \text{ g}^{-1}$ (Thompson et al. 2010). Contaminant remediation by NZVI is known to be a surface-mediated process (Li et al. 2006) and NZVI nanoparticles can react approximately 1,000 times faster than MZVI (Kanel et al. 2005, 2006).

NZVI is capable of removing arsenic from groundwater by surface precipitation or adsorption when arsenic is in a pentavalent oxidation state [As(V); Su and Puls 2001]. Trivalent arsenic [As(III)] removal by NZVI can be attributed to spontaneous adsorption and co-precipitation of iron oxides/hydroxides which are formed due to oxidation of NZVI (Kanel et al. 2005). While NZVI particles are very effective in remediating arsenic to low concentrations there are certain disadvantages associated with their small particle size. NZVI particles quickly become dispersed and mobile in the aquifer. They may also agglomerate if present in high concentrations resulting in the formation of larger particles which tend to precipitate out in the pores of the aquifer materials (Krajangpan et al. 2012). Reactivity of nanoparticles is reduced as the particles lose some of their reactive surface area due to such agglomeration. The nanoparticles may affect micro and higher organisms if present in unreacted (ZVI) stage (Phenrat et al. 2009). Further, arsenic sorbed onto NZVI may still be potent toxicant to human and other ecosystem components. Lack of control over the particles' dispersion behavior and their mobility

makes it difficult to use them on cases where a stationary treatment medium (e.g., a permeable reactive barrier) is needed.

Calcium (Ca)–alginate is a popular material used for entrapping microbial cells used in the food and beverage industries (Roy et al. 1987), pharmaceutical industries (Brachkova et al. 2010), and water treatment (Hill and Khan 2008). In recent years Ca–alginate has been used to entrap or encapsulate NZVI to treat nitrate (Bezbaruah et al. 2009) and trichloroethylene (Bezbaruah et al. 2011; Kim et al. 2010). Ca–alginate is porous enough to allow contaminants to diffuse through it and come in contact with the entrapped materials. Alginate is nontoxic, non-immunogenic, and relatively insoluble in water making it an ideal material for environmental applications (Hill and Khan 2008). Bezbaruah et al. (2009) have demonstrated that NZVI particles do not lose their reactivity when entrapped in Ca–alginate beads. This paper reports removal of pentavalent arsenic [As(V)] by NZVI entrapped in Ca–alginate beads and discusses mechanism of removal.

Materials and methods

Chemicals and reagents

Iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99 % pure, Alfa Aesar), sodium borohydride (NaBH_4 , 98 %, Aldrich), calcium chloride (CaCl_2 , ACS grade, BDH), sodium hydroxide (5 N NaOH , Alfa Aesar), sodium (Na)–alginate (production grade, Pfaltz and Bauer), diarsenic pentoxide (As_2O_5 , Alfa Aesar), nitric acid (HNO_3 , 68 %, J. T. Baker), methanol (production grade, BDH), and ethanol (ACS grade, Mallinckrodt Chemicals) were used as received unless otherwise specified.

NZVI synthesis and entrapment procedure

ZVI nanoparticles were produced using the borohydride reduction of ferrous iron (Bezbaruah et al. 2009). Ca–alginate beads were made (Fig. 1a) following the methodology previously described by the corresponding author's research group (Bezbaruah et al. 2009). One gram of Na–alginate was dissolved in 50 mL deoxygenated deionized (DI) water (2 % w/v) at room temperature ($\sim 22 \pm 2^\circ\text{C}$), and mixed using a

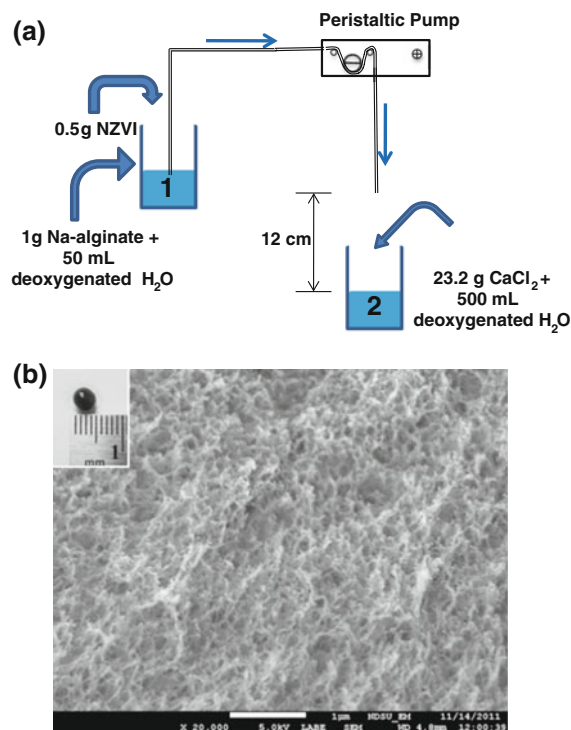


Fig. 1 **a** Schematic of Ca–alginate bead preparation process, **b** scanning electron microscopy (SEM) image of a Ca–alginate bead interior (*inset* Ca–alginate bead with entrapped NZVI particles)

magnetic stirrer for 3–5 h, until solution appeared uniform. After mixing was achieved the Na–alginate solution was allowed to sit for an additional period of no less than 30 min to allow any air bubbles to escape from the solution. NZVI (0.5 g) was then added expeditiously (to avoid oxidation) to the Na–alginate solution and stirred with a glass rod to get a well-mixed solution (Solution 1). A deoxygenated aqueous calcium chloride solution was prepared separately by adding 23.2 g of CaCl_2 to 500 mL of deoxygenated DI water (Solution 2). Next, Solution 1 was added dropwise into Solution 2 using a peristaltic pump (Masterflex, Cole Parmer, 0.5 mm ID tubing, 2.5 mL min^{-1} flow rate) from a height of 12 cm (optimized based on a number of trials) to form Ca–alginate beads. Solution 1 was continuously stirred with a glass rod while pumping it to ensure that almost all NZVI was transferred into the beads. Additional amount of Na–alginate solution was used if needed to ensure that all NZVI particles were transferred to the beads. About 0.19 % NZVI might not have been possibly transferred in this process

(Bezbaruah et al. 2009). The beads were allowed to harden in the CaCl_2 solution for 6–9 h to achieve adequate hardness and porosity (Bezbaruah et al. 2009), and then rinsed and stored in deoxygenated DI water.

Batch studies

Batch arsenic removal studies were performed under anaerobic conditions in reactors made of 500 mL commercial-grade polyethylene terephthalate bottles fitted with a sleeve-type silicone septum seal. The minimal head space left after 500 mL solution was added to the reactor was purged with N_2 gas to flush out air (oxygen). A 100 mg L^{-1} As(V) stock solution in DI water was prepared using As_2O_5 , and used to make solutions with initial As(V) concentrations of 1, 5, and 10 mg L^{-1} . Four study groups were analyzed with different concentrations of arsenic. Group 1 used 0.5 g bare NZVI particles, Group 2 used Ca–alginate-entrapped NZVI particles (0.5 g NZVI), Group 3 had only Ca–alginate beads (made from 50 mL Na–alginate) with no entrapped NZVI, and Group 4 consisted of blanks run with only arsenic solution (no NZVI or Ca–alginate beads). The reactors were rotated end-over-end at 28 rpm in a custom-made shaker. The samples were collected at 0, 5, 15, 30, 45, 60, 90, and 120 min using a syringe (10 mL, Becton-Dickinson) fitted with a needle. This technique protected against possible oxygenation of the test solution in the reactors during sample collection. The samples were then filtered using a syringe filter (Whatman ANOTOP 25, $0.02 \mu\text{m}$) to remove any leaked out NZVI from the beads, and preserved using nitric acid for ICP analysis later. All experiments were conducted in triplicate (for each study group).

Analysis and characterization

ICP analysis

The concentration of arsenic was measured using Spectro Genesis SOP ICP-OES (Scott double-pass nebulizer). SmartAnalyzer (version v. 3.013.0752) software was used. The machine was set with a specific plasma power (1,425 W), constant flow (13.5 L min^{-1}), auxiliary flow (1.2 L min^{-1}), nebulizer flow (0.9 L min^{-1}), and the integration time of 21 s. A four-point standard calibration was done using single element standards with a matrix of 5 % HNO_3 . All samples were randomized prior to analysis and the

results were reported as the mean of three replicate measurements. A control check standard was analyzed after every 20 samples to ensure that the values measured were within 10 % of the expected value.

XRD analysis

Powder X-ray diffraction (PXRD) analysis was done to determine the crystalline materials [e.g., magnetite (Fe_3O_4) and iron (Fe^0)] in alginate beads, NZVI, NZVI that sorbed arsenic (NZVI–As), alginate-entrapped NZVI (Alginate–NZVI), and alginate-entrapped NZVI that sorbed arsenic (Alginate–NZVI–As beads). The samples were dried in vacuum oven under nitrogen environment for 2 days. The dried samples were ground finely using a mortar with pestle. The powdered samples were placed/spread on microslides ($15 \times 15 \text{ mm}$) and experiments were performed on Philips X'Pert MPD system with Cu $K\alpha$ radiation. Bragg–Brentano parafocusing optics (fix divergence slit = 1° , receiving slit = 0.2, 15 mm mask) was used for all five samples, which were scanned by an applied current of 40 mA and a voltage of 45 kV with 2θ step 0.05° and step time 5 s.

FT-IR analysis

Fourier transform infrared spectroscopic (FT-IR) spectra were obtained with a Nicolet 6700 FT-IR Spectrometer operated with OMNIC software. The spectra were observed from 400 to $4,000 \text{ cm}^{-1}$ using potassium bromide (KBr) as a background. The samples were dried in vacuum oven under nitrogen environment for 2 days. The dried samples were mixed with KBr corresponding to approximate mass ratio of 1:10 (sample:KBr) for pellet preparation. Spectra were recorded at a resolution of 4 cm^{-1} with each spectrum corresponding to the coaddition of 64 scans. The background collected from KBr was automatically subtracted from the sample spectra. The spectral information were collected and plotted in the same scale on absorbance axis.

Results and discussion

NZVI synthesis and entrapment in Ca–alginate beads

The NZVI produced during this study had $\sim 35 \text{ nm}$ average particle size (range 10–90 nm), and an

average BET surface area of $25 \text{ m}^2 \text{ g}^{-1}$ (Bezbaruah et al. 2009). The NZVI-entrapped Ca-alginate beads produced during this study had an average size of $3.4 \pm 0.13 \text{ mm}$ (Fig. 1b, inset). The beads were hardened in CaCl_2 for more than 6 h to ensure adequate porosity for contaminant diffusion into the beads (Bezbaruah et al. 2009). Scanning electron microscopy image of the beads shows a porous interior (Fig. 1b). Earlier Aksu et al. (1998) reported no problem with diffusion of contaminants into the beads after adequate hardening in CaCl_2 solution. Bezbaruah et al. (2009) reported that agglomeration is reduced if NZVI particles are entrapped in Ca-alginate beads.

Treatability studies

Both bare and entrapped NZVI showed similar As(V) removal characteristics. In a 2-h period bare NZVI ($1 \text{ g L}^{-1} \text{ Fe}^0$) reduced arsenic concentration from 9.834, 4.380, and 1.447 mg L^{-1} to 0.042 (99.57 % reduction), 0.058 (98.68 %), and 0.230 mg L^{-1} (84.11 %), respectively (Fig. 2). The entrapped NZVI particles (1 g L^{-1}) used in this study reduced arsenic concentrations from 9.259, 4.974, and 1.305 mg L^{-1} to 0.042 (99.55 % reduction), 0.042 (99.16 %), and 0.187 mg L^{-1} (85.67 %), respectively. Controls (with only Ca-alginate beads and no NZVI) had only a slight arsenic reduction ($<10.00\%$) in the first 30 min of the reaction at all concentration levels but no further reduction of arsenic was observed over time (data not shown). The small initial change observed can be attributed to physical sorption to the Ca-alginate bead. Others also have observed similar initial minor reduction of contaminant concentrations with alginate beads (Bezbaruah et al. 2009; Hill and Khan 2008). Blanks (only arsenic with no Ca-alginate beads or NZVI) showed no change in arsenic concentration over time (data not shown).

The possible mechanisms of arsenic removal by NZVI have been reported by others. Water oxidizes iron (Fe^0) to Fe^{2+} even when no dissolved oxygen is present (Eq. 1; Kanel et al. 2006; Su and Puls 2001). The Fe^{2+} formed then reacts with OH^- to produce ferrous hydroxide $\text{Fe}(\text{OH})_2$ (Eq. 2; Kanel et al. 2005). As(V) is possibly removed by NZVI via reduction, and hydrous ferric oxides adsorbs arsenic (Kanel et al. 2006). There is also a possibility of Fe^{3+} formation due to oxidation by water (Han et al. 2011). NZVI particles similar to those used in this experiment were

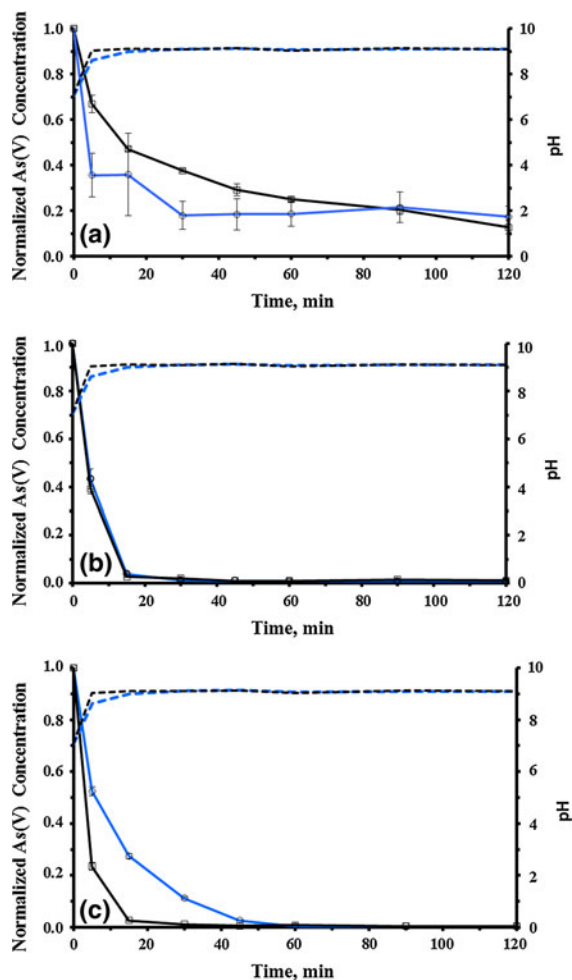
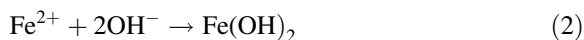
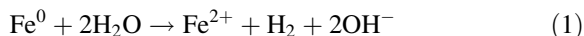


Fig. 2 Removal of As(V) by bare NZVI (circles) and entrapped NZVI (squares). Observation of change of pH over time indicates initial increase of pH in the presence of both bare NZVI (thick blue dashed lines) and entrapped NZVI (thick black dashed lines). **a** Initial As(V) = 1 mg L^{-1} [actual average initial As(V), $C_{0,\text{Act}}$ (mg L^{-1}) = 1.305 (entrapped), 1.447 (bare)], **b** initial As(V) = 5 mg L^{-1} [$C_{0,\text{Act}}$ = 4.974 (E), 4.380 (B)], and **c** initial As(V) = 10 mg L^{-1} [$C_{0,\text{Act}}$ = 9.259 (E), 9.834 (B)]. The normalized concentrations are calculated as the fraction of initial As(V) remaining over time (C_t/C_0). The straight lines joining the data points are for ease of reading only and do not represent trend lines. The vertical error bars indicate \pm standard deviations. (Color figure online)

found to have a NZVI core and FeOOH shell structure (Martin et al. 2008). The corresponding author's group has earlier reported a thin ($\sim 2\text{--}5 \text{ nm}$) passivating iron oxide layer on freshly produced NZVI (Krajangpan et al. 2012). The presence of mixed oxides might have helped in arsenic removal; arsenic might have been reduced from As(V) to As(III) and As(0), and then

adsorbed and/or co-precipitated (Bang et al. 2005; Ramos et al. 2009; Wan et al. 2010). Recent theory of dual redox functionality of NZVI by Yan et al. (2010) needs special reference here; they suggested that while oxide layer sorbs As(V), the core ZVI reduces As(V)–As(III) and then to As(0). A schematic of possible arsenic removal mechanism in deoxygenated water environment is presented in Fig. 3.



Kinetics

Analysis of the relevant data points indicates that the arsenic reduction reactions followed pseudo first-order kinetics for both bare and entrapped NZVI. The observed reaction rate constants (k_{obs}) were found to be in the range 9.81×10^{-2} – $11.08 \times 10^{-2} \text{ min}^{-1}$ for bare NZVI, and 8.51×10^{-2} – $14.90 \times 10^{-2} \text{ min}^{-1}$ for entrapped NZVI (Table 1). Kanel et al. (2006) reported a k_{obs} value of $7.1 \times 10^{-1} \text{ min}^{-1}$ for As(V) removal by bare NZVI. In the case of small-sized ZVI, the reaction is known to be surface mediated (Matheson and Tratnyek 1994), and it is, therefore, pertinent to relate the reaction rate constant to the total NZVI surface area. Surface area-normalized reaction rate constant, k_{sa} (Eq. 3), makes it easier

to compare efficacy of nanoparticles produced via different synthesis routes (i.e., having different surface characteristics). It should, however, be noted that the adaptation of k_{sa} is debatable. While Cwiertny and Roberts (2005) did not find linearity of surface area-normalized rate constants with iron loading, Matheson and Tratnyek (1994) did. A surface area-normalized rate equation can be proposed after Johnson et al. (1996) as:

$$dC/dt = -k_{\text{sa}}C = -(k_{\text{obs}}/a_{\text{np}})C, \quad (3)$$

where k_{sa} is the surface area-normalized rate constant ($\text{L m}^{-2} \text{ min}^{-1}$) and a_{np} is the iron surface area concentration ($\text{m}^2 \text{ L}^{-1}$).

The surface area-normalized rate constants (k_{sa}) are calculated here (Table 1) using an iron surface area of $25 \text{ m}^2 \text{ g}^{-1}$ reported for bare NZVI (Bezbaruah et al. 2009). The reaction rate constants obtained from bare and entrapped NZVI were compared. Two-way analysis of variance shows no significant difference between the reaction rate constants at 95 % confidence (p value >0.05) with the exception of the 1 mg L^{-1} arsenic concentration. At the end of 120 min entrapped NZVI (1 mg L^{-1} arsenic) showed a significantly greater removal efficiency than bare NZVI (p value = 0.01) even though arsenic removal by bare NZVI was much better till about 90 min (Fig. 2a). The fact that entrapped NZVI particles removed arsenic as efficiently as bare NZVI has great ramifications in environmental remediation and opens up the possibilities of use of entrapped NZVI in water purification (as filter media).

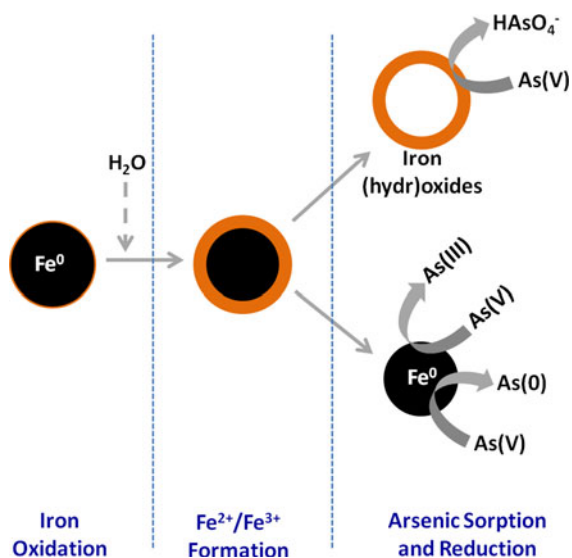


Fig. 3 Schematic of possible mechanisms of As(V) removal by NZVI. Both sorption and reduction of arsenic are expected within the Ca-alginate–NZVI beads

XRD and FT-IR analyses

PXRD is very powerful and common technique for characterization of crystalline phases in materials. Magnetite and iron are known to crystallize in $Fd3m$ and $Im3m$ space groups, respectively (Downs and Hall-Wallace 2003). In order to identify them in the beads, the XRD studies were performed in 2θ range from 20 to 70° . The five most intensive peaks of Fe_3O_4 in this 2θ range are at: 30.39° (attributed to 220 plane), 35.48° (311), 43.52° (400), 57.57° (511), and 63.23° (440). Fe(0) has only two characteristic peaks in this region at 44.68° and 65.03° which are assigned to (110) and (200) planes in $Im3m$ space group. All XRD results and simulated spectra of Fe_3O_4 and Fe(0) are shown in Fig. 4. As can be seen, the

Table 1 First-order reaction rate constants (k_{obs}) and surface area-normalized rate constants (k_{sa}) for arsenic removal with bare and entrapped NZVI

Batches	Initial As(V) concentration (mg L ⁻¹)	Observed reaction rate constant, k_{obs} (min ⁻¹)	Surface area-normalized rate constant, k_{sa} (L m ⁻² min ⁻¹)	R^2
Bare NZVI	1	No good fit		
	5	9.81×10^{-2}	3.92×10^{-3}	0.8174
	10	11.08×10^{-2}	4.43×10^{-3}	0.8753
Entrapped NZVI	1	14.90×10^{-2}	5.96×10^{-3}	0.9137
	5	10.40×10^{-2}	4.16×10^{-3}	0.8569
	10	8.51×10^{-2}	3.40×10^{-3}	0.9852

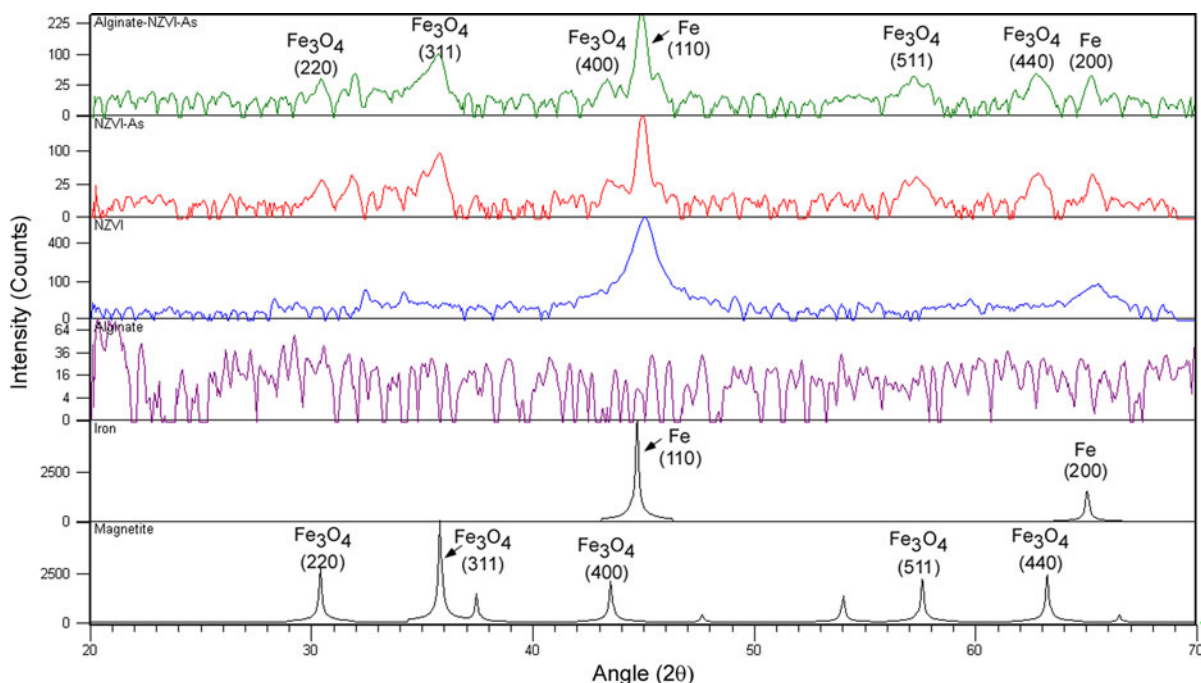


Fig. 4 X-ray diffraction results for bare NZVI, entrapped NZVI, and alginate beads under different conditions. *Alginat-NZVI-As* alginate-entrapped NZVI that sorbed arsenic, *NZVI-As* bare NZVI that sorbed arsenic, *NZVI* bare NZVI not exposed

to arsenic, *Alginat* Ca-alginate bead (no NZVI inside and no arsenic), *Iron* zero-valent iron (modeling data), *Magnetite* magnetite (modeling data)

alginate-NZVI-As and NZVI-As samples (samples after arsenic removal study was complete) have all characteristic peaks of both, Fe_3O_4 and Fe(0) while virgin bare NZVI has only Fe(0). The additional oxide peaks for NZVI after reaction with arsenic is consistent with the theory of arsenic removal by NZVI (Fig. 4). The similarity of the spectra from bare and entrapped NZVI after reaction with arsenic reconfirms that the degradation reactions were same. A few feeble peaks around 32–35° in virgin bare NZVI spectrum are indicative of the presence of the passivating oxide

layer around the particles. Obviously these peaks are shifted from the observed magnetite peaks. These peaks can be assigned to the two most intensive peaks of Fe_2O_3 (hematite) at 33.12° (104) and 35.61° (110). The spectrum for only alginate does not show any crystalline materials and is given here for comparison. The two spectra at the bottom are simulated to indicate the exact positions of the peaks of the crystals of interest.

FT-IR analyses were carried out to elucidate the binding of arsenic to Ca-alginate-entrapped NZVI.

Figure 5 provides the spectra for the samples of bare NZVI and only alginate bead before reaction with arsenic, and bare NZVI, alginate-entrapped NZVI after reaction with arsenic, and only alginate after sorbing arsenic. FT-IR spectra of alginate (only) and bare NZVI were collected to serve as references. There are no significant peaks in the spectra for NZVI. Even though NZVI has a layer of iron oxides, the oxide layer was very thin and concentration is not high enough to get a sharp peak in the FT-IR spectra. The spectra for alginate (only), Alginate-As, and Alginate-NZVI-As shows the carboxymethyl group that has two peaks at $\sim 1,620$ and $\sim 1,433$ cm^{-1} . The spectra have C-O (ether) stretching at $\sim 1,030$ cm^{-1} . The additional peaks in NZVI-As and Alginate-NZVI-As at ~ 470 , and ~ 660 cm^{-1} are As-O stretch vibration, and the peak at ~ 809 corresponds to As-O-Fe bond. The absence of sharp peak in Alginate-As at 809 cm^{-1} shows the absence of binding of arsenic to alginate, and the presence of a weak band at ~ 870 cm^{-1} is for As-O stretching for pure sodium arsenate. This confirms simple absorption of arsenic by alginate beads in the first few minutes during treatability studies. The observation that Ca-alginate is not participating in any As-alginate is important because the authors wanted to use the alginate as the dispersing matrix for NZVI and it is not expected to participate in As removal in a significant way.

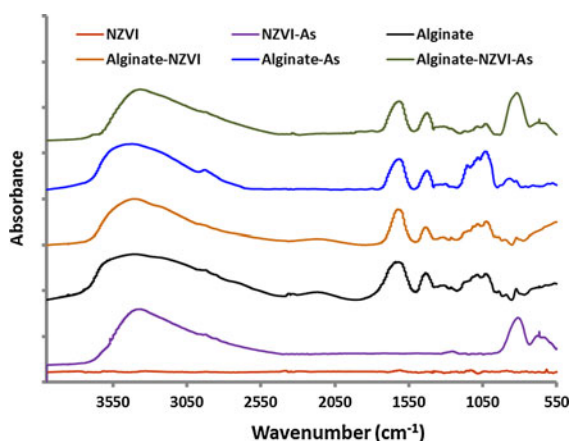


Fig. 5 FT-IR analysis data for (starting from the bottom most plot) bare NZVI with no arsenic (NZVI), NZVI with sorbed arsenic (NZVI-As), Ca-alginate-entrapped NZVI but no arsenic sorbed (Alginate-NZVI), Ca-alginate-entrapped NZVI with sorbed arsenic (Alginate-NZVI-As), Ca-alginate beads with no NZVI entrapped (Alginate), and Ca-alginate beads (no NZVI) with arsenic absorbed (Alginate-As)

Low-concentration arsenic studies

Batch experiment were conducted to find out effectiveness of the Ca-alginate-entrapped NZVI in removing As(V) when present in low concentrations (~ 100 $\mu\text{g L}^{-1}$ or lower) and in the presence of other ions (Na^+ , Ca^{2+} , Cl^- , and HCO_3^-). The experiments were conducted following the same protocol discussed earlier in this paper. Ca-alginate-entrapped NZVI removed As(V) in DI water from 104 $\mu\text{g L}^{-1}$ initial concentration (C_0) to below instrument detection limit (10 $\mu\text{g L}^{-1}$) in 120 min (90.38 % removal, Fig. 6). Then a calculated amount of NaHCO_3 was added to the As(V) solution to prepare 10 mM solutions of NaHCO_3 and batch studies were conducted using Ca-alginate-entrapped NZVI. Control experiments were carried out with blank alginate beads (no NZVI). Na^+ and HCO_3^- did not affect arsenic removal by entrapped NZVI. The experiments were repeated for 10 mM CaCl_2 and it was found that neither Ca^{2+} nor Cl^- interfered in As(V) removal (90.38 % removal from 104 $\mu\text{g L}^{-1}$ to below detection limit). To find out the effectiveness of the alginate-NZVI beads under actual groundwater conditions water was collected from a

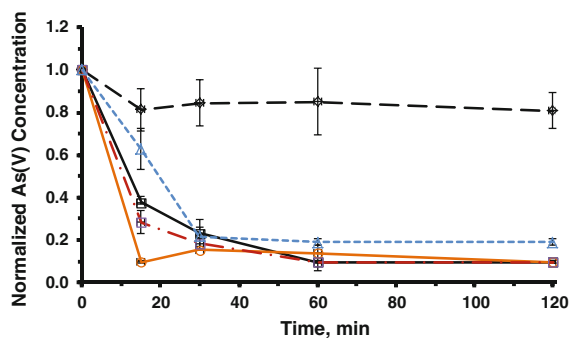


Fig. 6 As(V) removal by Ca-alginate-entrapped NZVI when arsenic is present in low concentrations. The normalized concentration is calculated as the fraction of initial As(V) remaining over time (C_t/C_0). Average C_0 for the groundwater sample (Well 50, $\text{---}\blacktriangle\text{---}$) was ~ 50 $\mu\text{g L}^{-1}$ (actual average concentration was 53 $\mu\text{g L}^{-1}$) and C_0 for the rest of the samples was ~ 100 $\mu\text{g L}^{-1}$ (actual average 104 $\mu\text{g L}^{-1}$) As(V) solution (~ 100 $\mu\text{g L}^{-1}$) with (1) CaCl_2 (CaCl_2 100, 10 mM CaCl_2 , $\text{---}\circ\text{---}$); (2) NaHCO_3 (NaHCO_3 100, 10 mM NaHCO_3 , $\text{---}\square\text{---}$); (3) As(V) in DI water (DI 50, $\text{---}\blacksquare\text{---}$); and control (blank alginate beads with no NZVI entrapped, Control 100, $\text{---}\blacklozenge\text{---}$) were tested. Any As(V) concentration below the instrument detection limit (10 $\mu\text{g L}^{-1}$) is represented as 10 $\mu\text{g L}^{-1}$. The straight lines joining the data points are for ease of reading only and do not represent trend lines. The vertical error bars indicate \pm standard deviations. (Color figure online)

City of Moorhead (MN) extraction well. The well water was reported to contain arsenic above the MCL ($10 \mu\text{g L}^{-1}$). However, no arsenic was detected in the samples and so experiments were conducted by spiking the groundwater with As(V) to have a C_0 of $\sim 50 \mu\text{g L}^{-1}$ (actual initial average value, $C_{0,\text{Act}} = 53 \mu\text{g L}^{-1}$). Ca–alginate-entrapped NZVI removed As(V) to below detection limit within 60 min (81.01 % removal). The experiments done with low As(V) concentrations show that the present technology is effective in removing arsenic from geochemically complex water. The mechanism of arsenic removal by NZVI is a combination of sorption and reduction and it was feared that the sorbed arsenic may become available in drinking water if iron leaches out of the alginate beads. The iron content was monitored in the bulk water during all batch experiments involving low-concentration arsenic. Iron was not detected (instrument detection limit $7 \mu\text{g L}^{-1}$) in the samples indicating no leaching of entrapped NZVI from the beads.

Conclusions

Ca–alginate-entrapped NZVI removed ~ 85 – 100 % aqueous arsenic ($50 \mu\text{g L}^{-1}$ – 10mg L^{-1}) within 2 h. While the reaction kinetics differs between bare and entrapped NZVI, the overall reductions of arsenic are comparable. Surface area-normalized arsenic (1 – 10mg L^{-1}) reduction reaction rate constants for bare and entrapped NZVI [1 – 10mg L^{-1} As(V)] were 3.40 – 5.96×10^{-3} and 3.92 – $4.43 \times 10^{-3} \text{L m}^{-2} \text{min}^{-1}$, respectively. The results indicate that entrapment of NZVI in Ca–alginate does not reduce reactivity of the nanoparticles. Low arsenic concentration (~ 50 – $100 \mu\text{g L}^{-1}$) studies indicated that alginate-entrapped NZVI can effectively remove arsenic from actual groundwater to below instrument detection limit ($10 \mu\text{g L}^{-1}$). FT-IR analysis indicated that arsenic does not bind with Ca–alginate but only with iron.

Environmental significance

The NZVI particles were used by others (Kanel et al. 2006) for arsenic removal in laboratory experiments. However, there was no easy way to use the nanoparticles for drinking water arsenic removal as it would be

difficult to remove the particles from the solution and, thus, keeping the contaminant in the solution itself. By immobilizing the NZVI particles in alginate, it will be easier to retrieve them from solutions and dispose the nanoparticles in a safer way. Ca–alginate is an excellent choice for entrapment as it is non-toxic and has little solubility in water. That iron did not leach out from the beads during the batch studies again indicates that alginate reduces the mobility of the NZVI particles and, thus, making it a safer technology. While the present work has proved the feasibility of the technology, additional column studies and determination of useful life of the alginate-entrapped NZVI will be necessary to finally use the technology in actual drinking water treatment.

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Conflict of Interests The authors declare no competing financial interest.

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