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RESEARCH PAPER

Encapsulation of iron nanoparticles in alginate biopolymer for trichloroethylene remediation

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Abstract Nanoscale zero-valent iron (NZVI) particles (10–90 nm) were encapsulated in biodegradable calcium-alginate capsules for the first time for application in environmental remediation. Encapsulation is expected to offers distinct advances over entrapment. Trichloroethylene (TCE) degradation was 89–91% in 2 h, and the reaction followed pseudo first order kinetics for encapsulated NZVI systems with an observed reaction rate constant (k_{obs}) of 1.92–3.23 $\times$ 10^{-2} min^{-1} and a surface normalized reaction rate constant (k_{sa}) of 1.02–1.72 $\times$ 10^{-3} L m^{-2} min^{-1}. TCE degradation reaction rates for encapsulated and bare NZVI were similar indicating no adverse affects of encapsulation on degradation kinetics. The shelf-life of encapsulated NZVI was found to be four months with little decrease in TCE removal efficiency.

Keywords Nanoscale zero-valent iron (NZVI) · Encapsulated NZVI · Trichloroethylene (TCE) · Calcium-alginate · Biopolymer · Environmental remediation

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Introduction

Nanoscale zero-valent iron (NZVI) particles have been used to remediate a wide range of groundwater contaminants including chlorinated compounds (Liu and Lowry 2006), pesticides (Bezbaruah et al. 2009b; Joo and Zhao 2008), heavy metals (Alowitz and Scherer 2002), and explosives (Gregory et al. 2004). NZVI particles are ideal for the degradation of environmental contaminants because of their environment friendly nature, high reactivity, and low cost (Zhang 2003). The mode of degradation by which the NZVI breaks down such contaminants is reductive dehalogenation and sorption (Matheson and Tratnyek 1994). The small sized (<100 nm) NZVI particles have very high reactive surface area (25–54 m^2 g^{-1}) (Bezbaruah et al. 2009a; Liu and Lowry 2006), and that makes them highly efficient for contaminated water remediation. However, NZVI particles are highly mobile in the aquifer or they settle down into the aquifer pores once they agglomerate due to interparticulate magnetic and van der Waals forces (Bezbaruah et al. 2009a). There are also increasing concerns about high mobility of the small nanoparticles and they reaching undesired receptors including

endemic microorganisms and humans (Phenrat et al. 2009b).

In order to overcome the inherent mobility problem, NZVI can be encapsulated in calcium (Ca) alginate. In encapsulation, particles are put inside hollow Ca-alginate capsules without individually restraining them. Encapsulation ensures that the particles do not come out of the capsules and become mobile. This is in contrast to entrapment (Bezbaruah et al. 2009a) where particles are embedded into a polymer matrix for the same purpose. Encapsulation also needs less alginate as compared beads (from entrapment), and may result in major material savings.

Calcium-alginate is non-toxic, biodegradable, and sparsely soluble in water making it an ideal polymer for use in environmental applications (Bezbaruah et al. 2009a; Chan et al. 2010; Lai et al. 2008). The porous nature of Ca-alginate allows solutes to diffuse and come in contact with the entrapped NZVI (Bezbaruah et al. 2009a; Huang and Zhihui 2002). Results from previous studies indicate that entrapped nanoparticles perform equally well as bare nanoparticles with little change in their reactivity (Bezbaruah et al. 2009a). While entrapment has been tried for environmental remediation (Bayramoğlu and Arica 2009; Bezbaruah et al. 2009a; Bleve et al. 2011; Hill and Khan 2008; Lin et al. 2005; Önal et al. 2007; Pramanik et al. 2011), encapsulation has not been reported as a possible remediation technique. Encapsulation is expected to ensure better contacts between contaminants and encapsulated nanoparticles. In addition successful encapsulation of NZVI is expected to lead to the development of more effective and robust environmental remediation techniques involving co-encapsulation of nanoparticles, microorganisms, and/or enzymes.

The objective of this paper is to examine the effectiveness of the encapsulated iron nanoparticles for aqueous contaminant remediation with TCE as the test contaminant. Comparisons between TCE remediation by bare and encapsulated NZVI were made to see if the NZVI particles lose their reactivity due to encapsulation. Diffusion studies were performed to check whether Ca-alginate creates any additional mass transfer resistance for contaminant diffusion. Shelf-life studies were conducted for the encapsulated NZVI to know if the particles lose their reactivity upon storage and during transport.

Materials and methods

Chemicals and reagents

Calcium chloride ($CaCl_2$, ACS grade, BDH), sodium-alginate (production grade, Pfaltz & Bauer), methanol (production grade, BDH), maltodextrin (food grade, Aldrich), and trichloroethylene (TCE, ACS Grade, 99.5% pure) were used as received.

Synthesis of NZVI

NZVI particles were synthesized using the borohydride reduction of ferrous iron and passivation technique reported by others (Eq. 1, Bezbaruah et al. 2009a; Liu and Lowry 2006).

$$2Fe^{2+} + BH_4^- + 3H_2O \rightarrow 2Fe^0 \downarrow + H_2BO_3^- + 4H^+ + 2H_2 \quad (1)$$

Preparation of alginate capsules and characterization

A sodium (Na)-alginate solution was prepared by dissolving 10 g of Na-alginate in 1 L of de-ionized (DI) water. Alginate capsules were made using a variable flow mini-pump (VWR, 0.1 mm ID tubing, 1.5 mL min^{-1} flow rate). $CaCl_2$ (0.25 g) and maltodextrin (4.0 g) were dissolved in DI water (6 mL). Maltodextrin was added to control the viscosity and obtain spherical shape of capsules (Tanriseven and Doan 2001). Fifty milliliters of the Na-alginate solution (10 g L^{-1}) was transferred to a 250 mL glass beaker and continuously stirred at 600 rpm using a magnetic stirrer. The $CaCl_2$/maltodextrin mixture was then pumped dropwise into the Na-alginate solution from a height of 6 cm from the solution surface (Fig. 1). Capsules were formed as soon as the $CaCl_2$/maltodextrin mixture hit the stirred alginate solution. The capsules formed were continuously stirred in the Na-alginate solution for $\sim$10 min and rinsed several times using DI water. They were then transferred into a 2% $CaCl_2$ solution for 30 min with constant stirring. The resulting capsules were allowed to harden in a 2% $CaCl_2$ solution for 6 h before being used in batch studies. To store the capsules for longer time, 2% $CaCl_2$ was used. All procedures were carried out at room temperature (22 $\pm$ 2 °C). To know the number of capsules synthesized in each batch, the capsules formed during the synthesis of 10 different batches

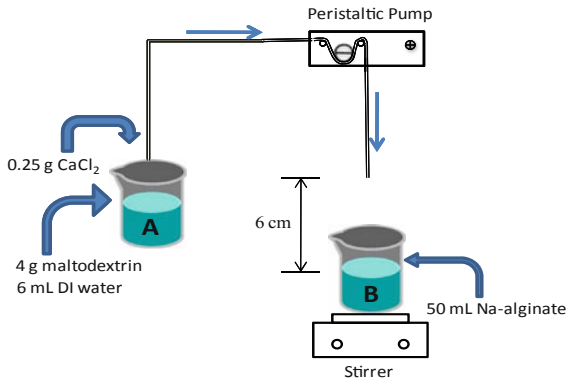

Fig. 1 Schematic of Ca-alginate capsule preparation process. For NZVI encapsulation, 30 mg NZVI particles were added to the solution in beaker A and deoxygenated solutions were used

were manually counted and the results were averaged. The diameter and skin thickness of the capsules were measured using a vernier caliper for a number of capsules ($n = 25$) from different batches and the average value is reported.

Encapsulation of iron nanoparticles

Encapsulation of NZVI in Ca-alginate was done following the capsule preparation method described earlier. The $CaCl_2$ (0.25 g) and maltodextrin (4.0 g) were mixed with 30 mg of NZVI in 6 mL deoxygenated DI water, and the mixture was stirred to ensure homogeneity. The alginate–maltodextrin–NZVI mixture was then purged with N_2 gas (ultra high purity grade) for $\sim$20 min to remove any air bubbles present before being dropped into the Na-alginate solution.

There were possibilities that NZVI particles might have got attached to the pipes and the pump system, and these particles would not be accounted for in the final results. This NZVI loss during the encapsulation was estimated by flushing the pipes and the pump with copious amount of methanol. The methanol flushed NZVI was collected and dried in the oven for a short period and the NZVI was weighed. This exercise was repeated for five independent batches of encapsulated NZVI and the results were averaged.

Diffusion studies

Diffusion studies were conducted in reactors (40 mL amber glass vials) with 25 mL TCE solution (30 and 40 mg L^{-1}) and 300 alginate capsules without NZVI. The reactor caps were fitted with a Teflon septum seal to avoid possible sorption by the plastic caps. The diffusion of TCE from the bulk solution into the capsules was monitored over time. The reactors were shaken in a custom-made end-over-end rotary shaker (28 rpm) to reduce mass transfer resistance. Aliquots (40 μL) of bulk solution were collected at 0, 5, 15, 30, 45, 60, 90, and 120 min and analyzed for TCE. All experiments were performed in triplicates and average values are reported.

TCE degradation studies

Batch TCE degradation experiments were conducted with bare and encapsulated NZVI at room temperature in 40 mL amber glass vials (reactors) fitted with Teflon septum. Deoxygenated TCE solution (25 mL) of specific concentration (1, 10, 30, and 40 mg L^{-1}) was used in each reactor along with a definite amount of encapsulated NZVI (30 mg NZVI). The reactor headspace was purged with N_2 gas. All the reactors were rotated end-over-end at 28 rpm in the custom-made rotary shaker. Experiments with (a) only TCE (blank), (b) alginate capsules (with no NZVI) and TCE (control), (c) bare NZVI (not encapsulated) and TCE, and (d) encapsulated NZVI and TCE were conducted. Samples were withdrawn at 0, 5, 15, 30, 45, 60, 90, and 120 min, and then analyzed for TCE. All experiments were performed in triplicates and average values are reported.

Shelf-life studies

Shelf-life study was conducted for the encapsulated NZVI for a 6-month period. NZVI particles were synthesized in a single batch ($\sim$3 g) and encapsulated in Ca-alginate (30 mg NZVI in each batch of capsules). Each batch of encapsulated NZVI was stored in a 45-mL vial containing 2% $CaCl_2$ (made with deoxygenated DI water). The vials were purged with N_2 gas and closed air tight to prevent possible NZVI oxidation. The vials were wrapped in aluminum foils to prevent any possible photo reactions and stored in a cabinet at room temperature. At least two sacrificial vials were taken out every month and TCE (initial concentration 30 mg L^{-1}) degradation batch studies were conducted using the encapsulated NZVI as described earlier (see "TCE degradation studies").

Analytical methods

A gas chromatography (GC, Agilent 6890A PLUS with a capillary column, HP-5MS, 30 m long, and 0.25 mm inner diameter) and mass selective detector (Agilent 5973 Network) coupled with a purge and trap auto sampler system (Tekmar–Dohrmann trap concentrator with Tekmar 2016 autosampler) was used for TCE analysis (APHA et al. 2005; USEPA 1992). The samples were purged with helium gas at a flow rate of 35 mL min^{-1} for 11 min at ambient temperature after they were loaded into the purge and trap concentrator. Desorption of the trapped sample components was done by heating the trap column at 225 °C for 2 min. The purge and trap concentrator was in a bake mode between the analyses of samples for 6 min at 270 °C. For GC, the carrier and split gases (Helium in both cases) had a flow rate of 1.5 and 28 mL min^{-1}, respectively. The analyses were performed with an initial oven temperature of 40 °C for 1 min, followed by ramping up at 5 °C min^{-1} to 45 °C, 8 °C min^{-1} to 125 °C, and 25 °C min^{-1} to a final temperature of 180 °C where it was held for 1 min. The injector and detector temperatures were 250 and 275 °C, respectively. A five-point TCE calibration was performed with 5–50 μg L^{-1} standards ($R^2 = 0.9794$). The method detection limit for TCE was ~0.2 μg L^{-1}. The internal standard was fluorobenzene and a response factor method was used for the calibration and estimation of TCE in the samples.

Statistical analysis

Standard deviations for results were calculated and have been reported in this paper. Two-way ANOVA was used to determine whether there is any significant difference between the reaction rates of bare and encapsulated NZVI for TCE removal. Statistical analyses were performed using Minitab software.

Results and discussions

NZVI characteristics

NZVI synthesized (Fig. 2a–c) in the laboratory had a size <100 nm (average size 35 nm) and an average BET surface area of 25 m^2 g^{-1}. The synthesized particles were black in color (Fig. 2a) and majority of them were ≤50 nm (Fig. 2b). Transmission electron microscope (TEM) image (Fig. 2c) showed the particles as clustered chains.

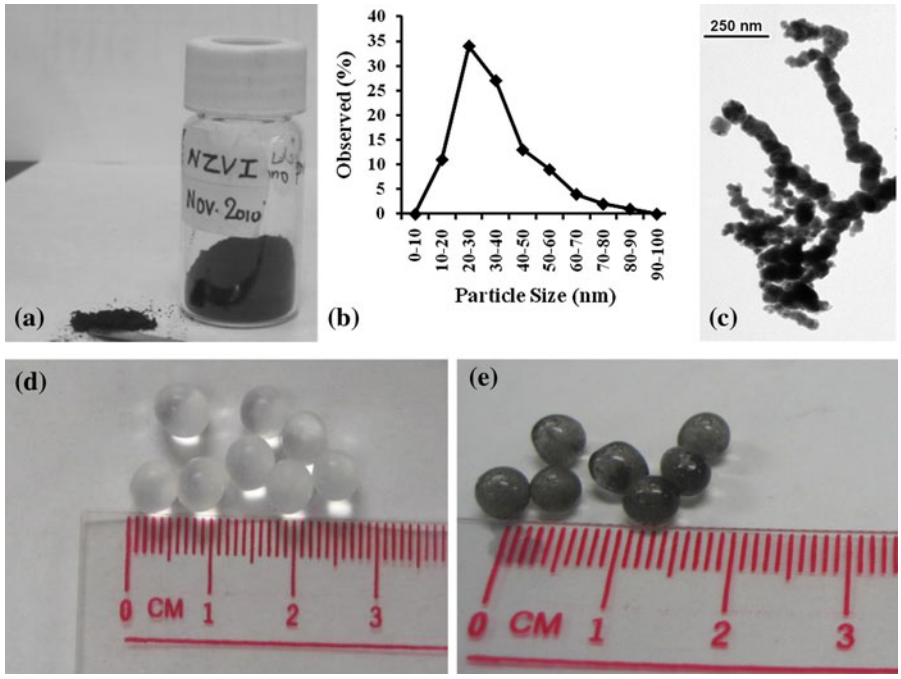

Fig. 2 **a** NZVI synthesized in the laboratory; **b** NZVI particle size distribution. The particle size distribution (average ~35 nm) was determined by measuring individual particles in TEM images ($n = 200$); **c** TEM image of clustered NZVI particles; **d** bare Ca-alginate capsules (without NZVI); and **e** NZVI encapsulated in Ca-alginate. Average capsule size = 3.96 mm

Calcium-alginate capsule characteristics

Alginate capsules (Fig. 2d, e) were successfully prepared in the laboratory and had an average diameter of 3.96 ± 0.01 mm (average of 25 capsules from 5 batches) and skin thickness of 0.2736 ± 0.0036 mm. It is important to have skin as thin as possible to reduce contaminant mass transfer resistance during diffusion and materials used. Capsule diameter of ~2.96 mm and skin thickness of ~0.11 mm have been reported by other researchers (Wang et al. 2010). Literature indicates that the concentration of Na-alginate influences the characteristics of the capsules as Ca-alginate gel formation depends on the cross-linking between alginate from Na-alginate and Ca^{2+} from $CaCl_2$ (Augst et al. 2006). In this study different concentrations of Na-alginate (i.e., 4, 6, 8, 10, and 12 g L^{-1}) were tried to obtain the optimum capsules characteristics which include small diameter, thin membrane, ease of capsule preparation, and effective NZVI particle retention. A 10 g L^{-1} of Na-alginate was found to be the optimum concentration for capsule preparation. It is worth noting that $CaCl_2$ used in capsule formation remained inside the capsules, and possibly helped in better hardening of the capsules (Aksu et al. 2002; Garbayo et al. 2002).

The stirring speed of the Na-alginate solution and dropping height of $CaCl_2$–maltodextrin–NZVI mixture (onto the stirred Na-alginate solution) also influenced the shape and size of the capsules formed. A stirring speed of 600 rpm and 6 cm dropping height from the solution surface were selected as the optimal values for capsule formation based on a number of trials (data not shown).

During NZVI encapsulation, there was negligible loss (~0.15%) of NZVI. A very small number of particles were stuck in the tubing and the beaker.

Diffusion studies

During the diffusion studies conducted with bulk TCE concentrations of 30 and 40 mg L^{-1}, the TCE concentration in bulk solution decreased gradually and leveled off within ~60 min to attain equilibrium (Fig. 3a, b). It can be inferred from the results from the diffusion studies that there was no major mass transfer resistance for contaminant diffusion through Ca-alginate. The diffusion characteristics observed within this research are comparable with similar

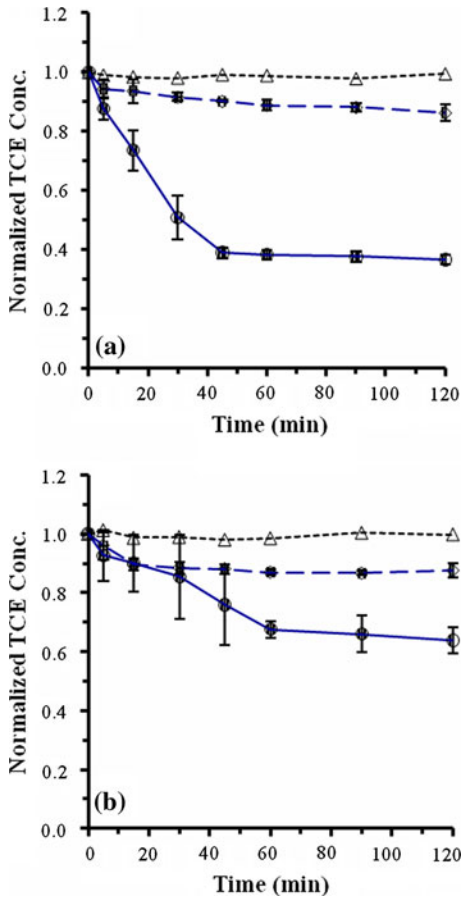

Fig. 3 TCE diffusion characteristics for the Ca-alginate capsules: **a** initial TCE concentration = 30 mg L^{-1}; **b** initial TCE concentration = 40 mg L^{-1}. *Triangle*, blank (only TCE solution), *diamond*, TCE solution with capsule skins; and *circle*, Ca-alginate capsules in TCE solution. The *vertical error bars* indicate ± standard deviations. The data points are joined by *straight lines* for ease of reading only and they do not represent any trend

results obtained by others (Garbayo et al. 2002; Lu et al. 2005; Srimornsak and Sungthongjeen 2007; Wang et al. 2011). While TCE is a low molecular weight (MW 131.5) non-polar compound, there are reports of effective diffusion of polar and other non-polar compounds with a wide range of MW through Ca-alginate capsule (Wang et al. 2011) and beads (Lu et al. 2005; Westrin and Axelsson 1991). Diffusion of Vitamin B_{12} (MW 1355.37) through Ca-alginate has been reported by Wang et al. (2011). Nicotinamide adenine dinucleotide (NADH, MW 709.4) diffused from the bulk solution into Ca-alginate beads and attained equilibrium in ~30 min (Lu et al. 2005).

The controls run with only the capsule skins did show a small initial decrease in bulk TCE concentration, but no further decrease was observed. Similar decreases were reported by others (Bezbaruah et al. 2009a; Hill and Khan 2008) and have been attributed to physical sorption by Ca-alginate.

Diffusion into Ca-alginate (beads) has been reported to be a function of the residence time (for hardening) of the beads in the $CaCl_2$ solution. Diffusion can be optimized with a long enough residence time in the solution (Garbayo et al. 2002). A 6-h residence time was used in this study to ensure proper hardening and, hence, contaminant diffusion into the alginate capsules.

TCE degradation

The encapsulated NZVI removed 89–91% of TCE in a 2-h period during the batch experiments. Bare NZVI also showed similar decrease (88–90%) over the same time period (Fig. 4a–d). The pH was not adjusted during the experiment and the pH of the bulk solution changed from 6.4 to 8.9 during the 2-h period (Fig. 4e). These results suggest that the encapsulated iron performed similar to bare NZVI. Comparable TCE degradation efficiencies with bare and encapsulated NZVI indicate that Ca-alginate did not create a barrier for contaminant transport. The controls (capsules with no NZVI) did not show any marked TCE decrease

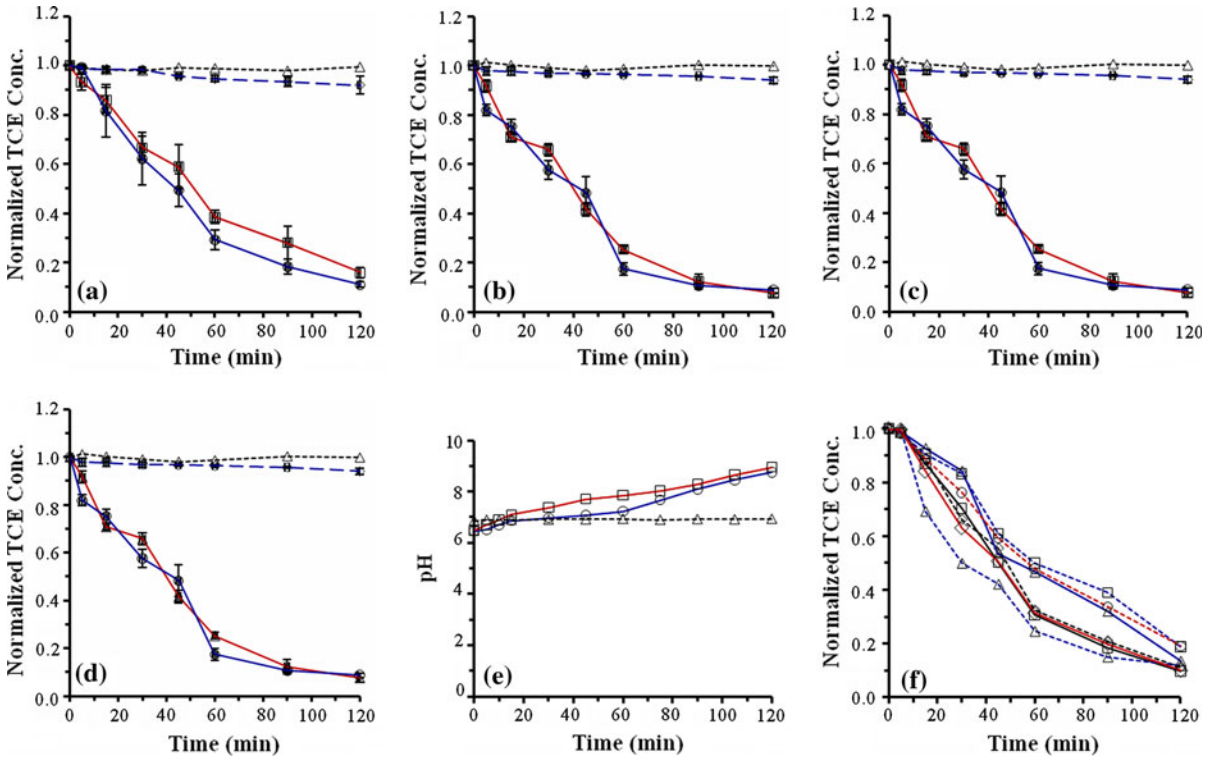

Fig. 4 **a–d** Reduction of TCE by bare and encapsulated NZVI over time. **a** The initial TCE concentration was 40 mg L^{-1}; **b** initial TCE concentration was 30 mg L^{-1}; **c** the initial TCE concentration was 10 mg L^{-1}; **d** the initial TCE concentration was 1 mg L^{-1} **e** representative pH trend during TCE degradation. The pH plot for 30 mg TCE L^{-1} is shown here. *Triangle over dashed line* TCE solution, *diamond over dashed line* TCE solution with capsule skin, *square over continuous line* TCE + Bare NZVI, *circle over continuous line* TCE + Encapsulated NZVI. The *vertical error bars* indicate ± standard deviations. **f** Reduction of TCE by encapsulated NZVI system over a time span of 6 months (shelf-life study). *Diamond over continuous line* month 0, *diamond over dashed line* month 1, *square over continuous line* month 2, *triangle over dashed line* month 3, *triangle over continuous line* month 4, *square over dashed line* month 5, *circle over dashed line* month 6. The data points are joined by *straight lines* for ease of reading only and they do not represent any trend

except a minor reduction (compared to the blank) possibly due to physical adsorption onto the Ca-alginate (Bezbaruah et al. 2009a; Hill and Khan 2008). Results obtained by Kim et al. (2010) indicate ~60% reduction in TCE with NZVI immobilized along with powdered activated carbon (PAC) in alginate beads. Kim et al. (2010) also reported entrapment NZVI and palladium (Pd) in alginate beads and achieved ~99.8% TCE removal. TCE removal efficiency in this study without PAC or Pd was ~90%.

TCE degradation kinetics

TCE degradation by both bare and encapsulated NZVI has been found to follow pseudo first order kinetics (Table 1). The observed reaction rate constant (k_{obs}) for the bare NZVI system was found to be 1.53–2.92 $\times$ 10^{-2} min^{-1}. The value of k_{obs} ranged from 1.92 to 3.23 $\times$ 10^{-2} min^{-1} for the encapsulated system. Statistical analyses (two-way ANOVA) indicate that there is no significant difference between the TCE degradation reaction rate constants when bare and encapsulated NZVI particles were used ($\alpha = 0.005$, $P = 0.211$). The reactions are known to be surface area controlled in NZVI, and it is, therefore, prudent to normalize the reaction rate constants to the NZVI surface area used/unit volume of treated water (Matheson and Tratnyek 1994; Thompson et al. 2010). Surface normalized reaction rate, k_{sa} (Eq. 2, Johnson et al. 1996), for bare and encapsulated NZVI are presented in Table 1 and compared with results reported by others in Table 2.

$$dC/dt = -k_{sa}\rho_{np}C \quad (2)$$

where dC/dt is the reaction rate (mg L^{-1} min^{-1}), k_{sa} is the surface area normalized reaction rate constant

Table 1 Reaction rate constants calculated based on the results obtained during this study

Batch	Initial TCE concentration (mg L^{-1})	Reaction rate constant		R^2
		k_{obs} (10^{-2} min^{-1})	k_{sa} (10^{-3} L m^{-2} min^{-1})	
Bare NZVI	1	2.92	1.6	0.9689
	10	2.35	1.3	0.9801
	30	1.53	0.8	0.9897
	40	2.24	1.2	0.9868
Encapsulated NZVI	1	3.23	1.7	0.9832
	10	2.45	1.3	0.9491
	30	1.92	1.0	0.9921
	40	2.21	1.2	0.9425

Table 2 Comparison of results from the present research with other reported studies on TCE removal with NZVI

Source	Type of NZVI	TCE removal (%)	Reaction rate constant	
			k_{obs} (min^{-1})	k_{sa} (L m^{-2} min^{-1})
He et al. (2010)	NZVI/Pd in CMC	80	2.40 $\times$ 10^{-1}	–
Kim et al. (2010)	NZVI/Pd in alginate beads	99.8	1.01 $\times$ 10^{-1}	1.06 $\times$ 10^{-2}
	NZVI/PAC in alginate beads	~62	–	–
Wang et al. (2010)	Bare NZVI	69.1	1.96 $\times$ 10^{-4}	–
	NZVI in PMMA	62.3	5.67 $\times$ 10^{-5}	–
Liu et al. (2005)	NZVI	100	–	2.33 $\times$ 10^{-4}
Schrick et al. (2002)	Bare NZVI	–	1.5 $\times$ 10^{-3}	3.3 $\times$ 10^{-5}
Wang and Zhang (1997)	Bare NZVI	~100	–	5.0 $\times$ 10^{-5}
Present work	Bare NZVI	88–90	1.53–2.92 $\times$ 10^{-2}	8.16 $\times$ 10^{-4}–1.56 $\times$ 10^{-3}
	NZVI in alginate capsules	89–91	1.92–3.23 $\times$ 10^{-2}	1.02–1.72 $\times$ 10^{-3}

CMC Carboxymethyl cellulose, *Pd* Palladium, *PAC* Powdered activated carbon, *PMMA* Poly (methyl methacrylate)

(L m^{-2} min^{-1}), C is the contaminant concentration (mg L^{-1}), t is time (min), and ρ_{np} is the concentration of iron surface area (m^2 L^{-1}).

Typically NZVI coated with polymers or electrolytes show reduced reaction rates possibly because of reduction in exposed reactive surface area or reduced diffusion through the coatings (Phenrat et al. 2009a; Wang et al. 2010). The results from the present research indicate no significant difference in the values between bare and encapsulated NZVI possibly because the particles are only restrained within the confined space and no surface modification was observed. Such a confinement reduces the mobility of the particles without sacrificing their reactivity and, hence, will be ideal for in situ applications for groundwater remediation (e.g., in permeable reactive barriers). As durability of the capsules and long-term effectiveness of the NZVI are important for such applications, shelf-life studies were conducted.

Shelf-life of NZVI

The NZVI particles are expected to have long shelf-life to be commercially viable. Long shelf-life would ensure that they can be stored for an extended period of time after production, and shipped out to distant remediation sites without the change in their characteristics. Results from the shelf-life study experiments revealed that the efficiency of the encapsulated NZVI for TCE removal did not decrease in the first 4 months (~89% TCE removal) and decreased marginally by 5–7% over the fifth (84%) and the sixth (82%) months (Fig. 4f). The first-order reaction rate constant (k_{obs}) for TCE removal decreased from 1.95 to 1.37×10^{-2} min^{-1} over the 6-month study period. A 4-month shelf-life can be considered to be very good for transportability and storage of the encapsulated NZVI and increases the relevance of the present technique for real world applications.

Conclusions

This study has demonstrated that NZVI particles can be encapsulated in Ca-alginate without significant reduction in their reactivity. The TCE removal using encapsulated NZVI was 89–91% when compared to 88–90% removal using bare NZVI over a 2-h period. The TCE degradation followed pseudo first order kinetics for encapsulated NZVI systems. The shelf-life of the encapsulated NZVI was 4 months within which there was little decrease in its TCE degradation efficiency. The use of Ca-alginate encapsulated NZVI can overcome the mobility and settlement problems associated with bare NZVI and can be a potential technique for in situ remediation of groundwater.

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