Contaminant diffusion and degradation studies with alginate encapsulated iron nanoparticles

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Introduction

Zero-valent iron (Fe^o) nanoparticles (nZVI) are used to remediate a range of groundwater contaminants include chlorinated compounds[1], pesticides.[2, 3] Iron is inexpensive, non-toxic and environmentally compatible for in-situ uses. The reported mode of contaminant degradation by nZVI is reductive dehalogenation.[4] Nanoscale ZVI has certain advantages over other ZVI (microscale ZVI and iron filings). It has a high reactive surface (25-54 m^2g^{-1}) and a small particle size (diameter < 100 nm).[1, 3, 5, 6]

While having high surface is an advantage, being highly reactive makes nZVI nonselective towards contaminants. They react rapidly with surrounding media (water and non target compounds) in the subsurface and significantly lose their reactivity.[7] Because of their small size the particles are mobile and at the same time they agglomerate with each other. The agglomerated particles settle down quickly into subsurface media pores. As such it is difficult to use nZVI in aqueous environment where they are particularly expected to be relatively stationary (for example in permeable reactive barriers). Higher mobility, sedimentation and oxidation by non-target compounds remain as major challenges for wide spread nZVI use in remediation.[6] To overcome these problems, nZVI can be encapsulated within a biocompatible matrix and the encapsulated particles can then be used effectively.

Entrapment in solid calcium (Ca) alginate beads is one of the most common methods for immobilizing living cells in food and beverage industries.[8] Immobilization of cells and enzymes in hollow Ca-alginate capsules is also a common procedure.[9] Most importantly, Ca-alginate entrapped bacterial cells have been used in environmental remediation.[10] Thompson (2008) entrapped nZVI in Ca-alginate beads and successfully demonstrated its effectiveness to degrade contaminants in aqueous solution.[3] The porosity in Ca-alginate allows contaminants to diffuse through the beads and come in contact with the entrapped cells[11] or nZVI.[3]

Alginate is commonly used in entrapment because it is nontoxic, biodegradable, and nonimmunogenic. Sodium (Na) Alginate is extracted from brown algae belonging to Laminariaceae family (e.g., *Macrocystis pyrifera, Laminaria digitata* Lmx., *Laminaria hyperborea*).[12,13] Alginates are block co-polymers composed of D-mannuronic acid (M) and L-guluronic acid (G). Alginates have the ability of forming gels in presence of divalent ions (e.g., Ca^{2+}) and that makes it attractive for use in entrapment. [13]

The objective of this study is to demonstrate that nZVI can be effectively encapsulated in a biopolymer matrix (alginate) without significant reduction in their reactivity towards contaminants when compared with bare nZVI. Calcium alginate hollow capsules were fabricated and optimized for size, membrane thickness and bursting strength. The capsules were analyzed for contaminant diffusion characteristics and degradation studies were conducted.

Experimental

Synthesis of nZVI. Iron nanoparticles were synthesized by borohydride reduction method proposed by Li et al. (2006)[1] and modified by Krajangpan et al (2008)[6] and Thompson (2008).[3]

Preparation of Capsules. Na-alginate solutions (5, 6, 8, 10, 12 and 14 g/L) were prepared using alginate from Sigma. $CaCl_2$ solution containing 0.25g of $CaCl_2$ and 4.0 g of maltodextrin in 6 ml of deionized water was prepared.[14] Malodextrin was used to regulate the viscosity and to ensure spherical shape of the capsule.[9] By using a variable mini flow pump (VWR, 0.1 mm ID tubing, 1.5 mL min^{-1} flow rate) the $CaCl_2$ solution was added drop wise (5.5 cm dropping distance) into a 100 ml of Na-alginate solution in a beaker. The solution was stirred using a magnetic stirrer at 600 rpm. Capsules were formed instantly when $CaCl_2$ solution came in contact with Na-alginate solution. Approximately 30 capsules were formed per minute. The capsules formed were constantly stirred in the Na-alginate solution for ~10 min and rinsed several times using distilled water and transferred into a 2% $CaCl_2$ solution for ~30 min with constant stirring. The resulting capsules were stored in 2% $CaCl_2$. All procedures were carried out at room temperature.

Encapsulation of Iron Nanoparticles. Same procedure was followed as in capsule preparation for nZVI encapsulation expect that all the solutions were purged with N_2 gas (ultra high purity grade) for ~15 min to remove dissolved oxygen (DO). DO removal was necessary to ensure that nZVI do not get oxidized during encapsulation. The $CaCl_2$ was stirred and mixed with 20 mg of nZVI. The mixture was then sonicated, purged with N_2 again, stirred continuously with a glass rod and dropped into 100 ml of deoxygenated Na-alginate solution. Capsules were formed as described in the previous method.

Characterization of Ca-Alginate Capsules. The diameter of the capsules and the membrane thickness were measured manually using a digital vernier caliper. The capsules were dried using filter paper before diameter measurement and ruptured using needle and dried to measure the membrane thickness. The shape and circularity were decided visually. At least 10 capsules were measured to get the average value of each parameter. The bursting force (strength) of the capsule was determined using a Texture Analyzer (TAXt2i Analyzer, USA).[15] A 2 mm probe was gradually pressed onto a capsule placed on the aluminum platform till rupture. 10-15 capsules were busted to get the average value.

Diffusion of Solutions into the Ca-Alginate Capsules. Xylose and alachlor were used in diffusion experiments as substrate. Diffusion experiments were conducted in a 100 ml beaker (reactor). A definite number (400) of capsules were added into the well stirred (300 rpm) 30 ml bulk substrate solution. Different concentrations of xylose ($C_5H_{10}O_5$, MW 150.14) and alachlor ($C_{14}H_{20}ClNO_2$, MW 269.8) were used. The aliquots of 200 μL were withdrawn from the reactor at definite time intervals (0, 5, 10, 15, 20, 25, 30, 60, 120, 240 min). Control experiments were carried out with an equal number of 400 capsule skins. The xylose and alachlor were analyzed using HPLC.

Degradation Experiments. Alachor degradation experiments were conducted in a series of batches. The experiments were performed in a 60 ml vial fitted with teflon septum seal (reactor). The reactor was covered with aluminum foil to prevent possible photo degradation of alachlor. Ca-alginate capsules (400) encapsulated with 20 mg of nZVI were used in 50 ml of 5 mgL^{-1} deoxygenated alachlor in the reactor. The head space of the reactor was purged with nitrogen avoid possible oxygen transfer into the bulk solution. The reactors (triplicates), controls (with capsule skins), and blanks were rotated end-over-end at 28 rpm in a custom made shaker. Aliquots (500 µl) were withdrawn periodically (at 0, 3, 6, 12 h, 1, 2, 3, 4, 6, 8 and 10 days) and filtered using a 0.02 µm pore size syringe filter (Whatman, Anatop 10). All experiments were conducted at room temperature.

Results and Discussion

To optimize the Ca-alginate capsules for size, membrane thickness and bursting strength were determined for capsules made with different Na-alginate concentrations. Concentration of Na-alginate influences the characteristics of the capsules as alginate gel formation depends on cross-linking between Na-alginate and $CaCl_2$.[13] When the concentration of Na-alginate was increased, the diameter and membrane thickness also increased (**Table 1**). The increase in concentration of Na-alginate increases the Ca^{2+} binding sites and better capsules are formed. At lower Na-alginate concentrations relatively slimy and fragile capsules were formed. Again at high Na-alginate concentrations (12 g and 14 g/L) the capsules did not retain the desired spherical shape. Lumps of alginate were formed from the relatively high viscous solution. The capsules with 10 g/L Na-alginate formed and retained good shape. At higher Na-alginate concentrations, better gel formation and hence better membranes were observed. The bursting strength of the capsules increased as the Na-alginate concentration increased (**Table 1**). The bursting force is related to the thickness of the membrane.[16]

Considering the characteristics of the prepared capsules (diameter, membrane thickness and bursting strength), ease of capsule preparation and nZVI retention, we selected 10 g/L of Na-alginate to be the optimum concentration.

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Diffusion Studies. Xylose and alachlor were used as model substrates for diffusion studies. The diffusion of xylose and alachlor from the bulk solution into the capsules was examined. The concentration of xylose (**Figure 1**), and alachlor (**Figure 2**) decreased rapidly just after the addition of the capsules into the bulk solution and slowed down over time. The substrate concentrations started leveling off after ~30 min to reach equilibrium. There was also an initial decrease in substrate concentrations in the controls. Similar decrease was also observed by others and that was attributed to physical adsorption by alginate.[3, 10]

Solutions with different xylose and alachlor concentration behaved in a similar fashion and reached equilibrium state after ~30 min. From the results we can say that our model substrate xylose and alachlor can diffuse freely into the capsules and would be available for degradation within the capsules.

Table 1. Optimization of Ca-alginate Capsules

Alginate Concentration in g/L	Bursting Force in g	Diameter in mm	Membrane thickness in mm	Visual observation
5	114.6±7.076	3.10±0.0611	0.215±0.0137	Slimy
6	118.8±4.915	3.17±0.0156	0.224±0.0035	Slimy
8	127.0±5.325	3.23±0.0076	0.240±0.0223	Slimy
10	169.1±5.577	3.40±0.0055	0.276±0.0036	Best
12	176.2±4.36	3.46±0.0264	0.276±0.0058	Stiff
14	193.4±5.29	3.49±0.0100	0.288±0.0045	Stiff

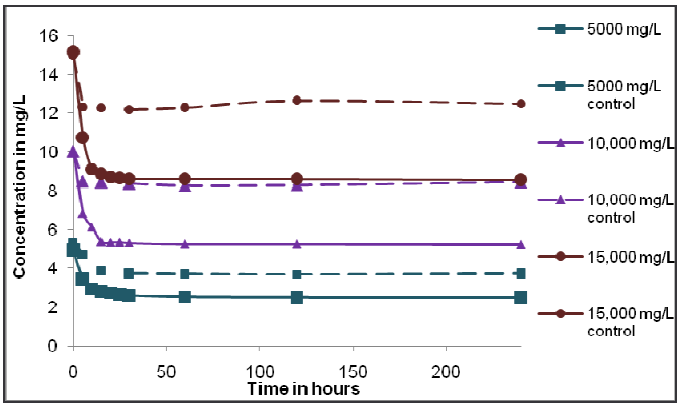

Figure 1. Data for Xylose Diffusion Studies

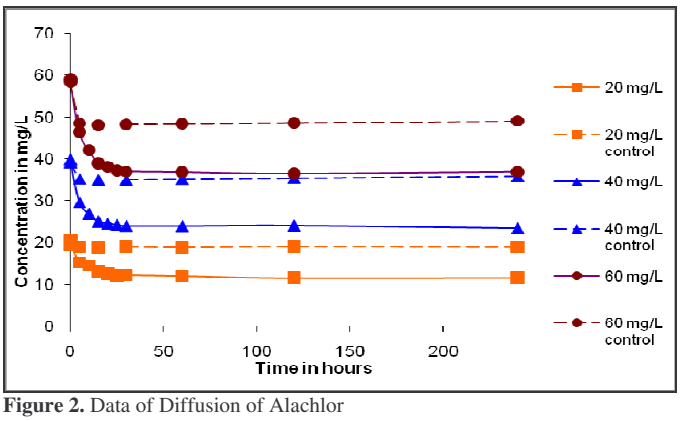

Figure 2. Data of Diffusion of Alachlor

Degradation of Alachlor. Bare nZVI decreased alachlor from 4.14 mgL^{-1} to 1.2 mgL^{-1} over a period of 10 days. For the encapsulated nZVI, the decrease was from 4.8 mgL^{-1} to 1.8 mgL^{-1}. The alachlor degradation reaction was found to obey first-order kinetics (**Figure 4**). Comparison degradation data for bare and encapsulated nZVI indicates that there is decrease in degradation rate for the encapsulated nZVI even though it is not significant. Further studies are needed to characterize the encapsulation process and look at corrosion characteristics of the nZVI used.

Figure 3. Encapsulated nZVI in a Ca-alginate Capsule

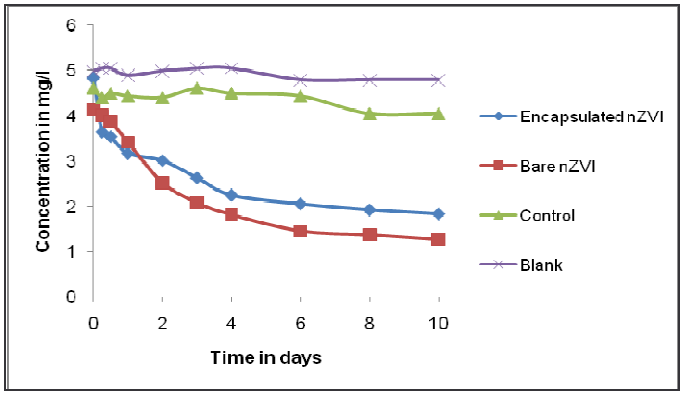

Figure 4: Data from Alachlor Degradation Study

Conclusions

Iron nanoparticles were successfully encapsulated in Ca-alginate capsules. Even though there was some reduction in degradation rate when encapsulated (as compared to bare), encapsulation in Ca-alginate capsules can be used efficiently to retain the nanoparticle in specific locations in the subsurface and hence can possibly be used in permeable reactive barriers.

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