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Nitrate removal from aqueous solution: using zero-valent iron (Fe°) fixed on Ca-alginate bead

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ABSTRACT

Drinking water pollution by nitrate in the world has a major environmental problem. The aim of this study was to investigate the synthesis and entrapment of nanoscale zero-valent iron (nZVI) in Ca-alginate beads for preventing the aggregation of Fe° particles in aqueous solution in order to remove nitrate efficiently. The nZVI with concentrations of 0.5 to 4 g Fe° was immobilized in the alginate bead by applying the barium and ferric ions to replacement of Fe° instead of the cations in the bead. The kinetics of the process was investigated by preparing the nitrate solution in concentrations of 20, 50, 100, 150, and 200 mg/L of NO_3^- at pH 2–10 and retention time 15–90 min. Nitrate removal efficiency by Fe°/Ca-alginate column was between 58% and 98% at retention time 90 min. Nitrate removal efficiency at pH 10 was 62% and also the removal efficiency at pH 4 was about 90%. The reduction capacity for nitrate has been increased with increasing time and nZVI dosage, while it decreased with increasing the nitrate concentrations and pH. This study results showed that the use of nZVI entrapped in Ca-alginate beads can be applied for in situ remediation of nitrate.

Keywords: Calcium alginate; Nanoscale zero-valent iron; Nitrate

1. Introduction

The concentration of nitrate in groundwater supplies has been increased over the past three decades [1]. The high nitrate concentration in groundwater supplies was associated with fertilizers and organic waste materials used [1]. Consumption of drinking water containing nitrate might lead to an acute fatal disease in infant called methemoglobinemia through oxygen deprivation by nitrite ions, which are formed by the reduction of nitrate inside the gastrointestinal tract [2]. Several other adverse health effects related to the high levels of nitrate in drinking waters have been reported such as cancers, birth defects, eutrophication, hypoxia and promoting algae growth in water bodies (algae bloom) [2]. To prevent these adverse health effects, the environmental protection agency (EPA) has established a maximum contaminant level (MCL) of 10 mg/L for nitrate (as N) in public water systems [3]. There are different methods available for removing nitrate from the water (e.g., adsorption, electrodialysis, ion exchange, reverse osmosis) [4]. The applications of these methods in large scale are very expensive since they are based on physicochemical properties [5]. Recently, researchers have paid more attention to the application of nanoscale zero-valent iron (nZVI) [6]. Following using nZVI (Fe°) in-situ groundwater supplies, it will remove nitrate and also several other water pollutants such as chromate, pesticides, heavy metals and chlorinated organics [7,8]. The application of nZVI for the nitrate reduction has been extensively studied [8,9]. The major problems for using nZVI are the agglomeration, rapid oxidation of non-target compounds, and higher mobility [10–12]. To overcome these problems, nZVI has been modified by using several surface stabilizers such as porous media [10,11], clay templates [13], noble

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metals [14,15], and chitosan [16]. Further, using gel materials such as alginate gel have been suggested to remove pollutants from aqueous solution [12,17–19]. The purpose of this study was the synthesis and production of stable nZVI on alginate beads for efficient removal of nitrate from contaminated water.

2. Materials and methods

2.1. Chemicals

Chemicals used in this study include iron chloride ($FeCl_3.6H_2O$), ferrous sulfate ($FeSO_4.7H_2O$), hydrogen peroxide (H_2O_2, 30% by weight), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), potassium nitrate, acetic acid (CH_3COOH), sodium borohydride ($NaBH_4$), methanol and ethanol (30%), calcium chloride and sodium nitrate with 95% purity. All of which were purchased from Merck company, Germany. Additionally, we used sodium alginate (production grade, Pfaltz & Bauer) and maltodextrin (food grade, Sigma-Aldrich, USA).

2.2. Preparation of nano-sized Fe°

Fe° nanoparticles were synthesized with ferrous iron ($FeCl_3.6H_2O$) reduction by borohydride ($NaBH_4$) in 30% ethanol. The borohydride solution ($NaBH_4$, 0.94 M) was slowly added to iron chloride ($FeCl_3.6H_2O$, 0.18 M) with stirring ≈400 rpm at room temperature as following:

$$4Fe\,(H_2O)_6^{3+} + 3BH_4^- + 9H_2O \rightarrow 4\,Fe^{\circ}\downarrow + 3B\,(OH)_3 + 10.5H_2 \tag{1}$$

The synthesized Fe° nanoparticles can be easily separated from the liquid by vacuum filtration through papers filter 0.2 µm. Fe° particles were then washed three times with deionized (DI) water and ethanol and then were dried in a furnace [20]. Freshly prepared Fe° immediately added to the Ca-alginate bead to replace with Ca^{2+} ions.

2.3. Preparation of column

One gram of sodium alginate was dissolved in 50 mL deoxygenated deionized water (2%, w/v). A concentration of 0.5, 1, 2, and 4 g of Fe° added to $CaCl_2$ 3.5% (v/v) and continuously stirred (400 rpm) for 10 min at room temperature (22°C ± 2°C). Maltodextrin was added to control the viscosity and obtain a spherical shape of capsules. Fig. 1(A) shows Fe° replacement with calcium in alginate solutions. To remove deposits of iron in solution, beads were washed with pure water and methanol. The gel beads were retained in the deoxygenated $CaCl_2$ solution for ≈9 h for hardening and then washed with deoxygenated deionized water [21].

A plexiglass column with a diameter of 30 mm and length of 60 cm with four outlets was employed as the column. The column study was also carried out in down flow mode using a Fe°/Ca-alginate bead for treatment of prepared nitrate solution at various times (Fig. 1(B)). The sample was taken from the bottom of the column. Peristaltic pump was used to feed the solution uniformly. The schematic of the process is given in Figs. 1(A) and (B).

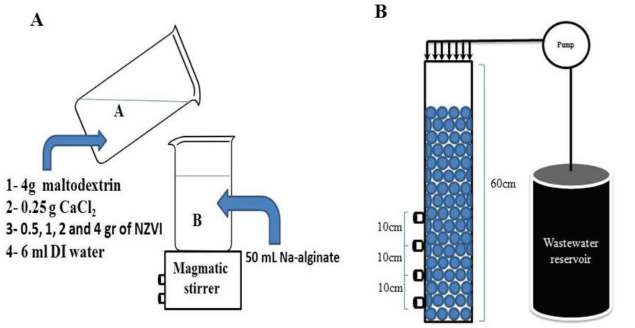

Fig. 1. (A) Preparation of Ca-alginate capsule. (B) The schematic of Ca-alginate column.

2.4. Preparation of nitrate solutions

Different concentrations of nitrate (20, 50, 100, 150, 200, and 300 mg/L) in aqueous solution were prepared by dissolving $NaNO_3$ in deionized water. After filtration of solution, three samples were collected at 15, 30, 45, 60, and 90 min. Then concentration of nitrate was studied.

2.5. Analysis and kinetics of study

The concentrations of nitrate (NO_3^-) and ammonia (NH_4^+) were measured by UV–Vis spectrophotometer (DR5000 model methods 4500, Hach) [22]. Nitrogen (N_2) was analyzed using gas chromatography (Tremetrics Inc., Austin, TX). Sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were used to adjust the pH (pH meter HQ 40d, Hach, USA) of solutions. The removal efficacy of nitrate was calculated by following the formula:

$$\%\ \text{Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

where C_o is the initial concentration of nitrate and C_e is the final concentrations of nitrate.

Scanning electron microscope (SEM) was used in determining the surface morphology of calcium alginate bead (Carl Zeiss, Germany). The particle size distribution was determined by a scanning mobility particle sizer.

The adsorption performance measured through the adsorption kinetics study at an equilibrium condition (pH 4, residence time 90 min, 2 g Fe° on Ca-alginate beads and nitrate concentrations 20 mg/L). The equilibrium adsorption capacity (q_e) of the Fe°/Ca-alginate bead was calculated by the following formula:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{3}$$

where q_e is the adsorption capacity at equilibrium (mg/g), C_o is the initial concentration of nitrate in the solution (mg/L), C_e is the final concentration of nitrate in the solution (mg/L), V is the volume of a nitrate solution (g), and m is the mass of Fe° on Ca-alginate bead (g).

The pseudo-first-order kinetic model was applied as given as follows [23]:

$$q_t = q_e\left[1-\exp\left(-k_1 t\right)\right] \quad (4)$$

where k_1 is the pseudo-first-order kinetic rate constant (1/min). Statistical analysis was performed using STATA software version 12 (STATA Corporation, College Station, TX).

3. Results and discussion

3.1. Characteristics of Fe°/Ca-alginate column

Fe° synthesized in the laboratory had a particle size of less than 100 nm with an average size of 25 nm. Fig. 2 shows SEM images of zero valent iron (Fe°) entrapped on calcium alginate bead.

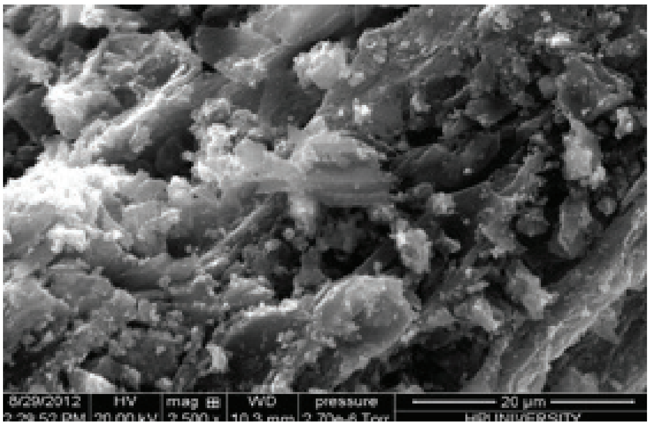

Fig. 2. Scanning electron microscope images of calcium alginate bead with zero valent iron (Fe°).

3.2. Effect of nitrate concentration

The efficiency of nitrate removal by this study was 58%–98% during 90 min (Fig. 3(A)). At Fe° concentration, 2 g on Ca-alginate column and pH 4, the efficiency of nitrate removal at nitrate concentrations of 20, 50, 100, 150, and 200 mg/L were, respectively, 88.5%, 83%, 85%, 78.5%, 82.5%, and 87%. A significant difference was found between different nitrate concentrations and nitrate removal ($p = 0.00$).

3.3. Effect of pH

The synthetic water samples containing 100 mg/L of nitrate were treated at various pHs (2–8), the retention time of 90 min and Fe° of 0.5–2 g/L, on Ca-alginate bead 5%. The effect of pH on nitrate removal by 2 g Fe° on Ca-alginate beads is shown in Fig. 3(B). By decreasing pH, the efficiency of nitrate removal increased. Nitrate removal efficiency at pH 8 was approximately 50%, while at pH 4 reached to 90%.

3.4. Column performance with time

At retention times of 10, 15, 30, 45, 60, and 90 min, and the Fe° concentration 2 g on Ca-alginate column, the nitrate removal efficiency were 87.5%, 89.5%, 83.5%, 92%, and 94.6%, respectively (Fig. 3(C)). The mean percent of N_2 and NH_3^- production in Ca-alginate column at retention time of 90 min were 36% and 42.5%, respectively (Fig. 3(D)).

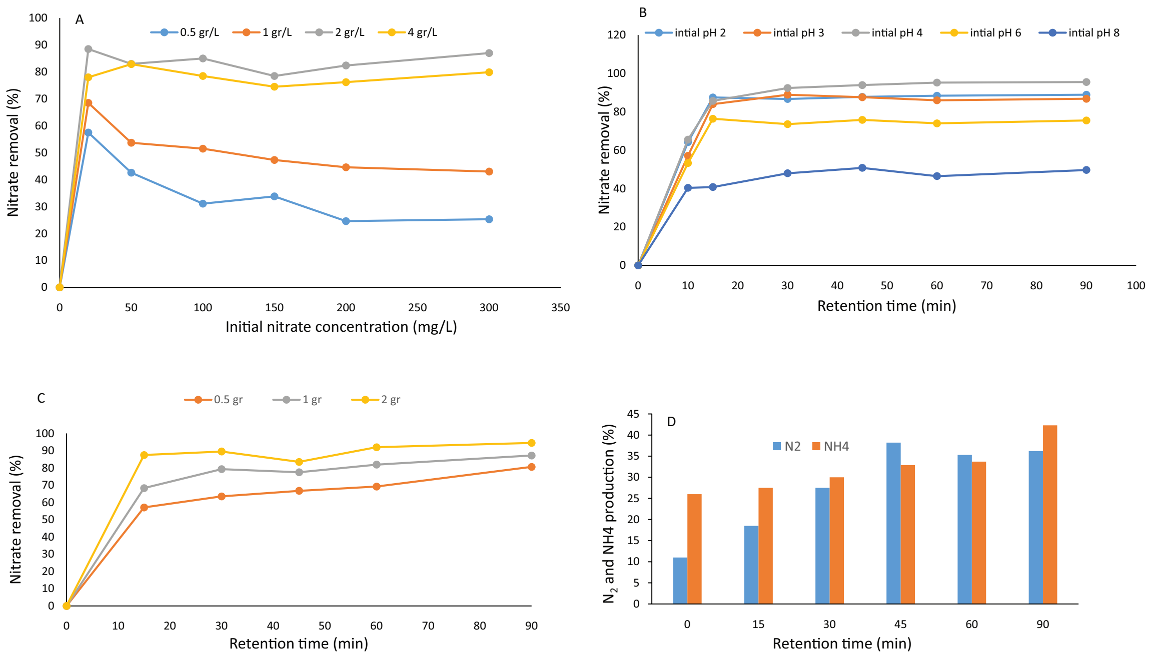

Fig. 3. (A) Nitrate removal (%) as a function of nitrate initial concentration in Fe°/calcium alginate bead with initial pH = 4, residence time 90 min and flow rate = 20 mL/min. (B) Nitrate removal (%) as a function of residence times and pH, with Fe° dosages 2 g, flow rate = 20 mL/min and initial nitrate concentration of 100 mg/L. (C) Nitrate removal efficiency (%) as a function of the residence times (min) at pH 4.0, flow rate = 20 mL/min and initial nitrate concentration of 100 mg/L. (D) N_2 and NH_3^- production (%) as function of the retention time (min) at pH 4.0, Fe° = 2 g and flow rate = 20 mL/min.

Table 1
Linear regression coefficients for nitrate (mg/L) removal by time, pH, and Fe◦ dose

Term	Unstandardized coefficients		Standardized coefficients	*t*	Sig.
	B	Standard error	Beta	–	–
(Constant)	50.5	2.35	–0.043	26.975	0.000
Time	1.851	0.024	–0.325	–4.476	0.005
pH	3.48	0.058	–0.431	–2.179	0.002
Fe◦ dose	–5.45	1.55	–0.024	–3.449	0.000

Table 2
First-order rate constant (*k*) for the NO_3^- reduction in the Fe°/Ca-alginate column

pH	*k* (min⁻¹)	
	Calcium alginate column with Fe◦	Calcium alginate column without Fe◦ as control
4	0.605 ± 0.124	0.021 ± 0.050
6	0.374 ± 0.075	0.021 ± 0.050
8	0.123 ± 0.058	0.021 ± 0.050
10	0.075 ± 0.005	0.021 ± 0.050

3.5. Analysis

The results of multiple linear regression model for nitrate (mg/L) removal by time, pH, and Fe° dose are given in Table 1. Table 2 shows the first-order rate constant (*k*) for a NO_3^- reduction in the Fe°/Ca-alginate column.

4. Discussion

The average removal efficacy of nitrate by Fe°/Ca-alginate columns was 75%, ranged from 58% to 98%. The same result was found by Bezbaruah et al. [24]. In general, lower values of pH had greater removal efficiency of nitrate, and the highest removal efficiency was at pH 4. Kanel et al. [25] found nitrate reduction from solution by Fe° to be inversely related to pH. Huang and Zhang [26] observed more rapid reduction of nitrate by Fe° at pH 4 than pH 8. The nitrate removal efficiency at retention time of 90 min increased from 50% in pH 8 to 94.5% in pH 4. The results of other studies were found to be similar [25–27].

The highest nitrate removal with a dosage of 2 g Fe° was 94.5% at 90 min. To support our result, Chen et al. [28] reported that the treatment of NO_3 solution with 2 gr Fe° completely transformed all nitrate to ammonium in 24 h. Similarly, Han et al. [29] reported that under neutral pH and Fe° dosage of 2 g, the maximum nitrate removal was obtained.

Fe° is thermodynamically unstable in water and causes iron to react with water producing hydrogen gas and hydroxide. The consumption of H^+ through NO_3^- removal is illustrated by Eq. (1). Also, the release of a hydroxyl group and the increase in the pH of solution are illustrated by Eqs. (1) and (2) [26]. The use of buffer compounds such as KH_2PO_4 can lead to better adjustment of the pH and more precipitation of iron compounds [16]. The linkage between nitrate removal and pH can be described by the reaction stoichiometry where 10 mol of protons were consumed for every mole of nitrate converted to ammonium ion [30]:

$$\begin{aligned} &5\,Fe^\circ + 2NO_3^- + 12H^+ \rightarrow 5Fe^{2+} + N_2 + 6H_2O \\ &\quad Fe^\circ \rightarrow Fe^{2+} + 2e^- \qquad E^\circ = -0.44\ V \end{aligned} \tag{5}$$

$$\begin{aligned} &4\,Fe^\circ + NO_3^- + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \\ &\quad Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad E^\circ = -0.77\ V \end{aligned} \tag{6}$$

Fe° takes oxygen from nitrate to reach higher capacities and finally it is converted to the precipitation of iron and ammonia or nitrogen gas [31]. The N_2 and ammonia production increased with retention time. The ammonia did not react with nZVI, and the removal mechanism could be the ammonia stripping followed by nitrate reduction only. Therefore, the pH of the solution was increased during the reaction. Singh et al. [32] hypothesized that iron corrosion by-products (e.g., Fe^{2+}, $Fe(OH)_2$), produced by reactions of Fe° with oxygen, were thermodynamically capable of reducing nitrate to ammonia. Nitrate can be stoichiometrically reduced to ammonium in the presence of iron compounds, and lead to the production of Fe^{2+} as an oxidation by-product [32].

In this study, nitrate was completely converted into ammonium and N_2 over 90 min. The recovery of N_2 was between 3.5% and 13.5% and for ammonium was between 35.5% and 60.6%. The same results reported by Hwang et al. [21,33], and Huang and Zhang [26].

The use of iron compounds to remove nitrates can be suitable when drinking water is contaminated with nitrate. The advantages of utilizing iron compounds include high efficiency, less power consumption, and very simple method.

Some compounds such as chlorides, sulphates, phosphates, citrate, borates, and oxalate ions can act as ligands and subsequently they can interfere with the nitrate removal when only using Fe°. In the present study, these compounds were not associated with nitrate removal when using Fe° fixed on Ca-alginate bead. On the other hand, the application of Fe° fixed in Ca-alginate bead has few disadvantages such as water contaminated with ammonium as well as daily monitoring and evaluation of downstream water.

5. Conclusion

In this study, the synthesis and entrapment of Fe° on Ca-alginate bead was used for preventing the aggregation of Fe° particles in aqueous solution to remove nitrate from groundwater. The reduction capacity for nitrate has been increased with elevated time and Fe° dosage, while it is conversely associated with nitrate concentrations and pH values. Fe°/Ca-alginate column successfully reduced the concentration of nitrate and also NH_4^+ and N_2 produced over the reduction process. As a result, the high nitrate removal capacity suggests that Fe°/Ca-alginate column may be a potential material for in situ remediation of nitrate contaminated water.

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