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Remediation of Cr(VI) contaminated soil by Zero-Valent Iron Nanoparticles (nZVI) entrapped in Calcium Alginate Beads

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Abstract— **Hexavalent Chromium (Cr(VI)) is a potential soil and groundwater contaminant and is considered as a priority pollutant. In the present study zero-valent iron nanoparticles (nZVI) entrapped in calcium alginate beads was investigated as a potential remediation technology for the decontamination of Cr(VI) contaminated soil. Results of batch experiments conducted with varied doses of nZVI entrapped in alginate beads and Cr(VI) spiked soil showed that 1.5 g of nZVI entrapped in alginate beads removes 98% Cr(VI) from spiked soil within a contact time of 60 min. Further studies were carried out to investigate the effect of contact time on reduction of Cr(VI) concentration in spiked soil. Cr(VI) concentration shows an decreasing trend with increasing contact time, indicating an increase in removal rate of Cr(VI) with increasing contact time. Cr(VI) removal percentage shows an increasing trend with increase in contact time and dose of nZVI entrapped in alginate beads. Results of kinetic study reveals that the removal of Cr(VI) by nZVI entrapped in alginate beads follows a pseudo first order kinetics with a kinetic rate constant of 0.53, 1.17 and 1.69 min^{-1} for 0.5, 1.0 and 1.5 g of nZVI entrapped in alginate beads respectively.**

Keywords: Calcium alginate bead; hexavalent chromium; entrapment; remediation; nZVI.

I. INTRODUCTION

Hexavalent Chromium (Cr(VI)) is a potential carcinogen, teratogen, mutagen and is on the top priority list of toxic pollutants defined by USEPA. Contamination of soil with Cr(VI) is a worldwide problem and the remediation of contaminated site has become an environmental challenge. Thus a cost effective, easy to use and environment friendly technique has been sought for the remediation of contaminated sites.

The use of Zero-valent iron nanoparticles (nZVI) has been gaining increasing interest in the area of environmental remediation [1-2]. Transformation of a wide variety of environmental contaminants such as heavy metals, chlorinated hydrocarbons, pesticides, nitrate etc has been extensively documented [3-5]. nZVI is an excellent electron donor and has high capacity to reduce an array of toxicants, however its tendency for rapid oxidation and aggregation, reduces its reactivity. In the present work an attempt has been made to entrap nZVI in an anionic biopolymeric alginate to overcome these problems. Earlier studies have reported the use of calcium alginate beads for the entrapment of metal hydroxides [6], surfactants [7], activated carbon [8], algae [9], bacteria [10] etc. Calcium alginate beads has also been used for the removal of Cr(VI) from aqueous solution with several type of adsorbents such as grape stalks wastes [11], humic acid [12] etc.

The objective of this work is (a) to entrap nZVI in calcium alginate beads and (b) to study the kinetics and removal rate Cr(VI) from Cr(VI) spiked soil.

II. EXPERIMENTS

A. *Synthesis of nZVI*

nZVI was synthesized by adding 1:1 volume ratio of $NaBH_4$ (0.2 M) into $FeCl_3.6H_2O$ (0.05 M) solution. Fe (III) ion was reduced to Fe (0) by borohydrate according to the following eq:

$$4Fe^{3+} + 3BH^{4-} + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2 \quad (1)$$

B. *Preparation of nZVI entrapped in alginate beads*

The method for the preparation of nZVI entrapped in calcium alginate beads was adopted from Papageorgiou et al. [13] with little modification. In brief, desired amount of nZVI was added to 10 ml of 4% (w/v) sodium alginate solution. This mixture was promptly dropped into a 3.5% (v/v) deoxygenated aqueous solution of $CaCl_2$ using a peristaltic pump with continuous stirring to obtain a homogeneous mixture. Finally the beads formed were allowed to harden and then rinsed with distill water. For the preparation of calcium alginate beads without entrapment of nZVI, similar procedure was employed except the addition of nZVI.

C. *Batch Experiments*

Batch experiments were carried out in the laboratory to evaluate the efficacy of nZVI entrapped in alginate beads for the removal of Cr(VI) from spiked soil. Various doses of nZVI entrapped in alginate beads (0.5, 1.0, 1.5 g) were applied on Cr(VI) spiked soil (Cr(VI) initial conc. = 100 μg/g). The reaction mixture was allowed to react for 60 minutes with continuous shaking. After that the mixture was centrifuged and the supernatant was analyzed for residual Cr(VI) by colorimetric technique. To study the trend of Cr(VI) removal with contact time, reaction mixture was taken out at predetermined time interval (15, 30, 45,.....120 min), filtered through 0.22 μm syringe driven micropore filter and then analyzed for Cr(VI). Cr(VI) removal percentage was also calculated using (2).

$$\text{Cr(VI) removal (\%)} = (C_0 - C)/C_0 \times 100 \qquad (2)$$

where C and C_0 (µg/g) is the final and the initial conc. of Cr(VI) in the spiked soil [14]. To determine the reaction kinetics of Cr(VI) removal, various doses of nZVI entrapped in alginate beads (0.5, 1.0, 1.5 g) were added to the spiked soil. At selected time intervals, samples were taken out, filtered and tested for residual Cr(VI).

III. RESULTS AND DISCUSSIONS

Fig 1. shows the effect of varied doses of nZVI entrapped in alginate beads on Cr(VI) concentration in spiked soil. It is clear from the fig. that as the dose increases, Cr(VI) concentration in spiked soil decreases. At 1.5 g dose of entrapped beads Cr(VI) concentration decreases up to 2 µg/g within 60 min. This may be explained by the increase in the reactive sites of nZVI with the increase in the dose. These results are consistent with the results of earlier studies conducted on Cr(VI) reduction by nZVI. Alginate beads without entrapped nZVI did not show any removal under similar reaction condition.

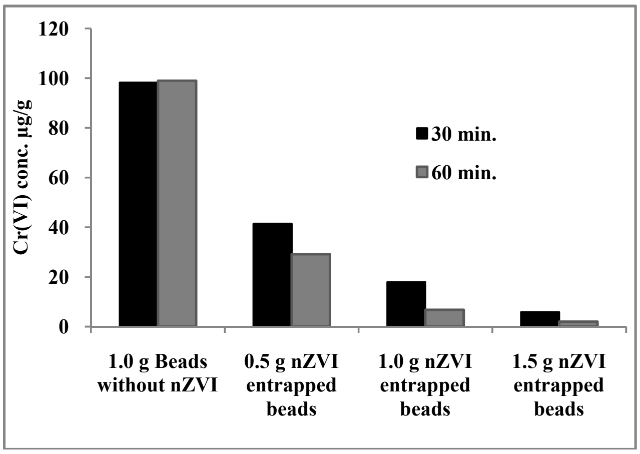

Figure 1. Effect of various doses of nZVI entrapped in alginate beads on Cr(VI) concentration; Cr(VI) initial conc. = 100 µg/g; nZVI entrapped in alginate beads dose = 0.5, 1.0, 1.5 g; reaction period = 60 min.

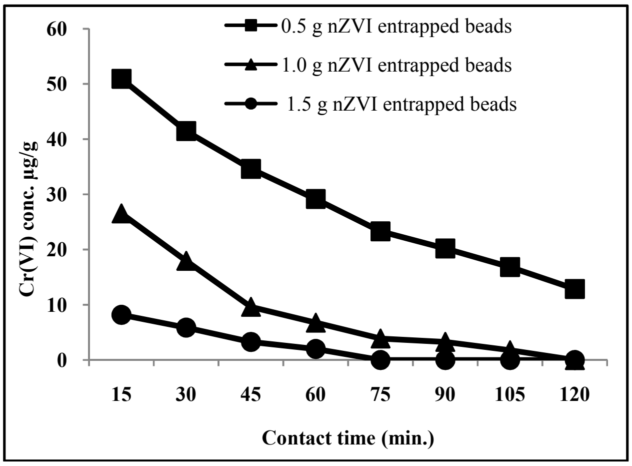

Figure 2. Cr(VI) removal by nZVI entrapped in alginate beads as a function of reaction time; Cr(VI) initial conc. = 100 µg/g; nZVI entrapped in alginate beads dose = 0.5, 1.0, 1.5 g.

The length of contact time between nZVI entrapped in alginate beads and Cr(VI) spiked soil has a significant effect on Cr(VI) removal. Results of the experiments carried out to determine the effect of contact time on Cr(VI) concentration is shown in fig. 2. Cr(VI) concentration shows a decreasing trend with increasing contact time. At a contact time of 75 min., 1.5 g of nZVI entrapped in alginate beads reduces Cr(VI) concentration below detection limit.

Cr(VI) removal percentage is shown in fig. 3. Results showed that 0.5, 1.0 and 1.5 g of nZVI entrapped in alginate beads resulted in 59, 82 and 94% Cr(VI) removal in 30 minutes respectively.

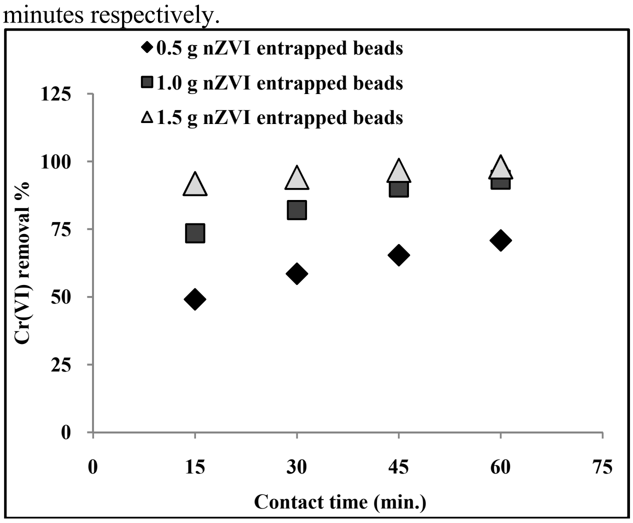

Figure 3. Cr(VI) removal percentage (%); Cr(VI) initial conc. = 100 µg/g; nZVI entrapped in alginate beads dose = 0.5, 1.0, 1.5 g.

However when the reaction period increases from 30 minutes to 60 minutes, percent reduction also increases and reach up to 71, 93 and 98% for 0.5, 1.0 and 1.5 g of nZVI entrapped in alginate beads respectively.

As reported in previous studies [15, 16], reaction rate of nZVI mediated Cr(VI) reduction could be estimated by pseudo first order kinetic equation which is as follows:

$$dC/dt = - k_{obs}C \quad (3)$$

Integration of (3) yields:

$$\ln C/C_0 = - k_{obs}t \quad (4)$$

where C and C_0 are the instantaneous and initial concentration of Cr(VI) in µg/g respectively, 't' is the reaction time in min, and 'k_{obs}' is the kinetic rate constant representing the overall Cr(VI) removal rate (min^{-1}).

Fig. 4. shows the reaction kinetics of nZVI mediated Cr(VI) removal. Analysis of the kinetic data reveals that the overall removal rate of Cr(VI) from soil follows a pseudo-first order kinetic model.

Table 1 shows the value of kinetic rate constant for different doses of nZVI entrapped in alginate beads. Analysis of the data reveals that, the value of kinetic rate constant (k_{obs}) increases from 0.53 to 1.69 min^{-1} as the concentration of nZVI entrapped in alginate beads increases from 0.5 to 1.5 g.

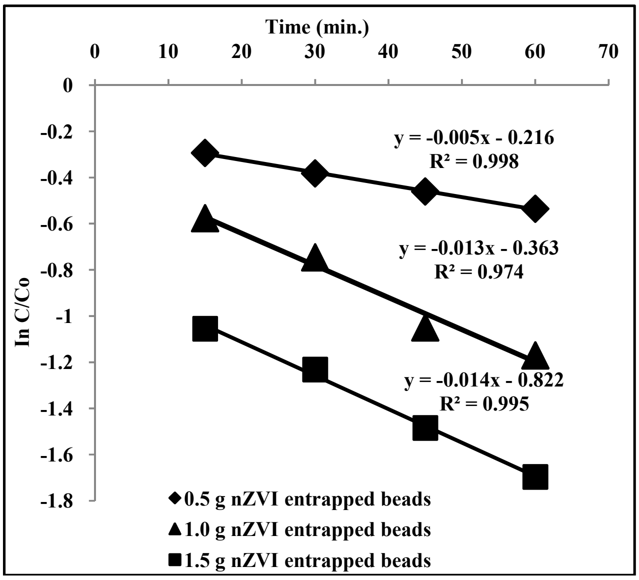

Figure 4. Pseudo first order kinetics for Cr(VI) removal from spiked soil by nZVI entrapped in alginate beads; Cr(VI) initial conc. = 100 µg/g; contact time = 60 min.

TABLE 1. PSEUDO FIRST ORDER RATE CONSTANT (KOBS) FOR CR(VI) REMOVAL FROM SPIKED SOIL USING NZVI ENTRAPPED IN ALGINATE BEADS.

Cr(VI) conc. (µg/g)	nZVI entrapped in alginate beads dose (g)	Pseudo first order kinetics	
		k_{obs}	R^2
100	0.5	0.535	0.998
100	1.0	1.170	0.994
100	1.5	1.696	0.974

Removal of Cr(VI) by zero-valent iron nanoparticle is based on the transformation of Cr(VI) to Cr(III). nZVI has shown high removal capacity and fast reaction kinetics for Cr(VI) reduction which makes it an effective tool for in situ immobilization of Cr(VI) contaminated soil and groundwater. However its high affinity for oxidation and rapid aggregation reduces its overall reactivity. To overcome this drawback, nZVI was entrapped in calcium alginate beads which will provide protection to nZVI from oxidation and aggregation.

Calcium alginate beads have been reported to successfully entrap adsorbents like grape stalks, activated carbon, humic acid, dithionite [17], surfactants etc. for the treatment of organic and inorganic pollutants [6-8, 11, 12]. Alginate immobilized algal and bacterial cells also have been used for the remediation of inorganic contaminants [9, 10]. According to the literature, adsorbents entrapped alginate beads removes Cr(VI) by either of these two processes,

(a) sorption process controlled by mass transfer and intra particle diffusion [11] or
(b) by reduction of Cr(VI) to Cr(III) [17].

In the present work reduction by nZVI is the predominant mechanism for the removal of Cr(VI). Alginate beads without nZVI entrapment have not shown any reduction and adsorption. The results of the work presented here demonstrate the efficacy of the nZVI entrapped in alginate beads for the treatment of contaminated sites.

IV. CONCLUSION

In the present study, nZVI was entrapped in calcium alginate beads and applied on Cr(VI) spiked soil to demonstrate its potential for the remediation of Cr(VI) contaminated soil. Results shows that nZVI entrapped in alginate beads effectively removes Cr(VI) from soil following a pseudo first order kinetics. Cr(VI) concentration decreases with the increase in the contact time and dose of nZVI entrapped in alginate beads. 1.5 g of nZVI entrapped in alginate beads shows 98% removal within 60 min. However additional research will be required in order to optimize the overall process to increase the efficiency of nZVI entrapped in alginate beads for the remediation of Cr(VI) contaminated soil.

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