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Nitrate Removal in Porous Media Using Nanoscale Zero Valent Iron: Column Experiment

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Abstract: *The use of nanoscale zero valent iron (nZVI) as a reactive media in porous media has become a promising technology for contaminants removal from soil and groundwater. Therefore, the main aim of current work is to investigate nitrate removal from water using nZVI in an upflow packed sand column. The effects of one layer, multilayer and different thicknesses of nZVI/sand on nitrate removal were reported in this study. The initial nitrate concentration was 200 mg/L. The distribution of nitrate trapped inside the columns was evaluated by measuring nitrate concentration at various intermediate sampling points along the depth of the column in addition to the column outlet. The results indicated that the best condition to remove nitrate was observed when using single 10-cm high layer of nZVI/sand and more than 97% of influent nitrate was removed.*

Keywords: Nanoscale zero valent iron (nZVI); Porous media; Nitrate removal; Packed sand column.

1. INTRODUCTION

Nitrate contamination of groundwater has become a real environmental and public health alarm worldwide. Nitrate contamination usually originates from chemical fertilizers for agriculture, animal manure, wastewater discharges, fertilizers factories and landfills [1, 2]. Excessive nitrate exposure can cause cancer, methemoglobinemia and blue baby disease in infants due to the potential reduction of nitrate to nitrite [3]. Due to threats of nitrate contamination, World Health Organization (WHO) and many countries restricted the maximum contaminant level (MCL) of nitrate in drinking water to 50 NO₃⁻ mg/L and NO₃⁻-N 10 mg/L, respectively [4, 5].

Several physico-chemical and biological technologies have been proposed for removing nitrate from contaminated water like ion exchange, reverse osmosis, chemical reduction, electrodialysis and biological denitrification [6]. However, these processes are relatively expensive and are often limited due to potential of side effect on water quality [7]. Therefore, there is a need to explore alternatives for resolving the problem of nitrate contaminated sites.

In recent years, zero valent iron (ZVI) has been employed intensively to remediate soil and groundwater contaminants such as As(III), As(V), Cr(VI), Pb, Ni, Cu, Zn, PO₄³⁻ and NO₃⁻. Nano-zero valent iron (nZVI) has shown higher reactivity compared with micro- or milli-sized iron for the effective removal of a wide range of contaminants [8]. The higher surface reactivity of nano-zero valent iron is the result of larger surface area due to small size of particles. In addition, these particles are nontoxic to aquatic organisms, available and cheap [9].

For in situ nitrate treatment from groundwater, permeable reactive barrier (PRB) is one of the well-known technologies owing to their effective operation and maintenance costs. ZVI PRB has been successfully used to remediate groundwater contaminated by nitrate.

Several researches have focused on evaluating the behavior and efficiency of nitrate treatment by ZVI in laboratory scale column. Tehrani et al. [10] investigated nitrate removal using nZVI/Ni particles. They concluded that nitrate remediation was mostly influenced by seepage velocity, freshness and quantity of nZVI/Ni and particle size of porous media and the maximum nitrate removal did not exceed 85% in column experiment.

Huang and Zhang [11] observed that adding certain selected cations (Fe(II), Fe(III), or Al(III)) in feed solution can greatly enhance nitrate reduction and extending hydraulic retention time, increased nitrate removal by Fe⁰ packed columns. Tang et al. [12] indicated that ZVI PRB is a potential technique for in situ remediation of soil and groundwater nitrate contamination in the alkaline conditions.

Hosseini and Tosco [13] assessed nitrate removal in a laboratory bench-scale aquifer system (60 cm length × 40 cm width × 50 cm height) using nZVI and carbon substrates. The results of this study demonstrated that the model has a great possibility for nitrate reduction in-situ contaminated groundwater. Araújo et al. [14] showed that the use of nZVI in PRBs is, indeed, a suitable technique for denitrification with high performance record but the long-term impact of nZVI on the environment and on the human health needs further work.

Westerhoff and James [15] studied removal of nitrate under laboratory and field conditions using ZVI packed columns. They noticed that only 70% of the applied nitrogen was recovered as nitrate, ammonium, or nitrite during short-term column operations and less than 25% of the applied nitrogen was recovered during long-term column tests. They also reported that a pH increase, DO decrease, and soluble iron increase were accompanied during nitrate removal. Hosseini et al. [1] applied a modified surface of nZVI using Cu nano-particles to remove nitrate through packed sand column. The results

revealed that 75% of influent nitrate was removed when nano-Fe/Cu concentration=8 g/L, initial nitrate concentration=100 mg/L and pore water velocity through sand=0.125 mm/s. Despite these studies, sufficient data cannot be found in the literature concerning the removal of nitrate using nZVI packed columns.

In the present article, the main objective of this research was to study the effectiveness of nZVI for the removal of nitrate in porous media using an upflow packed sand column. To attain this goal, the effects of different configurations of nZVI/sand like one layer, multilayer and different thicknesses of nZVI/sand on nitrate removal were investigated. Four columns were operated simultaneously using 10 g of nZVI in each in addition to fifth column filled with sand only. Nitrate concentration was monitored in the effluent and at different sampling ports along the various depths of the column. To the best of our knowledge, this research is the first study that uses nZVI in layers in the length of packed sand column to remediate nitrate contaminant.

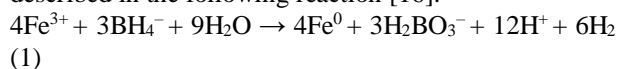
2. MATERIALS AND METHODS

2.1. Materials and chemicals

Ferric chloride (>99.0%, Junsei Chemical Co., Japan), sodium borohydride (>98.0%, Sigma-Aldrich Inc., USA) and ethanol (99.5%, Wako Co., Japan) were purchased for nZVI synthesis. Potassium nitrate (>99.0%, Wako Co., Japan) was used to make the nitrate solution, while hydrochloric acid (35–37%, Wako Co., Japan) was used for pH adjustment. All solutions were prepared using deionized water and purged with nitrogen for 20 min for de-oxygenation process. Standard sand (As One Co., Japan) was used as a porous medium. Maximum and minimum diameter of sand particle was equal to 2 mm and 0.075 mm, respectively. The sand properties were estimated as bulk density ($\rho_b = 1.3 \text{ g/cm}^3$) and average porosity ($n = 0.35$). All chemicals and minerals were used as received without any pretreatment.

2.2. Synthesis of nZVI

nZVI was synthesized based on an aqueous reduction of ferric chloride hexahydrate using sodium borohydride as described in the following reaction [16]:



In order to make 10 g of nZVI, sodium borohydride solution (NaBH_4 , 28 g/L) was added slowly into ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 40 g/L) in 5000 mL four-neck glass flask at a rate of 1 L/h using a roller pump. The synthesis was processed under a continuous flow of nitrogen gas to create anoxic condition. The synthesis was conducted with vigorous stirrer 250 rpm, under temperature $25 \pm 0.5 \text{ }^\circ\text{C}$ using water bath and left for 20 min as aging time to complete the reaction. The resulting black precipitates were filtered by vacuum filtration, washed with deoxygenated deionized water and ethanol three times, and then applied immediately in column experiments.

2.3. Column experiment setup and operation

Column experiments were conducted using a Plexiglas column with a length of 25 cm and an internal diameter of 8.5 cm. The columns were pumped continuously with

nitrate synthetic water in an up-flow mode using a multiport peristaltic pump (RP-1000, As One, Japan). Four sampling ports were installed along the height of the column at 5 cm (S1), 10 cm (S2), 15 cm (S3) and 20 cm (S4) from the column inlet to allow for water collection (Fig. 1). 10 g of nZVI were introduced in each column. The column experiments were comprised of five columns. The first column (C1) was first filled with a 5-cm high layer containing sieved sand; the second 10-cm high layer was filled with a homogenous nZVI/sand mixture (10 g of nZVI) while the third layer (10cm) contained just sand (Fig. 1a). The second column (C2) was composed of a first layer at the bottom containing sand only (5 cm long); the second layer containing a homogenous mixture of nZVI/sand (5 g of nZVI) (5 cm long); the third layer was packed with 5 cm of sand; the fourth layer was filled with a mixture of nZVI/sand and the last layer containing only sand (5cm long) (Fig. 1b). The third column (C3) was packed with a 5-cm high layer of sand as a first layer; the second layer was packed with a 5-cm high layer of a homogenous mixture of nZVI/sand and the remaining of the column was filled with sand only (Fig. 1c). C4 was similar to C1 but was filled with nZVI supported on porous media (sand particles were added to ferric chloride during nZVI synthesis) (Fig. 1d). C5 was prepared with only sand as a control column. The sand layers at the inlet and the outlet were used to improve flow distribution and limit nZVI loss from each column. During the whole experiments, each column was fed with 200 mg/L of nitrate from a 20 L tank. Flow rate was set to 5 mL/min and the residence time was thus 99 min. The pH of the influent solution in all experiments was nearly 7. The water samples were collected from effluent and intermediate sampling ports and analyzed for pH, oxidation reduction potential (ORP), nitrate, nitrite, ammonium and total soluble iron.

2.4. Analytical methods and instruments

Samples were filtered using 0.45 mm syringe filters for nitrate, nitrite, ammonium and dissolved total iron analyzes. Nitrate, nitrite, ammonium and dissolved total iron were determined using an UV-visible spectrophotometer (DR 3900, Hach Co., USA), employing dimethylphenol method at 345 nm, USEPA diazotization method at 515 nm, salicylate method at 690 nm and TPTZ method (2,4,6-tri(2-pyridinyl)-1,3,5-triazine) at 590 nm, respectively. pH and ORP were measured using a pH/ORP digital meter (D-72, Horiba Co., Japan).

3. RESULTS AND DISCUSSION

3.1. Nitrate–nitrogen removal

The changes in NO_3^- -N, NH_4^+ -N and NO_2^- -N concentrations in column experiments C1–C4 over time are presented in Figs. 2–5, respectively. No significant variations in NO_3^- -N, NH_4^+ -N and NO_2^- -N were observed in C5 (not given). Fig. 2 presents the temporal changes in nitrogen species in C1. NO_3^- -N concentration decreased quickly and more than 96% of NO_3^- -N was removed after 1 hr. After this time, the concentration of NO_3^- -N relatively remained constant until 22 hr and then NO_3^- -N removal dropped from 93% after 22 hr to 70% after 25 hr. NH_4^+ -N concentration increased gradually over the first 5 hr to reach 8.35 mg/L and subsequently decreased slightly 35% of the added NO_3^- -N was recovered as NH_4^+ -N.

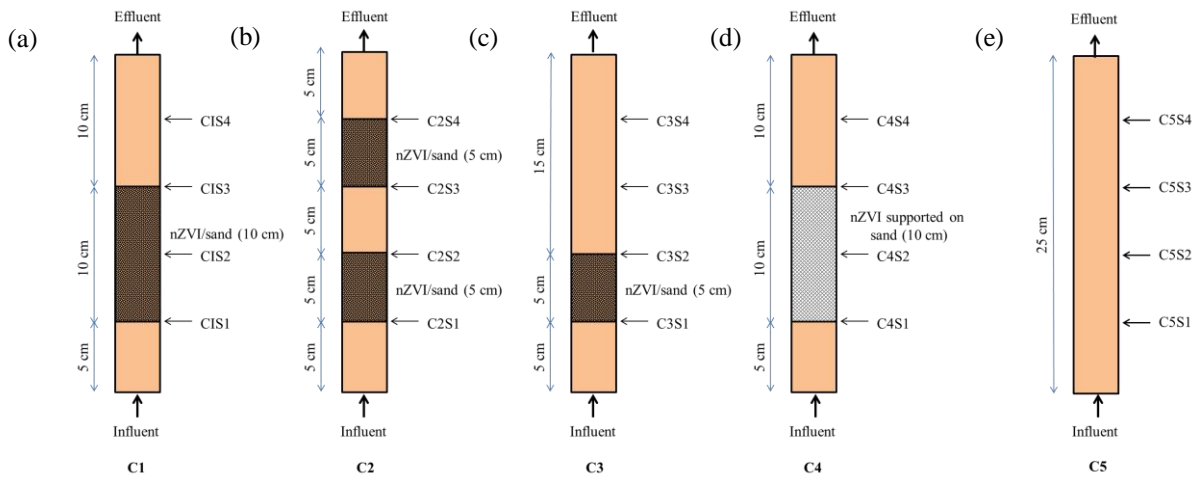


Fig. 1. Schematic representation of the columns design.

until 17 hr and at the end of experiment approximately Low formation of NO_2^- -N was observed over time in C2 ($< 1.62 \text{ mg/L}$). The nitrogen mass balance was about 69% in which nitrogen as NO_3^- -N, NH_4^+ -N and NO_2^- -N.

Fig. 3 presents the temporal changes in nitrogen species in C2. The NO_3^- -N concentration decreased sharply and greater than 95% of the influent NO_3^- -N was removed after 5 hr and afterward NO_3^- -N concentration increased steadily and reached 5.06 mg/L after 17 hr. After this time, NO_3^- -N removal dropped from 89% after 17 hr to 71% after 25 hr. The effluent NH_4^+ -N concentration increased gradually and about 61% of the NO_3^- -N removed was recovered as NH_4^+ -N. Little formation of NO_2^- -N was detected ($< 1.05 \text{ mg/L}$) during C2 experiment.

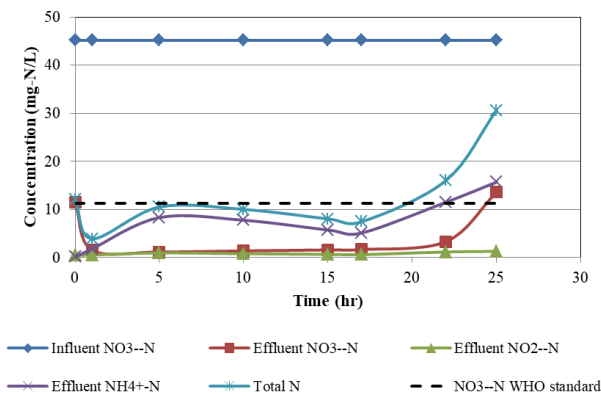


Fig. 2. Changes in nitrogen concentrations in C1 over time.

About 91% of total applied nitrogen was recovered as NO_3^- -N, NH_4^+ -N and NO_2^- -N after 25 hr of operation. Fig. 4 exhibits the temporal changes in nitrogen species in C3. The NO_3^- -N concentration at the outlet showed 98% of NO_3^- -N removal during the first hour and thereafter increased slowly to more than 4.02 mg/L after 17 hr. A gradual decrease in the rate of NO_3^- -N removal from 91% to 76% after 17 and 25 hr was observed, respectively. High accumulation of NH_4^+ -N was noted in C3 over time and almost 70% of the influent NO_3^- -N was recovered as NH_4^+ -N. Low NO_2^- -N formation was detected with a maximum of 0.91 mg/L after 25 hr. The final mass balance of nitrogen showed 95 % of the initial nitrogen was recovered as NO_3^- -N, NH_4^+ -N and NO_2^- -N.

Fig. 5 shows the temporal changes in nitrogen species in C4. Only 75% of the influent NO_3^- -N was removed within the first 5 hr and afterward NO_3^- -N concentration increased gradually and the removal efficiency dropped to 30% at the end of experiment. NH_4^+ -N was produced remarkably in C4 with a maximum of 19 mg/L and little NO_2^- -N formation was detected ($< 1.39 \text{ mg/L}$). The nitrogen mass balance at the end of experiment was 96% as NO_3^- -N, NH_4^+ -N and NO_2^- -N.

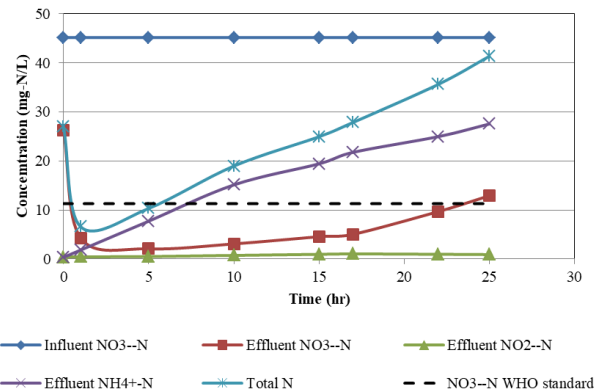


Fig. 3. Changes in nitrogen concentrations in C2 over time.

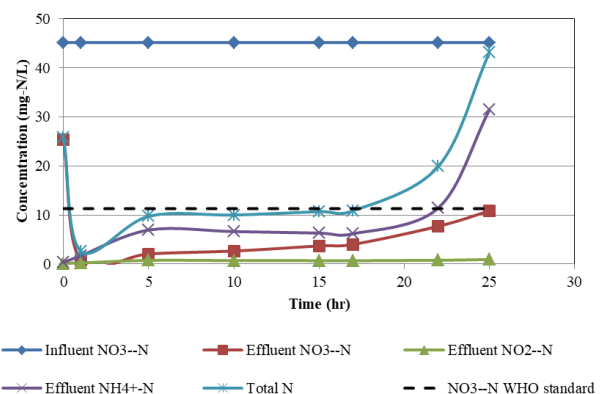


Fig. 4. Changes in nitrogen concentrations in C3 over time.

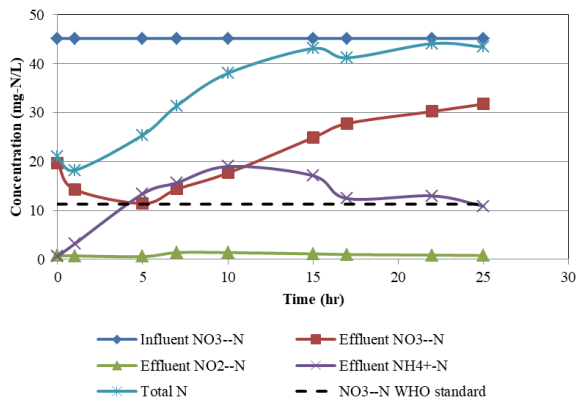


Fig. 5. Changes in nitrogen concentrations in C4 over time.

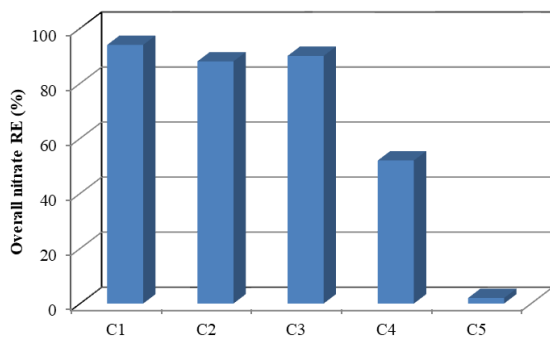


Fig. 6. Overall nitrate removal efficiency in column experiments C1–C5 after 25 hr of operation.

Comparison among C1–C5, C1 showed the maximum nitrate removal efficiency (> 97%). In addition, C1 showed the highest overall nitrate removal among C1–C5 (Fig. 6). These results indicated that the optimum condition to reduce nitrate among nZVI/sand columns (C1–C4) was C1 by using a 10-cm high layer containing nZVI/sand.

4. CONCLUSION

This study evaluates the application of nZVI in porous media in multilayer system to remove nitrate through an up flow packed sand column. The results indicated that using single 10-cm high layer containing nZVI/sand demonstrated the best performance to remove nitrate among nZVI/sand columns and more than 97% of influent nitrate was removed. Low formation of nitrite and always less than 1.39 NO₂⁻-N mg/L was noted during nZVI/sand columns. High generation of ammonium was found during nZVI/sand and more than 69% of applied nitrogen were recovered as nitrate, ammonium and nitrite at the end of experiments after 25 hr of operation.

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