

DEGRADATION OF NITRATE BY MODIFIED SURFACE OF NANO-ZERO VALENT IRON IN FLOW THROUGH PERMEABLE REACTIVE BARRIER: DIFFERENT CONFIGURATIONS

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Abstract - Permeable reactive barrier (PRB) is one of the well-known technologies for in situ nitrate removal from groundwater owing to their effective operation and maintenance costs. This work aims using modified surface of nanoscale zero valent iron (known as bimetallic nano-Fe/Cu particles) as a reactive material in the porous media of PRB for nitrate removal. In order to simulate the real situation of PRB, column experiments were conducted in this study under different configurations. The effect of one layer, two layers and different thickness layers of nano-Fe/Cu particles was investigated. 10 g of nano-Fe/Cu particles were applied in each column. The initial nitrate concentration was 200 mg/L. Solid analysis was performed after dismantling using X-ray diffraction (XRD), transmission electron microscopy (TEM), and Brunauer-Emmett-Teller (BET) surface area analysis to characterize nitrate removal mechanism in each column. The results revealed that using double 5-cm high layers of bimetallic nanoparticles showed the highest nitrate removal efficiency. In addition, high accumulation of ammonium was observed during (nano-Fe/Cu)/sand column experiments. Little formation of nitrite was detected during the initial stages of (nano-Fe/Cu)/ sand columns whereas relatively high accumulation was obtained at later stages.

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

I. INTRODUCTION

Nitrate contamination of groundwater has become a real environmental and public health problem around the world. Nitrate contamination usually originates from chemical fertilizers, wastewater discharges, fertilizers factories and landfills [1]. Excessive nitrate exposure can cause many diseases like cancer and met-hemoglobinemia due to the potential reduction of nitrate to nitrite [1, 2]. There are several physico-chemical and biological technologies for removing nitrate from contaminated groundwater like ion exchange, reverse osmosis, chemical reduction and biological denitrification [3]. However, these processes are relatively expensive and are often limited due to potential of side effect on water quality [4]. Therefore, there is a need to explore new technologies for removing the problem of nitrate contaminated sites.

In recent years, nanoscale zero valent iron (nZVI) has been employed heavily to remediate contaminants of soil and groundwater. nZVI has shown higher reactivity for the effective removal of a large range of contaminants compared with micro- or milli-sized iron [5, 6]. The higher reactivity of nZVI can be the result of larger surface area due to smaller particles size [7]. Coating the surface of nZVI using another metal (known as bimetallic nano-particles) such as copper (Cu), nickel (Ni), palladium (Pd) or platinum (Pt) has been recorded to enhance the nZVI reactivity towards a variety of contaminants [8, 9].

Permeable reactive barrier (PRB) is one of the well-known processes for in situ nitrate removal from groundwater owing to their effective operation and

maintenance costs [10, 11]. ZVI PRB has been used to remediate groundwater contaminated by nitrate [12]. Several studies have focused on evaluating the behavior and efficiency of nitrate removal by ZVI in lab scale column. Tehrani et al. [13] concluded that nitrate removal did not exceed 85% in column experiment and removal of nitrate was mostly influenced by seepage velocity, freshness and quantity of nZVI/Ni. Hosseini and Tosco [14] investigated nitrate removal in a lab-scale aquifer (60 cm length × 40 cm width × 50 cm height) using nZVI and carbon substrates. The results demonstrated that the system has a great possibility for nitrate removal in-situ contaminated groundwater. Araújo et al. [15] depicted that the use of nZVI in PRBs is a suitable technique for denitrification with high performance record. Jeong et al. [16] studied the nitrate removal efficiency by ZVI in packed sand reactor bipolar electrolytic cell. The results showed that 99% of nitrate was removed and the main final product of nitrate reduction was ammonia. In spite of these studies, sufficient data cannot be found in the literature concerning the removal of nitrate using nano-Fe/Cu particles in packed sand column.

In the present paper, the main objective of this research was to study the efficiency of nZVI and nano-Fe/Cu particles for the removal of nitrate in porous media using an upflow packed sand column. To attain this goal, the effect of multibarrier and different thicknesses of nZVI and nano-Fe/Cu and on the nitrate removal rate were investigated. Four columns were operated using 10 g of nZVI and nano-Fe/Cu particles in each under different configurations in addition to fifth column filled with sand only as a

control column. 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, there is no literature that uses nZVI and nano-Fe/Cu particles in multibarrier system to remediate nitrate contaminant in porous media using packed sand column.

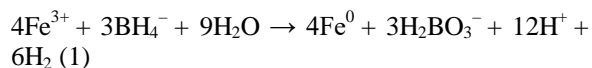
II. MATERIALS AND METHODS

2.1 Materials and chemicals

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99.0%, Junsei Chemical Co., Japan), sodium borohydride (NaBH_4 , 98.0%, Sigma-Aldrich Inc., USA) and ethanol (99.5%, Wako Co., Japan) were purchased for nZVI synthesis. Potassium nitrate (KNO_3 , 99.0%, Wako Co., Japan) was used to make the nitrate solution, while hydrochloric acid (HCl , 35–37%, Wako Co., Japan) was used for pH adjustment. Anhydrous copper chloride (CuCl_2 , 99.9%, Aldrich Inc., USA) was used to prepare nano-Fe/Cu particles. All aqueous solutions were prepared using deionized deoxygenated water. The sand properties were estimated as particle size (2–0.075 mm), bulk density ($\rho_b = 1.3 \text{ g/cm}^3$) and average porosity ($n = 0.35$).

2.2 Synthesis of nZVI

nZVI particles were synthesized based on chemical reduction of ferric chloride using sodium borohydride as depicted in the following reaction:



To make 10 g of nano-Fe/Cu particles, sodium borohydride solution (0.74 M) was added slowly into ferric chloride hexahydrate (0.15 M) in 5000 mL four-neck glass flask at a rate of 1 L/h using a roller pump. The synthesis was conducted under a continuous flow of nitrogen gas to create anoxic condition. The synthesis was processed with vigorous stirrer 250 rpm, under temperature $25 \pm 0.5 \text{ }^\circ\text{C}$ and aging time 20 min. The resulting black particles were filtered by vacuum filtration, washed with

deoxygenated deionized water and ethanol three times and then used immediately in column experiments. CuCl_2 was added to ferric chloride before pumping sodium borohydride. Based on Khalil et al. [17] study, the best coating rate in case of nano-Fe/Cu was 5% wt/wt of CuCl_2/Fe .

2.3 Column experiment setup and operation

Column experiments were applied 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 contaminated water in an up-flow mode using a peristaltic pump. Four sampling points were positioned along the length 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. 10 g of nZVI and nano-Fe/Cu particles 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. 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 nano-Fe/Cu) (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). C3 and C4 were similar to C1, C2, respectively but with using nano-Fe/Cu particles instead of nZVI. C5 was prepared with only sand as a control column.

The sand layers were used at the inlet and the outlet to enhance flow distribution and reduce nanoparticles loss from each column. During the whole experiments, each column was fed with 200 mg/L of nitrate from a 60 L tank. Flow rate was set to 5 mL/min and the retention time was thus 99 min. The pH of the influent solution in all experiments was adjusted to 7. The water samples were analyzed for pH, oxidation reduction potential (ORP), nitrate, nitrite, ammonium and total soluble iron.

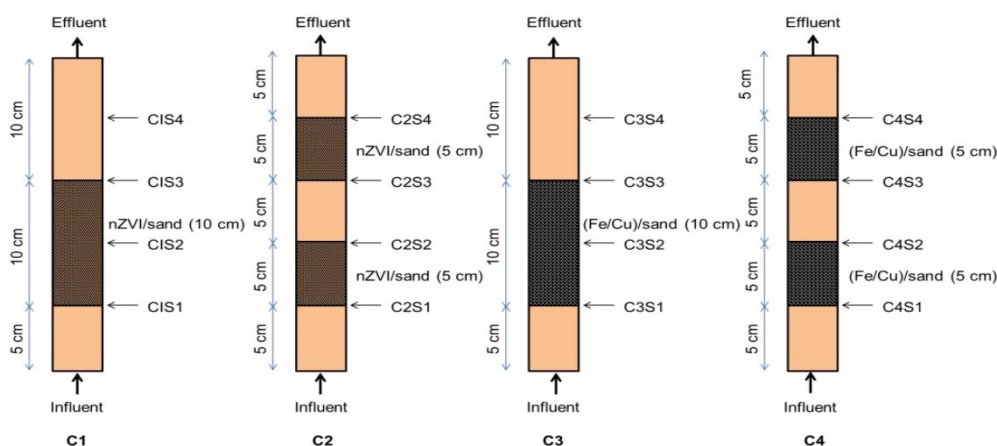


Fig. 1. Schematic representation of the columns design.

2.4 Analytical methods and instruments

Nitrate, nitrite, ammonium and dissolved total iron concentrations were measured 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 determined using a pH/ORP digital meter (D-72, Horiba Co., Japan).

III. RESULTS AND DISCUSSION

3.1 Nitrate-nitrogen removal

The variations 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 changes in NO_3^- -N, NH_4^+ -N and NO_2^- -N were noticed in C5 (not given).

Fig. 2 shows the temporal changes in nitrogen concentrations in C1. NO_3^- -N concentration decreased rapidly and more than 95% of NO_3^- -N was removed after 1 hr. After this time, the concentration of NO_3^- -N approximately remained constant until 22 hr and then NO_3^- -N removal declined from 93% after 22 hr to 70% after 25 hr. NH_4^+ -N concentration increased steadily over the first 5 hr to reach 8.35 mg/L and subsequently decreased slightly until 17 hr and approximately 35% of the added NO_3^- -N was recovered as NH_4^+ -N at the end of experiment. Little formation of NO_2^- -N was detected over time in C2 (less than 1.62 mg/L). The nitrogen mass balance was about 70% as NO_3^- -N, NH_4^+ -N and NO_2^- -N.

Fig. 3 presents the temporal changes in nitrogen concentrations in C2. The NO_3^- -N concentration decreased significantly and more than 95% of the influent NO_3^- -N was removed after 5 hr and NO_3^- -N concentration afterward increased steadily and reached 5.06 mg/L after 17 hr. After this time, NO_3^- -N removal decreased from 89% after 17 hr to 71% after 25 hr. The NH_4^+ -N formation increased gradually and about 60% of the NO_3^- -N removed was recovered as NH_4^+ -N. Low formation of NO_2^- -N was observed (less than 1.05 mg/L) during C2 experiment.

Fig. 4 depicts the temporal changes in nitrogen concentrations in C3. NO_3^- -N concentration decreased sharply within the first 5 hr and was removed by more than 90%. After that, NO_3^- -N concentration increased steadily until the end of experiment. The production of NH_4^+ -N was increased remarkably in C1 with a maximum of 34.14 mg/L. The formation of NO_2^- -N was low during the first 10 hr and then increased gradually and reached a maximum of 6.64 mg/L after 22 hr. At the end of experiment, the nitrogen mass balance was 98% as NO_3^- -N, NH_4^+ -N and NO_2^- -N.

Fig. 5 shows the temporal changes in nitrogen concentrations in C4. NO_3^- -N was removed

completely (100%) after 1 hr and the removal of NO_3^- -N was maintained constant until 10 hr. After this time, NO_3^- -N concentration increased drastically and the removal efficiency declined to about 50% after 25 hr. NH_4^+ -N formation was significantly produced in C4 with a maximum of 29.85 mg/L. Low effluent NO_2^- -N was formed during the first 10 hr and then NO_2^- -N increased steadily to 5.57 mg/L after 25 hr. Nearly 94% of nitrogen mass recovery was observed as NO_3^- -N, NH_4^+ -N and NO_2^- -N at the end of the experiment.

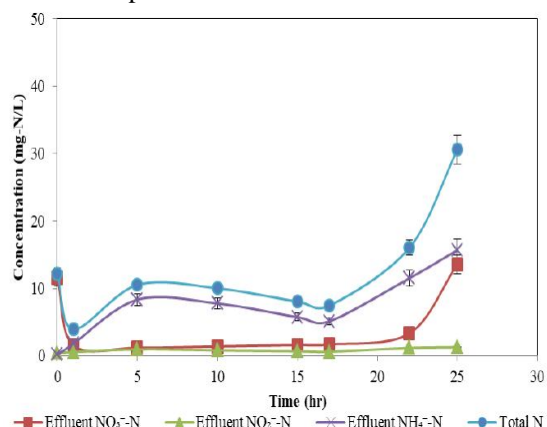


Fig. 2. Changes in nitrogen concentrations in C1 over time.

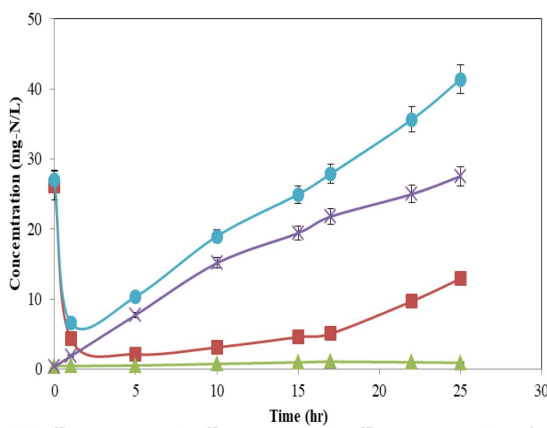


Fig. 3. Changes in nitrogen concentrations in C2 over time.

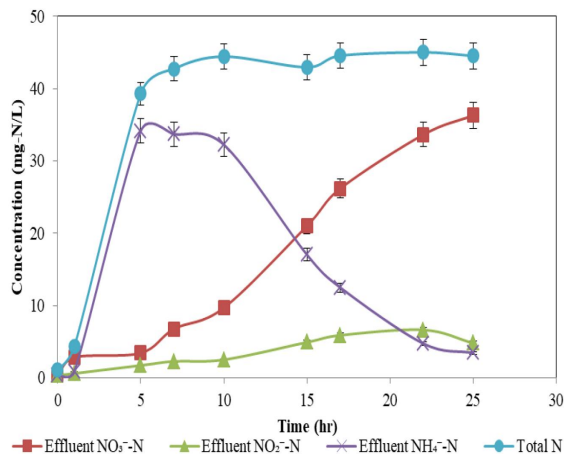


Fig. 4. Changes in nitrogen concentrations in C3 over time.

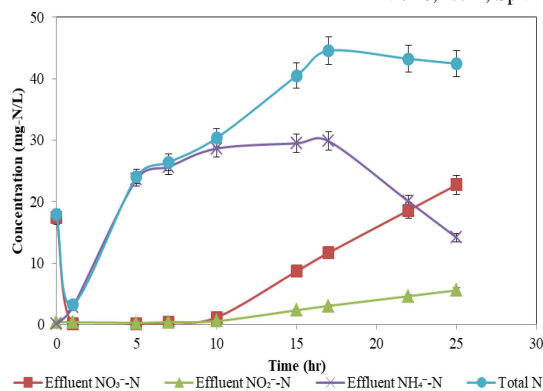


Fig. 5. Changes in nitrogen concentrations in C4 over time..

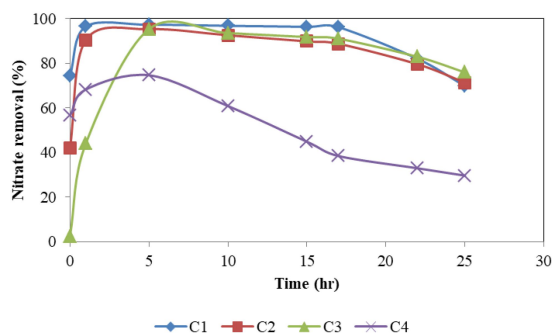


Fig. 6. Overall nitrate removal efficiency in column experiments C1–C5 after 25 hr of operation.

Comparison among C1–C5 (Fig. 6) indicated that the optimum condition to reduce nitrate among nZVI/sand columns was C1 (overall nitrate removal efficiency = 94%) by using single 10-cm high layer containing nZVI/sand whereas in (nano-Fe/Cu)/sand columns, C3 (overall nitrate removal efficiency = 83%) with two 5 cm (nano-Fe/Cu)/sand layers showed the highest performance to remove nitrate.

CONCLUSION

This study investigates the application of nZVI and bimetallic nano-Fe/Cu particles in porous media in multibarrier 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 optimum performance to remove nitrate among nZVI/sand columns and more than 97% of influent nitrate was removed while using double 5-cm high layer containing (nano-Fe/Cu)/sand achieved the best removal performance among (nano-Fe/Cu)/sand columns and nitrate removal was complete (100%). Little nitrite formation (< 1.32 NO₂⁻-N mg/L) was detected during nZVI/sand columns while relatively high formation (> 3.9 NO₂⁻-

N mg/L) was found during the later stages of (nano-Fe/Cu)/sand columns. High formation of ammonium was observed during nano-Fe/Cu column experiments and more than 94% of applied nitrogen were recovered at the end of experiments as nitrate, ammonium and nitrite.

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