Effect of Nano Zero Valent Iron Delivery Method into Porous Media on Phosphorus Removal from Groundwater

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Effect of Nano Zero Valent Iron Delivery Method into Porous Media on Phosphorus Removal from Groundwater

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Abstract: *The main aim of this study is to investigate the effect of the delivery method of nano zero valent iron (NZVI) into porous media on the removal of phosphorus from groundwater. Different column experiments were conducted considering injection and permeable reactive barrier (PRB) approaches using sand-packed column with 65 cm length and 10 cm inner diameter. Results revealed that Injecting 10 g of NZVI into C4 resulted in the highest sorption capacity and average removal efficiency of 25 mg/L phosphorus concentration over 14 days with 197.76 mg-P/g-NZVI and 84.8% respectively. The dissolved oxygen levels in the effluent samples of the NZVI column were declined due to the oxidation process of NZVI, which was accompanied by a lower ORP values. The change of the delivery methodology of NZVI into porous media affected its capacity to remove phosphorus, revealing that injection could be better than PRB in terms of the reactive performance.*

Keywords: Phosphorus; nano zero valent iron; permeable reactive barrier; injection; delivery method.

1. INTRODUCTION

Phosphorus (P) is one of the major nutrients and it is essential element for all forms of life. However, the excessive use of fertilizers and the uncontrolled discharge of untreated sewage could increase the phosphorous concentration in groundwater [1,2]. Correspondingly, the migration of such contaminated groundwater into water bodies could be one of the possible factors in speeding up eutrophication [3]. Therefore, phosphorus removal from groundwater plays a significant role in decreasing the harmful impact of eutrophication on the aquatic systems and the drinking water quality as well [4,5]. Meanwhile, nano zero valent iron (NZVI) has been widely used as an efficient adsorbent for phosphorus removal from water, because of its unique core-shell structure which increases its reactivity towards several water pollutants [6,7]. In addition, its nano-size features lead to larger specific surface area which provides more available sorption sites on the surface. Moreover, owing to its position in the chemical reactivity series it can react with most of the soluble contaminants in water. When it comes to applying NZVI into in-situ groundwater remediation applications, there are two main methodologies that has been widely used. The first one is injecting NZVI solution into the porous media using screened wells which penetrates the medium to the desired contamination depth. The second approach is the PRB, which basically conducted by digging a trench into porous media in which NZVI is packed to Intersect the contaminated plume [8]. Therefore, the main objectives in this study are; a) conducting column experiments to determine the best delivery method of NZVI into porous media, and b) investigating the effect of the delivery method on the reactivity and longevity of NZVI towards phosphorus.

2. MATERIALS & METHODOLOGY

2.1 NZVI Synthesis

Chemical reduction method of ferric chloride ($FeCl_3$) by the drop-wisely injected sodium borohydride ($NaBH_4$) was used to synthesize NZVI [9]. To prepare 1 g of NZVI, the two solutions ($FeCl_3/NaBH_4$: 5/3.5) were mixed mechanically at 250 RPM and at constant temperature of $25 \pm 0.5°$ C. Nitrogen purging was provided for all the prepared solutions before use and also during the whole synthesis steps to ensure the anaerobic environment. After 20 min aging time the black precipitates of NZVI were collected using vacuum filtration and washed by DIW.

2.2 Column Experiments

Different column experiments were conducted in order to investigate the effect of the NZVI delivery method into porous media on phosphorus removal from groundwater. In our experiments, three NZVI delivery methods were considered: a) supporting NZVI on sand using a PRB layer of NZVI/Sand mixture (mixing mass ratio of Fe/Sand: 1/100), b) Bare NZVI using a PRB layer of pure NZVI, and c) Injecting NZVI solution. The same dosage of 10 g NZVI was considered in the three approaches for a reasonable and fair comparison. Moreover, the injection rate of NZVI solution into the column was 2 g/day distributed over the experiment time.
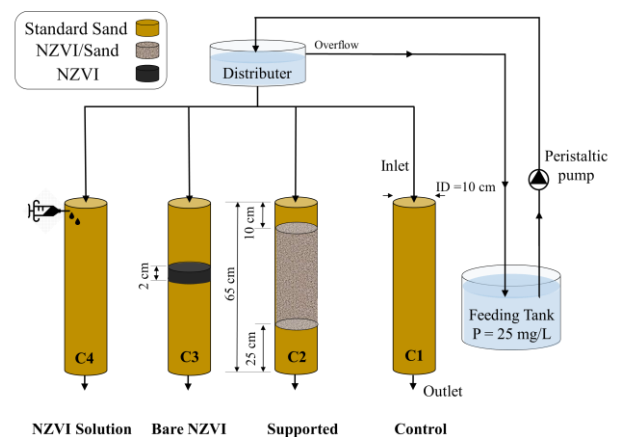
Fig. 1. Schematic of column experiment configurations.

A Plexiglas column (65 cm height and 10 cm inner diameter), packed with standard sand as the main porous medium, was used in the column experiments. Four columns (C1-C4) were considered including the three delivery methods to be investigated as well as the control column. The configurations of the 4 columns are shown in detail in Fig. 1. Feeding phosphorus solution with initial concentration of 25 mg-P/L was pumped downward into the column at 15 mL/min flowrate. The initial geochemical measurements of the inlet solution are; pH = 7 ± 0.5, oxygen reduction potential (ORP) = -25 mV and dissolved oxygen (DO) = 8 mg/L. Effluent samples and samples along the column height were collected for phosphorus analysis over 14 days of experiment time. Samples were directly analyzed using UV-Vis spectrophotometer (DR3900, HACH, USA) for phosphorus concentration.

3. RESULTS & DISCUSSION
3.1 Sorption Capacity & Removal Efficiency
Sorption capacity and removal efficiency were calculated using Eq. 1 and 2 respectively based on the phosphorus concentration in the effluent samples. Results are plotted with respect to experiment days as shown in Fig. 2 and 3.

$$q_e \ (mg/g) = \frac{(C_o - C_e)\,V}{m} \qquad (1)$$

$$R \ (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

Where; C_o and C_e (mg/L) are inlet and effluent phosphorus concentration, m (g) is NZVI dosage, and V (L) is accumulated inflow volume.
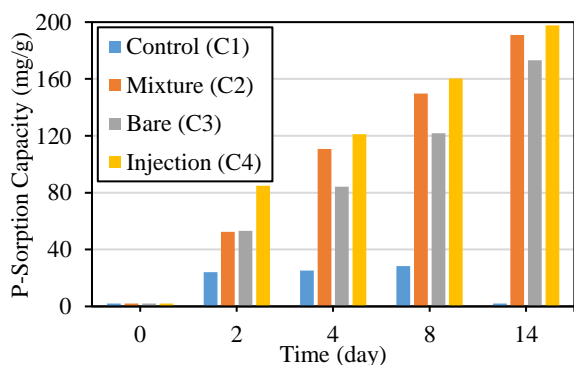

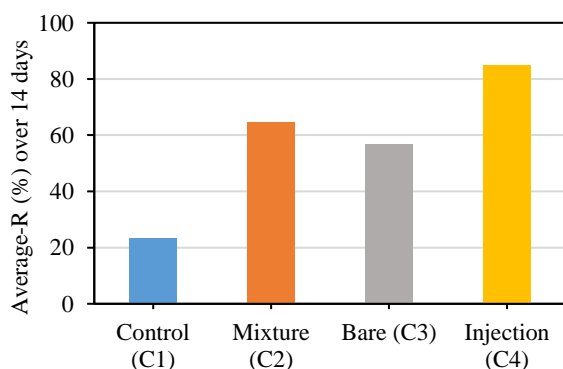Fig. 2. Effect of delivery method on NZVI sorption capacity towards phosphorus.

Fig. 3. Average phosphorus removal efficiency (R %) over the 14 days experiment time.

Sorption capacity gradually increased for C2, C3 and C4 to reach its maximum values after 14 days of the experiment of 190.94, 173.12 and 197.76 mg-P/g-NZVI respectively. Whereas, the maximum sorption capacity in the control column was around 28.42 mg-P/g-NZVI. Results showed an obvious enhancement in the sorption capacity for the injection column (C4) comparing to the PRB columns (C2 and C3). However, it is worth to be said that the performance of the supported NZVI in C2 was comparable to C4. Meanwhile, the results of the average removal efficiency of phosphorus were consistent with what have been concluded. Injecting NZVI into C4 resulted in an average removal efficiency of 84.8% which was the highest comparing with the other two PRB columns (C2 and C3) with 64.4% and 56.8% respectively.

3.2 Geochemical Measurements
Over the experiment time, geochemical measurements (pH, ORP and DO) of the effluent samples were recorded, as presented in Fig. 4.
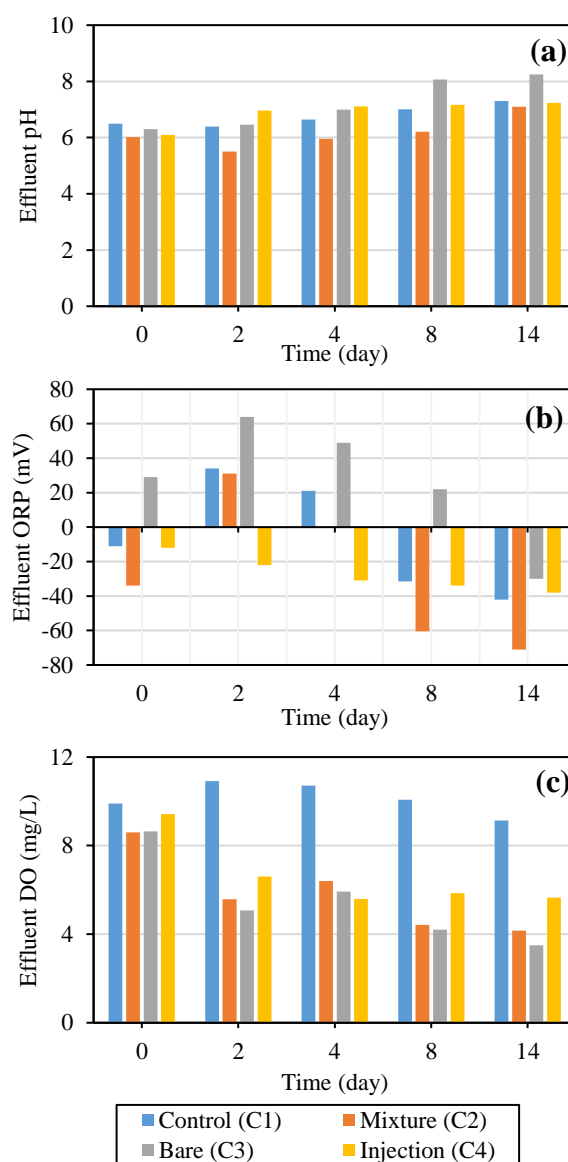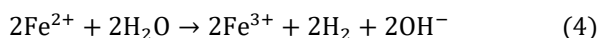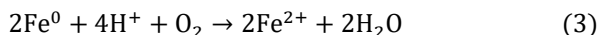

Fig. 4. Effect of NZVI delivery methods in the effluent's geochemical values of: (a) pH, (b) ORP, and (c) DO.

Results showed that there was no significant difference in the pH values at the effluent of the 4 columns.

However, there was a slight increase in case of bare NZVI in C3 comparing to the supported one in C2 to reach pH value above 8 at the later stages of the experiment, which could be attributed to the easy oxidation of the bare NZVI which accompanied with the release of iron oxides (Fe^{2+} and Fe^{3+}) and OH^- anions:

$$2Fe^0 + 4H^+ + O_2 \rightarrow 2Fe^{2+} + 2H_2O \qquad (3)$$

$$2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + 2H_2 + 2OH^- \qquad (4)$$

ORP measurements was fluctuated for all the columns except for the injection column (C4), in which it had a clear trend with a final value of -38 mV, which is not so far from the initial value. Meanwhile, DO levels significantly decreased in the effluent of the three NZVI columns (C2-C4) comparing to that in the control column (C1), indicating the oxygen consumption which occurred by the presence of NZVI within the medium.

3.3 P-Profiles
Phosphorus concentration along the column's height at the 14th day of the experiment time are shown in Fig.5. Results depicted that phosphorus concentration in case of injecting NZVI into the column decreased dramatically comparing to that of the other columns. That could be attributed to both the fresh state of the injected (as-synthesized) NZVI slurry in addition to the possible rapid surface oxidation of the packed-NZVI particles during the packing process in C2 and C3.
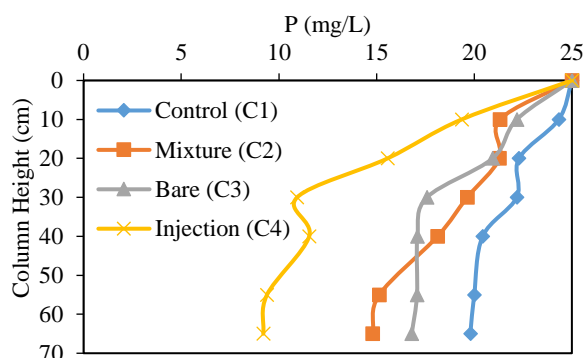

Fig. 5. Phosphorus profiles along the columns at the end of the experiment.

4. CONCLUSIONS
In this study, different delivery approaches of NZVI into porous media were investigated through a set of laboratory column experiments for a better performance in groundwater treatment. Results implied that injecting the solution of the as-synthesized NZVI into porous media showed superiority over packing it as a PRB layer. Injecting 10 g of NZVI into C4 resulted in the highest sorption capacity and average removal efficiency of 25 mg/L phosphorus concentration over 14 days with 197.76 mg-P/g-NZVI and 84.8% respectively. Meanwhile, mixing NZVI with sand as a PRB material showed a comparable performance to the injection method. Geochemical measurements were consistent with the obtained results showing the decline in the dissolved oxygen levels in the effluent samples due to the oxidation process of NZVI, which was accompanied by a lower ORP values. Generally, it could be concluded that the change of the delivery methodology of NZVI into porous media affected its capacity to remove phosphorus, revealing that injection could be better than PRB in terms

of the reactive performance. However, further investigation is needed on the use of NZVI/Sand mixture as PRB material because of its comparable depiction. Also, it is important to conduct a feasible comparison between Injection and PRB in terms of the installation and operating costs, which represents a crucial factor in the real field applications.

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