Using cation exchange resin for ammonium removal as part of sequential process for nitrate reduction by nanoiron

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1. Introduction

The problem of nitrate contamination in groundwater and surface water is of concern. The sources of nitrate contamination are from industrial waste, landfill leachate, agriculture runoff, and human disposal [1–4]. For human health, nitrate will be reduced to nitrite, and then oxidized by ferrous iron in haemoglobin, leading to serious lack of oxygen in organ tissue, called methemoglobinemia or “blue baby syndrome”. In addition, nitrate is associated with formation of carcinogens in stomach and other organs [3]. As a result of the health issue of nitrate in drinking water, the United States Environmental Protection Agency set a maximum contaminant level at 10 mg-NO3 L−1 as N [2,3].

There are many nitrate treatment technologies including reverse osmosis, ion exchange, biological denitrification and chemical reduction processes [3]. However the reverse osmosis and ion exchange are quite expensive and may generate brine water [5,6]; biological denitrification is difficult to maintain and operate. The chemical reduction process is the most suitable for use in the in situ treatment of nitrate-contaminated groundwater because the reducing chemicals can be easily injected, dispersed and transported in groundwater and soil. Among various chemical reduction processes, the process of zero-valent iron (ZVI) is effective and widely used in permeable reactive barriers to remediate groundwater contaminated with organics and inorganics [6,7]. Furthermore, the ZVI was also developed in nanoscale to improve its performance because of its favourable characteristics of small particles, high specific
surface area, high rate of nitrate reduction, and stable reactivity [2,4,8].

Reaction of nitrate removal by nanoscale zero-valent iron (nZVI) process results in the formation of ammonium as the major product, as in Reactions 1–6 [9]:

\[
\begin{align*}
\text{Fe}^0 & \rightarrow \text{Fe}^{2+} + 2e^- \\
\text{Fe}^0 + 2\text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \\
\text{Fe}^0 + \text{NO}_3^- + 2\text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O} + \text{NO}_2^- \\
4\text{Fe}^0 + \text{NO}_3^- + 10\text{H}^+ & \rightarrow 4\text{Fe}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O} \\
4\text{Fe}^0 + \text{NO}_3^- + 7\text{H}_2\text{O} & \rightarrow 4\text{Fe(OH)}_2^+ + \text{NH}_4^+ + 20\text{H}^- \\
3\text{Fe}^0 + \text{NO}_3^- + 3\text{H}_2\text{O} & \rightarrow \text{Fe}_3\text{O}_4 + \text{NH}_4^+ + 20\text{OH}^- 
\end{align*}
\]

Ammonium may cause toxicity to aquatic animal and ecosystem [5,10–12]. There are many technologies used to remove ammonium such as air stripping, breakpoint chlorination, ion exchange, and biological methods [13]. Although the biological method is most effective, disadvantageous situation can occur when the effluent ammonium concentration shock load and unacceptable peak appear [14]. So, ion exchange and adsorption method are promising because of its short contact time, low energy consumption, easy operation. In addition, ammonium can be reclaimed as fertilizers from the regenerated resins. Many researchers chose natural zeolites for ammonium removal, but it appears to be unsatisfied for large scale treatment because it has high cost of mining, transporting and processing [15]. Therefore, cation exchange resins were selected for the alternative technology on ammonium removal.

The work of this study was carried out by using cation exchange resin type C160H for removing ammonium from the effluent of nZVI-induced nitrate removal process. Experiments were investigated to determine the kinetic rate constant with respect to initial pH and initial nitrate concentration of solution. In addition, effects of the competitive ions and initial solution pHs on the equilibrium of cation exchange resin were performed to obtain the relevant parameters.

2. Experiments and methods

2.1. Chemicals

All chemicals used in this work are analytical reagent grade. Solution was prepared using deionized water (18.2 MΩ cm Milli-Q). The KNO₃ (99%, Merck) was used to prepare the synthetic nitrate solutions. Both NaBH₄ (>96%, Merck) and FeCl₃·6H₂O (99%, Merck) were used for the nZVI synthesis. Synthetic water for equilibrium batch experiments were prepared with the use of KNO₃ (99%, Merck), nitrite Standard (Panreac), FeCl₃·6H₂O (99%, Merck) and FeSO₄·7H₂O (99%, Merck).

2.2. Ion exchange resins

The ion exchange resins used are Purolite C160H (Macroporous Strong Acid Cation Exchange Resin). The particle size range of resins is from 300 to 1200 μm, and the functional group is sulfonic acid with macroporous polystyrene crosslinked with divinylbenzene. The exchanged ions are hydrogen ions. The uniform coefficient and the moisture content are 1.7 (maximum) and 43–48%, respectively. The resins were washed by deionized water prior to use.

2.3. Synthesis of nZVI

The nanoiron particles were synthesized from aqueous mixture [16] under ambient conditions. The aqueous mixture was prepared by adding 100 mL of 0.045 M FeCl₃ dropwise (1 drop s⁻¹) into an equal volume of 0.25 M NaBH₄. The solution was stirred vigorously, and formation of black particles was observed. The nZVI formation reaction is presented in the following:

\[
\text{Fe(}\text{H}_2\text{O)}_{\text{3}^+} + 3\text{BH}_4^- + 3\text{H}_2\text{O} \rightarrow \text{Fe}^0 + 3\text{B(OH)}_3^- + 10.5\text{H}_2
\]

2.4. Batch experiments

The kinetic experiments were carried out in a 2 L glass batch reactor under ambient temperature of around 23 °C. 1 L of the solution was introduced into the reactor to ensure homogeneous mixing. An amount of 0.25 g nZVI dosage was applied for all the batch experiments. Samples were taken at a certain time interval and were filtered by a 0.2 μm membrane filter prior to analysis for residual nitrate as well as nitrite and ammonium.

The equilibrium batch experiments were conducted in a beaker containing 1 L of the solution and 10 g resins, and mixed by a stirrer. Samples taken at a certain time interval were filtered with 0.2 μm membrane filter. Concentrations of ammonium that adsorbed on resins were calculated according to Eq. (8) [17–20]:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

where \(q_e\) (mg g⁻¹) is the amount of adsorbed ions (mg) per mass of the resin applied (g), \(C_0\) and \(C_e\) are defined as concentrations at initial and equilibrium time, respectively. \(V\) is the volume of solution, and \(m\) mass of resin.

2.5. Instrumental analysis

Ammonium was analysed by using the Phenate method through spectrophotometric reading (CT 2400) at 640 nm [21]. Analyses of residual nitrate and nitrite were performed by using Ion Chromatography (IC; DIONEX-120, USA). The conversion of ammonium is based on initial and final concentrations of nitrate. In addition, the pH was monitored by pH metre (Suntex TS-1).

3. Results and discussions

3.1. Nitrate reduction by nZVI

Nitrate reduction was carried out in a batch reactor under the conditions of 100 mg NO₃⁻ L⁻¹, un-buffered pH, and 0.25 g of nZVI. Fig. 1 illustrates that nitrate was rapidly reduced in the first 1 min. Nitrate was converted to nitrite, ammonium, and nitrogen gas, according to Suzuki et al. [22]. They reported that nitrate disappeared via directly receiving electrons released from corrosion of Fe⁰. The experimental results show that 77% of nitrate was removed according to Suzuki et al. [22]. They reported that nitrate dis-
conditions of un-buffered pH and 0.25 g of nZVI. Fig. 2a–b shows that the removal of NO$_3^-$ decreased significantly along with the reaction time. The nitrate removal efficiencies of 88, 71, 61, 47, and 42% were obtained with the initial nitrate concentrations at 50, 100, 150, 200, and 250 mg NO$_3^-$/L$^{-1}$, respectively. It appears that the nZVI dosage of 0.25 g was not adequate to reduce much higher NO$_3^-$ concentrations. In view of ammonium formation, 50–80% of nitrates were transformed to ammonium at the end of reaction. The highest ammonium formation of 14.9 mg NH$_4^+$ as N was achieved. The kinetics of nitrate reduction and rate constants are shown in Fig. 2c and Table 1, respectively. The experimental data were fitted into both the pseudo-first and second order equations. It appears that the pseudo-second-order reaction, rather than the pseudo-first order reaction, could better describe the kinetics of nitrate reduction under various initial nitrate concentrations. It’s noticed here that, when the initial nitrate concentration was more than 100 mg L$^{-1}$, the lower $R^2$ values were observed. This is to say that the initial nitrate degradation within the range of 0–100 mg L$^{-1}$ could be strongly explained by the pseudo-second order reaction, but, as the initial nitrate concentration increased, the pseudo-second order reaction kinetics became weakly followed. Based on the pseudo-second order reaction, the rate constants ($k_{2,\text{obs}}$) of various nitrate concentrations fall within the range of (0.058–2.1) × 10$^{-3}$ M$^{-1}$ min$^{-1}$. In addition, the reaction rate was observed to decrease quite significantly when the initial nitrate concentration increased from 50 to 250 mg L$^{-1}$. Finally, it is further noticed here that the final solution pH reached approximately 9.8 under the conditions of the five different initial nitrate concentrations.

### 3.2. Effect of initial nitrate concentration

Five different initial NO$_3^-$ concentrations were employed to investigate the efficiency of NO$_3^-$ removal by nZVI under the experimental conditions of un-buffered pH and 0.25 g of nZVI. Fig. 2a–b shows that the removal of NO$_3^-$ decreased significantly along with the reaction time. The nitrate removal efficiencies of 88, 71, 61, 47, and 42% were obtained with the initial nitrate concentrations at 50, 100, 150, 200, and 250 mg NO$_3^-$/L$^{-1}$, respectively. It appears that the nZVI dosage of 0.25 g was not adequate to reduce much higher NO$_3^-$ concentrations. In view of ammonium formation, 50–80% of nitrates were transformed to ammonium at the end of reaction. The highest ammonium formation of 14.9 mg NH$_4^+$ as N was achieved. The kinetics of nitrate reduction and rate constants are shown in Fig. 2c and Table 1, respectively. The experimental data were fitted into both the pseudo-first and second order equations. It appears that the pseudo-second-order reaction, rather than the pseudo-first order reaction, could better describe the kinetics of nitrate reduction under various initial nitrate concentrations. It’s noticed here that, when the initial nitrate concentration was more than 100 mg L$^{-1}$, the lower $R^2$ values were observed. This is to say that the initial nitrate degradation within the range of 0–100 mg L$^{-1}$ could be strongly explained by the pseudo-second order reaction, but, as the initial nitrate concentration increased, the pseudo-second order reaction kinetics became weakly followed. Based on the pseudo-second order reaction, the rate constants ($k_{2,\text{obs}}$) of various nitrate concentrations fall within the range of (0.058–2.1) × 10$^{-3}$ M$^{-1}$ min$^{-1}$. In addition, the reaction rate was observed to decrease quite significantly when the initial nitrate concentration increased from 50 to 250 mg L$^{-1}$. Finally, it is further noticed here that the final solution pH reached approximately 9.8 under the conditions of the five different initial nitrate concentrations.

### 3.3. Effect of initial pH

In this study, four different initial pH values were used, including 4, 6, 8, and 10. The profiles of initial pH effect are presented in Fig. 3a–c. Similarly, both the pseudo-first and second order reactions were tested and the results are summarized in Table 1. The removal efficiencies of NO$_3^-$ were found to decrease with increasing initial pH. In view of reaction kinetics, the pseudo-second order reaction of nitrate reduction was more closely followed than the pseudo-first order reaction. Interestingly, the latter one seems to be also statistically acceptable as the pH was within the range of 6–10. But when the pH dropped further down to a pH value of 4, a relatively lower $R^2$ value (0.61) was obtained. This implies that the pseudo-first order reaction was no longer strongly observed under a more acidic pH condition, and it can be explained well only by the pseudo-second order reaction, where the $R^2$ value (0.9485) is relatively higher. Therefore, in general, it is concluded here that the reaction kinetics of nitrate degradation belongs to a pseudo-second order as the pH varies from 4 to 10. In addition, the reaction rate was observed to decrease quite significantly when the initial nitrate concentration increased from 50 to 250 mg L$^{-1}$. Finally, it is further noticed here that the final solution pH reached approximately 9.8 under the conditions of the five different initial nitrate concentrations.

### Table 1

Observed kinetic rate constant and nitrate removed under various initial nitrate concentrations (initial pH = 5.8) and initial pHs (initial nitrate = 100 mg L$^{-1}$).

<table>
<thead>
<tr>
<th>Initial conc. (mg L$^{-1}$)</th>
<th>$k_{2,\text{obs}}$ (10$^{-3}$ M$^{-1}$ min$^{-1}$)</th>
<th>$R^2$</th>
<th>Initial pH</th>
<th>$k_{2,\text{obs}}$ (10$^{-3}$ M$^{-1}$ min$^{-1}$)</th>
<th>$R^2$</th>
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<tr>
<td>50</td>
<td>2.1</td>
<td>0.962</td>
<td>4</td>
<td>0.56</td>
<td>0.945</td>
</tr>
<tr>
<td>100</td>
<td>0.41</td>
<td>0.834</td>
<td>6</td>
<td>0.34</td>
<td>0.936</td>
</tr>
<tr>
<td>150</td>
<td>0.26</td>
<td>0.790</td>
<td>8</td>
<td>0.32</td>
<td>0.907</td>
</tr>
<tr>
<td>200</td>
<td>0.079</td>
<td>0.891</td>
<td>10</td>
<td>0.24</td>
<td>0.970</td>
</tr>
<tr>
<td>250</td>
<td>0.058</td>
<td>0.633</td>
<td></td>
<td></td>
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</table>
in contact with dissolved oxygen in water. At a lower pH, the H\(^+\) would dissolve ferrous hydroxide and other protective layers (the so-called acid washing) on the surface of nZVI, yielding more fresh active sites for chemical reduction of NO\(_3^-\).

3.4. Ammonium removal by cation exchange resin

The experiments for ammonium removal from the effluent of nZVI-induced nitrate reduction process were carried out by using a batch reactor. The synthetic effluent solution was prepared and used in this study to simulate the worst case of high ferric and ferrous concentrations. The effects of solution pH’s and competitive ions on ammonium removal were investigated by using cation exchange resins.

3.4.1. Effect of pH in the presence of competitive ions

Fig. 4 shows the efficiency of ammonium removal by cation exchange resins under various pH conditions and with the presence of competitive ions. The results indicate that the efficiency of ammonium removal exhibits 40% difference between without and with the presence of competitive ions. Such a result explains that Fe\(^{2+}\), Fe\(^{3+}\), and H\(^+\) compete with ammonium ions for the active functional group on the resins. In addition, the highest ammonium removal of 70% was obtained under acidic condition of pH 4, which was followed by 60% at both pH 7 and 9. In general the percentage of ammonium removal increased significantly within 10 min and then it reached the equilibrium state. Furthermore, since a higher pH condition could result in the precipitation of ferrous or ferric ions and, in turn, the clogging of resins-packed column (the so-called iron fouling), the removal of ammonium is thus retarded.

3.4.2. Equilibrium isotherm test

The initial pH effect on equilibrium distribution of ammonium ions between the ion exchange and aqueous phases was studied to examine the behaviour of ammonium removal by cation exchange resins (10 g of C160H). Note that the removal of NH\(_4^+\) (250 mg-NH\(_4^+\) L\(^{-1}\)) in the test solution was studied with the initial pH varying from 4 to 9. Langmuir and Freundlich isotherm were applied to describe the process of ammonium uptake onto cation exchange resins using the following equations [25]:

**Langmuir equation**

\[
q_e = \frac{q_m b C_e}{1 + (b C_e)}
\]

**Freundlich equation**

\[
q_e = K C_e^{1/n}
\]

where \(q_e\) is the amount of ammonium ions (mg) per mass of the resin applied (g), \(C_e\) is the equilibrium concentration (mg L\(^{-1}\)), \(q_m\) is the maximum specific uptake corresponding to the site saturation, \(b\) is the Langmuir isotherm constant, \(K\) and \(1/n\) are the Freundlich constant related to uptake capacity and intensity, respectively.

The Langmuir isotherm is based on one solute molecule per well-defined sites (functional groups of ion exchange for this case), one ion per site; all sites are energetically equivalent, and there’s no interaction between ions. The Freundlich isotherm was also chosen to estimate the chemisorption intensity between solution species and ion exchange resins, and was derived by assuming a heterogeneous surface (multilayer adsorption) [25]. Although the aforementioned models have been widely used for adsorption process [26–30], it can be seen that the assumption and experimental data fit well for ion exchange process used in this study. As presented in Table 2, both Langmuir and Freundlich isotherms have R\(^2\) values larger than 0.99. In addition, the values of 1/n, which is defined as the measured intensity and surface heterogeneity, range from 0 to 1. In this study, the 1/n was negative, suggesting that it was reversible uptake for ammonium ions. As can be seen from Table 2, the R\(^2\) values of Langmuir (0.9983–0.9992) are slightly higher than those of Freundlich (0.9949–0.9983). Although this cannot really imply that the Langmuir isotherm model was strongly followed, somehow, the kinetics of ammonium removal by the ion exchange resins in this study was described by the Langmuir model satisfactorily.
4. Conclusions

Nitrate removal by nZVI was significantly affected by both initial nitrate concentration and initial pH. The pseudo-second order reaction for nitrate reduction was more closely followed in this study under various initial nitrate concentrations (50–250 mg L⁻¹) and pHs (4–10), with their respective value range as follows: (0.058–2.1) × 10⁻³ M⁻¹ min⁻¹ and (0.24–0.56) × 10⁻³ M⁻¹ min⁻¹. Besides, the highest nitrate removal was 77% at pH 4, and it was 88% corresponding to the initial nitrate concentration of 50 mg L⁻¹ at pH 5.8.

Using cation exchange resins, ammonium removal was simulated in the synthetic solution. It was aimed to investigate the effect of competition ions and the effect of initial pH on the behaviour of ammonium uptake by cation exchange resin. As a result, Langmuir isotherm is seemingly more appreciated than Freundlich to describe ammonium removal kinetics in the cation exchange resin process. At higher pH like 7 and 9, the competing ion species can precipitate to clog the resin-packed column and thus retard further exchange of ammonium.

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Table 2

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
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</thead>
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<tr>
<td></td>
<td>R²</td>
<td>b (1/mg)</td>
</tr>
<tr>
<td>Un-buffered</td>
<td>0.9989</td>
<td>0.064</td>
</tr>
<tr>
<td>pH 4</td>
<td>0.9990</td>
<td>0.075</td>
</tr>
<tr>
<td>pH 7</td>
<td>0.9992</td>
<td>0.069</td>
</tr>
<tr>
<td>pH 9</td>
<td>0.9983</td>
<td>0.063</td>
</tr>
</tbody>
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References