Original research article

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

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ABSTRACT

Ammonium was reported as a major undesired product in the nitrate reduction by nanoscale zero-valent iron (nZVI). Hence, the focus of this study was aimed to remove ammonium by the cation exchange resin (Purolite C160H). The preliminary study involved optimizing pH condition (4–10) for nitrate (100 mg NO_3^- L^{-1}) removal by nZVI (0.25 g L^{-1}). The highest nitrate removal of 77% was obtained at pH 4, which was followed by 70% at pH 6, 69% at pH 8, and 64% at pH 10. In addition, the maximum NH_4^+–N formation of 60% (based on the initial NO_3^-–N) occurred at pH 4. As for the nitrate reduction, it appears that the pseudo-second order reaction has been followed for both cases of various nitrate concentrations (50–250 mg L^{-1}) and initial pHs (4–10). The rate constants for the former fall within the range of (0.058 –2.1) × 10^{-3} M^{-1} min^{-1}, and the range of (0.24–0.56) × 10^{-3} M^{-1} min^{-1} for the latter. In view of formation of ammonium in the nZVI preliminary study, two consecutive experiments were performed to determine the effects of competitive ions (Fe^{2+}/Fe^{3+}, NO_2^-/NO_3^-) and initial pH's on its removal. As a result, the equilibrium time for the removal of ammonium was 10 min at initial pH 4, 7, and 9. Fe^{2+} and Fe^{3+} significantly reduced the ammonium removal efficiency by 40%, while the NO_3^- and NO_2^- residues showed insignificant effect on its removal. In addition, there is no significant effect on the removal of ammonium when various initial pHs were applied.

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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-NO_3^- 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
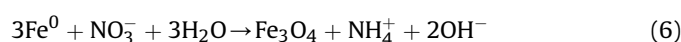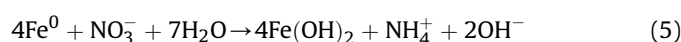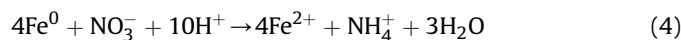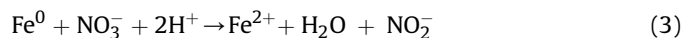
surface area, high rate of nitrate reduction, and stable reactivity [2,4,8].

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]:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \tag{1}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \tag{2}$$

$$Fe^0 + NO_3^- + 2H^+ \rightarrow Fe^{2+} + H_2O + NO_2^- \tag{3}$$

$$4Fe^0 + NO_3^- + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \tag{4}$$

$$4Fe^0 + NO_3^- + 7H_2O \rightarrow 4Fe(OH)_2 + NH_4^+ + 2OH^- \tag{5}$$

$$3Fe^0 + NO_3^- + 3H_2O \rightarrow Fe_3O_4 + NH_4^+ + 2OH^- \tag{6}$$
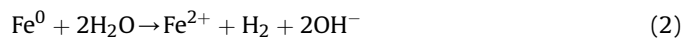
Ammonium may cause toxicity to aquatic animal and ecosystem [5,10–12]. There are many technologies used to remove ammonium such as air stripping, breakpoint chlorination, ion exchange, and biological methods [13]. Although the biological method is most effective, disadvantageous situation can occur when 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 Mill-Q). The KNO_3 (99%, Merck) was used to prepare the synthetic nitrate solutions. Both $NaBH_4$ (> 96%, Merck) and $FeCl_3 \cdot 6H_2O$ (99%, Merck) were used for the nZVI synthesis. Synthetic water for equilibrium batch experiments were prepared with the use of KNO_3 (99%, Merck), nitrite Standard (Panreac), $FeCl_3 \cdot 6H_2O$ (99%, Merck) and $FeSO_4 \cdot 7H_2O$ (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 $FeCl_3$ dropwise (1 drop s^{-1}) into an equal volume of 0.25 M $NaBH_4$. The solution was stirred vigorously, and formation of black particles was observed. The nZVI formation reaction is presented in the following:

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5H_2 \tag{7}$$
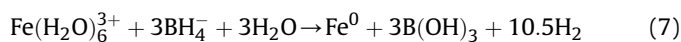
2.4. Batch experiments

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]:

$$q_e = \frac{(C_0 - C_e) * V}{m} \tag{8}$$

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 nitrate 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 NO_3^- 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 Fe^0. The experimental results show that 77% of nitrate was removed and 60% of NH_4^+–N (based on the initial NO_3^-–N) was produced. Lubphoo et al. [23] reported 77% of nitrate being transformed to ammonium under the conditions of 100 mg NO_3^- L^{-1} and 0.25 g of nZVI. The nitrate reduction reaction can be described by Eqs. (1)–(7). However, the intermediate of nitrite was negligible (< 0.25 mg NO_2^- L^{-1} as N).