

Experimental effect of medium ratio on removal efficiency of nitrate nitrogen in groundwater by zero-valent iron, activated carbon and zeolite

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ABSTRACT

In this study, column experiments in the laboratory were set up to examine how the concentrations of nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen changed when a nitrate-rich solution was passed through a medium comprising zero-valent iron, activated carbon, zeolite, and coarse sand. We varied the proportions of the components of the medium to determine how it influenced the nitrate removal and nitrogen fractions. Three different scenarios were used, with: (1) iron, activated carbon, and coarse sand at a ratio of 3:1:6; (2) iron, activated carbon, and zeolite at a ratio of 3:1:6; and (3) iron, activated carbon, and zeolite at a ratio of 3:3:4. The nitrate nitrogen concentration decreased from 25 mg/L to 2 mg/L in the first scenario. Removal was better when zeolite was added to the medium as most of the nitrate nitrogen broke down to ammonia nitrogen, with nitrite nitrogen as an intermediate product. The results of the tests showed that nitrate removal was best when the medium was iron, activated carbon, and zeolite, mixed at a ratio of 3:1:6. This study provides a scientific reference for *in situ* remediation of nitrate pollution in groundwater.

Key words | activated carbon, column experiment, groundwater, nitrate, zero-valent iron

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INTRODUCTION

Nitrate-contaminated groundwater is harmful to human health (Ganesan *et al.* 2013; Goudarzi *et al.* 2017). Methods such as ion exchange, biological deoxygenation, permeable reactive barriers (PRB), reverse osmosis, and electro dialysis have been used to reduce the nitrate concentrations in groundwater (Lu *et al.* 2014; Ghaemini & Mokhtarani 2018; Peng *et al.* 2018). Of these, PRB, considered environmentally friendly and non-intrusive, have become an increasingly popular method for *in situ* remediation of groundwater in recent years.

The reaction media used in *in situ* remediation include sepiolite, activated carbon, zero-valent iron (ZVI), zeolite, bimetallic materials, solid carbon, and denitrifying bacteria. The main types of ZVI used include nanometre iron and sponge iron. Shi *et al.* (2016) found that nanometre iron

performed well when removing nitrate nitrogen from water. However, applications of nanometre iron are limited because the particles are very small, they oxidize easily and aggregate in water, and are influenced by the pH (Shi *et al.* 2013). An *et al.* (2013) reported that ammonia nitrogen accounted for between 74.3% and 98.6% of the amount of NO₃-N removed, so ammonia nitrogen was the main by-product of the reaction between sponge iron and NO₃-N. Because nanometre iron is small and aggregates easily in water, the specific surface area, reactions, and fluidity all decrease. Nanometre iron oxidizes easily and the surface passivation layer is not conducive to reducing pollutants (Babaei *et al.* 2015; Jiang *et al.* 2015). And the physical and chemical properties of the particles' surfaces need to be modified, so that stable uniform particles are dispersed in the system.

ZVI is used instead of either nanometre or sponge iron to remove nitrate from groundwater because it is not expensive and is easy to use. Many recent studies have reported how ZVI has been used to remediate nitrate pollution (Suzuki *et al.* 2012; Fu *et al.* 2014). Tang *et al.* (2012), from their studies of PRB, found that as well as producing nitrate nitrogen, reactions could occur in alkaline conditions with ammonia nitrogen as the main product, and the corroding products of Fe^{2+} and Fe^{3+} strengthened the denitrification. Zeolite can be used to reduce the ammonia nitrogen concentrations. Natural zeolite is a kind of porous silicate mineral with a frame structure. Thanks to its well-developed pores, channel-like structure, and exchangeable cations, the physical adsorption and cation exchange capacities of zeolite are high (Gennaro *et al.* 2016). Given its limited ability to absorb ammonia and nitrogen, many researchers have tried to improve the adsorption capacity of natural zeolite. Natural zeolite can be activated by roasting at a high temperature, treating with acid (alkali), or immersing in a salt solution and baking (Soh *et al.* 2017). Once activated, impurities, such as organic matter, can be removed and retained in the zeolite pores or in the channel network, and the adsorption performance of zeolite is improved (Arzumanov *et al.* 2014). Therefore, nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen, pH, the overall nitrogen balance, and

soluble iron in nitrate-rich water were monitored to facilitate the detection of changes that occurred when activated zeolite was added to the test medium. Changes in the dielectric permittivity of the medium when the activated zeolite was added were also explored.

The above discussion of recent literature shows that different media can influence the removal of nitrate, and that ammonia nitrogen is frequently produced when nitrate is removed with ZVI. This study demonstrates how the performance of PRB technology was improved using ZVI; the nitrate-removal ability of a medium comprising ZVI, activated carbon, coarse sand and activated zeolite, combined at different ratios, was investigated.

MATERIALS AND METHODS

Experimental set-up

The main test unit included a Markov bottle with a capacity of 18 L, an acrylic circular tube (10 cm inner diameter, length 100 cm), and a total of four horizontal sampling tubes, spaced 20 cm apart along the acrylic circular tube (Figure 1). These four tubes were used for the sampling and also to calculate the permeability coefficient. A glass tube with an inner diameter of 5 mm was placed in the Markov bottle, and the glass tube was inserted below the liquid level in the bottle to keep the head difference constant. The constant flow rate of $0.005 \text{ m}^3/\text{d}$ was controlled by a flow meter. The bottom of the pipe was supported by a porous plate and a nylon mesh. A water buffer of about 5 cm was reserved to prevent water from washing the reaction material directly.

The test materials were granular activated carbon, iron powder, homogeneous coarse sand, and activated zeolite. The particles of the granular activated carbon were between 1 and 2 mm; the iron, pre-treated with water, had an average diameter of 40 mesh, specific surface area of $30\text{--}35 \text{ m}^2/\text{g}$ as reported by the manufacturer (see also <http://www.bjyxch.cn/>); the homogeneous uncontaminated coarse sand (from Hefei Huaguang Quartz Sand Company) was between 0.25 and 2 mm with measured bulk density of $1.27 \text{ g}/\text{cm}^3$ and porosity $n=0.34$, and the particles of zeolite were between 0.5 and 1 mm.

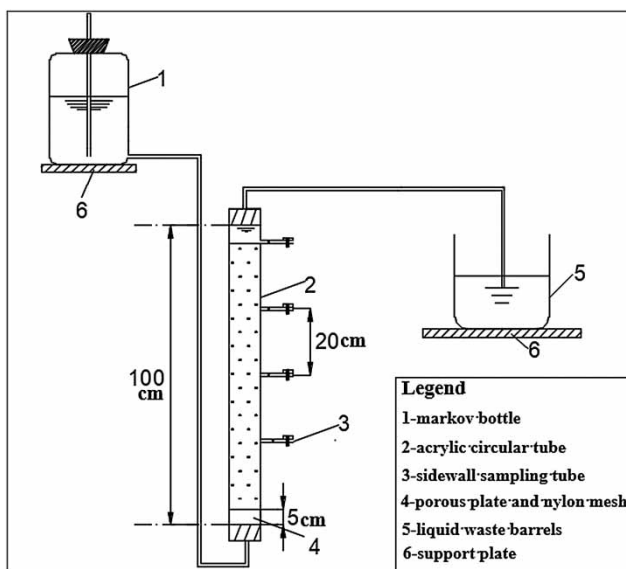


Figure 1 | Experimental set-up.

Experimental scenarios

Three sets of test protocols were set up to compare and examine the ability of zeolite to remove ammonia nitrogen during the test. Other studies have shown that ZVI has an important role in the removal of nitrate, and that activated carbon can accelerate the removal of nitrate. Coarse sand can prevent clumping of the iron powder, maintain good hydraulic conditions, and extend the useful life of PRB. The medium in scenario I was iron, activated carbon, and coarse sand, mixed at a volume ratio of 3:1:6. After receiving the test results of the first scenario, the medium was changed, and the coarse sand was replaced with zeolite so the excess ammonia nitrogen was adsorbed, and called scenario II. The volume ratio remained unchanged, with iron, activated carbon, and zeolite at a ratio of 3:1:6. To look more closely at the role of activated carbon in the reaction process, the ratio of the activated carbon in scenario II was adjusted, so that the ratio of iron, activated carbon, and zeolite was 3:3:4, and this was called scenario III. The hydraulic conductivity of the mixed media of scenarios I, II, and III is 298 m/d, 287 m/d and 234 m/d, respectively; the corresponding porosity is 0.30, 0.27 and 0.22, respectively.

Different nations have different threshold concentrations for $\text{NO}_3\text{-N}$. For example, the World Health Organization drinking water quality standards state that the maximum allowable $\text{NO}_3\text{-N}$ concentration is 10 mg/L, while the thresholds for the United States and China are 11.3 and 20 mg/L, respectively. In this test, because the groundwater is polluted by nitrate, the initial concentration should be greater than 20 mg/L, and we set it at 25 mg/L. The test was conducted at an environmental temperature of 22 °C–24 °C.

Experimental procedures

- Iron powder and sand were pre-treated by washing with water. The sand was washed to remove some impurities and the iron powder was washed to increase the activity and speed of the reaction.
- The test columns were set up. Depending on the required ratio of the test materials, the materials were evenly mixed and filled into the test columns. The materials had the same dry density and were loaded into the

columns in layers. The air was discharged from the dielectric materials as the columns became gradually saturated. The experiment was set up so that a saturated flow state could be maintained.

- Nitrate solution with a concentration of 25 mg/L was prepared with KNO_3 and distilled water.
- The prepared nitrate solution was put into the Markov bottle, and was supplied to the reaction columns from the Markov bottle.
- When the outflow stabilized, samples were collected once every day at the outlet. The test was stopped when the total nitrogen concentrations stabilized.
- The samples were tested spectrophotometrically. The concentrations of nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen were determined by UV spectrophotometry, double nitrogen coupled spectrophotometry, and Nessler reagent spectrophotometry.

RESULTS AND DISCUSSION

Changes in the concentrations of the different nitrogen forms

When the ratio of the medium (iron, activated carbon, and sand) was 3:1:6, the concentrations of $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NH}_3\text{-N}$ changed as shown in Figure 2. After 1 day, the $\text{NO}_3\text{-N}$ concentrations had rapidly dropped to 1.5 mg/L,

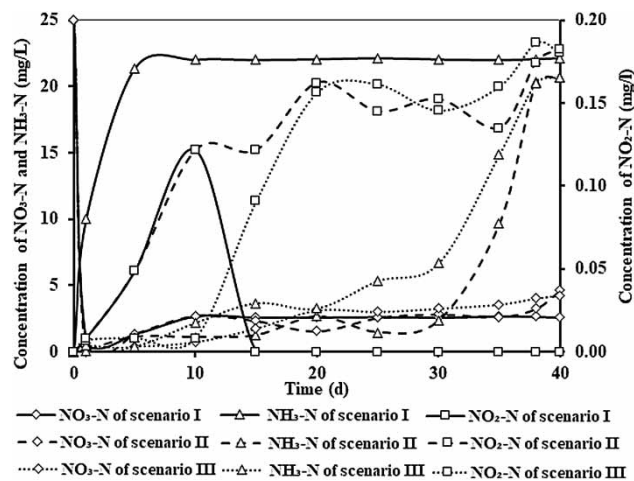


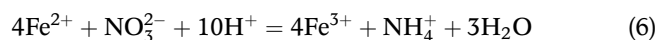
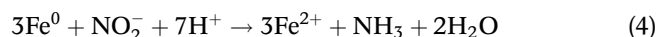
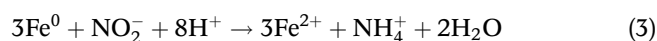
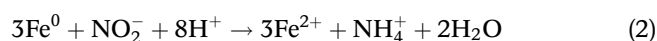
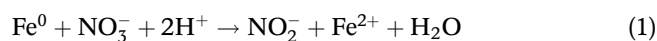
Figure 2 | Changes in the $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NH}_3\text{-N}$ concentrations over time.

after which, because of the reaction rate, the concentration stabilized and fluctuated between 1.5 and 2 mg/L. The concentration reduction represented a removal rate of 95%. The concentration of the intermediate product of the reaction, $\text{NO}_2\text{-N}$, remained low, and was below 0.1 mg/L. As the experiment progressed, the $\text{NH}_3\text{-N}$ concentration increased, and stabilized after 6 days at around 22 mg/L, and about 95% of the $\text{NO}_3\text{-N}$ was converted to $\text{NH}_3\text{-N}$. The concentration was higher than the safety limit, which indicates that, for this medium and at this ratio, ammonia nitrogen was the main product from the nitrate reaction. Therefore, when iron, activated carbon, and coarse sand were used as the reaction materials, the nitrate concentration decreased, but ammonia nitrogen was generated at high concentrations, which is not ideal. As reported by Suzuki *et al.* (2012), who analyzed the crystal structure of the zeolite, the volume of the holes in the zeolite crystal structure can account for more than 50% of the total volume of the zeolite crystals. The zeolite pores are uniformly distributed but have a small pore size. The inner surface of the zeolite crystals is greater than the inner surface of the average particle; solid particles generally have a surface area of only a few square metres per gram, but the inner surface area per gram of zeolite can reach more than 1,000 square metres, so the adsorption of zeolite is particularly large, and the zeolite can effectively adsorb ammonia nitrogen. Because of these properties, zeolite was used instead of sand in the second scenario, but the iron, activated carbon, and zeolite ratio was maintained at 3:1:6. The changes in the concentrations of $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NH}_3\text{-N}$ in scenario II are shown in Figure 2. The concentration of $\text{NO}_3\text{-N}$ remained at around 2.0 mg/L for the 30 days of the test, representing a removal rate of more than 90%. The concentration of $\text{NH}_3\text{-N}$ was less than 0.5 mg/L, and was lower than the safety limit. Once the zeolite became saturated, the concentration of $\text{NH}_3\text{-N}$ at the outlet increased rapidly, and finally stabilized at around 20 mg/L, and accounted for about 93% of the decrease in the $\text{NO}_3\text{-N}$ concentration. The results show that when iron powder is the main component of the medium for removing nitrates from groundwater, ammonia nitrogen is the main by-product, and $\text{NO}_2\text{-N}$ is produced at low concentrations as an intermediate product (around 0.2 mg/L). When the iron, activated carbon, and zeolite

were used at a ratio of 3:1:6, the $\text{NO}_3\text{-N}$ removal rate was over 90%, and the ammonia nitrogen concentration was lower than the safety limit for 30 days. This shows therefore that when the medium comprises iron, activated carbon and zeolite at a ratio of 3:1:6, the nitrate concentrations can be maintained within the required standards for 30 days under laboratory conditions.

Activated carbon has a large specific surface area, which means that it can improve the permeability of the reaction column and promote nitrate reactions. Therefore, the ratio of iron, activated carbon, and zeolite in the medium in scenario II was adjusted to 3:3:4 (scenario III). The changes in the concentrations of $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NH}_3\text{-N}$ in scenario III are shown in Figure 2. After 25 days, the $\text{NO}_3\text{-N}$ concentration was 1.5 mg/L, representing a decrease of about 98%, which was higher than the concentration decrease for scenarios I and II. When the medium in the column was ZVI, activated carbon, and zeolite, the activated carbon and iron powder formed many tiny battery systems during the nitrate reaction process that accelerated the electron transfer, promoted the reaction, and improved the reaction efficiency. However, because the volume of the zeolite was lower than in scenario II, the adsorption was lower and the time to saturation was less, so that the concentration of $\text{NH}_3\text{-N}$ was significantly higher on day 35 than earlier in the experiment, and finally stabilized at about 20 mg/L.

It can be known from the column experiment that under the condition that the reaction system was neutral, the ZVI can react with NO_3^- to form a reduction product mainly composed of trivalent nitrogen and Fe in an oxidation state according to the following reactions (Adeleye *et al.* 2013):



Total nitrogen concentrations

The changes in the total nitrogen concentrations over time were plotted to facilitate further analysis of the transformations and time taken to achieve equilibrium between $\text{NO}_3\text{-N}$, $\text{NH}_3\text{-N}$, and $\text{NO}_2\text{-N}$ during the reaction (Figure 3). The concentration curves in Figure 3 show that the total nitrogen concentrations decreased rapidly at the beginning of scenarios I, II and III, and then increased, and gradually stabilized. The changes in the total nitrogen concentrations mainly reflect the adsorption of $\text{NO}_3\text{-N}$ or $\text{NH}_4^+\text{-N}$, which was facilitated by the activated carbon. The iron powder and the compounds produced in the iron powder reactions, Fe_3O_4 and Fe_2O_3 , will also affect the adsorption of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$. There was no gaseous escape of nitrogen from the experimental set-up.

The difference observed between scenarios I and II reflects the difference in the medium. The coarse sand used in scenario I had almost no adsorption capacity, so the total nitrogen concentrations began to increase rapidly on day 2 of the experiment. Because the zeolite had not reached its saturation capacity, the total nitrogen concentration in scenario III first decreased, and then changed gradually from day 2 until day 30, after which the total nitrogen concentrations increased rapidly when the zeolite became saturated. This shows that the removal efficiency of the medium is directed controlled by the zeolite adsorption capacity. The total nitrogen and $\text{NH}_3\text{-N}$ concentrations in the effluent of scenarios II and III followed similar patterns (Figure 3); the $\text{NO}_3\text{-N}$ concentration was relatively stable

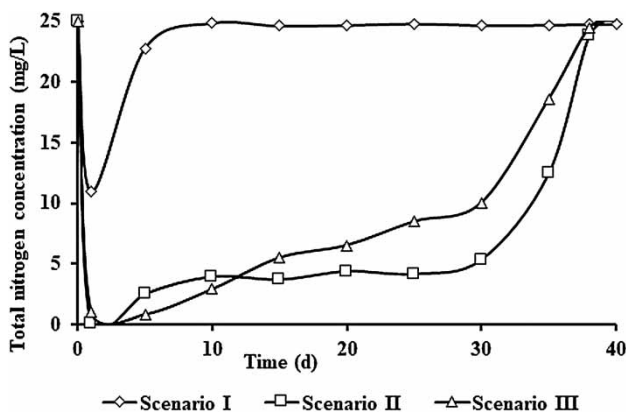


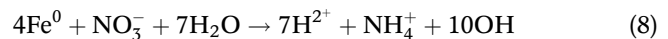
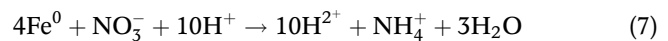
Figure 3 | Changes in the total nitrogen concentrations during the experiments.

during the experiment, and $\text{NO}_2\text{-N}$ made a very small contribution to the overall total nitrogen content. In the later stage of the reaction, the $\text{NH}_3\text{-N}$ concentrations increased rapidly as the zeolite became saturated. The three main forms of nitrogen basically reached equilibrium during the test period, which once again demonstrates that nitrogen was in equilibrium when nitrate nitrogen was being removed by the industrial iron powder. Because there was more zeolite in scenario II than in scenario III, the sum of the concentrations of the main nitrogen components was lower in scenario II than in scenario III from day 10 until day 35, which highlights the large contribution of ammonia nitrogen to the total nitrogen balance.

Changes in the pH

The remediation of nitrate in groundwater using iron powder as a reducing agent is mainly controlled by the pH. The pH in scenario I had stabilized at about 8.5 by the end of the test period. Scenarios II and III consumed more H^+ , and the pH gradually stabilized at about 10.

Ammonia nitrogen is produced when ZVI reacts with nitrate nitrogen, as shown in Equations (7) and (8):



The higher pH in scenario I reflects the lack of zeolite and the rapid accumulation of ammonia nitrogen in the reaction system. Most of the ammonia nitrogen in the water was in the form of NH_4^+ , which formed a hydrous ammonia and so the reaction system appeared to be weakly alkaline. In scenario III however, the zeolite material absorbed ammonia nitrogen, and the reaction system gradually became weakly alkaline, but over a longer time.

Hydraulic conductivity

The hydraulic conductivity K is frequently used to characterize the permeability of rock and soil, and is calculated with a fixed water head test. According to Darcy's Law, before and after the tests, seepage tests were carried out in the

experimental device with a one-dimensional steady flow water supply.

The permeability coefficient of the media for the three different tests decreased dramatically after the test. The permeability coefficient of scenarios I, II, and III decreased from 298 to 73 m/d, from 287 to 68 m/d, and from 234 to 59 m/d, respectively. In scenario II, the coarse sand was replaced by zeolite. Zeolite was more rounded and absorbent, and had a longer operating time, so the results of the hydraulic conductivity test for scenario II were lower than those for scenario I. The lower permeability coefficient in scenario III corresponds with the lower volume of zeolite used.

The permeability coefficient can reflect the permeability of a geotechnical soil or medium, and the permeability coefficient of the medium was lower after the test. Insoluble in water, Fe_3O_4 and Fe_2O_3 block the device, and impede the progress of the reaction so that the removal rate gradually decreases. This problem must be considered when promoting and applying ZVI to reduce nitrate in groundwater.

CONCLUSIONS

In this study, iron powder, activated carbon, zeolite, and coarse sand were used in the reaction medium. Using a laboratory column experiment, three tests were carried out with the medium components at different ratios to treat the nitrate pollution. In our tests, the $\text{NO}_3\text{-N}$ concentration decreased from 25 to 2 mg/L when iron powder was the main component of the medium. Most of the nitrate nitrogen was transformed into ammonia nitrogen, nitrite nitrogen was the intermediate product, and the treatment effect decreased gradually as the reaction time increased. Zeolite is a good medium for treating ammonia nitrogen. Therefore, so that the concentrations of $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{NH}_3\text{-N}$ can be maintained within the quality thresholds for groundwater quality, we suggest using the medium tested in scenario II, with iron, activated carbon, and zeolite at a ratio of 3:1:6.

The results from this study will be useful when selecting the ratio of the components for a medium to remediate nitrate pollution in groundwater by PRB technology. However, because Fe_3O_4 and Fe_2O_3 , which are insoluble in

water, were generated in the reaction, the device blocked, which caused a decrease in the permeability coefficient of the medium. And as this is a laboratory-scale study, there may need to be added more data about the long-term effects of using the materials (e.g. ion exchange and biological denitrification) at the full scale. These two problems will be explored in the next step of our research.

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