

Original Research

Laboratory Tests for Efficient Nitrate Removal with Water-Washed Zero Valent Iron and the Associated Mixed Mediums

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Abstract

The acid pre-washing of zero valent iron for improving removal efficiency would deduce the secondary pollution in groundwater, and more fine particles of zero valent iron would reduce the permeability of aquifers. In order to better understand the approaches of nitrate removal, a series of laboratory experiments was conducted in this study. Batch tests showed that washed zero valent iron powder and activated carbon are more efficient for removing nitrate than cemarite and zeolite, similar with the acid pre-washing zero valent iron. X-ray diffraction phase analysis showed that a kind of oxide Fe_3O_4 generated on the surface of the washed iron powder particles, which is mixed with Fe_2O_3 and FeO , is relatively loose and can improve the efficiency of nitrate removal. A continuous flow column system test showed that the coarse sand-zero valent iron mix (R1), the coarse sand-zero valent iron-activated carbon mix (R4), and the coarse sand-zero valent iron-sawdust mix (R5) are more effective for reducing nitrate than the coarse sand-activated carbon mix (R2) and the coarse sand-sawdust mix (R3). Components such as $\text{NO}_2\text{-N}$ and $\text{NH}_4^+\text{-N}$ would have environmental concerns as well. Further chemical analysis on the fluids from nitrate removal treatment indicates that R1 and R4 are the most effective and also environmentally friendly media for nitrate removal. This study showed that R1 and R4 media could be developed into a viable technology for the removal of nitrate in high concentration of polluted groundwater.

Keywords: nitrate removal, zero valent iron, batch test, column system, groundwater

Introduction

Nitrate contamination in groundwater has become an increasingly serious environmental problem, especially to the people living in underdeveloped countries where many still rely on groundwater for

drinking water [1]. Nitrate pollution is considered as a nonpoint source that results from agriculture runoff, nitrogenous fertilizers, animal manure, industrial and domestic wastewaters, septic systems waste, etc. [2-5]. The nitrate contamination of groundwater is hidden and irreversible, its spatial and temporal variation is great, and its removal from groundwater has been a great challenge to the environmental community [6]. So it is a hot and difficult topic in nitrate removal and

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groundwater remediation aspects [7-8]. At present, many active materials have been successfully applied to nitrate removal, especially in the PRB system, which is used to deal with the nitrate pollution in groundwater [9-13]. The zero-valent metals such as Fe, Al, Zn, and Mg have been frequently used for reducing nitrate anions [9, 14]. Among these zero-valent metals, zero-valent iron possesses a great importance for this purpose because it possesses a high specific surface area, which leads to high surface reactivity [15-16]. The use of zero-valent iron (Fe⁰) in the treatment of nitrate in groundwater has been studied [17-20]. Many factors were believed to affect the performance of zero-valent iron toward nitrate removal, and many studies have been conducted over the past decades [21-22]. pH is one of the most important characteristics of water that affects the rates of nitrate removal by zero-valent iron since pH greatly affects the rate of zero-valent iron corrosion [23-24]. Iron's intrinsic characteristics, especially particle size, has been identified as an important feature that influences the sequestration kinetics of nitrate by zero-valent iron. Some researchers use the nanoiron as reaction medium, as its surface area (>31.4 m²·g⁻¹) and surface activity (25.8 kJ·mol⁻¹) are larger than colloidal iron and industrial iron powder, which increase the contact chance of iron and NO₃⁻. So the nitrate removal of nanoiron is better than colloidal iron and industrial iron powder [25-26]. Another factor is acid washing, one of the earliest examples used to pretreat virgin zero-valent iron and which can remove the passive oxide layer and thus increase the reduction rates in laboratory tests [27].

However, there are also some defects during the treatment process. On the one hand, acid washing could produce strongly acidic wastewater with a high concentration of iron ions, and could make the loss of iron mass, which could cause secondary pollution of groundwater. This limited the widespread use of nitrate removal using zero-valent iron to a certain extent. On the other hand, as the major issues including long-term reactivity, mobility, and possible eco toxicity of nZVI are still unanswered, and the high cost is another consideration issue, especially the nanoiron with catalyst and chemical stabilizing agent whose price up to 120 U.S. \$/kg [28], therefore the nZVI could not be widely used for nitrate removal until these issues are resolved. So researches that combine the biological and chemical methods such as adding the activated carbon and sawdust to the iron powder to remove the nitrate in groundwater were conducted.

This study discussed the feasibility and efficiency of nitrate removal by using the water-washed iron powder in comparison with other mediums. It was also discussed that the removal efficiency and the associated permeability of the mixed mediums, which include iron powder and adding other mediums in the near-neutral pH conditions in the field. The target was to improve the reaction efficiency and at the same time avoid the secondary pollution of groundwater. The objectives of

this study were to: 1) select the suitable industrial iron powder for nitrate removal through batch experiments, 2) compare the nitrate removal efficiency of acid pre-washed and water pre-washed of pristine ZVI, and 3) select the best composition mediums based on industrial iron powder through continuous flow column systems for nitrate removal under field conditions.

Material and Methods

Materials

Groundwater samples contaminated with nitrate were replaced by nitrate solution, which was prepared in the laboratory by dissolving a predetermined amount of KNO₃ in the distilled water.

Zero-valent iron (Fe⁰) with particle sizes of 250 μm, 420 μm, and 840 μm, activated carbon, cemarite, and zeolite with particle sizes of 0.3-0.8 mm were used as the reaction mediums, respectively. Quartz sand was used as aquifer media.

Apparatus and Methods

Batch Experiments

Laboratory-scale batch experiments and continuous flow column systems experiments were conducted to evaluate nitrate reduction by different reaction mediums. Batch experiments were used to evaluate the nitrate removal efficiency in different residence

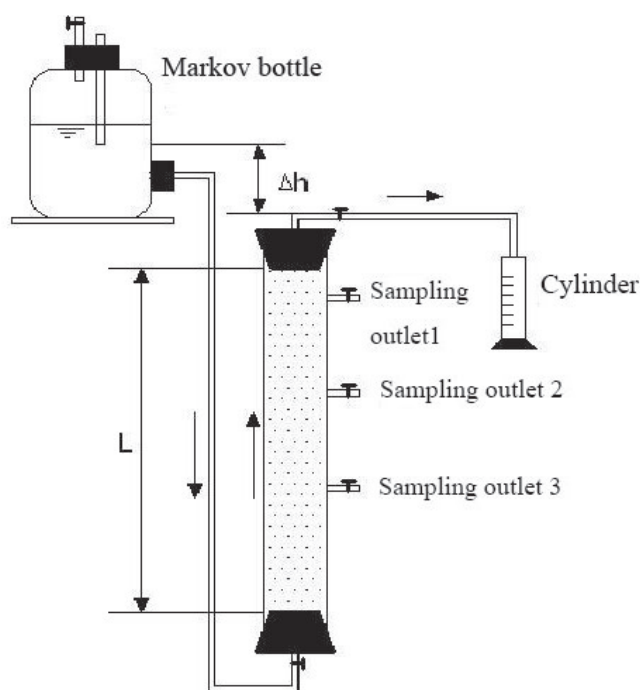


Fig. 1 The apparatus of the continuous flow column systems experiments.

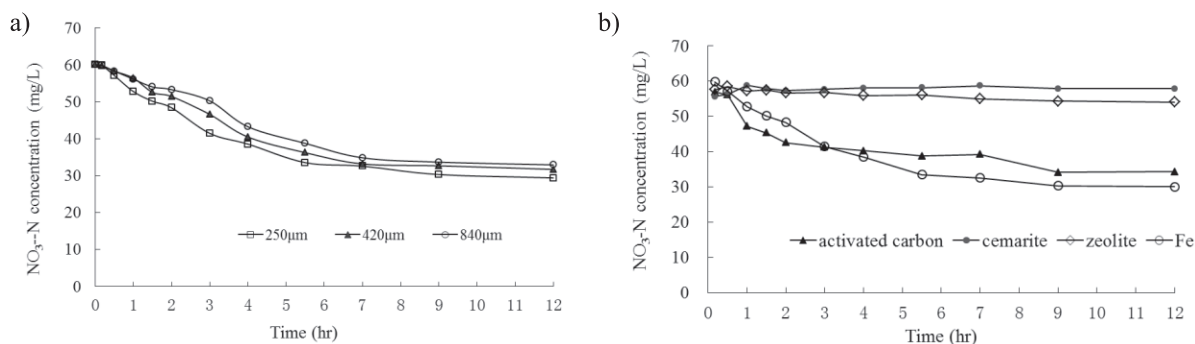


Fig. 2 Nitrate reduction by different particle size iron powder and different reaction mediums.

times. Jars were used as the reaction vessel containing the nitrate solution and the reaction mediums. When the reaction was complete, the variation of nitrate concentration and nitrate removal efficiency by iron powder were analyzed.

Continuous Flow Column Systems Experiments

As shown in Fig. 1, the reactor mediums were put in a cylindrical reactor with the length of 500 mm and internal diameter of 50 mm, and the nitrate solution was put in an 11 L Markov bottle. The glass tube with internal diameter of 9 mm connecting the cylindrical reactor and the Markov bottle ensured a steady and continuous flow and kept the constant head difference Δh between the Markov bottle and the outlet of the cylindrical reactor. The nitrate solution outflowed from the Markov bottle to the bottom of the cylindrical reactor. After reaction in the reactor, the solution flowed from the top of the cylinder and into the measuring cylinder. In the outlet, there was 5 cm thick quartz sand to be the supporting layer to ensure continuous flow. Three sampling ports were set on the side of the cylindrical reactor.

Nitrate-N, nitrite-N, and ammonia-N were measured by standard colorimetric method using a spectrophotometer (UV757). pH was monitored by the pH meter (PHSJ-5). A scanning electron microscope (SEM, Hitachi S-450) was used to obtain the microstructure and size information of iron powder.

Results and Discussion

Batch Experiments in Single Medium

Nitrate Removal Efficiencies of Different Reaction Mediums

The batch experiments were conducted in jars at 25°C. The initial concentration of nitrate solution was 60 mg/L and the initial pH was 7. The reaction mediums were put into the nitrate solution in the jars and then put them in the oscillator at 200 r/min.

Fig. 2 shows the nitrate concentration variations with time in different reaction mediums. The nitrate removal

efficiency of different particle sizes iron powder is shown in Fig. 2a). The nitrate concentration decreased with time in all the particle size iron powders. The nitrate concentration decreased from 60 mg/L to 32.92 mg/L, 31.71 mg/L, and 29.40 mg/L, and the removal rates were 45%, 47%, and 51% in 12 hours when the iron powder particle sizes were 840 μm , 420 μm , and 250 μm , respectively. The nitrate removal rate increased with the decrease of iron particle size as a whole. However, there was no significant difference among these three particle sizes, so we could think the nitrate removal efficiency of the three particle size iron powders was almost the same within half a day.

As shown in Fig. 2b), the NO_3^- concentration gradually decreased with the increased reaction time in activated carbon and Fe^0 mediums, while in the cemarite and zeolite mediums there was almost no variation. In the activated carbon medium and Fe^0 medium, the NO_3^- concentration decreased from 60 mg/L to 34.34 mg/L and 30.12 mg/L in 12 hours, respectively. Therefore, the nitrate removal efficiency of activated carbon and Fe^0 medium was better than for the cemarite and zeolite mediums.

Nitrate Removal Efficiency under Different pH Conditions

As there was oxide film on the surface of the iron powder, it would influence the nitrate removal efficiency. The removal rate would increase after treatment by acid. However, this would increase the secondary pollution. Therefore, washing and acid treatment efficiencies on iron powder were compared through batch experiments.

As shown in Fig. 3, at the same treatment time the nitrate concentration decreased with pH decreasing, which showed that the stronger the acidity, the better the nitrate removal efficiency by iron powder.

Fig. 4 presents the nitrate concentration variation in water pre-washed and acid pre-washed. The nitrate removal efficiency by water-washed iron powder was basically the same as that by acid washing when $\text{pH} = 4.0$. This shows that the pretreatment of ZVI by acid washing could be replaced by water washing, which could avoid the secondary pollution.

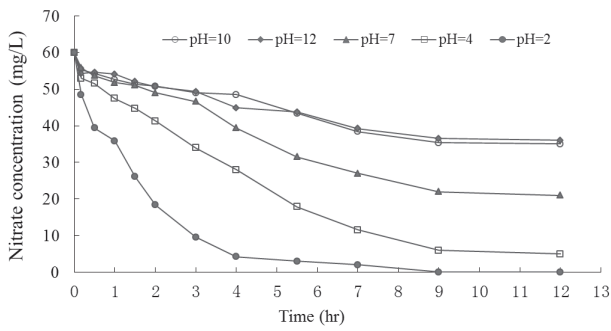


Fig. 3 Effect of pH on nitrate removal.

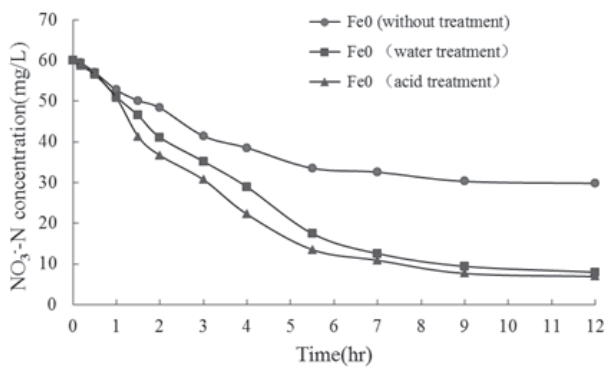


Fig. 4 The nitrate reduction by iron powder without treatment, washing by water and acid.

Analysis of Surface Morphology and Structure of Iron Powder

In order to further analyze the difference of the nitrate removal efficiency between iron powder before

treatments and washing by water or acid, the surface morphology was observed by scanning electronic microscope and the material structure was tested and analyzed using x-ray diffraction (XRD).

Fig. 5 is the camera captured image and scanning electronic microscope (SEM) image of iron powder before and after treatments. As shown in Fig. 5a), the surface of Fe⁰ was relatively smooth and the structure was compact before washing by water. While after washing by water (Fig. 5b), there were a lot of micro pores on the surface of Fe⁰ and the structure was loose. In addition, the specific surface area increased, which increased the contact frequency of iron powder and NO₃⁻. Therefore, the nitrate removal of the iron powder after water washing was much more efficient than without washing.

X-ray diffraction (XRD) analyses were performed to characterize mineralogical properties of Fe⁰ before and after the treatment (Fig. 6). XRD spectrum of iron powder before water washing showed 4 peaks corresponding to ferrite (Fig. 6a). Fig. 6b) showed the XRD spectrum of iron powder after water washing. It showed 11 peaks in the XRD spectrum analysis, of which the peak value was 3.021 cps. The main item on the sample surface was black grey magnetite with a proportion of 5.15 g/cm³, while inside it was mainly pure iron powder. This indicated that the surface of the iron powder particles was oxidized to loose MOX of Fe₂O₃ and FeO, which could improve the removal efficiency of nitrate.

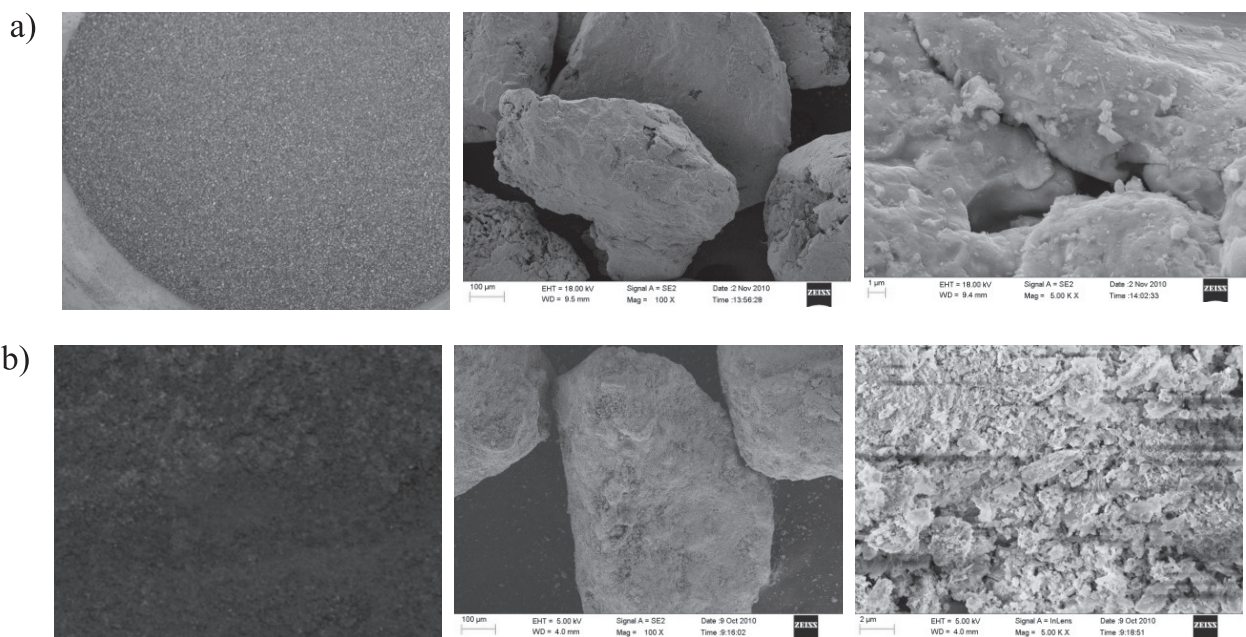


Fig. 5 SEM images of Fe⁰ a) without pre-treatment and b) after washing by water.

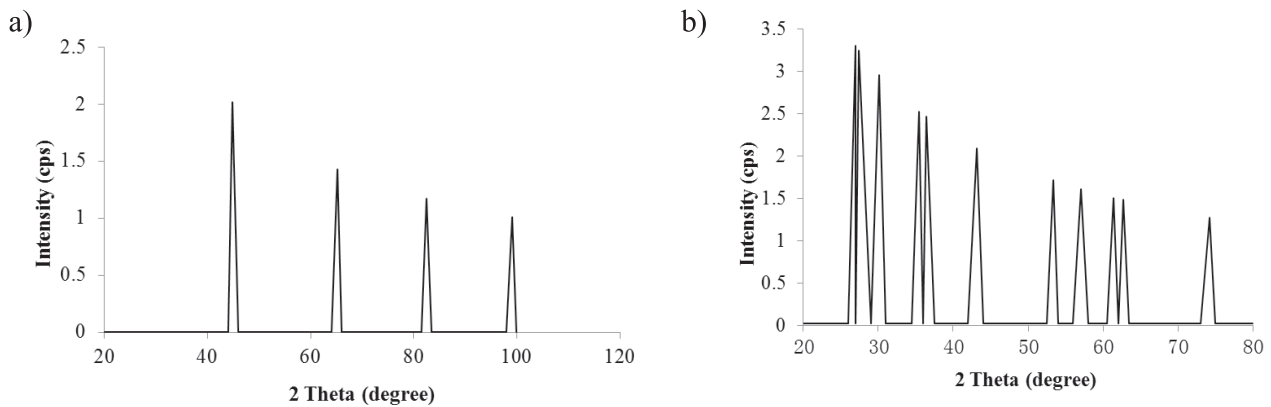


Fig. 6. X-ray diffraction patterns of Fe⁰ before and after treatment: a) before treatment, b) after treatment.

Composite Mediums Cylinder Experiments near Field Conditions

Nitrate Removal Efficiency of Composite Mediums

According to the batch experiment results, the nitrate removal efficiency of activated carbon and Fe⁰ mediums was better. However, when PRB for remediation of contaminated groundwater in the field, if the permeability of the reaction mediums was lower than the sandy aquifer, the groundwater would not pass through the PRB, which could not reach the effect of nitrate removal. So iron powder mixed with coarse sand and activated carbon would be a better choice as it could improve permeability and promote reaction. The initial concentration and pH of the nitrate solution in the Column system experiments was 80 mg/L and 7.0, respectively. Coarse sand-zero valent iron mix (R1), coarse sand-activated carbon mix (R2), coarse

sand-sawdust mix (R3), coarse sand-zero valent iron-activated carbon mix (R4), and coarse sand-zero valent iron-sawdust mix (R5) media were tested (Table 1). The hydraulic conductivity of the composite media was about 52 m/d. the nitrate concentration variation with time is shown in Fig. 7.

From Fig. 7 we see that there were obvious differences in the effects of different composite media on nitrate removal. In two-phase mixed medium the nitrate removal efficiency of R1 was best. The nitrate concentration dropped rapidly from 80 mg/L to less than 10 mg/L within 24 hours. For R2 composite media, the nitrate concentration decreased rapidly in the first day, and then gradually increased, which indicated that the activated carbon had a certain physical adsorption effect on nitrate and the activated carbon would lose its effect when it reached saturation. For R3 sawdust/coarse sand mix, the nitrate concentration decreased linearly. The nitrate removal rate of three-phase mixed medium (R4 and R5) was better than two-phase mixed medium, which the concentration of nitrate decreased less than 10 mg/L in 24 hours. Comparing the removal results of R4, R5, and R1, the nitrate concentration of

Table 1. The experiments scheme of different composite mediums.

Test scheme	Medium component	Particle size/mm	percent /%
R1	Coarse sand	0.25-2.0	70
	Iron powder	0.25-0.5	30
R2	Coarse sand	0.25-2.0	70
	Activated carbon	0.3-3.0	30
R3	Coarse sand	0.25-2.0	70
	Sawdust	0.25-2.0	30
R4	Coarse sand	0.25-2.0	40
	Iron powder	0.25-0.5	30
	Activated carbon	0.3-3.0	30
R5	Coarse sand	0.25-2.0	40
	Iron powder	0.25-0.5	30
	Sawdust	0.25-2.0	30

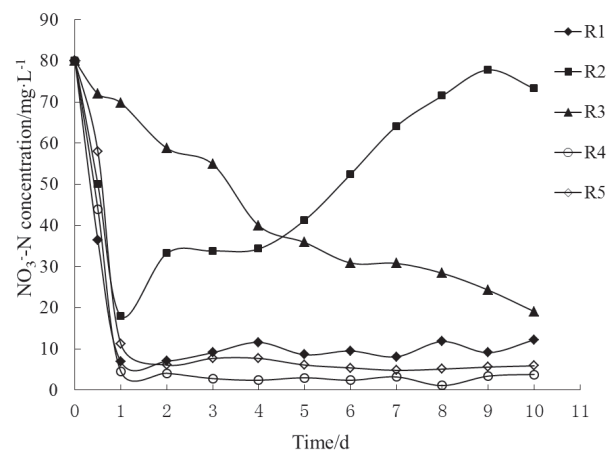


Fig. 7 The nitrate reduction across laboratory columns with different composite mediums.

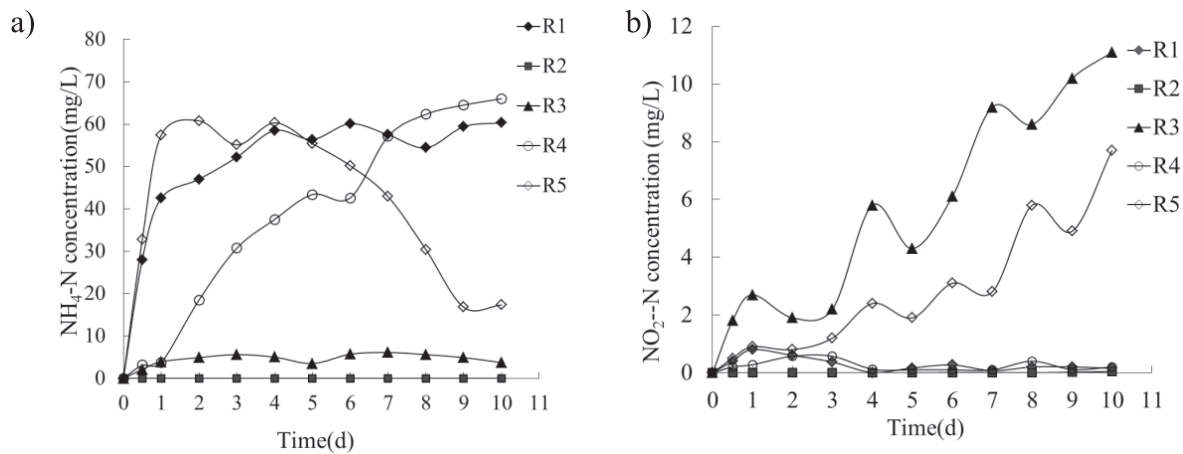


Fig. 8 The $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ produced from laboratory columns with different composite mediums: a) $\text{NH}_4^+\text{-N}$ concentration, b) $\text{NO}_2^-\text{-N}$ concentration.

R4 and R5 reactive medium was a bit lower than R1, which showed that coupling ZVI with activated carbon and with sawdust were better for nitrate removal.

Analysis of Intermediate Chemical Products

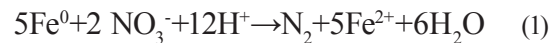
The nitrate removal process was a chemical reaction process. The ideal target is generating non-toxic and tasteless gas elements N_2 during the process of nitrate removal. However, the reaction process is very complex, with some intermediate products such as $\text{NO}_2^-\text{-N}$ and $\text{NH}_4^+\text{-N}$ being generated in the reaction process. When using sawdust as reaction media to remove nitrate, the sawdust could provide a carbon source for heterotrophic microorganisms, which could promote denitrification. Nitrate was converted to N_2O or N_2 under the action of denitrification bacteria (Fig. 8).

From Fig. 8, no $\text{NH}_4^+\text{-N}$ produced in the coarse sand/AC mix medium (R2), and less than 6 mg/L $\text{NH}_4^+\text{-N}$ was produced in coarse sand/sawdust mix medium (R3). In R1, R4, and R5 composite mediums, there was large $\text{NH}_4^+\text{-N}$ generation. There was a little $\text{NO}_2^-\text{-N}$ generated in R1, R2, and R4 composite mediums; however, in R3 and R5, there was large $\text{NO}_2^-\text{-N}$ generation. So, the reduction product of NO_3^- is mainly $\text{NH}_4^+\text{-N}$ in coarse sand/ZVI mix medium (R1), and $\text{NO}_2^-\text{-N}$ is the main reduction product in coarse sand/sawdust mix medium (R3). For R2 reactive medium, there was little by way of reduction products. If the concentration of the reduction products was larger than the drinking water standard (NH_4^+ : 0.2mg/L, NO_2^- : 0.066 mg/L), they need further processing. The treatment of ammonia nitrogen is relatively easy, while it is difficult for $\text{NO}_2^-\text{-N}$ processing.

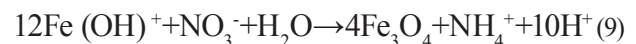
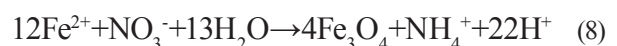
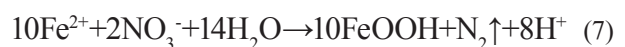
In all the mix mediums, the NO_3^- removal rate of coarse sand/ZVI mix medium (R1) and coarse sand/ZVI/AC mix medium (R4) was better, and the reduction product was mainly $\text{NH}_4^+\text{-N}$, so R1 and R4 are the best PRB mix medium for nitrate pollution remediation.

Discussions

The reduction of nitrate by iron powder is a high exothermic and spontaneous chemical reaction process. The main reactions involved in the production and consumption of NO_2^- anion are the following:



During the process, the by-products Fe^{2+} and $\text{Fe}(\text{OH})^+$ could also react with NO_3^- , in which case the reactions are as following:



It can be seen from the reaction equations that both Fe^2 and Fe^0 can react with NO_3^- . The oxide Fe_3O_4 generated on the surface of the iron powder washing by water and acid was the MOX of Fe_2O_3 and FeO , which indicated that Fe^{2+} was generated when the iron powder was washed by water and acid. Washing by water and acid accelerated the reaction process, and then the nitrate removal rate was also accelerated. This is the fundamental cause that the nitrate removal rate was better when the iron powder was washed by water or acid.

The ideal target is generating intermediate non-toxic and tasteless gas elements N_2 during the process of nitrate removal. However, the products including NO_2 -N and NH_4^+ -N were generated in the reaction process when the reaction mediums were iron powder and sawdust, of which the concentration exceeded the drinking water quality standards. So the water after treatments still influence drinking and need to be treated further. This is one of the limiting conditions that makes Fe^0 difficult to be widely used in nitrate removal of groundwater.

Although adding coarse sand to Fe^0 to improve the permeability of the reaction media, it is difficult to keep both permeability and reaction efficiency. Therefore, it is necessary to carry out field experiments and numerical simulation to analyze the application effect.

Conclusions

- 1) Through the batch experiments of different reaction media, including industrial iron powder, activated carbon, cemarite, and zeolite, the industrial iron powder and activated carbon could be well media for nitrate removal as they had better efficiency in removing the nitrate.
- 2) The stronger acid environments, the better the nitrate removal efficiency by iron powder. The removal efficiency of the iron powder washing by water was still well, and in the meanwhile washing by water could avoid the secondary pollution, which indicated that water washing iron powder would be a good choice.
- 3) Adding coarse sand and activated carbon to iron powder could improve the permeability of the reaction media and meanwhile not lose its reaction efficiency. The study results implied that it has important guiding significance to use Fe^0 -based PRB for in situ remediation of nitrate contamination in the field.

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Conflict of Interest

The authors declare no conflict of interest.

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