



Denitrification of nitrite by ferrous hydroxy complex: Effects on nitrous oxide and ammonium formation



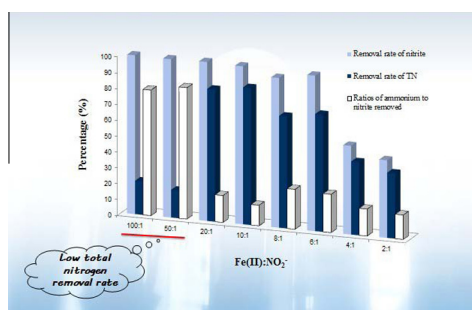
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HIGHLIGHTS

- Ferrous hydroxy complex was employed as an excellent reductant for nitrite.
- The production of nitrous oxide and ammonium highly depends on the dosage of Fe^{2+} , oxygen, OH^- and trace metals.
- Decreasing the yield of ammonium and increasing the removal rate of TN.
- The presence of trace metals accelerate the nitrite reduction.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrite reduction by structural Fe(II) associated with ferrous hydroxy complex (FHC) was performed in a batch reactor. The optimum Fe(II) : OH⁻ molar ratio for nitrite reduction is 7:12. FHC could totally remove nitrite within 60 min when the Fe(II) : NO₂⁻ molar ratio exceeded 10. Less than 30% of the removed nitrite was transformed to ammonium after 1.0 h when the Fe(II) : NO₂⁻ molar ratio was below 20, and the percentage of NH₄⁺-N in the products increased with increasing Fe(II) : NO₂⁻ molar ratio. However, more than 80% of the nitrite was reduced to ammonium when the Fe(II) : NO₂⁻ molar ratio was more than 50. Nitrite tended to be transformed to ammonium under high pH conditions, with a decline in the removal rate. The presence of oxygen reduced the production of ammonium. The addition of Cu²⁺ or Zn²⁺ might enhance the removal of nitrite and reduce NH₄⁺-N production and increase N₂O production.

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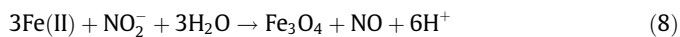
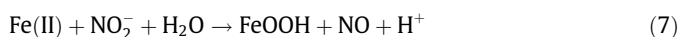
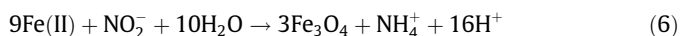
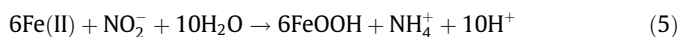
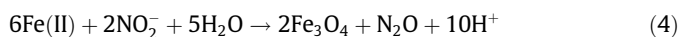
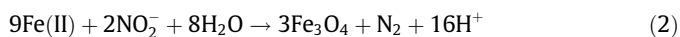
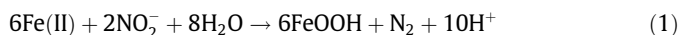
1. Introduction

Nitrate and nitrite contamination in groundwater and surface water constitutes a crucial environmental problem, especially when the water is used for public or private water supplies. Excessive nitrate and nitrite levels can cause serious health problems on human body. Chemical denitrification is widely used for the removal of nitrite and nitrate in water [1]. It degrades nitrogen oxides faster than biological methods and is more cost-effective than physicochemical approaches.

Fe⁰ is one of the most widely used reductants for denitrification in water, and nitrate and nitrite can be reduced by Fe⁰ under certain conditions at a relatively high rate [2–6]. Permeable reactive barriers containing zero-valent iron (ZVI) have been studied in situ and in the laboratory for the treatment of groundwater contaminants [7–9]. Furthermore, some researchers have started to use nano-scale Fe⁰ to reduce nitrate and nitrite because of its stable composition and high reactivity [10–12]. However, the end-product of the reaction between Fe⁰ and nitrate is always ammonium [13–15]. It is found that mixed ferrous/ferric hydroxides, known as green rust, are also effective reductants for denitrification in water [16–19]. The treatment of nitrate and nitrite with green rust has been investigated by several groups. Fe(II) acts as

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the main reductant in green rust, and it has been demonstrated that nitrate and nitrite can be completely degraded under anoxic conditions. The reduction ability of green rust can be enhanced by adding trace metals such as Ag^+ , Au^{3+} , Cu^{2+} , Pt^{2+} or Zn^{2+} [20,21]. Although green rust is highly effective in the removal of nitrate and nitrite in water, its primary reduction product is also ammonium, which means it cannot reduce the total nitrogen concentration in water. Fe^{2+} -containing minerals such as magnetite, pyrite, siderite, dolerite and wustite have proven to be capable of reducing nitrate or nitrite under appropriate conditions or time ranges [22–26]. Moreover, some researchers have found that $\text{Fe}(\text{II})$ can reduce nitrite and other nitrous oxides without the formation of green rust; however, the reduction of nitrate by $\text{Fe}(\text{II})$ will not occur spontaneously, even though the reaction is thermodynamically feasible [27,28]. The addition of trace metals such as Cu^{2+} , Ag^+ or Sn^{2+} can enhance the reaction rate between $\text{Fe}(\text{II})$ and nitrogen oxides, especially for the reduction of nitrate [29]:



Reactions 1–8 represent the most relevant processes that may be involved in the reduction of NO_2^- by $\text{Fe}(\text{II})$. The reduction products of $\text{Fe}(\text{II})$ are much more diversified, including NO , N_2O , N_2 and NH_4^+ [28,30]. The main product varies with different reaction conditions. Besides, under acid condition, NO_2^- could be transformed to NO and N_2O (reaction 9). NO_2^- is unstable under oxic environment and can easily be transformed to NO_3^- :



N_2O is a type of greenhouse gas, while it is also an important propellant for rockets and is difficult to produce. Therefore, it is economical if N_2O can be produced by water treatment processes: N_2O can be collected during the chemical denitrification process. Besides, ammonium is also an undesirable final product because of its biotoxicity. It is significant to control the products of N_2O and ammonium, which is an attractive research in this field.

Given that Fe^{2+} has some advantages over other reductants in terms of decreasing the ammonium in reaction products, and because the study of nitrate and nitrite reduction by Fe^{2+} is incomplete, the present paper will focus on using ferrous hydroxy complex (FHC) as a reductant. It has been reported that FHC could degrade several chemical compounds, such as nitrobenzenes and 2,5-dibromoaniline [31]. Thus, the reduction potential of FHC on nitrite is one of main issues in this paper.

Accordingly, the main objectives of this study were to (1) evaluate the removal efficiency of nitrite and total nitrogen by FHC at various $\text{Fe}^{2+}/\text{OH}^-$, $\text{Fe}^{2+}/\text{NO}_2^-$ molar ratios; (2) find the optimum conditions for more N_2O and less ammonium production; (3) investigate the influence of oxygen and metal ions (Cu^{2+} and Zn^{2+}) on NO_2^- reduction and N_2O , ammonium distribution; (4) explore the mechanisms of oxygen and metal ions (Cu^{2+} and Zn^{2+}) on NO_2^- removal and products distribution.

2. Materials and methods

2.1. Reagents and materials

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NaOH , NaNO_2 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent Co., Ltd and were used without further purification. High-purity (99.999%) argon was purchased from Shanghai Spring Specialty Gases. The 0.45- μm filters were purchased from Shanghai ANPEL Scientific Instrument Co., Ltd. The stock solutions of NaNO_2 were prepared before treatment. Ultrapure water was created using the Milli-Q ultrapure water system.

2.2. Preparation of FHC

Ferrous sulfate was dissolved in 94–100 mL deionized water to a concentration of 4–20 mM. A total of 0.8–4.3 mL of 8 M sodium hydrate was added to the solution after the metal sulfates were dissolved to prepare FHC with different $\text{Fe}^{2+}/\text{OH}^-$ molar ratios. A magnetic stirrer was used to maintain homogenous conditions. All steps were conducted under a flow of argon gas. Solid samples for SEM and XRD analysis were made by freeze-drying the FHC after centrifugation and rinsing.

2.3. Batch experiments

Stirred batch experiments were conducted in 500-mL sealed containers. The reactions were initiated by adding sodium nitrite to the FHC suspension, metal sulfates were added to investigate the role of metal ions on the reduction of nitrite by FHC suspension. Samples of approximately 5 mL were withdrawn at various time intervals and filtered with 0.45 μm membrane filter paper. Nitrate, nitrite and ammonium were subsequently analyzed.

2.4. Analytical and characterization methods

Solution after filtration was analyzed for nitrate and nitrite concentrations using a Dionex ICS-900 ion chromatograph with an IonPac AS23 Anion-Exchange Column with 4.5 mM $\text{Na}_2\text{CO}_3/1$ mM NaHCO_3 as the eluent. The retention times for NO_2^- and NO_3^- were 10 and 15 min, respectively. Ammonium was measured using the Nessler's reagent spectrophotometric method. Before the measurement of ammonium, the pH value of the solution was adjusted above 10, and then the solution was filtered by a 0.45 μm membrane filter to eliminate the influence of Fe^{3+} . N_2O was detected using an Agilent 7980A gas chromatograph using 95%Ar + 5%CH₄ as the carrier gas and an ECD detector.

Scanning electron microscope (SEM) images of the FHC were obtained by a field emission scanning electron microscope (SEM) (Hitachi S-4800, Hitachi, Japan). Solid samples were freeze-dried immediately once centrifugation and rinsing were finished. Powder X-ray diffraction (XRD) patterns of the solid-phase reaction products were collected using $\text{Cu K}\alpha$ radiation (40 kV, 40 mA) and a Bruker D8 Advance from 10° to $80^\circ 2\theta$, with 0.1-s steps and a step interval of 0.02° .

3. Results and discussion

Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to characterize the structure and morphology of FHC. The SEM image (Fig. A.1) showed that FHC had a layered and amorphous morphology which favors reactions with pollutants. XRD analysis (Fig. A.2) showed that the products of FHC (2:1; 1:1; 1:3) after reaction were goethite and Fe_2O_3 , indicating FHC was oxidized when nitrite was reduced.

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