

Original Research

Chemical Reduction of Nitrate Using Nanoscale Bimetallic Iron/Copper Particles

**Jifeng Guo*, Ping Guo, Miaomiao Yu, Zexin Sun, Pengtao Li,
Tong Yang, Jing Liu, Liyuan Zhang**

School of Environmental Science and Engineering, Key Laboratory of Subsurface Hydrology and Ecology in Arid Areas of Education Ministry, Chang'an University, Xi'an, China

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Abstract

Nanoscale zero-valent iron (NZVI) as an effective material has been applied to reduce nitrate. Yet NZVI has defects of aggregation and oxidation. To overcome these disadvantages, nanoscale bimetallic iron/copper particles were introduced to reduce nitrate in this work. In this paper, nanoscale bimetallic Fe/Cu particles were prepared by the liquid phase chemical reduction method; the particles were characterized by scanning electron microscopy (SEM) and x-ray diffraction (XRD). The effect of prepared particles was evaluated by reducing synthetic nitrate wastewater, and batch experiments were conducted to investigate the effect of initial nitrate concentration and various Cu loading on nitrate reduction by nanoscale bimetallic Fe/Cu particles. The results indicated that nitrate could be completely removed in 20 min reaction by nanoscale bimetallic Fe/Cu particles when Cu loading was 5% and initial nitrate concentration was 80 mg/L. As a result, the nitrate in wastewater was converted into ammonium and nitrogen gas, with nitrite as an intermediate by-product.

Keywords: nanoscale bimetallic iron/copper particles, chemical reduction, nitrate wastewater

Introduction

In recent years, human industrial and agricultural production such as farmland fertilization, sewage irrigation, and large amounts of contained nitrogen domestic sewage and industrial wastewater emissions have made nitrate pollution increasingly severe in water [1-2]. The content of nitrate and nitrite exceeded the standard and not only deteriorated water quality but also was a severe hazard to human and animal health. In the human body, nitrate can be reduced to nitrite,

which could react with hemoglobin in blood to form methemoglobin, preventing it from transporting oxygen to body tissues. It poisoned people by depriving them of oxygen, leading to methemoglobinemia, or "blue baby" syndrome. Moreover, nitrite worked with secondary amines form nitrosamines both inside and outside the human body. Nitrosamines were carcinogenic, teratogenic, mutagenic substances and harmful to human health when they reached a certain dose in the human body [3]. Therefore, it was significant to study how to effectively remove nitrate in water.

Nitrate in water had high solubility and fine stability, which was difficult to form co-precipitation or adsorption. Currently, methods of removing nitrate

*e-mail: guojifeng@chd.edu.cn

include physicochemical, such as ion exchange (IE) [4], reverse osmosis (RO) [5], electro-dialysis (ED) [6], biological denitrification (BD) [7-8], and chemical reduction (CR) [9] etc. These methods could remove nitrate to different extents. However, they all had definite disadvantages. In fact, physicochemical methods failed to remove nitrate completely, only to be transferred or concentrated [10]. Meanwhile, they would produce a large number of high concentration regeneration waste fluids and needed further treating, therefore the cost was high. Biological denitrification was characterized by a low biochemical reaction rate and complex operating conditions. Chemical reduction methods referred to use certain chemical reductants to remove nitrate, metal reductants including iron (Fe), aluminum (Al), and zinc (Zn) were applied extensively at present, and the iron powder was closely studied. Due to certain restrictions of iron powder in treatment effectiveness, nanoscale zero-valent iron has been rapidly developed.

NZVI has been extensively applied to reduce nitrate [11-13] due to its advantages of a large specific surface area and high reactivity. However, studies have indicated that NZVI had a tendency to agglomerate and oxidize, which led to decreased reactivity and limited its wide application [14]. Several carriers such as bentonite [15], silica [16], activated carbon [17], and chitosan [18] have been introduced on the surface of NZVI as an approach to improve the reactivity of NZVI. These composites had great improvement on contaminant removal, and the agglomeration of NZVI decreased. These indicated that the nitrate removal rate was enhanced when the carriers were introduced.

Coating NZVI by using another metal catalyst such as Pt, Pd, and Cu (named nanoscale bimetallic particles) was another effective and novel way to improve the reactivity of NZVI. It had been reported that nanoscale bimetallic particles were applied to degrade chlorinated hydrocarbons [19-20]. However, studies about nanoscale iron bimetallic particles for reducing nitrate wastewater have rarely been systematically reported.

Among the surface modifier metals for NZVI, Cu was known as a mild catalyst. In this study, metal Cu was introduced as a catalyst of NZVI. Nanoscale bimetallic iron/copper (Fe/Cu) particles (NZVI coating Cu as a catalyst) were prepared by the step liquid phase chemical reduction method. Batch experiments were conducted to reduce nitrate by the prepared nanoscale bimetallic Fe/Cu particles. The products of the reaction were also analyzed. This would provide more theoretical basis for the reduction of nitrite by nano-iron bimetallic particles. Meanwhile, this also provided an effective method for nitrate removal.

Material and Methods

Materials

Main chemical reagents used in the experiments included ferrous sulfate heptahydrate (CAS number: 7782-63-0, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Guangdong Guanghua Sci-Tech Co. Ltd, China), potassium borohydride (CAS number: 13762-51-1, KBH_4 , Guangdong Guanghua Chemical Factory Co. Ltd, China), absolute ethyl alcohol (CAS number: 64-17-5, Xi'an Chemical Reagent Factory,

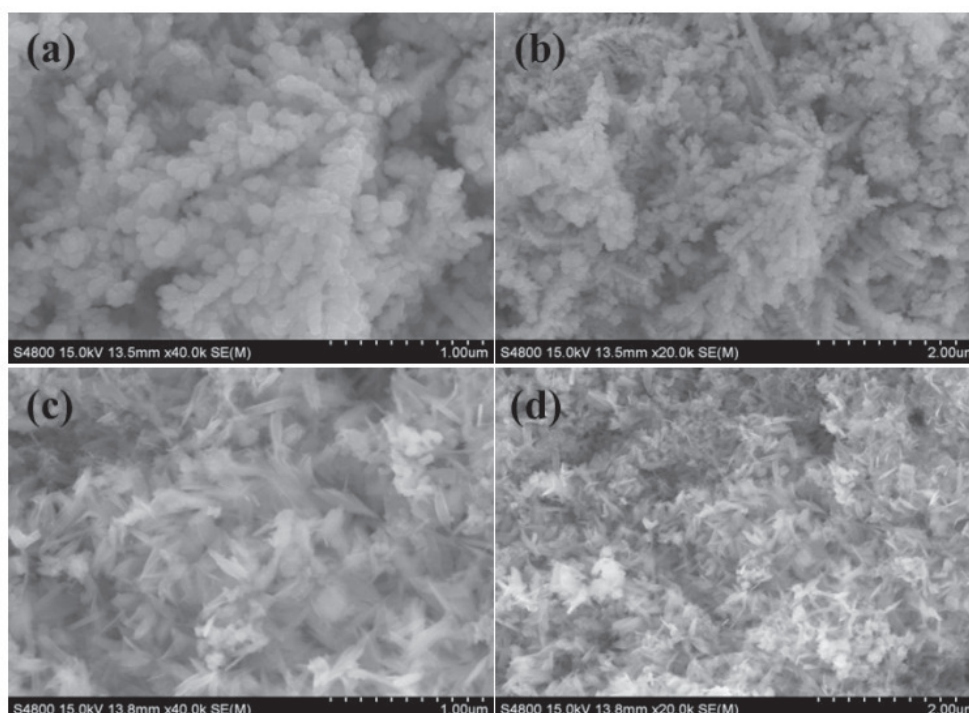


Fig. 1. SEM images of two bimetallic Fe/Cu particles.

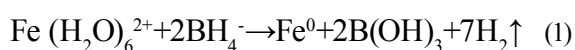
China), polyethylene glycol 4000 (CAS number: 25322-68-3, PEG-4000, Guangdong Guanghua Chemical Factory Co. Ltd, China), sodium nitrate (CAS number: 7631-99-4, NaNO₃, Guangdong Guanghua Sci-Tech Co. Ltd, China), and copper sulfate pentahydrate (CAS number: 7758-99-8, CuSO₄·5H₂O, Xi'an Chemical Reagent Factory, China) – all of which were of analytical grade. Iron powder was purchased from Tianjin University chemical reagent factory. The experimental water source was simulated nitrate wastewater prepared using analytically pure potassium nitrate.

Methodology of Bimetallic Fe/Cu Particles Preparation

Ordinary bimetallic Fe/Cu and nanoscale bimetallic Fe/Cu particles were prepared by liquid phase chemical reduction method [21-22].

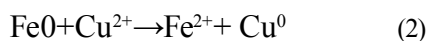
Ordinary bimetallic Fe/Cu particles: 0.2 g iron powder was added into a beaker with 100 mL CuSO₄·5H₂O solution (0.00156 mol/L). The solution was stirred to complete reaction under nitrogen atmosphere. In this way, ordinary bimetallic Fe/Cu particles were prepared. The prepared materials were filtered and stored in deoxidized deionized water (injected with nitrogen).

Nano Fe/Cu particles: 1.0 g FeSO₄·7H₂O was added into 500 mL beaker with 100 mL ethanol-water solution (ethanol: water = 2:5), the concentration of ferrous sulfate was 0.036 mol/L; 0.5 g PEG-4000 was also added. 100 mL 0.108 mol/L (KBH₄: Fe = 3:1) KBH₄ solution were added into the above solution dropwise and stirred constantly. After KBH₄ solution dropped completely, through nitrogen stirring for more than 5 min, so that the reaction was complete. Nanoscale iron particles were obtained as follows:



The products were washed with absolute ethyl alcohol and then washed with deoxidized deionized water several times. The whole process was carried out under nitrogen atmosphere.

The freshly prepared nanoscale iron particles were added to 50 mL deoxidized deionized water to form a suspension and ultrasonic dispersion for 10 minutes. 100 mL CuSO₄·5H₂O solution was slowly added to the suspension of nanoscale iron and stirred under nitrogen protection. After complete addition, the reaction was injected with nitrogen continually for 3 min. Nano Fe/Cu particles (5% Cu loading) were obtained according to the following reaction [23]:



The particles were filtered and washed with absolute ethyl alcohol and then washed with deoxidized deionized water several times.

Analysis Methods

The morphology of particles was characterized by SEM (S-4800, Hitachi, Japan) with 15.0 kV operating voltages. The crystal phase was measured by x-ray diffraction (D8ADVANCE, Brooke AXS Company, Germany), with Cu target K α radiation, working voltage was 40 kV, and scan area was 30~60°. Nitrate nitrogen was determined by ultraviolet spectrophotometry, nitrite nitrogen was measured by N-(1-naphthyl)-ethylene diamine spectrophotometry, and determination of ammonia nitrogen by nessler's reagent spectrophotometry.

Batch Nitrate Reduction Experiments

Batch nitrate reduction experiments were conducted in a 250 mL conical flask with 150 mL certain concentration simulated nitrate wastewater. Nano Fe/Cu particles dosage was 1.4 g/L. To ensure anaerobic conditions, wastewater was injected with nitrogen and flasks were sealed. The reaction was carried out in the condition of neutral pH and vibrated with a SHA-CT chilled water bath thermostat oscillator at 20°C at 150 rpm. Samples were periodically taken, filtered, and measured to investigate iron content.

Results and Discussion

SEM Analysis

Two prepared kinds of bimetallic Fe/Cu particles were adequately dried in vacuum. The morphologies were characterized by SEM. Figs 1a-b) showed SEM images of ordinary bimetallic Fe/Cu particles in which iron particles were white and granular, and dendritic copper was interspersed with large amounts of iron particles. The particles were well dispersed and the specific surface area of particles increased due to the joining of copper. Figs 1c-d) were the SEM image of nano Fe/Cu particles. It can be seen clearly that nano Fe/Cu particles were like chaotic feathers; the sample size was less than 100 nm. The dispersity of NZVI increased prominently when the Cu catalyst was introduced. The sample surface was uneven, which was conducive to increasing the surface area [24]. There were many channels and voids in the surface.

XRD Analysis

Fig. 2 was the XRD pattern of prepared nanoscale bimetallic Fe/Cu particles. Nano Fe/Cu particles had a sharp α -Fe diffraction peak at $2\theta = 44.67^\circ$, and the corresponding crystal plane was (110), which coincided with the standard PDF2 card. There were two Cu diffraction peaks at $2\theta = 43.39^\circ$ and $2\theta = 50.48^\circ$ in the 2θ angle range of 30° to 60° . In addition, iron oxide was not observed.

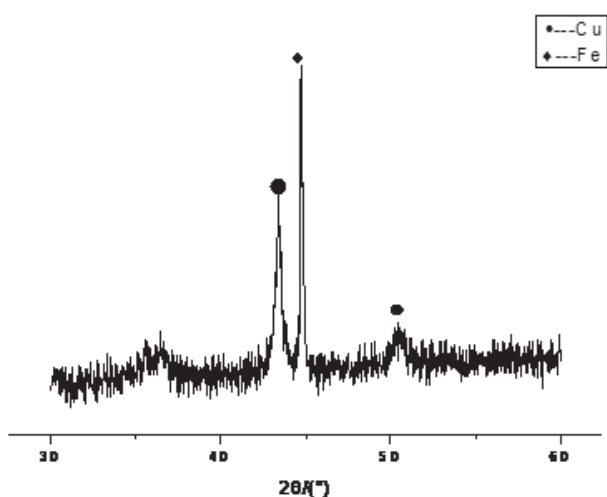


Fig. 2. XRD pattern of prepared nanoscale bimetallic Fe/Cu particles.

Nitrate Reduction by Two Bimetallic Fe/Cu Particles

The nitrate reduction abilities of two bimetallic Fe/Cu particles were compared in Fig. 3, where C/C_0 was the ratio of exploratory ion concentration to initial nitrate concentration in the solution. The results showed that nitrate removal rate was 24.8% at 20 min and only 30% when the reaction was complete by ordinary bimetallic Fe/Cu particles, while nitrate removal rate was 91.9% at 20 min and nearly 100% at 40 min by nano Fe/Cu particles under the same conditions. This was because the active mechanism for removing nitrate by nanoscale bimetallic Fe/Cu particles was utilizing its large specific surface area and high reactivity; the nitrate removal rate could reach nearly 100% in a short time. As can be seen in Figs 1(c-d), there were many channels and voids in the surface of nanoscale bimetallic Fe/Cu particles, which provided more adsorption sites and active sites for the reaction. This greatly enhanced

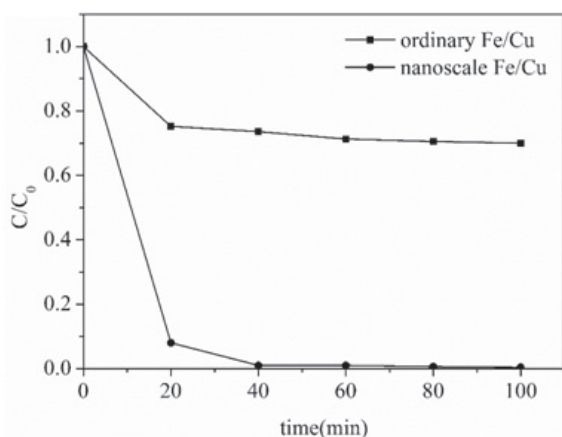


Fig. 3. Nitrate reduction ability of two bimetallic Fe/Cu particles (nitrate nitrogen concentration = 100 mg/L).

the activity of nanoscale bimetallic Fe/Cu particles.

Effect on Nitrate Reduction by Nano Fe/Cu Particles

Effect of Initial Nitrate Concentration

Effects of initial nitrate nitrogen concentration on nitrate reduction by nano Fe/Cu particles are shown in Figs 4(a-b), which shows that the initial nitrate nitrogen concentrations were 40, 80, 100, and 120 mg/L, respectively, and when the reaction time was 5 min, nitrate removal rates reached 80.6%, 71.2%, 70.2%, and 66%, respectively. When the nitrate nitrogen concentration was not higher than 80 mg/L, the nitrate removal rate was close to 100% at 20 min, while nitrate nitrogen concentration was 120 mg/L; nitrate removal rate was 89.6%, which indicated that the nitrate removal rate decreased with the increase of initial nitrate concentration. Nitrate reduction reaction needed to be adsorbed to the surface of nanoscale bimetallic Fe/Cu particles first, and then conducted redox reactions in reactive sites of the surface [25]. The increase of nitrate content occupied more reactive sites, resulting in a saturation effect; therefore, nitrate removal rate was slower.

Effect of Various Cu Loading

Liou [26] showed that Cu loading could markedly affect nitrate removal rates. Effects of various Cu loading on nitrate reduction are shown in Fig. 5, which clearly shows that nano Fe/Cu particles with 5% Cu loading had the best nitrate removal efficiency, with the nitrate removal rate reaching 100% within 20 min. While Cu loading was 1% and 20%, the removal rate was only 78% and 60%, respectively. The reactivity increased with the rise of Cu loading up to 5% and a further rise of Cu loading failed to increase reactivity. The loading was too small or too large; the reactivity of nanoscale bimetallic Fe/Cu particles would be decreased. This was because the small loading was not enough to cause surface property change of nanoscale iron particles, and excessive loading would cover the surface of nanoscale iron particles, thus failing to fully contact with the nitrate, and removal rate decreased.

Nitrate Reduction Product Analysis

Product analysis and total nitrogen balance of nitrate reduction by nanoscale bimetallic Fe/Cu particles are shown in Fig. 6. With the progress of the reaction, the nitrate nitrogen concentration decreased persistently and removal rate was almost 100% at 40 min. During the reaction, 22.4% nitrate was reduced to nitrite, which was as intermediate by-product remained in the solution. Nitrite was converted to ammonia nitrogen further with the reaction continued and 7.7% nitrite remained in solution in the final. Since the amount of nitrite was

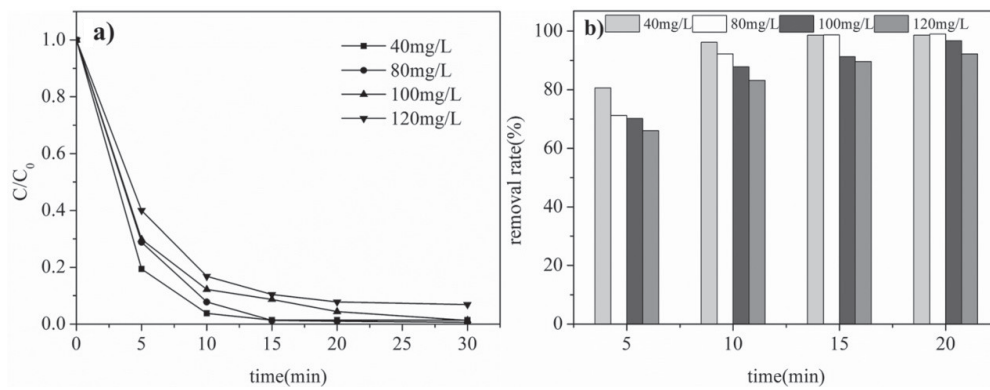


Fig. 4. Effect of different initial nitrate concentrations on nitrate removal rate (Cu loading = 5%).

small, it could be reduced further. So the amount of nitrite was not controlled deliberately in the experiment. 86.1% of the reaction final product was ammonia nitrogen. The total nitrogen (nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen) showed a tendency of first decreasing and then increasing, and the total nitrogen content decreased 5%. During the reaction, the pH increased from 7.24 to 10 or so. Here, the reduced total nitrogen was in the form of nitrogen gas (N_2) or ammonium. In addition, when nitrate nitrogen was removed quickly, there was still the presence of nitrite nitrogen, which indicated fully that the reaction process was a continuous stepwise reaction, namely $NO_3^- - N \rightarrow NO_2^- - N \rightarrow NH_4^+ - N$. The conversion from nitrate to nitrite was faster and from nitrite to ammonia was relatively slow.

Iron and copper could be converted into ions (Fe^{2+}/Fe^{3+} and Cu^{2+}) during the reaction. In this experiment, the pH value increased to 10 or so after reaction, Fe^{2+}/Fe^{3+} would precipitated in alkaline condition. Nanoscale bimetallic Fe/Cu particles dosage was 1.4 g/L and the Cu loading was 5% in the experiment. There was only 0.01 g Cu in 150 mL solution. By continuing to increase the pH value of the

solution, the purpose of further precipitation of Cu ion will be achieved.

Conclusions

In this study, the prepared nanoscale bimetallic Fe/Cu particles decreased the aggregation of NZVI, and dispersity of NZVI increased prominently when catalyst Cu was introduced. Iron oxide was not observed in the pattern of XRD. It can be concluded that the join of the catalyst Cu overcame the shortcomings of aggregation and oxidation of NZVI. The results indicated that nanoscale bimetallic Fe/Cu could effectively reduce nitrate. Nitrate could be completely removed in 20 min reaction by nanoscale bimetallic Fe/Cu particles when Cu loading was 5% and initial nitrate concentration was under 80 mg/L. As a result, the nitrate in wastewater was converted into ammonium and nitrogen gas, with nitrite as an intermediate by-product. This would provide more theoretical basis for the reduction of nitrite by nano-iron bimetallic particles. Meanwhile, this also provided an effective method for nitrate removal.

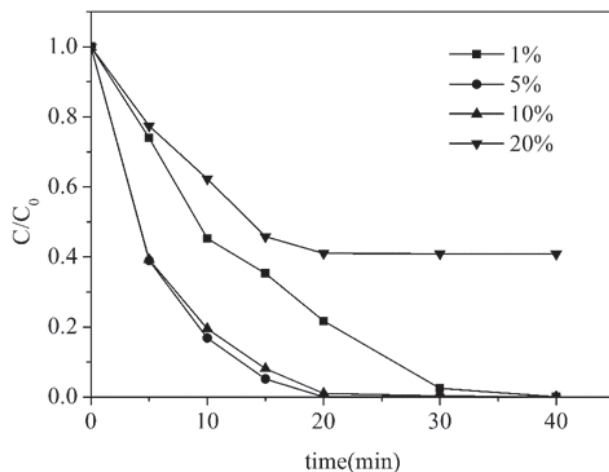


Fig. 5. Effect of various Cu loadings on nitrate reduction (nitrate nitrogen concentration = 80 mg/L).

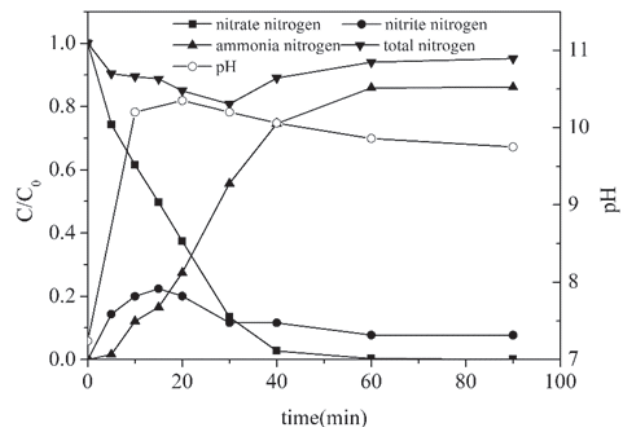


Fig. 6. Product analysis and total nitrogen balance of nitrate reduction by nanoscale bimetallic Fe/Cu particles (nitrate nitrogen concentration = 80 mg/L, Cu loading = 5%).

Acknowledgements

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