



Promoting nitrate reduction kinetics by nanoscale zero valent iron in water via copper salt addition



Ahmed M.E. Khalil^a, Osama Eljamal^{a,*}, Skander Jribi^{b,c}, Nobuhiro Matsunaga^a

^a Department of Earth System Science and Technology, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Koen Kasuga, Fukuoka 816-8580, Japan

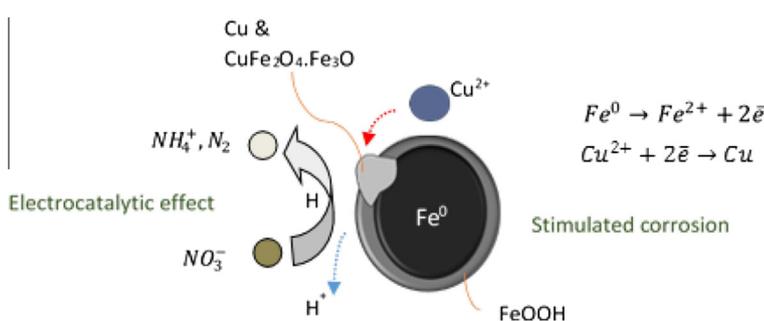
^b International Institute for Carbon-Neutral Energy Research (WPI-F²CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

^c Laboratory of Electro-Mechanical Systems (LASEM), National Engineering School of Sfax, University of Sfax, Route Soukra km 3.5, Sfax 3038, Tunisia

HIGHLIGHTS

- Copper salt addition during nitrate reduction increased iron corrosion rate and electron transfer.
- Copper compounds formed on nano iron surface catalyzed nitrate reduction.
- Kinetic rates and removal efficiencies were boosted more than three times the original values.
- Nitrate concentrations up to 500 mg/L were reduced to safe legal limits within one hour.
- Addition of copper salt enhanced air and pH stability of nano iron in the nitrate removal.

GRAPHICAL ABSTRACT



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ABSTRACT

Several methods were proposed to enhance nitrate reduction kinetics and removal from water by nanoscale zero valent iron (Fe⁰). One of them was the addition of other contaminants/components to nitrate-contaminated water, which is less common, but it can gain effective results and promote nitrate reduction kinetics. In this study, nano-Fe⁰ was synthesized under optimum conditions and characterized using transmission electron microscopy, surface area analyzer, X-ray diffraction and particle size analyzer. Nitrate removal performance was carefully investigated via batch experiments under different conditions of pH, presence/absence of oxygen and distinctive nitrate concentrations (50, 100, 200, 300, and 500 mg/L), comparing between nitrate removal by nano-Fe⁰ with and without copper salt (copper chloride) addition. Optimum addition ratio of CuCl₂/Fe (0.05 wt/wt) was collected from experimental results, which was used to conduct the rest of batch experiments. Kinetics of nitrate removal among several batch experiments were examined by applying different models, and it was found that most profiles obeyed first-order rate equation. The presence of copper ions during nitrate reduction imposes two electrochemical reactions; one stimulates iron corrosion and another reaction causes hydrogen-electrocatalytic reduction of nitrate. Both reactions boosted removal efficiency and kinetics around 3.5 times more than that by ordinary pristine nano-Fe⁰ alone, i.e. nitrate removal time was reduced from one hour to 20 min. Moreover, the stability of removal efficiency and kinetics under the influence of pH and dissolved oxygen was higher as well.

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* Corresponding author. Tel./fax: +81 92 583 8387.

E-mail address: osama-eljamal@kyudai.jp (O. Eljamal).

1. Introduction

Nitrate is one of the well-known hazardous contaminants, which is regarded as the main concern in the treatment of ground-water and surface water. Nitrate pollution is considered as a non-point source which resulted from agriculture runoff, nitrogenous fertilizers, animal manure, industrial and domestic wastewaters, septic systems waste, etc. This pollution has a great influence on the wells in the rural area in which shallow ground water exists, and residents mainly depend on them for drinking water purpose. In most cases, when nitrate (NO_3^-) is reduced to nitrite (NO_2^-), toxicity increases significantly, and the latter causes methemoglobinemia which is formed as a result of combining nitrite with blood hemoglobin. This methemoglobinemia leads to blue-tinged blood for babies, especially under six-month-old [1]. Furthermore, the human being is subjected to several diseases, such as cancer, liver damage and so forth, as a result of excessive release of nitrogen compounds and its consequences of eutrophication and drinking water pollution [2]. Thus, several entities and agencies, such as WHO (World Health Organization) and US-EPA (Environmental Protection Agency), have assigned the maximum contaminant level (MCL) for nitrate at 50 mg/L (NO_3^-) [3] and 10 mg/L (NO_3^- -N, measured as nitrogen) [4], respectively. The environmental quality standards for human health in Japan have set the limit of nitrate and nitrite contamination in water to 10 mg/L (N) [5].

There is an increasing interest on using zero valent iron (ZVI) for the removal of nitrate from groundwater and wastewater. During the last two decades, numerous researches were carried out on chemical reduction of nitrate by zero valent iron [6–10]. Reports have shown the reaction pathways of nitrate reduction by ZVI [8]. Iron reduces nitrate to ammonia, nitrite and nitrogen with relative amounts according to the reaction conditions. Also, the size of zero valent iron particle is an important factor to determine its efficiency and efficacy in nitrate removal. The nanoscale (n) ZVI has proven its high efficacy and efficiency in nitrate reduction from wastewater in several reports [7–9]. Thus, nZVI is considered reliable to employ in wastewater treatment systems because of its high cost effectiveness, high reactivity, easy operation and low dosage [11].

The search for methods to improve the removal efficiency of nitrate and its kinetic reduction rate by ZVI is unstoppable. Efforts were made at first to explain the reduction kinetics and mechanism of nitrate by zero valent iron [6,12]. To increase the denitrification rate of ZVI, Xu et al. [13] added ferrous ions and magnetite with micro size iron powder, which accelerated corrosion rate of iron and acted as a good conductor of electron transfer. In this case, the adsorption of nitrate on the iron surface increased along with a higher conductivity and transfer rate of electrons. Some other researchers were concerned about the effect of pH in promoting or inhibiting the denitrification rate using nZVI, proving that nitrate reduction by nZVI is an acid-driven surface-mediated process [8,14]. Then, during the last decade, numerous reports focused on three main methods to enhance nitrate reduction efficiency/conversion and kinetics: using a supported nZVI [15], dispersed nZVI by surfactant [16] and bimetallic nZVI particles [7,17].

Recently, contaminant removal was processed in the presence of another contaminant in which ZVI nanoparticles were capable of removing both contaminants with higher rate and efficiency than treating each contaminant solely. Su et al. [10] reported removal of cadmium and nitrate simultaneously via nitrate addition/presence. A benefit of high pH value (caused in the course of nitrate reduction) was embraced to increase cadmium hydrolysis and precipitation. In this study, the same basic principle could be employed to increase nitrate reduction rate with different mechanisms. When adding an optimized amount of copper salt to nZVI

and nitrate suspension mixture (instead of coating nZVI with copper during synthesis), two electrochemical reactions occur one after another, which greatly boost reaction kinetics and removal efficiency. In addition, copper salt addition cures some of nZVI defects in nitrate reduction reaction which appear in its dependence on pH and dissolved oxygen.

Based on previously mentioned, this study investigates the effect of adding different amounts of CuCl_2 and its impact on nitrate reduction by nZVI, and its influence on removing high nitrate concentrations by nZVI in presence/addition and absence/without addition of CuCl_2 (as the research on high concentrations of nitrate is poor). Additionally, the present research studies the effect of different conditions on nitrate reduction by nZVI with and without copper chloride addition. Batch experiments were performed under anaerobic and aerobic conditions and at different pH values. Finally, kinetics of reactions were carefully analyzed and studied.

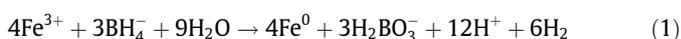
2. Materials and methods

2.1. Chemical reagents

Ferric chloride (>99.0%, Junsei Chemical Co., Japan), sodium borohydride (>98.0%, Sigma–Aldrich Inc., USA) and ethanol (99.5%, Wako Co., Japan) were purchased for nZVI synthesis. Potassium nitrate (>99.0%, Wako Co., Japan) was used to prepare a reactant stock solution, while pH buffer solution (Sansyo Co., Japan), hydrochloric acid (35–37%, Wako Co., Japan) and sodium hydroxide (>93%, Wako Co., Japan) were used for pH adjustment. Anhydrous copper chloride (99.9%, Sigma–Aldrich Inc., USA) was added with specific amounts in the investigated batch experiments. All solutions were prepared using deionized water after deoxygenating by purging with nitrogen gas for 20 min. All chemicals were used as received without further purification.

2.2. Synthesis of nZVI

The nZVI was synthesized according to the following chemical emulsion reduction method:



In this research work, the synthesis conditions were selected and optimized based on a previous research report [18]. Sodium borohydride (NaBH_4 , 98%, 1.1472 M) was pumped into anhydrous ferric chloride (FeCl_3 , 0.1434 M) using a roller pump at a rate of 1 L/h with a volumetric ratio of 1:1 in 500 mL four-neck glass flask. Anoxic condition was maintained by blowing a continuous flow of nitrogen gas. The synthesis mixture was stirred at 250 rpm, kept at 25 ± 0.5 °C using water bath, and left 20 min for aging to complete the reaction. After reduction, the jet-black iron nanoparticles were rinsed with deionized water ($\text{DW} > 100$ ml/g) and anhydrous ethanol three times each. The slurry was finally vacuum-filtered and anaerobically dried, then applied immediately in batch experiments.

2.3. Batch experiments

Batch experiments were conducted to investigate the effect of copper chloride addition and acquire the optimum addition ratio of CuCl_2 to nZVI among different values (0, 0.02, 0.05 and 0.25 g salt/g iron). These experiments were anaerobically carried out in 500 mL four-neck glass flask using 50 and 100 mg/L of nitrate solution with adding one gram of nZVI plus the corresponding amount of CuCl_2 . Before adding nZVI sample, nitrate solution was purged with a nitrogen stream for 20 min, and its initial pH was adjusted

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