



# Microbial reduction of nitrate in the presence of zero-valent iron and biochar



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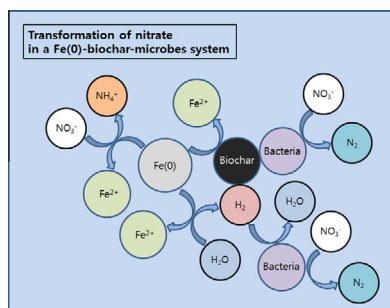
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## HIGHLIGHTS

- Biochar enhances the anaerobic denitrification of nitrate by microbes with Fe(0).
- Electron conductivity of biochar accounts for the enhancement.
- Increasing dosage of mixed culture promotes nitrate reduction with Fe(0) and biochar.
- A product of microbial reduction with Fe(0) and biochar is N<sub>2</sub>.
- A biochar–Fe(0)–microbes system may be an alternative option for NO<sub>3</sub><sup>−</sup> treatment.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 7 October 2015  
 Received in revised form 8 November 2015  
 Accepted 9 November 2015  
 Available online 14 November 2015

### Keywords:

Nitrate  
 Anaerobic denitrification  
 Biochar  
 Zero-valent iron  
 Microbes

## ABSTRACT

The denitrification of nitrate (NO<sub>3</sub><sup>−</sup>) by mixed cultures in the presence of zero-valent iron [Fe(0)] and biochar was investigated through a series of batch experiments. It was hypothesized that biochar may provide microbes with additional electrons to enhance the anaerobic biotransformation of nitrate in the presence of Fe(0) by facilitating electron transfer. When compared to the anaerobic transformation of nitrate by microbes in the presence of Fe(0) alone, the presence of biochar significantly enhanced anaerobic denitrification by microbes with Fe(0). Graphite also promoted the anaerobic microbial transformation of nitrate with Fe(0), and it was speculated that electron-conducting graphene moieties were responsible for the improvement. The results obtained in this work suggest that nitrate can be effectively denitrified by microbes with Fe(0) and biochar in natural and engineered systems.

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## 1. Introduction

Nitrate (NO<sub>3</sub><sup>−</sup>), a well-known contaminant in surface water and groundwater, has been extensively studied for its treatment in natural and engineered systems over the last few decades (Chafari et al., 2008). Nitrate can be discharged to the environment from a variety of sources, including agricultural activity, animal waste,

septic systems, atmospheric deposition from nitrogen oxide emissions, and industrial processes. Due to its toxicity to humans (e.g., blue baby syndrome) and the possibility of eutrophication, both the Korean Ministry of Environment and the U.S. Environmental Protection Agency have set a regulation level of 10 mg/L NO<sub>3</sub><sup>−</sup>-N in drinking water. While many techniques have been developed for the treatment of water with exceedingly high concentrations of dissolved NO<sub>3</sub><sup>−</sup> (e.g., ion exchange, reverse osmosis, biological denitrification, chemical reduction), such processes have the disadvantages of being prohibitively expensive, difficult to maintain, and likely to generate concentrated waste (Ahn et al., 2008).

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Zero-valent iron [Fe(0)] has been studied for its ability to reduce  $\text{NO}_3^-$  in natural water and wastewater (Westerhoff and James, 2003; Su and Puls, 2004; Yang and Lee, 2005). Fe(0) has also received much attention for the treatment of toxic contaminants because it is abundant, inexpensive, readily available, and has a strong reduction potential ( $E_0^{\text{Fe}} = -0.44 \text{ V}$ ). Furthermore, the Fe(0) reduction process requires little maintenance, and its corrosion products are relatively innocuous (Oh et al., 2002). Unfortunately, the Fe(0) reduction process for nitrate does not proceed in a straightforward manner. Many researchers have reported that it took several hours or even days to completely remove  $\text{NO}_3^-$  by Fe(0) in batch experiments under ambient conditions (Su and Puls, 2004). In other studies, acidic and highly buffered conditions were required to obtain significant  $\text{NO}_3^-$  reduction by Fe(0) (Alowitz and Scherer, 2002; Huang and Zhang, 2005). The use of nanoscale Fe(0) (Yang and Lee, 2005) or higher temperatures to overcome the kinetic barrier to reduction (Ahn et al., 2008) has resulted in a significant enhancement of the nitrate reduction rate (half-life range on the order of minutes). While sizable improvements have been achieved in the reduction of nitrate by Fe(0), the reduction products were reported to be mostly  $\text{NH}_4^+$  and thus, requiring additional treatments (e.g., ammonia stripping).

Biological denitrification is an attractive nitrate treatment option due to its low cost, high removal rate, and the high specificity of denitrifying bacteria for nitrate (Matéju et al., 1992). Previous studies have shown that Fe(0) can support the microbial reduction of nitrates to nitrogen gas (Till et al., 1998; Shin and Cha, 2008). Shin and Cha (2008) demonstrated that Fe(0) can serve as an electron donor for nitrate reduction by providing  $\text{H}_2$  to nitrate-respiring bacteria. It has also been suggested that the use of Fe(0) could eliminate the need for a continuous supply of expensive electron donors or hydrogen gas. Hydrogenophilic denitrifiers utilize cathodic hydrogen gas ( $\text{H}_2$ ) generated from the anaerobic corrosion of Fe(0) in water to transform nitrate to  $\text{N}_2$  during batch tests (Shin and Cha, 2008). Hydrogen gas ( $\text{H}_2$ ) is one of the most thermodynamically favorable electron donors for nitrate reduction (Till et al., 1998). It is an excellent electron source because of its clean nature and low biomass yield. Moreover, the reaction products of hydrogenophilic denitrification ( $\text{N}_2$  and water) are innocuous (Smith et al., 1994; Vasiliadou et al., 2006; An et al., 2010). Schaefer et al. (2007) reported the complete removal of 4 mg/L of nitrate-N with Fe(0) and bioculture. The continuous generation of  $\text{H}_2$  from the Fe(0) corrosion process may overcome the limitations associated with hydrogen-utilizing denitrification, as Fe(0) is a relatively inexpensive  $\text{H}_2$  source that eliminates the need to handle or store dangerous hydrogen gas.

Biochar, a carbon-rich product generated during the pyrolysis of organic materials, has received significant interest in recent years for the production of renewable energy (bio-oil and biogas) and the reduction of  $\text{CO}_2$  released via carbon sequestration (Lehmann and Joseph, 2009). Biochar has also been increasingly investigated as an adsorbent for organic chemicals and toxic metals in waters and soils (Mizuta et al., 2004; Loganathan et al., 2009; Ahmad et al., 2014; Mohan et al., 2014; Rajapaksha et al., 2014). Due to the presence of functional groups (acidity/basicity) on the biochar surface and  $\pi$ - $\pi$  electron donor-acceptor (EDA) interactions, toxic contaminants can be sorbed on biochar, thereby decreasing their mobility and bioavailability (Chun et al., 2004). However, enhancements in microbial nitrate reduction in the presence of biochar have not yet been extensively studied. Biochar-amended soil has reportedly been associated with improved absorbency to reduce the leaching of N, P, and organic carbons while increasing the soil surface area (Beck et al., 2011). In addition, higher water retention promotes the probability that microorganisms can uptake nutrients that would otherwise be leached from the soil (Coumaravel et al., 2011). Coelho et al. (1992) showed that activated carbon

particles could support wastewater denitrification. Due to their large adsorptive capacity and irregular surface shape, activated carbon particles serve to shelter bacteria from high fluid shear forces. This in turn allows bacteria to form a homogeneous biofilm with a uniform thickness, resulting in more effective denitrification rates. Bock et al. (2015) recently showed that the addition of biochar can significantly enhance nitrate removal in a denitrifying bioreactor.

In our previous work, we showed that biochar can act as an electron-transfer mediator to enhance the abiotic reduction of nitro explosives and pesticides by reductants (Oh et al., 2013, 2015). It was proposed that the graphene structure, surface functional groups (e.g., quinone), and possible embedded metals may be responsible for the observed improvement in the reduction of nitro explosives. However, the role of biochar in the biotic transformation of contaminants in the presence of Fe(0) has not yet been examined. In the present study, the microbial denitrification of nitrate in the presence of Fe(0) and biochar was investigated. It was hypothesized that biochar may provide electron-conducting porous structures in order to enhance the anaerobic biotransformation of nitrate by microbes in the presence of Fe(0) by facilitating electron transfer. Through a series of batch experiments, the influence of biochar and Fe(0) addition on microbial denitrification was examined. The effect of the graphene structure was investigated using graphite, a reference black carbon material; the impact of the pyrolysis temperature, biochar dosage, and mixed culture dosage was also examined. Lastly, possible products of denitrification and reduction are discussed.

## 2. Methods

### 2.1. Chemicals and materials

Potassium nitrate ( $\text{KNO}_3$ , >99%) was purchased from Duksan Pharmaceutical Co. (Kyunggi, Korea). The Fe(0) used in this study was Peerless iron (Peerless Metal Powders and Abrasives, Detroit, MI, USA); the specific surface area of the Peerless iron was  $1.67 \text{ m}^2/\text{g}$ , as determined by the Brunauer-Emmett-Teller (BET) method with nitrogen. The mean diameter of the Peerless iron, as evaluated with a size analyzer (Mastersizer 2000, Malvern, UK), was 1.2 mm, while the Fe content was more than 90%. Graphite powder (<20  $\mu\text{m}$ , 99.9%) was obtained from Aldrich (Milwaukee, WI, USA). Biochars were synthesized from rice straw generated in the city of Ulsan. The biochars were pyrolyzed using a laboratory-scale gas flow-controlled tube furnace maintained at 900 °C for 4 h under  $\text{N}_2$  flowing at a rate of 1000 cc/min. The properties of the graphite and the synthesized biochar (e.g., pH, BET surface area, cation exchange capacity (CEC), point of zero charge (PZC), and elemental composition) are described in a previous report (Oh and Seo, 2014). Mixed cultures were collected from a wastewater treatment facility in the City of Ulsan. The concentration of mixed liquor volatile suspended solids was 10,200 mg/L, while the contents of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N in the mixed cultures were 5.6 and 3.3 mg/L, respectively.

### 2.2. Batch experiments

Batch experiments were conducted using 250 mL borosilicate amber bottles. All experimental preparation was carried out in an anaerobic glovebox (JISICO, Seoul, Korea) under ambient  $\text{N}_2$  conditions. Each amber bottle contained 190 mL of deoxygenated nitrate solution (~55 mg/L), 10 mL of mixed culture, 10 g of Fe(0), and 0.5 g of biochar. The bottles were prepared in duplicates to ensure reproducibility and allow for experimental errors to be estimated. Mininert® valves (VICI Precision Sampling, Baton Rouge, LA, USA)

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