



# Enhanced nitrate removal by novel bimetallic Fe/Ni nanoparticles supported on biochar



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## ABSTRACT

In this study, a novel bimetallic iron/nickel nanoparticles supported on biochar (BC@Fe/Ni) was established to degrade nitrate pollution in water. The nanocomposite was prepared from steel pickling waste liquor and sugarcane bagasse, which are made at low cost. The particle sizes of the nanocomposite ranged from about 10 nm to 20 nm and its specific surface area (59.83 m<sup>2</sup>/g) was about 71% bigger than that of nanoscale zero valent iron prepared from steel pickling waste liquor (S-NZVI), which proved that biochar had an excellent dispersal effect on bimetallic iron/nickel particles. Without controlling the pH, high nitrate removal rates over 93% could be realized in nitrate concentrations below 50 mg/L. The results of batch experiments demonstrated that the kinetics curves fitted the pseudo-first-order reaction well. And it was also found that higher dosages of the nanocomposite, lower initial nitrate concentrations, and acid medium facilitated nitrate degradation. In addition, the observed pseudo-first order rate coefficient in nitrate (20 mg/L) degradation rate by 4 g/L of the bimetallic iron/nickel supported on biochar was 30% faster than that by 2 g/L the bimetallic iron/nickel nanoparticles, due to the existence of biochar. And it was 75% faster than that by 2 g/L the nanoscale zero valent iron due to the existence of both biochar and the nanoscale zero valent nickel catalyst. Furthermore, iron and nickel ion pollution occurred in the denitrification system with bimetallic iron/nickel nanoparticles but not in that with the bimetallic iron/nickel nanoparticles supported on biochar, due to the biochar's adsorption. After denitrification by the bimetallic iron/nickel nanoparticles supported on biochar, most of nitrate turned into ammonia (17.04 mg/L) and there only was a small amount of nitrite (0.024 mg/L) with high nitrate removal rate (99.5%). And most of ammonia can be absorbed by cation exchange resin with final ammonia concentration of 0.58 mg/L. At last, the concentrations of nitrate (0.24 mg/L), nitrite (0.021 mg/L), and total nitrogen (0.84 mg/L) were lowest in the nanocomposite system. Overall, the bimetallic iron/nickel nanoparticles supported on biochar exhibited clear advantages over bimetallic iron/nickel nanoparticles and nanoscale zero valent iron with respect to degrading nitrate efficiently, preventing iron and nickel pollution and removing ammonia pollution in combination with cation exchange resin.

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## 1. Introduction

Nitrate, possibly the most widespread contaminant in drinking water, can promote eutrophication (Hwang et al., 2011) and cause significant risk to human health, including cancer and methemoglobinemia (Shi et al., 2013; Soares et al., 2009) in infants. Therefore, many environmental protection departments, such as the

World Health Organization (WHO) and US Environmental Protection Agency (EPA), have set safety limits of no more than 10 mg/L for the allowable concentration of nitrate-nitrogen (NO<sub>3</sub>-N) in drinking water (Ahn et al., 2008). While various techniques such as the ion exchange (Mendez et al., 2008), reverse osmosis, electrodialysis (Bhatnagar and Sillanpää, 2011), and biological denitrification (Karanasios et al., 2010) have proved highly effective in the removal of nitrate contaminants, they cannot be employed in large-scale water treatment plants due to their high energy consumption, technological complexity, nitrate brine concentration (Barrabés and Sá, 2011), and secondary pollution by bacteria or other organic substrates (Sparis et al., 2013). With the rapid development of

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nanotechnology, the use of chemical denitrification, and especially the use of nanoscale zero-valent iron (NZVI) serving as a reduction agent has attracted the attention of many researchers due to its large specific surface area, high surface reactivity and low toxicity, which has proved to be faster and more effective in nitrate removal (O'Carroll et al., 2013).

Despite the above advantages, NZVI cannot be used alone for nitrate removal due to its aggregation behavior and easy oxidation on the surface (Fu et al., 2014; He et al., 2010). So, modified NZVI technologies such as those using Cu, Ni or Pb as catalyst (Ryu et al., 2011; Shi et al., 2016) and those supported by pillared clays, zeolites, or resins (Shi et al., 2013; Cai et al., 2014; Zhang et al., 2011) have been studied and proved to enhance its reduction activity effectively and separate the nanoparticles greatly. However, the chemical reagents used in the preparation of NZVI in the liquid phase reducing method are mostly ferric chloride or iron (II) sulfate heptahydrate, which makes the preparation cost of NZVI very expensive and limits its industrial application. In addition, nitrate degradation using NZVI or bimetallic nanoparticles as reduction agents would generate by-products such as high-concentration metallic ions (Chen et al., 2013; E.I.-Temsah and Joner, 2013) and ammonia, which then caused secondary pollution and cannot be neglected. However, there only have been a few of studies of secondary pollution removal (Fernando et al., 2015; Donald et al., 2014; Xiang et al., 2015; Anyika et al., 2016) so far, such as the removal metallic ions and ammonia generated by the nitrate degradation.

As is well known, the steel pickling waste liquor from the steel industry contains high concentrations of iron at zero cost. In addition, biochar has been proved to be porous (Song et al., 2014) with a large specific surface area. Moreover, biochar has great adsorption due to its functionalized surfaces, which is a combination of physical and chemical means (Cornelissen et al., 2005; Anyika et al., 2014; Lehanne and Joseph, 2009). If the chemical reagent used in the preparation of NZVI can be replaced by steel pickling waste liquor and supported by biochar prepared from sugarcane bagasse, production cost would be greatly reduced and the nanoparticles might be better dispersed and more stable with high activity. As yet, there have been no studies of nitrate reduction and the reaction mechanism of nitrate removal by S-NZVI prepared from steel pickling waste liquor.

In the current study, a novel bimetallic Fe/Ni nanoparticles supported on biochar (BC@Fe/Ni) was synthesized from steel pickling waste liquor and sugarcane bagasse to simultaneously remove nitrate and the possible pollution of iron and nickel ions. BC@Fe/Ni was characterized by transmission electron microscopy (TEM), scanning electron microscope (SEM), specific surface area analysis (BET) and energy-dispersive X-ray spectroscopy (EDX) to evaluate the difference between BC@Fe/Ni and S-NZVI. The batch experiments were conducted to investigate the effects of different parameters, including BC@Fe/Ni dosage, initial nitrate concentration, initial pH, and the use of biochar and Ni catalyst in the degradation of nitrate by BC@Fe/Ni. Whether the metallic ion contaminants appeared in nitrate degradation or could be removed by biochar would be detected by flameless atom absorption spectrophotometry. In order to achieve the complete degradation of nitrogen pollution, the cation exchange resin would be applied to remove the secondary ammonia pollution produced during the nitrate degradation by BC@Fe/Ni.

## 2. Experimental

### 2.1. Experimental materials

Potassium nitrate and sulphamic acid (chemical reagent,

Tianjin, China) were used to establish the standard curve of nitrate. The steel pickling waste liquor from steel industries, sugarcane bagasse, nickel chloride, and sodium borohydride (chemical reagent, Tianjin, China) were prepared for BC@Fe/Ni, Nano Fe/Ni, and S-NZVI. Sulfanilamide and hydrochloride naphthodiamide up to the standard of chemical reagent were purchased from Aladdin (Shanghai, China) and used as color-developing agent for measurement of nitrite.

A muffle furnace was supplied to prepare biochar from sugarcane bagasse with protection of nitrogen gas. An agate mortar and pestle was used to grind the nanoparticles after drying them in a vacuum chamber for 8 h.

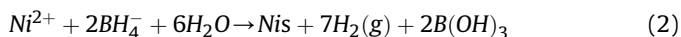
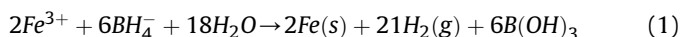
The concentrations of metallic elements, hydrogen ion and anions in raw waste liquor were measured by ICP-AES (IRIS Intrepid II XSP, Thermo Elemental Company, USA), pH meter and ion chromatography (DX-600, Dionex, USA), respectively. The chromatography of steel pickling waste liquor was detected in dilution multiple method. And the results were shown in Table 1.

### 2.2. Experimental methods

#### 2.2.1. Preparation and characterization

After being washed for impurities removing, sugarcane bagasse was dried in oven under 80 °C for one night and then smashed using a pulverizer. And then the smashed sugarcane bagasse was packed into crucibles and burned in muffle furnace at 600 °C for 2 h. In the burning process, nitrogen gas was passed over to isolate oxygen in muffle furnace. When cooled to room temperature, the combustion residue was ground into powder and sieved through 200 mesh strainer, which was called biochar. According to liquid phase reduction method, Nanoscale zero-valent iron (S-NZVI) was synthesized from steel pickling waste liquor (5 mL) reduced by dropwise addition of sodium borohydride (1.2 g) in ethanol solution (3:7 v:v). Similarly, bimetallic Fe/Ni nanoparticles (Nano Fe/Ni) were prepared in ethanol solution containing 5 mL of steel pickling waste liquor and nickel chloride (0.21 g), which was reduced by dropwise addition of sodium borohydride (1.2 g) with continuous stirring. The novel bimetallic Fe/Ni supported on biochar (BC@Fe/Ni) was synthesized in a co-reduction method (Chun et al., 2010) based on the principles shown in Eqs. (1) and (2). This process could be briefly outlined as follows: 1. Uniformly disperse 0.5 g biochar, 5 mL steel pickling waste liquor, and 0.21 g nickel chloride in ethanol solution in an Erlenmeyer flask on a magnetic stirrer by continuous stirring for 1 h; 2. Reduce the mixed solution by dropwise addition of sodium borohydride (1.2 g) with continuous stirring and precipitate the mixture by putting the Erlenmeyer on the surface of a big magnetic board; 3. Wash the precipitation three times by deionized water and rinse it three times by absolute alcohol and then dry it in a vacuum drying oven for 8 h.

Appropriate amount of biochar (0.5 g) and steel pickling waste liquor (5 mL) were dissolved uniformly in ethanol solution by continuous stirring for 1 h and then reduced by sodium borohydride. Lastly, a nickel chloride (0.21 g) solution was added into the mixed solution drop by drop for the preparation of Ni<sup>0</sup>. And so another bimetallic Fe/Ni supported on biochar abbreviated as BC@Nano Fe/Ni was prepared from steel pickling waste liquor but synthesized in a fractional precipitation method, as shown in Eqs. (1) and (3).



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