Research article

Nitrate reduction in water by aluminum alloys particles

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A B S T R A C T

Nano zero-valent iron (NZVI) particles have been extensively investigated for nitrate reduction in water. However, the reduction by NZVI requires acidic pH conditions and the final product is exclusively ammonium, leading to secondary contamination. In addition, nanomaterials have potential threats to environment and the transport and storage of nanomaterials are of safety concerns. Aluminum, the most abundant metal element in the earth's crust, is able to reduce nitrate, but the passivation of aluminum limits its application. Here we report Al alloys (85% Al) with Fe, Cu or Si for aqueous nitrate reduction. The Al alloys particles of 0.85–0.08 mm were inactivate under ambient conditions and a simple treatment with warm water (45 °C) quickly activated the alloy particles for rapid reduction of nitrate. The Al-Fe alloy particles at a dosage of 5 g/L rapidly reduced 50 mg-N/L nitrate at a reaction rate constant (k) of 3.2 ± 0.1 (mg-N/L)$^{1.5}$/min between pH 5–6 and at 4.0 ± 0.1 (mg-N/L)$^{1.5}$/min between pH 9–11. Dopping Cu in the Al-Fe alloy enhanced the rates of reduction whereas dopping Si reduced the reactivity of the Al-Fe alloy. The Al alloys converted nitrate to 20% nitrogen and 80% ammonium. Al in the alloy particles provided electrons for the reduction and the intermetallic compounds in the alloys were likely to catalyze nitrate reduction to nitrogen.

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1. Introduction

Water contamination with nitrate has caused public health problems (e.g. blue baby syndrome and stomach cancer) and a limit of 50 mg/L (i.e., 11.3 mg-N/L) in drinking water is set by the World Health Organization (WHO) (Fan et al., 1987; Loganathan et al., 2013; Mishra and Patel, 2009). For removal of low levels of nitrate around the WHO's standard limit from water containing low strength carbon sources, chemical reduction using hydrogen gas (Al Bahri et al., 2013; Jung et al., 2012; Kim et al., 2013, 2016) and zero-valent electropositive metals (e.g. Fe, Al, Zn, Mg, Sn) (Carlson, 1986; Hamid et al., 2016; Huang and Zhang, 2004; Hwang et al., 2011;

Kumar and Chakraborty, 2006; Murphy, 1991; Soares et al., 2012) as the reductant has been intensively investigated. The cost of zero-valent scrap iron is low and handling of the material is simple and safe as compared to hydrogen gas and therefore, zero-valent iron (ZVI) has been widely employed in laboratory studies for nitrate reduction (Huang and Zhang, 2004; Hwang et al., 2011; Liou et al., 2005b), chlorinated organic compounds degradation (Lee et al., 2006) and aerobic digestion of sludge (Zhen et al., 2015), and in engineering applications for groundwater contamination remediation by permeable reaction barriers (PBR) (Wilkin et al., 2005). However, the major shortcomings of ZVI for nitrate reduction are that the reaction condition requires relatively acidic pH conditions (pH < 5) (Choe et al., 2004; Hu et al., 2001; Huang and Zhang, 2004), the rates of reduction are relatively slow and the end-product of the reduction is exculsively ammonium ion (i.e. the selectivity of the reduction to N_2 is nil) (Alowitz and Scherer, 2002; Choe et al., 2004; Song et al., 2013). To increase the rates of nitrate reduction by Fe at neutral and near neutral pH conditions, practitioners investigated nano zero-valent iron (NZVI) materials (Choe

et al., 2000; Kim et al., 2012; Liou et al., 2005a; Liu et al., 2012). Excessive consumption of NZVI by water and rapid decline of reduction rates with increased pH of solution are the major concerns for NZVI (Hamid et al., 2016; Kim et al., 2012). In addition, the storage and transport of NZVI is a challenge and nanoparticles are considered as potential threats to the environment (Lee et al., 2013; Senjen and Hansen, 2011).

Aluminum, the most abundant metal element in the earth's crust and a stronger reductant than iron, has been investigated for nitrate reduction in water (Luk and Au-Yeung, 2002; Murphy, 1991; Zhao et al., 2014). However, use of Al for aqueous nitrate reduction has been far less studied, mainly because of its rapid passivation under ambient conditions and the protection of alumina layer on the surface (Lien and Zhang, 2002; Murphy, 1991). To eliminate the passivation and improve the surface reactivity of Al metal, researchers deposited a secondary metal catalyst (such as Pd, Cu, Fe) onto Al via a wet-chemistry approach (the secondary metal ions are reduced in aqueous solutions by Al and then deposited onto the surface of Al particles) to form bimetal particles for reductive dechlorination of chlorinated organic pollutants (e.g. carbon tetrachloride) (Chen et al., 2008; Lien and Zhang, 2002; Yang et al., 2013). Such Fe/Al bimetallic particles prevented formation of iron oxides/hydroxides at iron surface and increased the reactivity toward carbon tetrachloride by 10 times as compared to NZVI (Chen et al., 2008). However, it is difficult to obtain a uniform distribution of the secondary metal catalyst onto the surface of Al particles by this wet-chemistry approach. And the deposited catalyst (e.g. Fe) is subject to falling off the surface of Al metal particles when Al is gradually oxidized during the course of reaction, leading to unstable and unpredictable performance (Xu et al., 2012). In this context, Al alloy catalysts are an idea solution because the distribution of metal components in alloy particles is uniform through the surface to the core and the bonding of two metals in alloys is much stronger than the bimetallic particles. A typical example of Al alloy catalyst is Al-Ni alloy, which has been found spreadwide applications in chemical industry as hydrogenation catalyst and reductive debromination of 2,4,6-tribromophenol in aqueous solutions (Weidlich et al., 2013).

In previous studies (Hou et al., 2015; Xu et al., 2017), for the first time, we investigated Al-Fe alloys for aqueous nitrate reduction and found that Al-Fe alloys particles were able to reduce nitrate in a wide pH range between 2 and 12, increasing the alloy's Fe content from 10% to 58% enhanced the N_2 selectivity of nitrate reduction from 18% to 40% as compared to a zero N_2 selectivity by Fe, and depositing Cu on the surface of Al-Fe alloy particles significantly enhanced the rates of nitrate reduction. The catalytic effect of Cu on nitrate reduction by Fe has also been reported (Hou et al., 2015; Hwang et al., 2011; Khalil et al., 2016; Liou et al., 2005b). Lee et al. (2006) investigated the effect of Fe/Al ratios in the Fe/Al bimetal particles on reduction of carbon tetrachloride in water and found that a Al/Fe ratio of 85%:15% was of optimum performance. Therefore, the aim of this study was to investigate the performance of Al-Fe, Al-Cu, Al-Fe-Cu and Al-Fe-Si alloys with a mass ratio of 85% Al for aqueous nitrate reduction. Doping Si was to use its passivation role to adjust the reactivity of Al-Fe alloys.

2. Experimental

2.1. Chemicals and materials

Analytical grade chemicals were used throughout the study. Potassium nitrate, and aluminum, iron, copper and silicon powders (99.9% purity, 60–80 meshes) were obtained from Tianjin Fucheng Chemicals, China. Deionized water was used for preparation of solutions. Al, Fe, Cu and Si powders were added into a MgO crucible

(50 mm I.D. × 80 mm H., KF-M0.7, Dingsheng Technology, China) with a mass ratio of 85% Al and 15% Fe for Al-Fe15 alloy, 85% Al and 15% Cu for Al-Cu15 alloy, 85% Al, 9% Fe and 6% Cu for Al-Fe9Cu6 alloy, and 85% Al, 9% Fe and 6% Si for Al-Fe9Si6 alloy. The powders were mixed and then the crucible was put into a vacuum induction melting furnace (SGM.VB6/16, Sigma Furnace Industry, China) with initial vacuum pressure of 10 Pa, and the heating temperature process was 200 °C/12 min to 1500 °C at a vacuum pressure of <5 Pa. The melted liquid was refined for 2 min at 1500 °C and then cooled for 1.5 h in a copper mold by water under a vacuum pressure of 1–5 Pa. The Al alloy ingot was crushed into particles and sieved with desired sizes of 20–200 meshes (0.85–0.08 mm).

2.2. Characterization and analytical methods

The concentrations of nitrate and nitrite were determined by ion chromatography (Dionex, ICS-900, USA) using the eluent of 4.5 mM Na_2CO_3 and 0.8 mM $NaHCO_3$ mixed solution. Ammonium was determined by salicylate-sodium hypochlorite spectrophotometric method (Persee, TU-1900, China) at wavelength of 697 nm. Solution pH was measured by pH meter (Mettler Toledo, FE 20, China). Al, Fe and Cu ions in solutions were analyzed by ICP-AES (Thermo, iCAP 6000, USA). The morphology and chemical composition of the alloys were characterized by scanning electron microscopy (Hitachi, S4800-SEM, Japan) and X-ray diffraction (Bruker, D8 Advance, Germany) with a scanning range from 15° to 90° and a scanning speed of 5° min^{-1}.

2.3. Particles pretreatment and nitrate reduction

2.3.1. Pretreatment

The Al, Fe or alloy particles of 2 g were placed in a 500 mL glass reactor and 200 mL DI water were added. The reactor was purged with argon gas flow of 5 mL/min and heated in a water bath at 45 °C for 1–4 h. During the pretreatment, the mixtures in the reactor were stirred at 200 rpm. The reactor was cooled to 20 °C within 30 min.

2.3.2. Nitrate reduction

After pretreatment, an aliquot of 200 mL KNO_3 solution was added to the reactor. After shaking the reactor for 2 min, the pH of the solution was measured and the solution was then purged with argon gas at a flow rate of 5 mL/min for 5 min. The pH of the solution was adjusted to the required value using 1 M NaOH and 1 M HCl and stirred at 200 rpm with a magnetic bar at a reaction temperature of 20 °C unless otherwise specified. Samples of 5 mL were taken from the reactor at a given time interval and filtered with 0.22 μm membrane for analysis of nitrate, nitrite ammonium. The experiments were generally performed in duplicate batches and the results were averaged.

The rate constant (k) of the reduction was obtained via the following equation:

$$-d[NO_3^- - N]/dt = k[NO_3^- - N]^n \tag{1}$$

where n is reaction order calculated by MATLAB and t is the reaction time.

3. Results and discussion

3.1. Reduction of aqueous nitrate by Al, Fe and Al alloys

The reduction of aqueous nitrate by particles of Al, Fe and four Al alloys (Al-Fe15, Al-Cu15 and Al-Fe9Cu6) without pretreatment is