



Chemical removal of nitrate from water by aluminum-iron alloys



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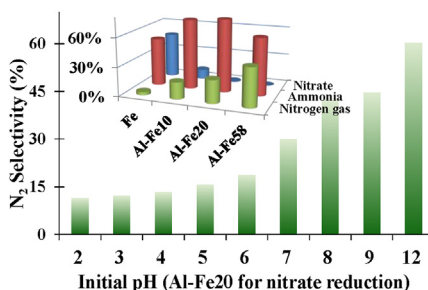
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HIGHLIGHTS

- Al-Fe alloy particles are efficient to reduce aqueous nitrate at a pH range of 2–12.
- Increasing Fe content of the alloy and solution pH improves the selectivity to N₂.
- Al-Fe alloys enhance removal efficiency while minimizing Fe contamination.

GRAPHICAL ABSTRACT



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ABSTRACT

Zero-valent iron has been intensively investigated in chemical reduction of nitrate in water, but the reduction requires acidic or weak acidic pH conditions and the product of the reduction is exclusively ammonium, an even more toxic substance. Zero-valent aluminum is a stronger reductant than iron, but its use for the reduction of aqueous nitrate requires considerably alkaline pH conditions. In this study, aluminum-iron alloys with an iron content of 10%, 20% and 58% (termed Al-Fe10, Al-Fe20 and Al-Fe58, respectively) were investigated for the reduction of aqueous nitrate. Al-Fe alloys were efficient to reduce nitrate in water in an entire pH range of 2–12 and the reduction proceeded in a pseudo-first order at near neutral pH conditions. The observed reaction rate constant (K_{obs}) of Al-Fe10 was 3 times higher than that of Fe and the K_{obs} of Al-Fe20 doubled that of Al-Fe10. The nitrogen selectivity of the reduction by Al-Fe10, Al-Fe20 and Al-Fe58 was 17.6%, 23.9% and 40.3%, respectively at pH 7 and the nitrogen selectivity by Al-Fe20 increased from 18.9% at pH 2–60.3% at pH 12. The enhanced selectivity and reactivity of Al-Fe alloys were likely due to the presence of an intermetallic Al-Fe compound ($Al_{13}Fe_4$).

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1. Introduction

High levels of nitrate in drinking water have been identified to cause blue baby syndrome and stomach cancer while nitrate

concentration in groundwater and surface aquifers has been increasing over the past decades owing to industrial and agricultural activities. Various methods such as physiochemical removal (Nguyen et al., 2015), bio-denitrification (Rezania et al., 2005), ion exchange (Meng et al., 2014), reverse osmosis (Kimura et al., 2002) and chemical reduction (Hou et al., 2015; Hu et al., 2001; Hwang et al., 2011; Liou et al., 2005c) have been investigated for nitrate removal from water. Ion exchange (Meng et al., 2014) and

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membrane technology (e.g. reverse osmosis (Kimura et al., 2002)) are highly efficient, but suffer high capital and running costs and usually generate brine wastes, which require further disposal (Schnoor, 2013). Bio-denitrification process is cost-effective and efficient for high strength wastewater, but is not readily applicable to relatively low levels of nitrate in ground and surface waters in which carbon sources are insufficient. In this context, chemical reduction using reductive zero-valent metals such as Fe (Huang et al., 1998; Huang and Zhang, 2004; Liou et al., 2005c; Ruangchainikom et al., 2006a), Al (Murphy, 1991), Zn (Carlson, 1986), Mg (Kumar and Chakraborty, 2006) particles is of great interest for groundwater nitrate contamination remediation.

Of the zero valent metals, Fe has been most employed as electron donor for nitrate removal from water (Zhu and Getting, 2012). Due to its availability and low cost (in particular zero valent scrap iron), Fe was also employed as electron donor to simulate the anaerobic digestion of sludge (Zhen et al., 2015). The major shortcoming of zero valent Fe (ZVI) is poor reactivity at neutral and near neutral pH conditions. In general, use of ZVI requires relatively acidic pH conditions (pH 2–5) to maintain the reactivity (Choe et al., 2004; Hu et al., 2001; Huang and Zhang, 2004). To increase the reactivity and reaction kinetics of aqueous nitrate with Fe at near neutral pH conditions, practitioners prepared nano-sized zero valent iron (NZVI) for denitrification of water (Choe et al., 2000; Kim et al., 2012; Liou et al., 2005a; Liu et al., 2012). However, the storage and transport of NZVI is a challenge due to its high reactivity and nanoparticles are considered potential threats to the environment (Lee et al., 2013; Senjen and Hansen, 2011). In addition, the final product of aqueous nitrate reduction by ZVI is ammonia, an even more toxic than nitrate to living organisms. And the secondary contamination due to leaching of Fe ions is additional concern of the water quality (Kim et al., 2012). Aluminum, the most abundant metal element in the earth's crust, has relatively stronger reductive properties and is able to reduce aqueous nitrate, but only in alkaline solutions (pH > 10) due to the protection of alumina layer on the surface (Murphy, 1991). To improve the performance of reductive metals for chemical removal of nitrate, bi-metals are prepared by chemical deposition of a second metal on the surface of the core metal (such as Cu/Fe (Khalil et al., 2016), Pd/Fe (Shi et al., 2016), Cu/Al (Lien and Zhang, 2002), Pd/Al (Yang et al., 2013), Fe/Al (Chen et al., 2008)).

Chen et al. 2008 reported Fe/Al bimetallic particles for chemical removal of carbon tetrachloride from water. The bimetallic Fe/Al particles can prevent formation of iron oxides/hydroxide at the iron surface and maintain the reactivity of iron because of galvanic effects (Chen et al., 2008). However, non-uniform distribution of the second metal on the surface of the core metal and a weak combination of the two metals are the shortcomings of such bimetal materials obtained by chemical deposition (Hou et al., 2015; Liou et al., 2005a). To avoid these shortcomings, we investigated Al-Fe alloy (10% Fe content) for aqueous nitrate reduction in a previous publication (Hou et al., 2015). We found that the reduction kinetics was slow, copper ions were required to catalyze the reduction and the final product of the reduction was exclusively ammonia (Hou et al., 2015). The objective of this study was to investigate the effect of Fe content of Al-Fe alloys on aqueous nitrate reduction, aiming at enhancing the reduction efficiency under neutral pH conditions and the formation of nitrogen.

2. Materials and methods

2.1. Materials preparation

Analytical grade chemicals were used throughout the study. Al and Fe powders (60–80 meshes, Fuchen Chemicals, China) were

added into a MgO crucible (50 mm I.D. × 80 mm H., KF-MO.7, Dingsheng Technology, China) with a mass ratio of 9:1, 8:2 and 42:58, respectively. 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 melting 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. After melting, the Al-Fe ingot was crushed into particles with different sizes (<0.8 mm, 0.8–2.0 mm, >2.0 mm). The Al-Fe alloys, Al and Fe particles were soaked in 45 °C deionized water overnight for activation prior to the reduction experiments.

2.2. Experimental methods

The activated alloy particles were loaded into a Perspex column (40 mm I.D. × 50 mm H.) and 40 g of 0.8–2 mm particles were used, unless otherwise specified. The porosity of the packed column was 50%. Potassium nitrate (Beijing Chemicals, China) solution of 25 mg-N/L (250 mL) was pumped upwards the column at a flow rate of 1.2 ml/s in a recycle mode. Samples of 1 mL were taken in a given time interval and filtered through 0.22 μm hydrophilic membrane and 0.6 ml of the filtered solution was diluted to 6 ml by deionized water prior to the analysis of nitrate, nitrite, ammonia, aluminum and soluble metal ions in water. Triplicate experiments were conducted for all of the experiments, and the confidential interval of the experimental data was 95%. The nitrate removal efficiency was calculated by $(1-C/C_0) \times 100\%$, where C was nitrate concentration (mg-N/L) and C_0 was the initial nitrate concentration (mg-N/L). The products of aqueous nitrate reduction by metals are nitrite, ammonia and nitrogen (Chen et al., 2005; Cheng et al., 1997; Daum and Vorlop, 1999; Murphy, 1991; Rodríguez-Maroto et al., 2009; Ruangchainikom et al., 2006b) and the N_2 selectivity was calculated by $(1-\text{Total-N}/C_0) \times 100\%$, where Total-N represents the sum of nitrate, nitrite, ammonia in aqueous solution in accordance with literature (Shi et al., 2016). To verify this calculation for N_2 selectivity, the volatile loss of aqueous ammonia was examined by stirring 250 mL of 13 mg-N/L ammonium chloride solution at different pH (9–12) with 9 g of Al-Fe₂₀ powders at 300 rpm and 26 ± 1 °C for 1 h in a beaker.

Nitrate and nitrite were determined by ion chromatography (ICS-900, Thermo Scientific, America). Ammonia was determined by UV-vis photometer (TU-1900, Persee, China) at wavelength of 420 nm according to Nessler's reagent spectrophotometry. Aluminum and iron ions in samples were determined by ICP-MS (iCAP 6000, Thermo Scientific, America).

3. Results and discussion

3.1. Nitrate reduction by Al, Fe and Al-Fe alloys

The nitrate concentration ratio in water with neutral pH passing a column packed with Al, Fe or Al-Fe alloys particles is shown in Fig. 1. For metallic Al particles, nitrate concentration decreased from 25 mg-N/L to 19.95 mg-N/L in the initial 15 min and then very slowly to 17.78 mg-N/L at the end of experiment (180 min). This indicates that the loss of nitrate was likely due to physiochemical adsorption on the surface of Al particles. By contrast, nitrate concentration by Fe and Al-Fe alloys decreased in a pseudo-first order and the observed pseudo-first-order reaction rate constant (K_{obs}) of the Al-Fe₁₀ alloy was 3 times higher than that of Fe (Fig. 1). The K_{obs} of Al-Fe₂₀ doubled that of Al-Fe₁₀ and that of Al-Fe₅₈ slightly increased. At the 90 min of reaction, almost 100% of nitrate was reduced by the three types of Al-Fe alloys whereas only 67.1% of

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