Nitrate reduction in water by aluminum–iron alloy particles catalyzed by copper

Mingtao Hou[a], Yang Tang[b], Jie Xu[a], Yuan Pu[a], Aijun Lin[a], Lili Zhang[a], Jinping Xiong[c], Xiao Jin Yang[a,*], Pingyu Wan[b]

[a] *School of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China*
[b] *Department of Applied Chemistry, Beijing University of Chemical Technology, Beijing 100029, China*
[c] *School of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China*

A B S T R A C T

Nitrate contamination is increasingly becoming a global health and environmental issue, because nitrate concentration in ground and surface waters has exceeded the safe limit in many places of the world. Removal of such low levels of nitrate from water by conventional processes in an efficient and cost-effective manner poses a significant challenge in water treatment industry. Chemical reduction using zero-valent iron and aluminum particles for nitrate removal from water has been extensively investigated. In this study, aluminum–iron alloy particles (containing 10% iron) were investigated for removal of nitrate from water and compared with zero-valent aluminum, iron and mixtures of aluminum and iron particles. The aluminum–iron alloy and metallic aluminum particles were inactive for nitrate reduction due to the presence of ubiquitous aluminum oxide layer on surface of the particles. Nitrate reduction was significantly promoted by copper chloride and the alloy particles showed the fastest rate and largest efficiency of the reduction. The significant promotion of the reduction was likely due to the catalytic effect of copper and an intermetallic alloy compound $Al_{13}Fe_4$. The catalytic mechanism of nitrate reduction by the alloy material was analyzed and the reduction pathway was identified as nitrite and ammonium to be intermediate and end product, respectively.

© 2015 Elsevier Ltd. All rights reserved.

Introduction

Nitrate contamination in ground and surface waters has become great health and environmental concern [1,2]. The World Health Organization (WHO) set a limit of 50 mg/L nitrate (i.e., 11.3 mg/L NO_3^-–N) in drinking water [3]. Biological denitrification is widely employed for nitrate removal from wastewater [4,5], but is not effective for water containing low levels of both nitrate (e.g., around the WHO's standard) and carbon sources. For removal of such low levels of nitrate from water, membrane technologies [6–8], ion exchange [9], electrochemical processes [10], hydrid processes by combining biological denitrification and electrodialysis [11], and chemical reduction have been investigated [12–22]. Of these processes, chemical reduction using metallic particles such as iron and aluminum has attracted extensive attention [12–19]. Nitrate reduction by metallic iron particles is generally carried out at relatively low pH conditions (preferably pH < 4) [13,18,19],

partly because nitrate increases iron surface passivation and reduces rates of iron corrosion. To improve reduction efficiency, nano-scale iron particles were investigated owing to greater surface area and reactivity [23–27]. However, high costs associated with the storage, preparation and stability of nano iron particles at ambient conditions and the rapid oxidation of nano iron particles in water limit their large-scale applications [26,27].

Metallic aluminum, a stronger reducing agent ($E° = -1.667$ V) and the most abundant metal element in earth's crust, has been reported to remove nitrate from water in conventional particle sizes (in micro- or millimeter) [12,15,28]. Nevertheless, pH conditions of alkaline (pH > 9) or acidic (pH < 3) were required to attack the passivation layer of aluminum oxide on the surface of aluminum particles [12,29]. To improve the reactivity of large size Fe or Al particles, single or dual metallic catalysts loaded on the surface of Fe or Al particles were investigated for chemical degradation of contaminants from water [22,28,30,31,32–34]. Such materials are generally prepared by depositing the catalytic metals (e.g., Cu, Ni, Pd) on the surface of Fe or Al particles via a wet-chemistry approach (i.e., the catalytic metal elements are reduced and deposited on the surface of Fe or Al particles in aqueous

* Corresponding author. Tel. +86 10 64421030; fax: +86 10 64421030.
 E-mail address: yangxj@mail.buct.edu.cn (X.J. Yang).

solutions) [22,28,31]. Zhao et al. [28] investigated Al particles on the surface of which a single metal (Cu or Ni) or bimetals (Pd–Cu, Pt–Cu, Au–Cu, and Ru–Cu) were loaded via the wet-chemistry approach to facilitate the reduction of nitrate in water. Chen et al. [30] prepared Al–Fe bimetallic particles by depositing Fe on the surface of Al particles for carbon tetrachloride dechlorination in water and found that bimetallic Al–Fe particles increased the reactivity toward carbon tetrachloride degradation by a factor of 10 as compared to the use of single metal Al or Fe. In principle, the dechlorination of carbon tetrachloride by Al–Fe bimetallic particles is similar to nitrate reduction, both of which utilize the reduction property of the materials. Therefore, Al–Fe bimetal materials can be of potential for nitrate reduction in water. However, weak combination of the two metals and uneven distribution of the catalytic metal on the surface of the active metal are the major shortcomings of such bimetallic particles, leading to unstable and poor performance in long-term applications [28,32,33].

Recently, de Sousa et al. [35] prepared mesoporous spheres of Al and Fe oxides containing 9% Cu oxide followed by reduction using hydrogen gas at high temperatures (100–900 °C) for nitrate reduction in aqueous solutions. They demonstrated catalysis of copper on nitrate reduction by reduced nano-iron supported on Al oxide. However, the preparation of such materials was rather complicated and nitrate reduction was determined by the degree of Fe and Cu oxide reduction in the spheres by hydrogen (i.e., the reduction activity of the spheres was quickly lost with the consumption of reduced Fe and Cu).

It was reported that corrosion rate (e.g., reduction reactivity) of Al was significantly enhanced by alloying with Fe [36,37]. Aluminum–iron alloy can maintain the reduction properties of Al and Fe and is expected to avoid the shortcomings of bimetallic Fe–Al materials prepared by the wet-chemistry method. Therefore, it is of great interest to explore the possibility of aluminum–iron alloy for nitrate reduction in water. In this study, we compared Al–Fe alloy particles (90% Al-10% Fe) with metallic Al and Fe and mixtures of Al and Fe particles for nitrate reduction in water and investigated catalytic effect of copper on nitrate reduction by aluminum–iron alloy.

Experimental

Chemicals and materials

Analytical grade chemicals were used throughout the study. Potassium nitrate, iron and aluminum powders were obtained from Tianjin Fucheng Chemicals, China. The size of metallic powders was 60–80 meshes. Copper chloride and hydrochloric acid (35%–37%) were purchased from Beijing Chemicals, China. Al–Fe alloy ingot was prepared by melting high purity Al and Fe metals (>99.9%) in a mass ratio of 9:1 in a vacuum induction melting furnace (SGM, RL91/X, China). The MgO crucible was dried for 10 h at 800–850 °C. The initial vacuum pressure of the system was 10 Pa and the materials were heated by increasing temperature 200 °C/ 12 min to 1500 °C at a vacuum pressure of <5 Pa. The moten 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 alloy particles were obtained by crushing the alloy ingot and sieved. The size of Al–Fe alloy particles used ranged between 60 and 80 meshes. All solutions were prepared using deionized water.

Nitrate reduction in aqueous solution

The reduction was conducted in a 400 mL flask with an overhead mechanical stirrer at room temperature. Metallic particles of 6 g were placed in the flask and 100 mL of 0.0–0.3% (w/v) copper chloride solution were added to the flask (corresponding to a copper loading of 0–5% w/w relative to 6 g particles). The solution was stirred at

150 rpm to allow Cu^{2+} to react with the alloy for 40 min (Cu^{2+} pre-reaction). Then, the pH of the solution was adjusted to the required value (in most cases at pH 4) with 0.1 M HCl and then 200 mL of 108.2 mg/L KNO_3 (i.e., 15 mg/L NO_3^-–N) were added to the flask to make an initial concentration of 10 mg/L for NO_3^-–N. The solution was stirred at 150 rpm and samples of 3 mL was taken for analysis for nitrate, nitrite and ammonium at a pre-set time.

Analytical methods and material characterization

Samples were filtered with 0.22 μm syringe filters prior to analysis. Nitrate and nitrite concentrations were analyzed by ion chromatography (Dionex, ICS-900, U.S.A.). Nessler photometric was used for the analysis of ammonium (Persee, TU-1900, China); pH meter (Mettler Toledo, FE 20, China) was used to measure solution pH. The morphology and structure of the prepared materials was examined with SEM (Zeiss, Supra55, Germany) and XRD (Bruker, D8 Advance, Germany), respectively. The localized elemental information of Al–Fe alloy particles were viewed with energy dispersed X-ray spectroscopy (EDX) in conjunction with SEM. The determination of Al, Fe and Cu in the reduction sample solution was carried out by ICP-AES (Thermo, iCAP 6000, U.S.A.) after proporiate dilution.

Results and discussion

Nitration reduction and the mechanism

Nitration reduction from aqueous solutions was compared among Al–Fe alloy (90% Al-10% Fe), metallic Al, Fe, and mixtures of
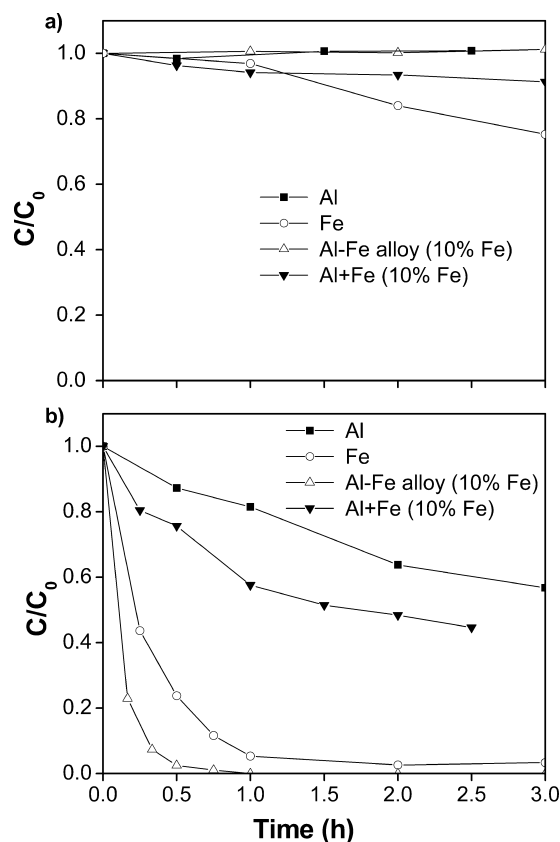

Fig. 1. Comparison of nitrate reduction by particles of Al, Fe, Al–Fe alloy and Al + Fe mixtures, (a) at pH 4 ± 0.3 adjusted by HCl; (b) with 3% copper loading, pH 4 ± 0.3 adjusted by HCl. Experimental condition: initial NO_3^-–N concentration (C_0) = 10 mg/L, 300 mL solution, 6 g particles.