Chemosphere 125 (2015) 41–49

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

The role of magnetite nanoparticles in the reduction of nitrate in groundwater by zero-valent iron

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HIGHLIGHTS

- Magnetite nanoparticles enhanced nitrate reduction by micro-sized Fe(0).
- Magnetite nanoparticles mediated electron transport from Fe(0) to nitrate.
- The presence of divalent cations promoted Fe(0)/magnetite reaction with nitrate.
- Fe(0)/magnetite can be a viable technology for contaminant reduction in groundwater.

ARTICLE INFO

Article history:
Received 28 March 2014
Received in revised form 29 December 2014
Accepted 14 January 2015
Available online 6 February 2015

Handling Editor: Y. Liu

Keywords:
Zero-valent iron (Fe(0))
Magnetite nanoparticles
Nitrate
Cations
Groundwater

ABSTRACT

Magnetite nanoparticles were used as an additive material in a zero-valent iron (Fe(0)) reaction to reduce nitrate in groundwater and its effects on nitrate removal were investigated. The addition of nano-sized magnetite (NMT) to Fe(0) reactor markedly increased nitrate reduction, with the rate proportionally increasing with NMT loading. Field emission scanning electron microscopy analysis revealed that NMT aggregates were evenly distributed and attached on the Fe(0) surface due to their magnetic properties. The rate enhancement effect of NMT is presumed to arise from its role as a corrosion promoter for Fe(0) corrosion as well as an electron mediator that facilitated electron transport from Fe(0) to adsorbed nitrate. Nitrate reduction by Fe(0) in the presence of NMT proceeded much faster in groundwater (GW) than in de-ionized water. The enhanced reduction of nitrate in GW was attributed to the adsorption or formation of surface complex by the cationic components in GW, i.e., Ca^{2+} and Mg^{2+}, in the Fe(0)–H_2O interface that promoted electrostatic attraction of nitrate to the reaction sites. Moreover, the addition of NMT imparted superior longevity to Fe(0), enabling completion of four nitrate reduction cycles, which otherwise would have been inactivated during the first cycle without an addition of NMT. The results demonstrate the potential applicability of a Fe(0)/NMT system in the treatment of nitrate-contaminated GW.

1. Introduction

Nitrate is a highly soluble form of nitrogen (N) and a common groundwater pollutant, especially in agricultural regions. Rapid growth of the world population over the last several decades has drastically increased global use of N fertilizer for enhanced crop production. This practice inevitably increases terrestrial nitrate levels, and a significant amount of nitrate is present in ground and surface waters. Ingestion of drinking water containing high levels of nitrate may cause methemoglobinemia in infants, known as blue baby syndrome (Kapoor and Viraraghavan, 1997). It has also been reported that nitrate induces carcinogenic or endocrine disrupting effects on sturgeon (US EPA, 2014). Recent occurrence survey studies have revealed that in many locations, nitrate contamination of groundwater is not limited to the local scale but occurs across wide regions (Kite-Powell and Harding, 2006; Hamlin et al., 2008; Fenton et al., 2009). Of concern is that high levels of nitrate are often found in shallow groundwater that is often used as a source of drinking water (Fenton et al., 2009). To protect human health, many countries put regulatory limits of nitrate-N on drinking water, ranging around 10 mg-N L^{-1}.

Zero-valent iron (Fe(0)) has been suggested as a treatment option for nitrate-contaminated water (Westerhoff and James,

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http://dx.doi.org/10.1016/j.chemosphere.2015.01.019
0045-6535/

2003; Burow et al., 2010; Ahn et al., 2012), but there is a great deal of variation in the overall efficiency of Fe(0). One of the key factors determining the overall performance of Fe(0)-based treatment systems is longevity of Fe(0) to maintain its reactivity over longer periods of time. Once placed in treatment units, Fe(0) undergoes various reactions with target contaminants as well as other coexisting redox-active components, and as a result, it gradually loses its reactivity as solid phase reaction products accumulate on the surface of iron, especially under alkaline conditions.

Several researchers have studied various water quality parameters including pH, coexistent ions, temperature, mass transport and dissolved oxygen that affect the reactivity of Fe(0) during reduction of nitrate (Ginner et al., 2004; Huang and Zhang, 2005; Ahn et al., 2008; Tang et al., 2012). Other investigations have focused on the use of external materials such as ultraviolet light, CO_2 gas bubbling, clay mineral, pillared clay, magnetite and CeO_2 in Fe(0) systems for enhancing nitrate reduction (Liao et al., 2003; Ruangchainikom et al., 2006; Cho et al., 2010; Zhang et al., 2011; Xu et al., 2012; Xu and Wang, 2013). Among those materials, magnetite is of particular interest because of its advantageous properties in improving the performance of Fe(0) systems (Wu et al., 2009; Lv et al., 2012). For example, Wu et al. (2009) observed a rate enhancement effect of magnetite in the removal of Cr(VI) by nano-scale Fe(0), and attributed its effects to preventing aggregation of reaction products on the Fe(0) surface and mediating electron transfer to adsorbed Cr(VI). Lv et al. (2012) also suggested nano-Fe(0)/nano-magnetite clusters to prevent superficial oxidation of the Fe(0) surface, thereby contributing to enhancement in Cr(VI) removal.

However, such an enhancement effect of magnetite was not apparent in nitrate reduction when magnetite was involved in the Fe(0) reaction in de-ionized water at neutral pH conditions, but in the presence of ferrous iron, magnetite significantly increased the extent and the rate of nitrate reduction (Xu et al., 2012). Furthermore, the favorable role of magnetite in nitrate reduction by Fe(0) has been demonstrated by Song et al. (2013), who used granular ferric hydroxide to induce magnetite formation under groundwater conditions. Also in their study, direct addition of magnetite nanoparticles increased nitrate reduction in groundwater conditions, although the extent of enhancement was lower than that obtained by granular ferric hydroxide amendment (Song et al., 2013). It appears the effect of magnetite on nitrate reduction is variable depending on solution conditions, with the groundwater environment providing more favorable conditions for nitrate reduction. Therefore, it is worth investigating the exact role of magnetite on the rate enhancement of the Fe(0) reaction in groundwater conditions, which is more relevant to actual field applications of Fe(0).

This study aimed to identify the effect of nano-sized magnetite on the reduction of nitrate by Fe(0) in groundwater based on the results of a series of batch experiments and spectroscopic analyses, and therefore get an insight into the mechanistic role of magnetite. The performance of magnetite-amended Fe(0) was compared with that of bare Fe(0). The dosage effect of Fe(0) and magnetite was also investigated to find the optimal ratio of Fe(0) and magnetite. The effect of major groundwater components was separately evaluated to understand the mechanisms involved in rate enhancement of nitrate reduction in the presence of magnetite. Finally, repetitive reduction of nitrate was carried out to investigate the longevity of Fe(0) amended with magnetite.

2. Materials and methods

2.1. Materials

High-density polyethylene (HDPE) vials (25 and 250 mL, Fisher Scientific, USA) were used as batch reactors. Nano-sized magnetite (NMT, particle size <50 nm, ⩾98%), with an average particle size of 20–30 nm and a density of 4.8–5.1 g cm^{-3}, was purchased from Sigma–Aldrich, USA. Iron powder (Fe(0), particle size 125–150 μm, 96%) was obtained from Junsei, Japan and used without pre-treatment. The surface areas of NMT and Fe(0), measured with ASAP 2010 (Micromeritics, USA), were 41.78 and 0.56 $m^2\ g^{-1}$, respectively. A groundwater (GW) sample heavily contaminated with nitrate was obtained from Hongseong district, South Korea, and delivered to the laboratory in a well-sealed plastic container and kept refrigerated until use. The ionic compositions of the groundwater were as follows (mM); Ca^{2+} (2.66), Mg^{2+} (1.44), Na^+ (0.43), K^+ (0.12), HCO_3^- (1.98), Cl^- (3.89), SO_4^{2-} (0.33) and NO_3^--N (2.19) (total moles of cations/total moles of anions concentration = 0.996), solution pH was 7.3 and dissolved oxygen concentration was 0.13 mM. Six electrolyte solutions containing sodium chloride (NaCl), sodium sulfate (Na_2SO_4), calcium chloride ($CaCl_2$), calcium sulfate ($CaSO_4$), magnesium chloride ($MgCl_2$) and magnesium sulfate ($MgSO_4$) were prepared by dissolving the corresponding salts into distilled de-ionized water (DW) to investigate the effect of coexisting ions on nitrate reduction. For nitrate reduction experiments in the DW solution, $NaNO_3$ was dissolved in DW similar to that in GW (2.13 mM NO_3^--N). All chemical reagents were of ACS grade (Sigma–Aldrich, USA).

2.2. Experimental methods

For the comparison of nitrate reduction by Fe(0) and Fe(0)/NMT under groundwater conditions, kinetic experiments were performed by transferring 20 mL GW solution into the reactors containing either 0.2 g of Fe(0) or 0.2 g Fe/0.2 g NMT, respectively, and the reactors were stirred at room temperature (23 ± 2 °C) and 150 rpm for 36 h. The dose effect of NMT or Fe(0) on the reduction of nitrate was examined by changing the amounts from 0.02 to 0.4 g at various Fe(0) loadings (0.02–1 g). The reactions were allowed to occur for 24 h. The effects of coexisting ions (Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}) on the reduction of nitrate by Fe(0) or Fe(0)/NMT were investigated by adding either 0.2 g Fe(0) or 0.2 g Fe(0)/0.2 g NMT to the electrolyte solutions. To investigate the lifespan of the Fe(0)/NMT reaction, 200 mL of 10 mM $CaCl_2$ solution containing 2.13 mM NO_3^--N was replenished to the reactor containing 4 g Fe(0)/4 g NMT when the nitrate concentration dropped to below 0.71 mM (10 mg-N L^{-1}) at each reduction cycle. During the replacement of nitrate solutions, the solid particles were held on the bottom of the reactors using a magnet to prevent loss of the particles, and the reacted solutions were completely removed using a pipette before adding fresh solution containing $CaCl_2$ and nitrate.

The samples obtained from all experiments were filtered with a 0.45 μm PVDF (Polyvinylidene Fluoride) syringe filter (Whatman, USA) at selected time intervals for the analysis of NO_3^-, NH_4^+ and pH. The concentration of nitrate was measured using a single-column ion chromatograph (Dionex CX-120). The concentration of cations in aqueous solution was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Ultima 2C, Horiba-Yuvon, France). The solution pH was measured using a pH meter (Horiba, Kyoto, Japan). The concentration of NH_4^+ in the solution was measured by a DR/4000 spectrophotometer (HACH, USA), using a C-MAC Nessler Kit. All the batch experiments were conducted in duplicate, and the average values are reported for each measurement, with the error bars representing the ranges of the measured values. The fresh NMT, fresh Fe(0) and reacted Fe(0)/NMT were analyzed by an X-ray diffractometer (D8 Advance, Bruker-AXS) to examine the mineralogical properties of the materials using Cu Kα radiation and a LynxEye position sensitive