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Simultaneous removal of cadmium and nitrate in aqueous media by nanoscale zerovalent iron (nZVI) and Au doped nZVI particles

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ABSTRACT

Nanoscale zerovalent iron (nZVI) has demonstrated high efficacy for treating nitrate or cadmium (Cd) contamination, but its efficiency for simultaneous removal of nitrate and Cd has not been investigated. This study evaluated the reactivity of nZVI to the co-contaminants and by-product formation, employed different catalysts to reduce nitrite yield from nitrate, and examined the transformation of nZVI after reaction. Nitrate reduction resulted in high solution pH, negatively charged surface of nZVI, formation of Fe_3O_4 (a stable transformation of nZVI), and no release of ionic iron. Increased pH and negative charge contributed to significant increase in Cd(II) removal capacity (from 40 mg/g to 188 mg/g) with nitrate present. In addition, nitrate reduction by nZVI could be catalyzed by Cd(II): while 30% of nitrate was reduced by nZVI within 2 h in the absence of Cd(II), complete nitrate reduction was observed in the presence of 40 mg-Cd/L due to the formation of Cd islands (Cd(0) and CdO) on the nZVI particles. While nitrate was reduced mostly to ammonium when Cd(II) was not present or at Cd(II) concentrations $\geq$ 40 mg/L, up to 20% of the initial nitrate was reduced to nitrite at Cd(II) concentrations < 40 mg/L. Among nZVI particles doped with 1 wt. % Cu, Ag, or Au, nZVI deposited with 1 wt. % Au reduced nitrite yield to less than 3% of the initial nitrate, while maintaining a high Cd(II) removal capacity.

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1. Introduction

Heavy metal pollution, especially cadmium (Cd), is a major environmental issue in China and many other parts of the world (Monteiro-Neto et al., 2003; An et al., 2010; Ju et al., 2007; Kaushik et al., 2003). The Guangzhou Food and Drug Administration recently reported that the content of Cd in 44% of sampled rice and rice products exceeded national standards of 0.2 and 0.1 mg/kg respectively (Bi et al., 2013), which underlined the severity of Cd pollution in China's main grain producing areas. Some of these grain producing areas (e.g. Jiangxi, Hunan) have large mines (Wang et al., 2012). Poor management of wastes from mining activities have resulted in severe water contamination (Lei et al., 2008) at levels of up to 3000–5000 mg Cd/L. Due to water shortages and lack of treatment facilities, water contaminated with nitrate (resulting from the overuse of synthetic fertilizers) and metals (e.g. Cd) is used for irrigating vegetables and grains (Yang et al., 2006), which could lead to high nitrate and heavy metal concentrations in vegetables and grains (Cheng, 2003; Cheng et al., 2010). While Cd damages lungs, kidneys, liver and reproductive organs (Guy et al., 2009), nitrate can cause methemoglobinemia in infants (Rogan and Brady, 2009). Hence, the importance of treating this kind of contamination cannot be overemphasized.

Nanoscale zerovalent iron (nZVI), with Fe(0) core and iron oxide shell, has been proposed for the treatment of Cd contamination (Kharisov et al., 2012; Li and Zhang, 2007; Boparai et al., 2011). However, there is a large discrepancy in Cd removal capacity of nZVI reported (e.g. 7.3 mg/g (Li and Zhang, 2007), 66.9 mg/g (Zhang et al., 2014), 769.2 mg/g (Boparai et al., 2011)). The discrepancies may arise from different initial Cd(II) concentrations, temperature, and water chemistry such as pH (Klimkova et al., 2011; Boparai et al., 2013; Liu et al., 2008), and concentrations of dissolved oxygen (Liu et al., 2008; Reinsch et al., 2010), phosphate (Reinsch et al., 2010; Su and Puls, 2004), and nitrate (Liu et al., 2008; Reinsch et al., 2010). According to previous studies (Li and Zhang, 2007; Boparai et al., 2011; Huang et al., 2013), X-ray photoelectron spectroscopy (XPS) analysis indicated that Cd(II) immobilization by nZVI was mainly through adsorption. However, reduction of Cd(II) to Cd(0) may also occur due to its slightly more positive standard electrode potential (E^0, $E_1^0 = -0.403$ V) than Fe ($E_2^0 = -0.447$ V) (Lide, 2004). As demonstrated in this study, X-ray diffraction (XRD) may help to better understand Cd(II) reduction on the nZVI particles, since it can show characteristic peaks of Cd(0) if present.

With regard to nitrate pollution, it has been widely observed that ammonium is the main reduction product in the presence of nZVI, with only a small fraction of nitrite detected; nitrite is regarded as an intermediate (Kim et al., 2012; Sohn et al., 2006; Ahn et al., 2008; Yang and Lee, 2005). Although ammonium is a toxic pollutant to some organisms (do Amaral et al., 2013; Dai et al., 2008, 2012), it serves as major nitrogen source for plants (Fuertes-Mendizabal et al., 2013; Cabezas and Couto, 2007). Furthermore, nZVI is mainly transformed into magnetite (Fe_3O_4) after reaction with nitrate (Su and Puls, 2004; Sohn et al., 2006; Ryu et al., 2011), which avoids significant increase of Fe^{2+} or exchangeable Fe concentration. This vastly reduces the potential environmental impact of nZVI (Adeleye et al., 2013; Keller et al., 2012). Hence, it is possible to employ nZVI to treat contaminated groundwater after it has been pumped out of the ground.

Given the prevalence of nitrate and metal contamination in many regions, it is important to understand the influence of one pollutant on the removal of the other using nZVI. In this study we focused on the interplay between nitrate and Cd. Nitrate may affect Cd removal in two ways: (1) in terms of Cd(II) adsorption, while nitrate may not affect adsorption significantly through changing ionic strength (Boparai et al., 2013), it may enhance Cd(II) removal by driving solution pH above 9 (Boparai et al., 2011, 2013; Sohn et al., 2006); and (2) in terms of Cd(II) reduction, nitrate reduction will consume a large part of Fe(0) and produce iron oxide— reducing electron supply and restricting electron flow for Cd(II) reduction. Likewise, the presence of Cd(II) may also have two important implications on nitrate reduction: First, similar to Cu islands (Sparis et al., 2013), Cd islands (Cd(II) compounds or Cd(0)) may be formed on nZVI, which may enhance electron transport to nitrate. Enhanced electron transport may occur given the lower electrical resistivity (ρ) of Cd ($\rho = 6.84 \times 10^{-8}\ \Omega$ m) than Fe ($\rho = 9.58 \times 10^{-8}\ \Omega$ m). Second, if Cd(II) is reduced to Cd(0), it can reduce nitrate to nitrite (Alonso et al., 1998; Wang et al., 1998; Oliveira et al., 2007), which may lead to an increased nitrite yield ratio (defined as $[\text{nitrite}]_{\text{final}}/[\text{nitrate}]_{\text{initial}}$). Nitrite tends to accumulate under strongly alkaline conditions created by nitrate reduction (Guy et al., 2009). However, nitrite accumulation is undesirable in natural environment as nitrite is highly toxic to several organisms, including humans (Hoque et al., 2008; Tenuta and Lazarovits, 2004; Bruning-Fann and Kaneene, 1993). Several previous studies have shown that catalysts, such as Cu (Hosseini and Tosco, 2013; Hosseini et al., 2011; Liou et al., 2009), Ag (Singh et al., 2012), or Au (Liou et al., 2009), can facilitate nitrite reduction.

In this study, Cd removal performance of nZVI in the presence or absence of nitrate was investigated. In addition, the effect of Cd on nitrate reduction was systematically examined. We also evaluated the potential of nZVI with 1 wt.% Cu, Ag, or Au to treat Cd and nitrate co-pollution with minimal nitrite yield. XRD was employed to detect Cd(0) and characterize the transformation of the nanoparticles under different conditions.

2. Materials and methods

2.1. Chemical reagents

Analytical grade cadmium acetate ($Cd[CH_3COO]_2 \bullet 3H_2O$), sodium nitrate ($NaNO_3$), copper chloride anhydrous ($CuCl_2$), sliver nitrate anhydrous ($AgNO_3$), gold chloride ($AuCl_3$), sodium borohydride ($NaBH_4$, 98%), ferric chloride anhydrous ($FeCl_3$), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Aladdin (Shanghai, China). Sodium acetate (CH_3COONa) and acetic acid (CH_3COOH) were obtained from Sinopharm Chemical Reagent (Shanghai, China). All chemicals were used without further purification.

2.2. nZVI Synthesis method

nZVI was synthesized based on the following reaction (Eq. (1)):

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 6H_2 + 12H^+ \quad (1)$$