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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 ($\rho$) 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)):

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

Sodium borohydride ($NaBH_4$, 98%, 0.25 M) was introduced into anhydrous ferric chloride ($FeCl_3$, 0.048 M) through titration (titration rate 1 L/h) with a volumetric ratio of 1:1. After reduction, the jet-black iron nanoparticles were collected and washed with deionized (DI) water (>100 ml/g) and anhydrous ethanol three times each. A neodymium–iron–boron magnet was used to separate solids and liquids. Fresh nZVI particles were stored in anhydrous ethanol solution at 4 °C in order to avoid oxidization.

To dope nZVI with 1 wt. % Cu, Ag, or Au, freshly-made nZVI was introduced to $Cu^{2+}$, $Ag^{+}$, or $Au^{3+}$ solutions separately (the weight ratio of Me/Fe was 1%, Me = $Cu^{2+}$, $Ag^{+}$, and $Au^{3+}$), and the mixture was ultra-sonicated (Crest, USA) for 20 min at 25 °C. The solid was then separated from the aqueous phase using the magnet, and an equal volume of anhydrous ethanol was added. After that, another 20 min ultra-sonication was performed. As soon as the bimetallic nanoparticles (denoted as nZVI–Cu, nZVI–Ag, nZVI–Au) were produced, batch tests for evaluating their reactivity to nitrate were carried out. Catalyst content was confirmed by inductively coupled plasma (ICP) analysis after digestion with 10% aqua regia.

### 2.3. *Batch experiments*

Batch Cd(II) adsorption experiments with and without nitrate addition were carried out in a 300 ml 3-neck flask. A 200 mg/L $Cd(CH_3COO)_2$ stock solution was prepared and used for all experiments. Final Cd(II)concentration was 10–40 mg/L and the load of iron nanoparticles was 500 mg/L. The flask was agitated by an electromagnetic stirrer (250 rpm, MaxQ 436HP, Thermo Fisher Scientific) at 25 °C under Ar atmosphere. In the series of tests with nitrate, the concentration of nitrate was 15 mg-N/L. After reacting for 90 min, solution pH was measured, and aqueous samples were collected for Cd(II) and total Fe analyses.

Batch tests for determining Cd(II) removal capacity under different nitrate loads were carried out in a series of 100 ml conical flasks sealed with screw caps. The concentrations of Cd(II) were 50, 100, and 150 mg/L while the concentrations of nitrate were 8, 12, 16 mg-N/L. The load of iron nanoparticles was 500 mg/L. The suspensions were mixed at 200 rpm for 90 min. At the end of the experiment pH was measured (preliminary experiments showed that pH increased significantly as soon as nZVI was added, and then remained stable), and aqueous samples were removed to determine concentrations of nitrogen compounds ($NO_3^-$, $NO_2^-$, $NH_4^+$) and metals (Cd(II), total Fe).

To further investigate the influence of nitrate on Cd(II) removal, two different series of tests were performed. In Series 1, nitrate was not present in the reaction system. 125 mg nZVI were added into 250 ml of a 40 mg-Cd/L solution, the solution pH was adjusted and maintained at 9.0, stirring for 30 min. After stirring, an aqueous sample was collected and analyzed for total Fe and Cd(II). The remaining mixture was then divided into 5 parts, which were adjusted to and maintained at pH 8.5, 8.0, 7.5, 7.0, or 6.5, stirring for another 30 min. Aqueous samples were then collected from the 5 subsamples for Cd(II) and Fe analyses. In Series 2, 125 mg nZVI was added into 250 ml of 40 mg/L Cd(II) and 15 mg-N/L nitrate. After 20 min, solution pH increased to 9, and remained stable for ~10 min, so it was not adjusted as in Series 1. As before, an aqueous sample was collected and analyzed. The suspension was divided into 5 parts whose pH was adjusted and kept at 8.5, 8.0, 7.5, 7.0, or 6.5. After stirring for another 30 min, aqueous samples were collected and analyzed. Additionally, we performed a control test to see the effect of pH on Cd removal, by adjusting the pH of 15 mg Cd/L solutions to 7, 7.5, 8.0, 8.3, 8.5, or 9.0, in separate vials. After 5 min mixing (150 rpm) and another 5 min standing, 1 ml aqueous media was collected for Cd measurement. Sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M) were used to adjust and maintain solution pH in all cases.

To examine the effect of different Cd(II) loads on nitrate reduction, nZVI (500 mg/L) was added into a series of 15 mg-N/L nitrate solutions with 10, 20, 30, 40, 50 or 100 mg/L Cd(II) in 100 ml conical flasks sealed with screw caps. After 120 min shaking (200 rpm, Thermo, MAXI MIX), samples were collected and nitrogen compounds in solution were analyzed.

To investigate the effect of Cd(II) addition on nZVI oxidation, 250 ml of a 500 mg/L nZVI suspension with or without 10 mg/L Cd(II) load was agitated vigorously by an electromagnetic stirrer (300 rpm) for 45 min in a 500 ml beaker without seal or Ar protection. Throughout the experiment, oxidation-reduction potential was carefully monitored.

In batch tests for determining the effect of pH on nitrate reduction in the presence of Cd(II), the pH of five 250 ml nitrate solutions (35 mg-N/L) with 500 mg/L nZVI and 20 mg/L Cd(II) was maintained for 60 min at pH 7.0, 7.5, 8.0, 8.5, or 9.0, using sodium hydroxide (0.05 M) and hydrochloric acid (0.05 M) to adjust pH. Aqueous samples were then collected for nitrate, nitrite, and ammonium analyses.

Tests for effect of Me catalysts on nitrate reduction and nitrite yield were carried out in a series of 100 ml conical flasks sealed with screw caps. Freshly-made nZVI–Cu, nZVI–Ag, or nZVI–Au was added into a 45 mg-N/L nitrate solution with or without 30 mg/L Cd(II) load. The nZVI load was 1500 mg/L. After 90 min, aqueous samples were collected for nitrate, nitrite, and ammonium analyses.

Based on the effect of Me catalysts on nitrate reduction, further investigation was done to see the effect of Au on nitrate reduction under different Cd(II) load conditions. nZVI–Au was introduced to a set of 15 mg-N/L nitrate solutions with 10, 20, 30, 40, 50, and 100 mg/L Cd(II). nZVI–Au concentration was 500 mg/L. Aqueous samples were isolated and analyzed ($NO_3^-$, $NO_2^-$, $NH_4^+$, Cd(II), total Fe) after 90 min of shaking at 200 rpm. To simulate Cd and nitrate contaminated groundwater, sodium nitrate and cadmium acetate were added into real groundwater (collected in Santa Barbara, California, USA) to achieve 15 mg-N/L nitrate and 20 mg/L Cd load. nZVI–Au concentration was still 500 mg/L. After 90 min shaking, aqueous samples were collected and analyzed. Characteristics of the groundwater are shown in Table S1.

Nitrite (15 mg/L) reduction by nZVI or nZVI–Au (500 mg/L) in the presence of Cd (10 mg/L) at different pH (8.0, 8.5, 9.0, or 9.5) was performed to better understand nitrite accumulation during nitrate reduction. Aqueous samples were collected for 2 h every 30 min and $NO_2^-$, $NH_4^+$ were analyzed. All tests were performed in triplicate.

### 2.4. Analyses methods and calculations

ORP and pH were monitored throughout using a HACH Sc200 (Loveland, CO). Cadmium and total iron in the collected samples were determined by inductively coupled plasma (ICP, Agilent 720 ES, Japan) after filtering with 0.22 μm filter and acidifying with 4% ultrahigh purity $HNO_3$. All nitrogen-containing compounds ($NO_3^-$, 420 nm; $NO_2^-$, 540 nm; and $NH_4^+$, 425 nm) in filtered samples were assessed spectrophotometrically (Shimadzu, UV-2550, Japan) based on a previous study that used a colorimetry technique (Third et al., 2003). A Zetasizer Nano-ZS90 (Malvern, UK) was used to determine the zeta (ζ) potential of particles. XRD was carried out on a Bruker D8 Advance X-ray diffraction instrument (Cu Kα) (Germany), and the diffraction angle (2θ) from 10° to 90° was scanned. For preparing samples, the collected solid samples were transferred into a vacuum freeze dryer (Labconco, Kansas City, MO) immediately. After 24 h, the dried samples were analyzed via XRD.

Cd(II) removal efficiency was calculated as:

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

where $C_0$ and $C_t$ (mg/L) are the initial and final concentrations of Cd(II) ions in solution respectively. Removal capacity was calculated using the equation:

$$\text{Removal capacity} = \frac{(C_0 - C_t)V}{m} \quad (3)$$

where $C_0$ and $C_t$ are the initial and final concentrations of Cd(II) (mg/L), $m$ is the mass of nZVI (g), and $V$ is the volume of solution (L).

## 3. Results and discussion

### 3.1. Cd removal performance of nZVI with and without nitrate addition

As shown in Fig. 1, in the absence of nitrate, 500 mg/L nZVI only completely removed Cd when the initial concentration was 10 mg Cd/L or less. However, with 15 mg-N/L nitrate in solution, complete Cd removal was observed even when the initial Cd concentration was increased to 40 mg/L. Cd removal capacity of nZVI was 40 mg/g in the absence of nitrate, while it reached 80 mg/g when nitrate was present at 15 mg/L. Several studies showed that nZVI reduces nitrate to ammonium, accompanied by increased solution pH (Eq. (4)) (Sohn et al., 2006; Ryu et al., 2011; Park et al., 2009; Liu et al., 2012), which could enhance Cd removal by nZVI through precipitation (e.g. $Cd(OH)_2$) (Boparai et al., 2013). Under these conditions (i.e. 15 mg-N/L nitrate) we observed that solution pH exceeded 9; while without nitrate the pH was below 8 (data not shown). Increased pH may therefore be responsible for increased Cd removal capacity of nZVI, due to the presence of nitrate. Additionally, final total Fe concentrations detected in these two reaction systems (with and without nitrate) were also very different. As seen in Fig. 1, total Fe in the supernatant at the end of the experiments exceeded 9 mg/L in all the conditions without nitrate while Fe was not detected in the supernatant of reaction systems with nitrate. The absence of Fe in suspension was probably due to the oxidation (Fe(II) to Fe(III)) and precipitation (e.g. formation of $Fe_3O_4$ (Sohn et al., 2006)) stimulated by nitrate.

$$NO_3^- + 3Fe^0 + 3H_2O \rightarrow Fe_3O_4 + NH_4^+ + 2OH^- \quad (4)$$

### 3.2. Cd removal capacity of nZVI at different initial Cd(II) and nitrate concentrations

In order to get further insight into Cd(II) removal performance of nZVI in the presence of nitrate, a series of experiments with different initial Cd(II) and nitrate concentrations were conducted. The results are shown in Fig. 2. When the initial Cd(II) concentration was 50 mg/L, Cd(II) ions in suspension were completely removed in the presence of 12 mg-N/L nitrate, while only 78% were removed when nitrate concentration was just 8 mg-N/L. Similarly, removal increased when the initial Cd(II) concentration was 100 mg/L, in the presence of 8–16 mg-N/L nitrate (Fig. 2a). However, when Cd(II) concentration increased to 150 mg/L, Cd removal efficiency peaked as nitrate increased from 8 mg-N/L to 12 mg-N/L, and plateaued thereafter (Fig. 2a). In Fig. 2b, Cd (II) removal capacity also increased with increasing nitrate concentration, from 78 mg/g (initial Cd(II) 50 mg/L, nitrate 8 mg-N/L) to 188 mg/g (initial Cd(II) 100 mg/L, nitrate 16 mg-N/L).

Cd removal efficiency decreased as initial concentration of Cd(II) increased regardless of nitrate concentration (Fig. 1). For instance, 78% of Cd(II) was immobilized when the initial Cd(II) concentration was 50 mg/L in the presence of 8 mg-N/L. However, Cd removal efficiency decreased to 43% when initial Cd(II) doubled to 100 mg/L. The actual amount of Cd(II) immobilized increased at higher Cd(II) concentration (as seen in the increased removal capacity, Fig. 2b), but the removal efficiency decreased because $C_0$ doubled while $C_t$ did not. Fig. 2b shows that high removal capacity is associated with higher levels of nitrate and Cd(II) ions. However, the high level of acetate (from cadmium acetate) may decrease solution pH, which can decrease Cd(II) removal capacity, For example,

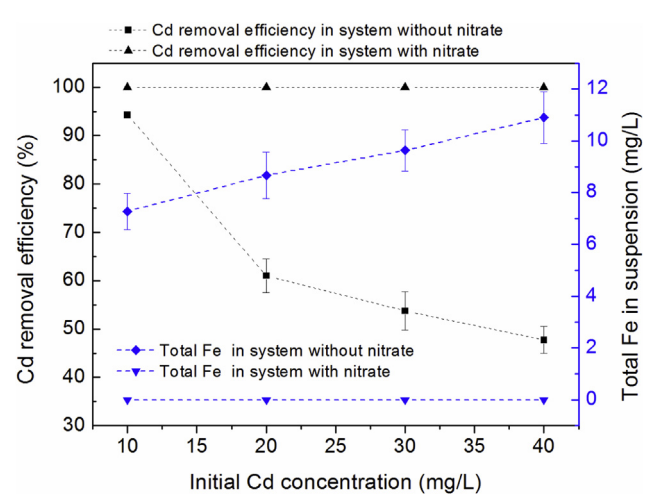


**Fig. 1 – Cd removal efficiency and total Fe concentrations at different Cd(II) loads with/without nitrate (15 mg-N/L, 500 mg nZVI/L).**

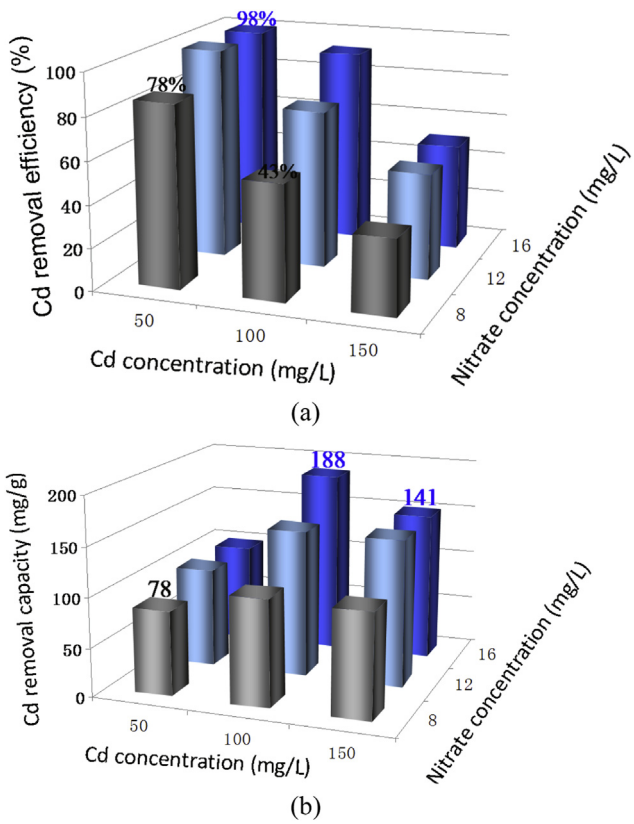


**Fig. 2 – (a) Cd removal rate at different initial Cd(II) (50, 100, 150 mg/L) and nitrate concentrations (8, 12, 16 mg-N/L); (b) Cd removal capacity under different initial Cd(II) (50, 100, 150 mg/L) and nitrate concentrations (8, 12, 16 mg-N/L).**

removal capacity decreased by about 25% when initial Cd(II) concentration increased from 100 mg/L (final pH 8.5) to 150 mg/L (final pH 7.8) in the presence of 16 mg-N/L nitrate (Fig. 2a).

### 3.3. *Further investigation on the role of nitrate in enhanced Cd(II) removal*

In the series of tests with pH control, Cd(II) removal efficiency decreased as pH decreased both in the presence and absence of nitrate (Fig. 3). At pH 9, Cd(II) removal efficiency of both reaction systems were very close. However, as pH decreased, Cd(II) removal efficiency in tests without nitrate addition was relatively higher than in tests with nitrate addition, especially at low pH conditions. This indicates that the removal capacity of iron hydroxide or iron oxide derived from the reaction between nZVI and nitrate is much lower than that of pristine nZVI. As seen in Fig. 3, the removal efficiency in both reaction systems increased by more than 20% when pH increased from 7.5 to 8.0, and 15% as pH increased from 8.0 to 8.5. Meanwhile, in a control test a significant increase in Cd removal efficiency was observed at pH 8.5 (Fig. S1), although Cd(II) started to precipitate out from water at pH $\geq$ 8.0 (Boparai et al., 2013). This meant the increase in Cd removal efficiency was mainly due to the presence of nZVI. The sharp increase in removal efficiency and capacity may be due to three main reasons: (1) the critical pH value for Cd(II) hydrolysis (formation of $Cd(OH)^+$ and $Cd_2(OH)_3^+$) and precipitation ($Cd(OH)_2$) is $\geq$ 8.0 (Boparai et al., 2013), which may have contributed to the increased removal rate through electrostatic interaction and deposition; (2) the isoelectric point (IEP) of nZVI is around 8.1 (Sun et al., 2006), below which nZVI particles are positively charged and above which they are negatively charged. The negatively charged surface at pH > IEP favors Cd(II) adsorption due to strong electrostatic attraction. Thus, the change of surface charge of nZVI may also have contributed to the increased removal of Cd(II); and (3) high pH, especially above 7, could also improve Cd adsorption on iron oxide (Benjamin and Leckie, 1981). Comparing the results of these two series of experiments, the enhanced Cd(II) removal capacity in the presence of nitrate most likely resulted from elevated solution pH. Specific sorption (chemisorption) may have also contributed to Cd(II) removal because of the relatively high removal efficiency (~50%) observed around pH 6 (Boparai et al., 2013).

### 3.4. *Effect of Cd(II) on nitrate reduction*

#### 3.4.1. *Cd(II) enhanced nZVI reactivity for nitrate reduction*

The presence of Cd(II) also had a significant influence on the reduction of nitrate by pristine nZVI (Fig. 4). Without Cd(II), less than 33% nitrate was reduced by nZVI. Reduction of nitrate was catalyzed by the presence of Cd(II) (Ottley et al., 1997), which was similar to the catalytic effect of Cu(II) (Sparis et al., 2013) or Ni(II) (Ryu et al., 2011). Nitrate reduction by nZVI increased with increasing Cd(II) concentration; 100% nitrate reduction was observed at 30–40 mg/L Cd(II) concentration. Enhanced reduction of nitrate by nZVI in the presence of Cd(II) was probably due to enhanced electron flow facilitated by Cd(0) and CdO islands (Fig. S2). XRD analysis confirmed the presence of Cd(0) and CdO in the final solids (Fig. 5). Cd(0) islands were detected from the characteristic peaks at 31.8, 34.7, 38.4, 47.8, 61.1, 62.3, 71.6 and 77.2° in 2$\theta$; and characteristic CdO peaks were observed at 33.0, 38.3, 55.3, 65.9, 69.3 and 81.9° in 2$\theta$. A similar phenomenon, formation of Cu islands on nZVI has been reported (Sparis et al., 2013). As

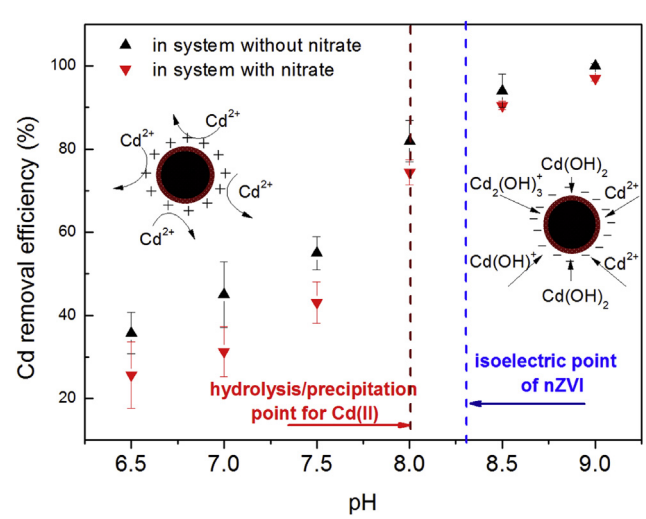


**Fig. 3 – Cd(II) removal rate at different pH values with/without nitrate addition.**

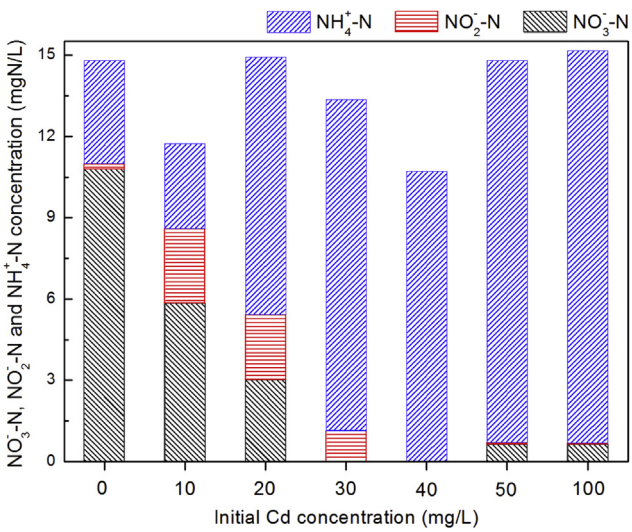


**Fig. 4 – Nitrate reduction under different Cd load (nZVI, 500 mg/L).**

shown in Fig. S3, the ORP of the nZVI system with Cd(II) present increased faster than that without Cd(II), indicating that Cd(II) addition led to faster electron flow and oxidation. The enhanced transport of electrons on Cd islands can contribute to nitrite production from nitrate under certain conditions.

### 3.4.2. *Effect of low levels of Cd(II) on nitrate reduction*

While almost no nitrite was observed in the reaction between nitrate and nZVI (Sohn et al., 2006; Hwang et al., 2011), a considerable amount of nitrite was produced when a low level of Cd(II) (≤30 mg/L) was present in the system (Fig. 4). In theory, Cd(II) in solution can be reduced to Cd(0), since it has a slightly more positive standard electrode potential ($E^0 = -0.403$ V) than that of Fe ($E^0 = -0.447$ V). According to previous studies, Cd(0) can reduce nitrate to nitrite but not to ammonium (Alonso et al., 1998; Haghighi and Tavassoli, 2001; Ma et al., 1998). This is due to low surface density of hydrogen on Cd(0) resulting from its low adsorption binding energy with H (28–29 kcal/mol (Jr., 1987)). The nitrite generated by Cd(0) can subsequently be reduced to ammonium or nitrogen by zerovalent iron (ZVI) (Liang et al., 2008). But the reaction is inhibited by high pH that results when nZVI and nitrate react. As shown in Fig. 6b, there was a clear decrease of nitrite reduction rate by nZVI in the presence of Cd from pH 8.5 to 9.0, and even at pH 9.5 less than 5% of original nitrite was reduced by nZVI within 2 h. It was also reported that while nitrite can barely be reduced at high pH (≥9) (Ginner et al., 2004), nitrate can still be reduced under these conditions (Sohn et al., 2006).

It seems that whether nitrite accumulation was observed or not was due to the relative kinetics of nitrate to nitrite and nitrite to ammonium (Ginner et al., 2004). The most likely reason for a decreasing nitrite reduction rate was that at high pH (low [$H^+$]), there are not enough protons for significant nitrite reduction (since adding a proton to form a reaction intermediate is necessary for nitrite reduction) (Guy et al., 2009; Alowitz and Scherer, 2002). In addition, nitrite

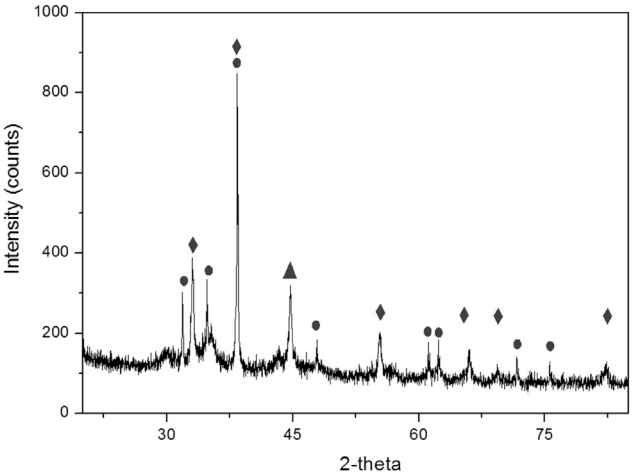


**Fig. 5 – XRD pattern of nanoparticles after reaction between nZVI (500 mg/L) and Cd(II) (40 mg/L) (▲peaks of Fe(0); ◆peaks of CdO; ●peaks of Cd(0)).**

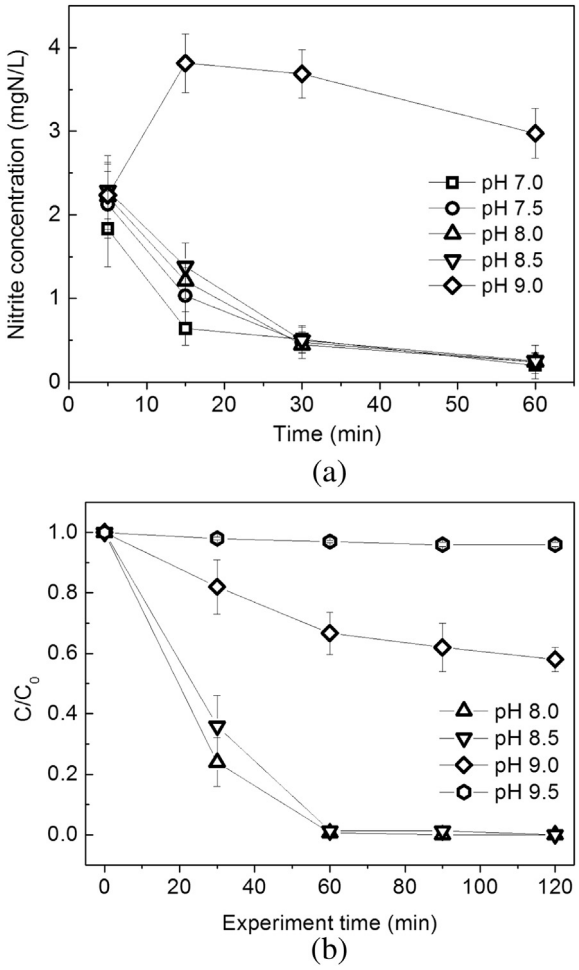


**Fig. 6 – (a) Trends of nitrite during nitrate reduction at different pH values (initial nitrate, Cd(II), and nZVI were 35 mg-N/L, 20 mg/L, and 500 mg/L, respectively); (b) nitrite concentration trend ($C/C_0$) in reaction system with nitrite (15 mg/L), Cd (10 mg/L), and nZVI (500 mg/L) at different pH values.**

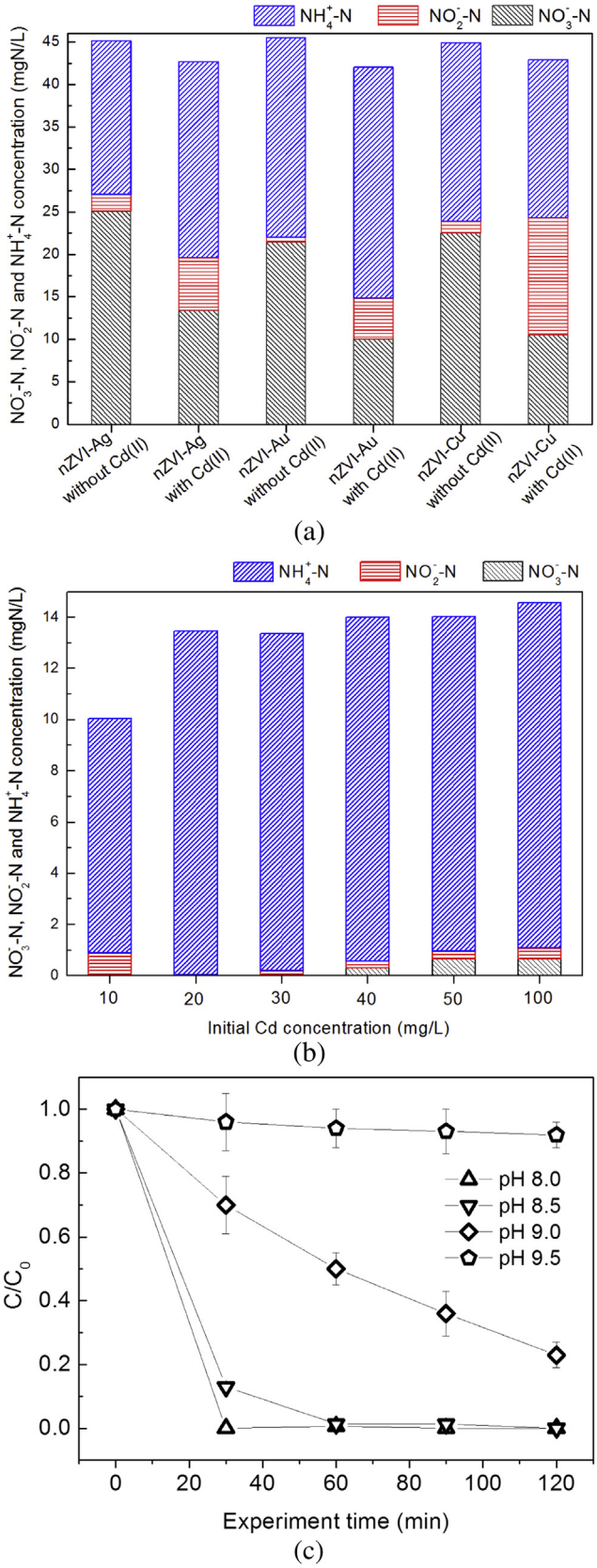


**Fig. 7 – (a) Nitrate reduction by nZVI–Ag, nZVI–Au, and nZVI–Cu with or without Cd(II) (initial nitrate, Cd(II), and bimetallic nanoparticles concentrations were 45 mg-N/L, 30 mg/L, and 1500 mg/L respectively); (b) Nitrate reduction by nZVI–Au under different Cd load (initial nitrate and nZVI–Au concentrations were 15 mg-N/L and 500 mg/L respectively); (c) Nitrite concentration trend ($C/C_0$) in reaction system with nitrite (15 mg/L), Cd (10 mg/L), and nZVI–Au (500 mg/L) at different pH values.**

accumulation, in a reaction system with Pd-based bimetallic catalysts at high pH conditions, was attributed to electrostatic repulsion between nitrite and the negatively charged surface of particles (Chaplin et al., 2006; Prusse and Vorlop, 2001). In our experiment, while nitrite accumulation was detected at pH 9, we did not observe nitrite accumulation at pH $\leq$ 8.5 despite the IEP of nZVI being pH 8.1. The change in nZVI surface charge from positive to negative did not appear to cause nitrite accumulation. However, the largely increased negative nZVI surface charge from pH 8.5 (−25 mV) to pH 9.0 (−46 mV) likely repels nitrite from the nZVI surface. Additionally, on the Cd(0) surface nitrate was still reduced to nitrite while nitrite was not reduced any more (Alonso et al., 1998; Wang et al., 1998), contributing to nitrite accumulation.

#### 3.4.3. *Decreased nitrite yield at high levels of Cd(II)*

Nitrite was not detected when Cd(II) increased to 40 mg/L. The number of Cd islands on the nZVI are likely to increase at higher Cd(II) concentration, further increasing electron transport. Also, when Cd(II) concentration increased (>50 mg/L), the solution pH decreased to < 9 (due to high concentration of acetate), which may also be responsible for the disappearance of nitrite in solution at the end of tests. In addition, precipitation of Cd species ($Cd(OH)_2$) on the surface of nZVI particles may inhibit the reaction between nitrate and ZVI to some extent. Consequently, a small fraction of nitrate remained in the solution at higher Cd(II) concentrations (Cd(II) > 50 mg/L).

#### 3.4.4. *Effect of Cd(II) on gaseous products of nitrate reduction*

The production of gaseous products (likely $N_2$ and/or $N_2O$) due to nitrate reduction was not expected as previous studies showed that nZVI mainly reduced nitrate to ammonium (Ryu et al., 2011; Hwang et al., 2011). However, certain amount of $N_2$ gas was observed when nitrate was reduced by nZVI with Pd and Cu deposits (Hosseini et al., 2011; Liou et al., 2009). Production of $N_2$ gas was adduced to the presence of the deposited metals on nZVI (Hosseini et al., 2011; Liou et al., 2009). $N_2O$, a common product of nitrate reduction (Hansen et al., 1994; Fanning, 2000), may have also been produced in our experiments. In our study, the presence of Cd(II) caused gaseous products generation due to the increase in pH, since basic conditions are favorable for $N_2$ generation (Liou et al., 2009).

### 3.5. *Influence of different catalysts on nitrate reduction with/without Cd(II) addition*

While the nitrite yield rate without Cd(II) or with high levels of Cd(II) ions (≥40 mg/L) was less than 3% of initial nitrate, a considerable amount of nitrite was detected in the final supernatant at Cd(II) concentrations of 10–30 mg/L (Fig. 4). In order to reduce the nitrite ratio in the final nitrate-reduction products, different catalysts were employed. 1 wt.% Cu, Ag and Au were deposited separately onto the nZVI surface. As seen in Fig. 7a, ammonium is the main reduction product when

nZVI is deposited with the three catalysts, and nitrite yield ratio was much higher in a system with Cd(II) than without Cd(II). nZVI–Au exhibited the highest nitrate reduction (over 77% of nitrate was reduced, Fig 7a) and lowest nitrite yield ratio, with and without Cd(II). nZVI–Au reduced nitrite yield ratio from 33% (Fig. 4) to about 6% (Fig. 7b) at 10 mg-Cd(II)/L load. Nitrite yield was very limited from 10 to 100 mg-Cd(II)/L, and we did not detect any nitrite in simulated contaminated groundwater (over 95% of initial nitrate was reduced to ammonium). In addition, Cd(II) ions were not detected below 50 mg-Cd(II)/L in the presence of nZVI–Au; and 85% removal efficiency was observed at 100 mg-Cd(II)/L load (Table S2). This Cd(II) removal efficiency was equal to that of pristine nZVI.

Ammonium yield ratio (defined as $[\text{ammonium}]_{\text{final}}/[\text{nitrate}]_{\text{initial}}$) during nitrate reduction is closely related to surface density of hydrogen (Yamauchi et al., 2011). Nitrate adsorption onto the Fe(0) surface is likely via Fe–O bonds rather than an Fe–N bond, since the N atom in nitrate does not have an unpaired electron. After adsorption, the electric potential difference between $Fe^{2+}/Fe$ and $H^{+}/H_2$ initiates the hydrogenation pathway (active H attacks any of the Fe–O bonds). H replaces all initial O sequentially (nitrate → nitrite → ammonium), and ammonium is generated.

While Fe(0) is mainly responsible for ammonium production, catalysts mainly facilitate the electron transport from reducer (Fe(0)) to oxidizer (nitrate) (Ryu et al., 2011; Hou et al., 2008; Shih et al., 2011). Of the three catalysts, Cu yielded the highest nitrite ratio, while Au had the lowest nitrite yield ratio. Without catalysts, nitrite accumulation was due to the slow transformation of nitrite to ammonium at high pH value. Nitrite reduction rate was accelerated significantly with Au as catalyst (Fig. 7c) compared to no catalyst (Fig. 6b). Even at pH 9, a reduction rate of 11.55 mg N per g nZVI–Au per hr was observed (while under the same reaction condition, 6.3 mg N per g zerovalent iron per hr was obtained by nZVI). In this respect, the accelerated nitrite reduction rate may contribute to lowering the nitrite yield ratio.

### 3.6. *The transformation of nZVI with/without nitrate presence*

XRD was employed to analyze the crystals in the final solids. The pattern of solid from the reaction between nZVI and Cd(II) (without nitrate) showed that along with the Fe(0) characteristic peak at 45.0° in $2\theta$ (Adeleye et al., 2013), Cd(0) and CdO were present (Fig. 5). The presence of Cd(0) solid indicated that Cd(II) was partly reduced by Fe(0); while the presence of CdO meant that chemical adsorption was also involved in Cd(II) immobilization by nZVI. However, in the presence of nitrate, peaks in the diffractogram were not distinct (Fig. 8a), except the characteristic peak of Fe(0). This suggested that a part of Fe(0) remained after reaction with Cd(II) and nitrate was completed.

Compared to the diffractogram derived in the Cd(II)/nZVI/nitrate system, the spectrum derived from Cd(II)/nZVI–Au/nitrate system was explicit (Fig. 8b). Although the characteristic peaks of Au were not observed in the diffractogram (probably because the amount or particle sizes of Au were below the detection limit), peaks of magnetite ($Fe_3O_4$) were detected. Magnetite is thermodynamically stable and the major species of iron oxide under the alkaline conditions (Sohn et al., 2006). The formation of magnetite reduces iron dissolution, thereby, reducing the probability of causing acute toxicity to microorganisms and plants via dissolved Fe (Adeleye et al., 2013; Keller et al., 2012). Also, the disappearance of Fe(0) peaks in the presence of Au suggests higher reactivity of nZVI–Au with nitrate.

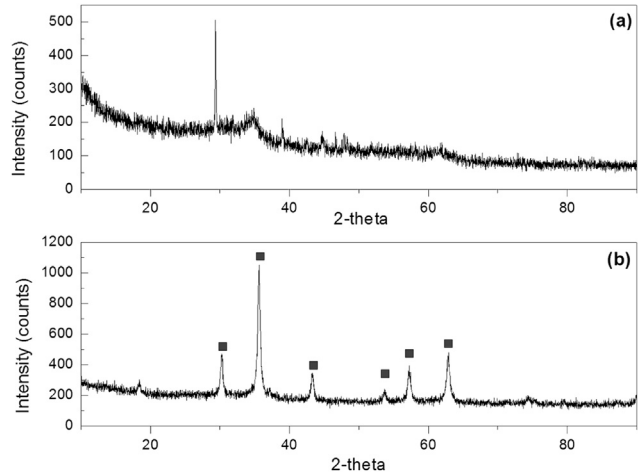


**Fig. 8 – XRD patterns of residual solid after reaction; (a): the pattern of solid after reaction of nZVI and Cd(II) in the presence of nitrate; (b): the pattern of solid after reaction of nZVI–Au and Cd(II) in the presence of nitrate (■peaks of $Fe_3O_4$).**

## 4. Conclusion

The co-occurrence of Cd(II) and nitrate in groundwater has a significant influence on each other's removal by nZVI. Nitrate stimulates enhanced removal of Cd(II) by nZVI, reducing Cd's bioavailability. In addition, nitrate stimulates the formation of stable iron oxide (magnetite) from nZVI instead of ionic iron. Magnetite formation prevents significant increase of exchangeable iron concentration, which has been acknowledged as a potential toxicant resulting from nZVI application in the environment. Cd(II), on the other side, has both positive and negative effects on nitrate reduction: Cd(II) (<50 mg/L) improves nZVI reactivity with nitrate significantly but a considerable amount of nitrite is produced. Doping of nZVI with Au (1%) appeared to significantly reduce nitrite yield ratio, much better than nZVI only, or doping nZVI with Cu or Ag. Also, nZVI–Au has equal Cd(II) removal capacity as nZVI in the presence of nitrate. This study indicates that it is possible to employ nZVI–Au to remediate Cd(II) and nitrate co-pollution.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2014.06.008.

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