Removal of nitrate from water by acid-washed zero-valent iron/ferrous ion/hydrogen peroxide: influencing factors and reaction mechanism

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ABSTRACT

In this paper, a system consisting of acid-washed zero-valent iron (ZVI), ferrous ion (Fe\textsuperscript{2+}), and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) was employed for the removal of nitrate (NO\textsubscript{3}\textsuperscript{-}) from water, and the reaction mechanism for this is discussed. The effects of acid-washed ZVI, Fe\textsuperscript{2+}, H\textsubscript{2}O\textsubscript{2}, and initial NO\textsubscript{3}\textsuperscript{-} concentration on nitrate removal were investigated. Acid-washed ZVI before and after reaction with nitrate were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Results reveal that the combined system can enhance the corrosion of ZVI and facilitate aqueous nitrate reduction. The products of nitrate reduction are mainly ammonium, with some N\textsubscript{2}. The ZVI particles after reaction may have a core of ZVI with an oxidation layer mainly consisting of Fe\textsubscript{3}O\textsubscript{4}.

Key words | ferrous ion, hydrogen peroxide, nitrate removal, zero-valent iron (ZVI)

INTRODUCTION

Nitrate contamination has become an increasingly serious water quality problem. High concentrations of nitrate seriously affect drinking water quality and risk public health: it cannot only cause methemoglobinemia in infants, but also lead to gastric cancer (Xu et al. 2017). Due to the toxic effects of nitrate, the US EPA has set a maximum concentration of nitrate-nitrogen (NO\textsubscript{3}\textsuperscript{-}-N) of 10 mg/L in drinking water (Ahn et al. 2012). The drinking water standard for NO\textsubscript{3}\textsuperscript{-}-N was also changed from 20 to 10 mg/L in 2000 in China (Fan et al. 2009).

The process of biological denitrification is one of the most widely used techniques for the removal of nitrate from wastewater. However, biological denitrification is difficult in inorganic wastewater treatment because additional carbon sources are required (Dhamole et al. 2009). Meanwhile, many treatment processes, including electrochemical, adsorption, and chemical reduction methods, have been applied for the removal of nitrate from water (Li et al. 2010; Anderson 2011; Bhatnagar & Sillanpää 2011).

Iron is the fourth most abundant element in the Earth’s crust. In the past decade, numerous researchers have focused on the removal of contaminants and environmental remediation by zero-valent iron (ZVI) for its strong reducing capacity (E\textsuperscript{0} = −0.44 V), non-toxicity, abundance, and cheapness (Fu et al. 2014). Nevertheless, the formation of passivation layers, which hinder the transfer of electrons from the ZVI core to the solid-liquid interface, restrain the reactivity of ZVI and thus inhibit the removal of contaminants, such as nitrate. To solve this problem, research has suggested that the addition of a certain amount of Fe\textsuperscript{2+} can increase the efficiency of nitrate reduction under initial neutral conditions (Xu et al. 2012). Common oxidants, such as O\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, MnO\textsubscript{4}\textsuperscript{-}, and CrO\textsubscript{4}\textsuperscript{2-}, have been used to enhance nitrate reduction from contaminated water (Guo et al. 2015).

Furthermore, some bimetals, such as Al/Fe and Cu/Fe, have also been synthesized and employed for nitrate reduction (Xu et al. 2017; Zeng et al. 2017).

In this paper, the behavior of the combined system of acid-washed ZVI/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} for the removal of nitrate from water and the removal mechanism were investigated. The performance of the acid-washed ZVI/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} system, with different acid-washed ZVI, Fe\textsuperscript{2+}, H\textsubscript{2}O\textsubscript{2}, and initial nitrate concentrations, was studied. The content of nitrogen gas product was calculated using the initial concentration of nitrate and subtracting from it the final...
concentrations of nitrate, nitrite, and ammonium (Shi et al. 2016). Furthermore, the acid-washed ZVI before and after reaction was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), so as to reveal the structure and composition of acid-washed ZVI as well as the nitrate removal mechanism.

MATERIALS AND METHODS

Materials and chemicals

All chemicals used were analytical grade or better. Deionized water was used to prepare all aqueous solutions. All the vessels used for the experiments and analyses were dipped in HCl solution, flushed with tap-water and rinsed three times with deionized water before use. The ZVI (analytical grade, 99% purity, specific surface area 0.50 m²/g) was purchased from Tianjin Kermel Chemical Reagent Company.

Batch experiments

Before the experiments, the ZVI powders were soaked in 0.1 M H₂SO₄ solution for 10 min and dipped in acetone for 30 min, then flushed with deionized water several times and put through suction filtration. The acid-washed ZVI powders were reserved in a vacuum desiccator before use. The experiments were conducted in 500 mL glass flasks containing 200 mL NaNO₃ solution. The initial pH of the NaNO₃ solution was adjusted using 1.0 M H₂SO₄ or 1.0 M NaOH. Different amounts of acid-washed ZVI, FeCl₂, and H₂O₂ were added into the above flasks and mixed at the speed of 200 rpm using a thermostatic cyclotron oscillator for 6 hours.

At regular time intervals, 10 mL of solution was withdrawn for chemical analysis immediately. All experiments were conducted at least in triplicate, and average values along with one standard deviation are presented.

Characterization

Scanning electron microscopy

The micro-structure of acid-washed ZVI surface before and after reaction was viewed using a field-emission scanning electron microscope (S-4800, Hitachi, Japan) with an accelerating voltage of 20 kV.

X-ray diffraction

XRD analysis was conducted by an X-ray diffractometer (Bruker D8, Germany) using Cu Kα radiation at the scanning speed of 10°/min between scanning angles 20° and 90°.

X-ray photoelectron spectroscopy

The XPS spectra of acid-washed ZVI particles before and after reaction were obtained by XPS (Amicus, Shimadzu Co., Japan), using normal Al Kα radiation (1486.8 eV) under a residual pressure of 2×10⁻⁹ Torr. Data analysis involved non-linear Shirley-type background subtraction and curve fitting by mixed Gaussian-Lorentzian functions. Spectral bands were deconvoluted into peaks (sum function of 90% Gaussian and 10% Lorentzian) with the software XPSPEAK from RCSMS laboratory using integrated background subtraction.

Analytical procedures

Each solution was diluted to an appropriate range of concentrations before analysis. NO₃⁻, NO₂⁻, and NH₄⁺ were analyzed by ultraviolet spectrophotometric method at 220 and 275 nm, N-(1-naphthyl)-ethylenediamine dihydrochloride colorimetric method at 540 nm, and Nessler’s method at 420 nm, respectively, using a spectrophotometer (UV2400, Sunny Hengping Scientific Instrument Co., Ltd, Shanghai) (Huang et al. 2015). The concentration of Fe²⁺ in solution was determined by using 1,10-phenanthroline method. Concentration of total iron ions was determined by a flame atomic absorbance spectrometer (AAS, Z-2000, Hitachi, Japan). All the detections of the above chemical constitutes yielded analytical regression coefficients R² > 0.9990.

RESULTS AND DISCUSSION

Comparison of nitrate removal by different reaction systems

The removal of nitrate by different systems was investigated and the results are shown in Figure 1. Clearly, by the Fe²⁺ as well as the Fe²⁺/H₂O₂ system, nitrate removal efficiencies are less than 10.0% in 6 hours, which indicates that the two systems lack sufficient electron donors for nitrate reduction. It can be seen that the concentration of nitrate displays a declining trend and the removal of nitrate reaches about 74.2% in 6 hours by acid-washed ZVI alone.
the commercial ZVI system just achieves 16.4% nitrate removal in 6 hours, indicating that the acid-washing procedure can effectively remove the oxidation film on the commercial ZVI surface and enhance its reactivity. Meanwhile, it can be observed that the acid-washed ZVI/H$_2$O$_2$ system exhibited a better nitrate removal efficiency compared with the ZVI system. The addition of H$_2$O$_2$ could corrode the surface of ZVI intensively and activate the reactivity of ZVI (Guo et al. 2013). The acid-washed ZVI and acid-washed ZVI/H$_2$O$_2$ system achieved 74.2% and 78.7% nitrate removal in 6 hours.

The presence of Fe$^{2+}$ can promote nitrate removal efficiency by ZVI, consistent with the results of some previous studies (Huang & Zhang 2005; Xu et al. 2012). Fe$^{2+}$ in aqueous solution can continuously convert into Fe$^{3+}$ oxides and then into Fe$_3$O$_4$ on the surface of ZVI by electron transfer between Fe$^{2+}$ and pre-existing Fe$^{3+}$ oxides, and it is the spontaneous electron transfer between the Fe$^{2+}$ and Fe$^{3+}$ oxides that accelerate the interfacial electron transfer between the iron species and nitrate (Han et al. 2016). It is worth noting that in the acid-washed ZVI/Fe$^{2+}$/H$_2$O$_2$ system, nearly all nitrate was removed within 4 hours. Compared with the acid-washed ZVI/Fe$^{2+}$ system, the acid-washed ZVI/Fe$^{2+}$/H$_2$O$_2$ system can more efficiently remove the nitrate in solution. So the acid-washed ZVI/Fe$^{2+}$/H$_2$O$_2$ system was used in the next stage of investigation, and the influencing factors as well as the reaction mechanism are discussed later.

**Nitrate removal by acid-washed ZVI/Fe$^{2+}$/H$_2$O$_2$ system**

The parameters which would affect the removal of nitrate, including the dosages of acid-washed ZVI, Fe$^{2+}$, H$_2$O$_2$, and initial concentration of nitrate were investigated.

The effect of different acid-washed ZVI dosages on nitrate removal was explored and the results are shown in Figure 2(a). The removal efficiencies of nitrate in 6 hours were 37.5%, 65.0%, and 91.8% by 17.8, 35.7, and 53.6 mM acid-washed ZVI, respectively. Nearly all the nitrate was removed in 6 hours when the dosage of acid-washed ZVI increased to 89.3 and 107.1 mM. Higher acid-washed ZVI loadings clearly activated the nitrate reduction, which corresponded to the results that nitrate reduction was conducted at the surface of ZVI particles and the removal of nitrate depended considerably on the loading of the ZVI surface mentioned by previous researchers (Liao et al. 2003; Zhang et al. 2010). Considering the results of nitrate removal efficiencies and economic considerations, 89.3 mM acid-washed ZVI was chosen for the following studies.

Figure 2(b) is the effect of Fe$^{2+}$ on nitrate removal in the acid-washed ZVI/Fe$^{2+}$/H$_2$O$_2$ system. Without Fe$^{2+}$, the nitrate removal efficiency just achieved 79.0% after 6 hours of reaction time. Better nitrate removal efficiency was observed in the presence of Fe$^{2+}$: the nitrate concentration decreased rapidly and nearly all the nitrate could be effectively removed in 6 hours. Fe$^{2+}$ in aqueous solution can be oxidized into Fe$^{3+}$ immediately as shown by Equations (1) and (2). Then the Fe$^{3+}$ may be attracted onto the surface of ZVI and Equation (3) would happen (Yoshino & Kawase 2013), resulting in the corrosion of ZVI being promoted. As a result, iron oxides/hydroxides may form on the surface of ZVI, and their components will be discussed in the following characterization.

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \quad (1)$$

$$\text{Fe}^{2+} + \cdot\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (2)$$

$$\text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+} \quad (3)$$

The effects of the dosage of H$_2$O$_2$ are presented in Figure 2(c). In presence of H$_2$O$_2$, nearly all the nitrate was removed in 4 hours. As the concentration of H$_2$O$_2$ increased from 0 to 15.0 mM, the removal efficiency of nitrate ranged from 18.1% to 50.2% in 1 hour and from 46.8% to 82.6% in 2 hours. Increase of H$_2$O$_2$ concentration results in better nitrate removal efficiency. The results can also be attributed to the reactions shown in Equations (1) and (2). Meanwhile, the surplus H$_2$O$_2$, serving as an oxidant, would continue to promote the corrosion of ZVI and enhance nitrate removal.
As can be seen in Figure 2(d), even at higher nitrate concentrations, nitrate can be removed efficiently by the acid-washed ZVI/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} system. A higher initial concentration of nitrate could achieve a greater reaction rate constant (Fan et al. 2013), which was attributed to better contact between the reactive sites and nitrate. This result also implies that the combined system of acid-washed ZVI/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} has the potential to remove higher concentrations of nitrate in water. Results in Figure S2 (available with the online version of this paper) show that nitrate can also be removed effectively under neutral pH in 6 hours, which indicates the acid-washed ZVI/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} system could be applied to water with different initial pH values.

To better investigate the effects of acid-washed ZVI dosage, Fe\textsuperscript{2+} dosage, H\textsubscript{2}O\textsubscript{2} dosage, and initial concentration of nitrate on nitrate removal, a pseudo-first-order kinetic model (Equation (4)) was employed (Rodríguez-Maroto et al. 2009; Zhang et al. 2010).

\[
-\ln\left(\frac{C}{C_0}\right) = k_1t
\]  

(4)

where C (mM) is the concentration of nitrate in solution at time t (h), C\textsubscript{0} (mM) is the initial concentration of nitrate in solution, k\textsubscript{1} (1/h) is the related first-order reaction rate constant.

The plots of the pseudo-first-order kinetic model are shown in Figure S3. Kinetic constants obtained from this model are listed in Table S1. It can be seen from Figure S3(a) and Figure S3(b) that k\textsubscript{1} increased from 0.0524 to 1.4685 h\textsuperscript{-1} and 0.2495 to 1.2003 h\textsuperscript{-1} when the ZVI dosage and Fe\textsuperscript{2+} dosage increased from 17.8 to 107.1 mM and 0 to 5.0 mM, respectively. Results in Figure S3(c) show that k\textsubscript{1} increased from 0.6281 to 1.0383--1.2898 h\textsuperscript{-1} in the presence of H\textsubscript{2}O\textsubscript{2}. As can be seen in Figure S3(d), k\textsubscript{1} increased at first and then decreased when the initial nitrate concentration increased from 0.7 to 1.2 mM. (Figure S3 and Table S1 are available with the online version of this paper.)

Conversion of nitrate and iron in solution

The transformations of N in the acid-washed ZVI/Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} system are shown in Figure 3. The highest concentration of nitrite occurred in 1 hour, followed by slower, steady decreases thereafter. Some previous studies also
proved that nitrite was the intermediate during nitrate reduction by ZVI (Hwang et al. 2011; Guo et al. 2015). Meanwhile, the concentration of ammonium increased sharply in 2 hours and then grew slowly to a stable concentration of about 0.65 mM during the removal of nitrate. About 83.9% of nitrate was reduced to ammonium. The concentration of total N dropped from 0.77 to 0.65 mM. The loss of total N may be attributed to the generation of N₂ gas. The nitrate reduction pathway under acidic conditions consists of reactions in series: nitrite is generated first, followed by ammonium or N₂ gas (Yoshino & Kawase 2013). So the process of nitrate reduction may be described by the following equations:

\[
\text{NO}_3^- + 2\text{H}^+ + 2e^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O} \quad (5)
\]

\[
2\text{NO}_2^- + 8\text{H}^+ + 6e^- \rightarrow \text{N}_2(\text{g}) + 4\text{H}_2\text{O} \quad (6)
\]

\[
\text{NO}_2^- + 8\text{H}^+ + 6e^- \rightarrow \text{NH}_4^+ + 2\text{H}_2\text{O} \quad (7)
\]

The transformations of Fe²⁺ and total iron ions are shown in Figure 4. The concentration of Fe²⁺ ions decreased from 4.0 to 3.1 mM in 1 hour because of the Fe²⁺ oxidation by H₂O₂. Then the concentration of Fe³⁺ almost remained in stable at around 3.0 mM, which may be attributed to ZVI corrosion and partly to Fe³⁺ reduction. The concentration of total iron ions increased from 4.0 to 11.6 mM during the reaction, which was mainly due to the corrosion of ZVI and oxidation of Fe²⁺ in solution.

**Characterization of acid-washed ZVI before and after reaction**

**Scanning electron microscopy**

The morphologies of the acid-washed ZVI before and after reaction were investigated by SEM, and the results are shown in Figure 5. The acid-washed ZVI before reaction exhibits apparent agglomeration and the surface is relatively smooth. In contrast, the surface of acid-washed ZVI after reaction becomes very uneven. As can be seen in Figure S4 (available with the online version of this paper), the pH value of the solution increases from 3.0 to 4.5 in 1 hour, then almost keeps in stable at around 4.5 for 1–4 hours, and finally drops slightly from 4.5 to 4.3. The above results imply the very uneven surface of the ZVI resulted from the iron oxide/hydroxide deposition process.

**X-ray diffraction**

As can be seen in Figure 6, the acid-washed ZVI particles after reaction exhibited a remarkable change in their composition compared with the acid-washed ZVI particles before reaction. The diffraction peaks of ZVI can be detected at 44.7°, 65.0°, and 82.3° before and after reaction. There were some new diffraction peaks detected from the acid-washed ZVI after reaction, which indicated the formation of some new compounds on the ZVI surface. The new peaks were found at 50.3°, 35.6°, 43.1°, 57.2°, and 62.7° after reaction, corresponding to the diffraction peaks of
magnetic Fe₃O₄ (Yang et al. 2015). This result reveals that during the removal of nitrate, ZVI was oxidized while magnetic Fe₃O₄ was generated on the surface of ZVI. Furthermore, it was also observed that some new inconspicuous diffraction peaks occurred, and the components of these peaks will be explained by the following XPS analysis.

XPS analysis

In order to get further insight into the nitrate removal mechanism by the acid-washed ZVI/Fe²⁺/H₂O₂ system, acid-washed ZVI before and after reaction were characterized by XPS. As is known, XRD and XPS do scan different depths, and XPS especially does not scan deeply enough to reach the ZVI layer. Figure 7(a) shows a full survey of the iron surface composition before and after reaction. The photoemission peaks of Fe(2p), O(1s), and C(1s) can be detected at 711.2, 530.2, and 284.7 eV, respectively. Furthermore, no obvious peaks of nitrogen occurred in the acid-washed ZVI particles after reaction. Figure 7(b) shows the Fe(2p) peaks at the binding energies of 711.2 eV (2p3/2)
and 724.8 eV (2p1/2), with a shakeup satellite at ~719.0 eV. Besides, no strong peak of ZVI at 706.9 eV (Ai et al. 2013) is observed in Figure 7(b), which is mainly due to the formation of an oxidation film on the iron surface.

In Figure 8, the broad peak of O(1s) can be fitted by three peaks at the binding energies of 529.9 eV, 531.2 eV, and 532.5 eV, respectively. The peak at 529.9 eV is characteristic of Fe-O, while the peaks at 531.2 eV and 532.5 eV are attributed to Fe-OH and excess oxygen (Volgmann et al. 2012; Xia et al. 2013; Eltouny & Ariya 2014; Yin et al. 2014), respectively. The fitting results in Figure 8(a) show that Fe-O, Fe-OH, and excess oxygen occupy 47.6%, 40.6%, and 11.8% before reaction, respectively. Meanwhile, the fitting results in Figure 8(b) indicate that Fe-O, Fe-OH, and excess oxygen occupy 55.8%, 34.0%, and 10.2% after reaction, respectively. The content of Fe-O increased after reaction, which may indicate that the Fe3O4 layer formed on the surface of ZVI during the reaction. The presence of Fe-OH may be attributed to the formation of iron oxyhydroxides. The Fe3O4 on the surface of ZVI is formed according to Equation (8) (Salam et al. 2015). The iron oxyhydroxides are probably formed according to Equation (9).

\[
\begin{align*}
\text{NO}_3^- + 3\text{Fe}^{2+} + 3\text{H}_2\text{O} & \rightarrow \text{NH}_4^+ + \text{Fe}_2\text{O}_4 + 2\text{OH}^- \quad (8) \\
4\text{Fe} + 3\text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{FeOOH} \quad (9)
\end{align*}
\]

From the combined results of XRD and XPS, it can be deduced that the ZVI particles after reaction may have a core of ZVI, and have a filmy layer mainly consisting of
The chemical reduction of nitrate by ZVI always depends on the efficiency of electron transfer from ZVI to active sites through the oxide layer on the ZVI surface (Xu et al. 2012). Electrons can transfer almost freely in the semi-conductive magnetite layer, but can hardly pass through the maghemite or lepidocrocite layer (An et al. 2014). The formation of Fe₃O₄ on the surface of ZVI during the reaction could expedite iron corrosion and facilitate electron transfer from ZVI to nitrate (Chao et al. 2015). So it can be inferred that the Fe₃O₄ layer may serve as a pathway for the transfer of electrons during the reaction and thus facilitated the removal of nitrate.

**Schematic mechanism for nitrate removal by acid-washed ZVI/Fe²⁺/H₂O₂ system**

The probable mechanism of nitrate removal by the acid-washed ZVI/Fe²⁺/H₂O₂ system is shown in Figure 9. During the reaction, the ZVI core served as the electron donor and was corroded by the H₂O₂ as well as Fe³⁺. The corrosion of ZVI yielded Fe²⁺ first and eventually resulted in the oxidation layer forming on the surface of ZVI. The oxidation layer mainly consisted of the Fe₃O₄, which could promote the electron transfer from the ZVI core to nitrate. Serving as one of the electron acceptors, NO₃⁻ was reduced to NO₂⁻ at first and then to NH₄⁺ or N₂ with the participation of H⁺.

**CONCLUSIONS**

The system of acid-washed ZVI/Fe²⁺/H₂O₂ was employed for the removal of nitrate. Compared with the acid-washed ZVI, acid-washed ZVI/Fe²⁺, and acid-washed ZVI/H₂O₂ systems, the acid-washed ZVI/Fe²⁺/H₂O₂ system was more effective for the removal of the nitrate from water. Under different initial NO₃⁻ concentrations, nitrate removal efficiency reached more than 99.0% within 6 hours using 89.3 mM acid-washed ZVI, 4.0 mM Fe²⁺, and 10.0 mM H₂O₂. Nitrite was the intermediate product of nitrate reduction while ammonium and nitrogen gas were the end products. The combined system can enhance the corrosion of ZVI and facilitate aqueous nitrate reduction. The oxide layer mainly consisting of Fe₃O₄, which could facilitate electron transfer from ZVI to nitrate formed on the surface of ZVI after reaction. The efficient removal of nitrate from water by the acid-washed ZVI/Fe²⁺/H₂O₂ system provides a promising method for nitrate remediation.

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