Sustaining reactivity of Fe^0 for nitrate reduction via electron transfer between dissolved Fe^{2+} and surface iron oxides

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GRAPHICAL ABSTRACT

HIGHLIGHTS

- NO_3^- reduction and the decrease of $\text{Fe}^{2+}_{\text{aq}}$ exhibited similar kinetics.
- The electron transfer between $\text{Fe}^{2+}_{\text{aq}}$ and the surface Fe(III) enhanced Fe^0 activity.
- The NO_3^- reduction produced surface iron oxides, supplying active sites for $\text{Fe}^{2+}_{\text{aq}}$.

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ABSTRACT

The mechanism of the effects of $\text{Fe}^{2+}_{\text{aq}}$ on the reduction of NO_3^- by Fe^0 was investigated. The effects of initial pH on the rate of NO_3^- reduction and the Fe^0 surface characteristics revealed $\text{Fe}^{2+}_{\text{aq}}$ and the characteristics of minerals on the surface of Fe^0 played an important role in NO_3^- reduction. Both NO_3^- reduction and the decrease of $\text{Fe}^{2+}_{\text{aq}}$ exhibited similar kinetics and were promoted by each other. This promotion was associated with the types of the surface iron oxides of Fe^0 . Additionally, further reduction of NO_3^- produced more surface iron oxides, supplying more active sites for $\text{Fe}^{2+}_{\text{aq}}$, resulting in more electron transfer between Fe^{2+} and surface iron oxides and a higher reaction rate. Using the isotope specificity of ^{57}Fe Mossbauer spectroscopy, it was verified that the $\text{Fe}^{2+}_{\text{aq}}$ was continuously converted into Fe^{3+} oxides on the surface of Fe^0 and then converted into Fe_3O_4 via electron transfer between Fe^{2+} and the pre-existing surface Fe^{3+} oxides. Electrochemistry measurements confirmed that the spontaneous

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electron transfer between the Fe^{2+} and structural Fe^{3+} species accelerated the interfacial electron transfer between the Fe species and NO_3^- . This study provides a new insight into the interaction between Fe species and contaminants and interface electron transfer.

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1. Introduction

Zero valent iron (Fe^0) has been extensively studied to reduce a wide range of contaminants, including halogenated aliphatics [1], nitro aromatic compounds [2], pesticides [3], heavy metals [4], and so on. Fe^0 -bearing technologies, such as permeable reactive barriers, which is a cost-effective technology, have been successfully applied for the remediation of contaminated groundwater [5,6]. However, the oxidation of Fe^0 results in the formation of an oxide layer, including goethite ($\alpha\text{-FeOOH}$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$), leading to a reduction in the reactivity of Fe^0 [7,8], although contaminant degradation can be continued when $\text{Fe}^{2+}/\text{Fe}^{3+}$ hydroxides, such as magnetite (Fe_3O_4) and green rust, are formed on the Fe^0 surface [9,10]. Different procedures have been developed to inhibit the formation of the oxide layer to maintain or enhance the activity of Fe^0 , including the use of sonication [11], external voltage [12], flash-drying after acid washing [13] and strong reductants [14].

Nitrates which is a widespread groundwater contaminant can also be reduced using Fe^0 -bearing technologies [15]. Recently, various modified Fe^0 by microbes [16], Fe oxides [17], minerals [18] and organic carbon [19] was used to improve the degradation effect of nitrate. It was found that the reductive efficiency of nitrate by Fe^0 increased as the concentration of dissolved ferrous ion ($\text{Fe}^{2+}_{\text{aq}}$) increased in solution [20,21]. In addition, dissolved $\text{Fe}^{2+}_{\text{aq}}$ was a strong contributor to trichloroethylene (TCE) reduction by Fe^0 coated with a Fe^{3+} crust [22,23].

Some researchers found that adsorbed Fe^{2+} on the mineral surfaces can promote the reductive transformation of different contaminants because of its relatively negative redox potential [24–26]. Klupinski et al. [25] verified that the degradation of pentachloronitrobenzene by adsorbed Fe^{2+} on iron oxide was a rate-affecting surface-association process rather than a direct reaction. Perchlorate reduction was not observed on pure Fe^0 or on a mixed-phase oxide, but perchlorate was reduced by a mixed valence iron hydr(oxide) coating or a adsorbed Fe^{2+} surface complex on the surface of Fe^0 [27]. Additionally, green rust with a high reactivity toward nitrate [28] and other contaminants [29] may be produced when Fe species with different valence states coexisted [30]. Moreover, Liu et al. [31] suggested that proton release during the adsorption of Fe^{2+} to iron oxide coatings can promote surface dissolution and enhance the extent of TCE reduction by aged Fe^0 . In addition, it has been reported that Fe^{2+} on the surface of Fe^{3+} oxides can catalyze the transformation of amorphous Fe^{3+} oxides or goethite to magnetite [23,32]. It is assumed that the semiconductive magnetite layer allows electron transfer from Fe^0 to nitrate [17,33] and other contaminants [23] at the oxide–water interface. The above results indicated that the reactivity of Fe^0 for nitrate and other contaminants reduction is relative to the interaction between Fe^{2+} and Fe^{3+} . Recently, Mossbauer spectra of Fe^{2+} adsorbed on Fe oxide demonstrated spontaneous electron transfer between adsorbed Fe^{2+} and $\alpha\text{-FeOOH}$, $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 , and ferrihydrite [34–36]. However, there have been no reports to confirm whether this spontaneous electron transfer behavior can catalyze electron transfer from Fe^0 to nitrate.

In this work, nitrate was chosen as a target pollutant to study contaminants degradation by Fe^0 and $\text{Fe}^{2+}_{\text{aq}}$ with different

conditions. During the reduction of nitrate, the electron transfer and Fe species transformation were investigated using Mossbauer spectroscopy and electrochemistry measurement. A new electron transfer mechanism was proposed among dissolved $\text{Fe}^{2+}_{\text{aq}}$, iron oxide, Fe^0 and nitrate for helping deepen the understanding of the mechanism of contaminants reduction.

2. Materials and methods

2.1. Materials

Fresh zero valent iron ($\geq 98.0\%$) was purchased from Sinopharm Chemical Reagent Co., Ltd. The specific surface area of fresh iron was measured by Micromeritics ASAP2000 analyzer (Micromeritics, Norcross, GA) and was calculated from the isotherms using the BET method. The surface area of the iron was $1.2563 \pm 0.0842 \text{ m}^2 \text{ g}^{-1}$. To research the role of the surface mineral, about 30 g the used Fe^0 was obtained from the reaction among fresh Fe^0 (60.0 g L^{-1}), NaNO_3 (20.0 mM) and FeSO_4 (10.0 mM) under anaerobic conditions. The used Fe^0 was filtered in the anoxic glovebox after 5 days, washed and dried naturally after the reaction for the further experiment. The surface area of used Fe^0 was $1.5617 \pm 0.0351 \text{ m}^2 \text{ g}^{-1}$. Iron metal isotopically enriched for ^{57}Fe ($\geq 99\%$) was purchased from Sigma–Aldrich Co., LLC. The reported purity was 95% for ^{57}Fe (compared to a natural abundance of 2.12%). The enriched $^{57}\text{Fe}^0$ was dissolved in 0.1 mM H_2SO_4 , and the resulting $^{57}\text{Fe}^{2+}$ sulfate solution was filtered through a 0.22 μm filter and stored in an anoxic glovebox (Thermo Fisher Scientific Inc.). All other chemicals were analytical grade and used without further purification. All aqueous solutions were prepared with deionized water.

2.2. Batch experiments

Deionized water was aerated with high-purity nitrogen (99.9999%) for 1 h to remove dissolved oxygen. The NaNO_3 stock solution (100.0 mM) and FeSO_4 stock solution (100.0 mM) were prepared in the anoxic glovebox using the O_2 -free deionized water. According to the experimental requirements, different quantities of Fe^0 , NaNO_3 , FeSO_4 and O_2 -free deionized water were added into a 100-mL vial. The total volume of the solution in the vial was 50 mL, and the pH of the solution was adjusted to 5.0–9.0 with 1.0 M NaOH or 1.0 M HCl. The vials were then sealed with butyl-rubber stoppers and aluminum caps. The vials were incubated in a thermostatic shaker at 200 rpm at 30 °C in the dark. The vials were opened in the anoxic glovebox at various reaction times. Samples were withdrawn by disposable syringes, passed through 0.22 μm membrane filters and analyzed within 4 h. All of the tests were performed in triplicate.

2.3. The reduction of NO_3^- under different condition

The transformations of NO_3^- by $\text{Fe}^{2+}_{\text{aq}}$ + different materials (Fe^0 , Al_2O_3 , SiO_2 , Fe_2O_3 and Fe_3O_4) and the effects of solution initial pH, NO_3^- initial concentration, $\text{Fe}^{2+}_{\text{aq}}$ initial concentration, and Fe^0 dosage on the reduction of NO_3^- were investigated. The concentrations of nitrate (NO_3^-) and nitrite (NO_2^-) were measured by ICS-2000 ion chromatography with an IonPac AS11-HC

Fig. 1. (A) NO_3^- reduction products, total nitrogen content and (B) $\text{Fe}^{2+}_{\text{aq}}$ consumption during NO_3^- reduction (initial concentration of $\text{NO}_3^- = 2.0 \text{ mM}$, $\text{Fe}^{2+}_{\text{aq}} = 1.0 \text{ mM}$, and $\text{Fe}^0 = 6.0 \text{ g L}^{-1}$).

column ($250 \times 4 \text{ mm I.D.}$) and KOH eluent (Dionex Corporations, USA) according to standard methods [37]. Ammonium (NH_4^+) was measured with the salicylate method at 697 nm on a UV-vis spectrophotometer [37]. The $\text{Fe}^{2+}_{\text{aq}}$ was determined by removing the suspended solids from the aqueous phase using a $0.22 \mu\text{m}$ syringe filter and then assaying the filtrate using 1,10-phenanthroline colorimetric assay at 510 nm on a UV-vis spectrophotometer (Hitachi UV-3100) [38]. The dissolved Fe^{3+} concentration was obtained from the difference between the dissolved $\text{Fe}^{2+}_{\text{aq}}$ concentration and the total dissolved Fe concentration, which was determined using 1,10-phenanthroline colorimetric assay after adding 10% hydroxylamine hydrochloride to reduce all dissolved $\text{Fe}^{3+}_{\text{aq}}$ to $\text{Fe}^{2+}_{\text{aq}}$. The pH value was measured using a pH meter (PHS-3C pH). The reduction of NO_3^- data were tested using the pseudo first-order and zero-order models. The rate is proportional to the dissolved NO_3^- concentration ($[\text{NO}_3^-]$) in a pseudo first-order kinetics model:

$$\frac{d[\text{NO}_3^-]}{dt} = -k[\text{NO}_3^-] \quad (1)$$

Integration of Eq. (1) and take $\ln$ of it results in:

$$\ln \frac{[\text{NO}_3^-]}{[\text{NO}_3^-]_0} = -kt \quad (2)$$

The correlation coefficients were calculated from linear regressions of $\ln([\text{NO}_3^-])$ vs. the time. The rate is constant in a zero-order kinetics model:

$$\frac{d[\text{NO}_3^-]}{dt} = -k \quad (3)$$

Integration of Eq. (1) results in:

$$[\text{NO}_3^-] - [\text{NO}_3^-]_0 = -kt \quad (4)$$

The correlation coefficients were calculated from linear regressions of $[\text{NO}_3^-]$ vs. the time.

2.4. Characterization

All powder samples were dried naturally in an anoxic glovebox and transported to the instrument using the sealed vials before tests. Powder X-ray diffraction (XRD) of the Fe^0 was recorded on an XDS-2000 Diffractometer (X'Pert PRO MPD, PANalytical, Almelo, The Netherlands). The morphology of the particles was observed using a scanning electron microscope (S-3000N, Hitachi, Japan). The X-ray photoelectron spectroscopy (XPS) data were taken on an AXIS-Ultra instrument (Kratos Analytical, UK) using monochromatic AlK α radiation (225 W, 15 mA, 15 kV). To compensate for surface charge effects, the binding energies were calibrated using the C1s hydrocarbon peak at 284.8 eV. Mossbauer spectra were collected in transmission mode with a constant acceleration drive system and a ^{57}Co source. Data were calibrated against an α -Fe metal foil collected at room temperature [34]. The Mossbauer spectroscopy of the samples was analyzed using the MossWinn 4.0 program.

2.5. Electrochemical tests

Cyclic voltammograms were carried out in a standard three-electrode cell using a CHI 660D Electrochemical Workstation. A glassy carbon (GC, 3 mm in diameter) electrode was used as the working electrode with a platinum wire electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All the reported voltages were vs. SCE. The Fe^0 -modified GC electrode was prepared as described by Liu et al. [31] but the procedures were slightly different. The GC electrode was polished with emery paper followed by Al_2O_3 powders of 1.0, 0.3 and 0.05 mm particle sizes. Between each polishing step, the electrode was thoroughly rinsed with deionized water. The polished electrode was successively cleaned with ethanol and water in an ultrasonic bath for 3 min. The Fe^0 (1 mg) was then dispersed in a dilute Nafion solution (0.5 wt.%, 50 μL) by vortex mixing for 1 min. An aliquot (2 μL) of the above suspension was coated on the clean GC electrode using a microsyringe, and the electrode with the coating was dried in air for 5 min prior to use. High purity nitrogen gas was bubbled through the electrolyte to remove the dissolved oxygen. Cyclic voltammetry was conducted at a scan rate of 50 mV s^{-1} in the cell containing 0.2 M Na_2SO_4 and different ions buffered with 28.0 mM 3-N-morpholinopropansulfonic acid (MOPS).

3. Result and discussion

3.1. Promoting effect of $\text{Fe}^{2+}_{\text{aq}}$ on NO_3^- reduction by Fe^0

The transformations of NO_3^- in solution for the different treatments at near-neutral pH were investigated (Fig. S1). No significant reduction of NO_3^- was observed with Fe^0 or $\text{Fe}^{2+}_{\text{aq}}$. In contrast, the reduction of NO_3^- was greatly enhanced with the simultaneous addition of Fe^0 and $\text{Fe}^{2+}_{\text{aq}}$. However, in different oxides (Al_2O_3 , SiO_2 , Fe_2O_3 and Fe_3O_4) and $\text{Fe}^{2+}_{\text{aq}}$ suspensions, the NO_3^- removal was just around 10% within 21 days (Fig. S2). With the reduction of NO_3^- , the concentration of NO_2^- increased to about 0.1 mM at 1 day and then decreased to about 0.001 mM at 5 days, while NH_4^+ gradually increased and reached a stable concentration of about 1.7 mM after 4 days. About 97% reduced NO_3^- was transformed into NH_4^+ . With the production of NH_4^+ , the concentration of $\text{Fe}^{2+}_{\text{aq}}$ rapidly decreased in 2 days (Fig. 1). Only 1.0 mM $\text{Fe}^{2+}_{\text{aq}}$ was added into the solution, while it needs 13.6 mM electrons that 1.7 mM NO_3^- was transformed into NH_4^+ . Therefore fewer electrons were provided by $\text{Fe}^{2+}_{\text{aq}}$ oxidation than the number of electrons required for the reduction of NO_3^- to NH_4^+ . The results indicated that Fe^0 predominantly provided the electrons to reduce

Fig. 2. Effects of the initial pH on the NO_3^- reduction by Fe^0 (6.0 g L^{-1}) and $\text{Fe}^{2+}_{\text{aq}}$ (initial concentration of $\text{NO}_3^- = 1.6 \text{ mM}$ and adding a concentration of $\text{Fe}^{2+}_{\text{aq}} = 1.0 \text{ mM}$).

NO_3^- , and its activity was enhanced by the $\text{Fe}^{2+}_{\text{aq}}$. Moreover, dissolved Fe^{3+} was not detected (data not shown), indicating that the $\text{Fe}^{2+}_{\text{aq}}$ was transferred to the surface of Fe^0 with the reduction of NO_3^- . Correspondingly, the solution pH gradually increased from 5.5 to 9 (Fig. S3) because alkalinity was produced from the reduction of NO_3^- by Fe^0 [39,40]. However, in the Fe^0 system, the solution's pH value quickly increased from 6.5 to 9, although only 10% NO_3^- was reduced at 5 days. The $\text{Fe}^{2+}_{\text{aq}}$ acted as a pH buffer in the reaction suspension of Fe^0 and $\text{Fe}^{2+}_{\text{aq}}$. As a control, the pH became acidic in the $\text{NO}_3^- - \text{Fe}^{2+}_{\text{aq}}$ system. These results were mainly contributed by the hydrolysis of $\text{Fe}^{2+}_{\text{aq}}$.

3.2. Effect of pH

The initial pH of the solution greatly influenced the reduction of NO_3^- in the Fe^0 and $\text{Fe}^{2+}_{\text{aq}}$ system (Fig. 2). Ninety-five percent and eighty-five percent of NO_3^- removal occurred at an initial pH of 6.0 and 7.0 after 4 days, respectively. The NO_3^- removal decreased to 78% at an initial pH of 5.0 in the same period and sharply decreased at an initial pH of 8.0 and 9.0, and only 40% and 20% of the NO_3^- was reduced, respectively. For the same $\text{Fe}^{2+}_{\text{aq}}$ dosage of 1.0 mM, the initial concentration of $\text{Fe}^{2+}_{\text{aq}}$ greatly decreased with increasing initial pH because $\text{Fe}^{2+}_{\text{aq}}$ was transformed into the insoluble complex of $\text{Fe}^{2+}_{\text{aq}}$ and hydroxyl ions at high pH (Fig. S4). At an initial pH of 8.0 and 9.0, the initial concentration of $\text{Fe}^{2+}_{\text{aq}}$ decreased to 0.31 and 0.06 mM, respectively, whereas they were 0.98, 0.92 and 0.73 mM at an initial pH of 5.0, 6.0 and 7.0, respectively. The results indicated that $\text{Fe}^{2+}_{\text{aq}}$ promoted NO_3^- reduction by Fe^0 rather than the insoluble complex of $\text{Fe}^{2+}_{\text{aq}}$ and hydroxyl ions. In the $\text{Fe}^0 + \text{Fe}^{2+}_{\text{aq}}$ system without NO_3^- , scanning electron microscope (SEM) analysis showed that amounts of round shape species embedded on the surface of Fe^0 while some of the round shape species was dissolved at initial pH 5.0. The species deposited as irregular shapes appeared on the Fe^0 surface when solution initial pH was 8.0 or 9.0 at which the insoluble complex of $\text{Fe}^{2+}_{\text{aq}}$ and hydroxyl ions would be expected to precipitate (Fig. S5). The initial $\text{Fe}^{2+}_{\text{aq}}$ was more at initial pH 5.0 than initial pH 6.0 and 7.0 (Fig. S4), while the rate of NO_3^- reduction was slower at initial pH 5.0 than initial pH 6.0 and 7.0 (Fig. 2). It should be because the round shape species was dissolved at initial pH 5.0. The results indicated that the round shape species on the surface of Fe^0 had also influence on the reduction of NO_3^- .

3.3. Kinetics for the reduction of NO_3^-

Previous studies showed that the reduction rate of NO_3^- by Fe^0 was described by a pseudo-first-order kinetics [40–42]. However, the reaction kinetics of NO_3^- reduction had a greater tendency

Fig. 3. (A) Effects of the $\text{Fe}^{2+}_{\text{aq}}$ concentrations in the range of 4.0–10.0 mM with 1.6 mM NO_3^- and $6.0 \text{ g L}^{-1} \text{ Fe}^0$ and (B) effects of the $\text{Fe}^{2+}_{\text{aq}}$ concentrations in the range of 4.0–10.0 mM with 1.6 mM NO_3^- and $12.0 \text{ g L}^{-1} \text{ Fe}^0$.

to a zero-order reaction with a different $\text{Fe}^{2+}_{\text{aq}}$ concentration at $6.0 \text{ g L}^{-1} \text{ Fe}^0$ and 1.6 mM NO_3^- (Fig. 3A). The correlation coefficients of linear regression for $[\text{NO}_3^-]$ vs. the time curve (R^2_{CT}) were larger than for $\ln [\text{NO}_3^-]$ vs. the time curve (R^2_{LCT}) (Table S1). However, the rate of NO_3^- reduction was improved, and the reaction kinetics of NO_3^- reduction turned into a pseudo-first order reaction kinetics at $12.0 \text{ g L}^{-1} \text{ Fe}^0$ and the same initial concentration of NO_3^- (Fig. 3B). The results indicated that the amount of the active site on the surface of Fe^0 was the limiting factor for NO_3^- reduction. The rate of NO_3^- reduction increased as the initial $\text{Fe}^{2+}_{\text{aq}}$ concentration increased from 4.0 mM to 6.0 mM and remained steady as the initial $\text{Fe}^{2+}_{\text{aq}}$ concentration continued to increase (up to 10.0 mM). The adsorption amount of $\text{Fe}^{2+}_{\text{aq}}$ monotonically increased with increasing $\text{Fe}^{2+}_{\text{aq}}$ initial concentrations from 1.0 mM to 10.0 mM (Fig. S6). Larese-Casanova et al. [35] reported that the adsorbed Fe^{2+} species are transient and quickly undergo interfacial spontaneous electron transfer with structural Fe^{3+} in hematite at low Fe^{2+} concentrations ($100 \mu\text{M}$). A stable adsorbed Fe^{2+} phase is formed on hematite at higher Fe^{2+} concentrations. The results were in good agreement with the spontaneous electron transfer behavior between the adsorbed Fe^{2+} and hematite. The same phenomenon was observed at an Fe^0 dosage of 12.0 g L^{-1} . Moreover, at $\text{Fe}^{2+}_{\text{aq}}$ 4.0 mM with Fe^0 6.0 g L^{-1} , the rate constant of NO_3^- reduction increased with increasing NO_3^- initial concentration and increased to $0.22 \text{ mmol L}^{-1} \text{ h}^{-1}$ at an initial NO_3^- concentration of 6.4 mM from $0.12 \text{ mmol L}^{-1} \text{ h}^{-1}$ at initial NO_3^- 1.6 mM (Fig. S7). In addition, both the decrease of the $\text{Fe}^{2+}_{\text{aq}}$ concentration and the reduction of NO_3^- showed similar tendency within 12 h (Fig. S8). After 12 h, the concentration of $\text{Fe}^{2+}_{\text{aq}}$ did not decrease further when NO_3^- was consumed below the limit of detection at an initial $\text{Fe}^{2+}_{\text{aq}}$ concentration of 6.0–10.0 mM. At a given $\text{Fe}^{2+}_{\text{aq}}$ concentration of 4.0 mM, with the reduction of NO_3^- , the concentration of $\text{Fe}^{2+}_{\text{aq}}$

Fig. 4. (A) NO₃⁻ reduction and (B) Fe²⁺_{aq} consumption by fresh Fe⁰/used Fe⁰ (6.0 g L⁻¹) in the absence or presence of Fe²⁺_{aq} (initial concentration of NO₃⁻ = 2.0 mM, and Fe²⁺ = 1.0 mM).

continuously decreased because the NO₃⁻ was not consumed below the limit of detection under this condition (Fig. 3A). The results indicated that the reduction of NO₃⁻ induced the Fe²⁺_{aq} transferred to the surface of Fe⁰, suggesting more active sites were produced with the reduction of NO₃⁻ for Fe²⁺_{aq}. Therefore the increase of NO₃⁻ initial concentration can accelerate the formation of active sites and cause the increase of the rate constant of NO₃⁻ reduction.

The active sites transformed from Fe²⁺_{aq} were different from the intrinsic active sites on the surface of Fe⁰, because the increase of the initial concentration of NO₃⁻ only improved the rate of NO₃⁻ reduction. It cannot change the reaction kinetics of NO₃⁻ reduction. Commercially available Fe⁰ particles have a Fe³⁺ oxide or oxyhydroxide shell such as α-FeOOH and γ-Fe₂O₃ [23,43]. The Fe 2p XPS spectra of fresh Fe⁰ showed obvious peaks at about 711, 719 and 725 eV (Fig. S9), which were assigned to the 2p_{3/2}, shake-up satellite 2p_{3/2}, and 2p_{1/2} of Fe³⁺ ions in Fe₂O₃ or FeOOH, respectively [44]. In addition, the Fe 2p XPS spectrum of used Fe⁰ showed a broader peak at about 710.5 eV, which may contribute from both Fe²⁺ and Fe³⁺ [45]. No significant XPS spectra were observed for Fe⁰ species in the two samples, indicating that both the fresh and used Fe⁰ were completely covered by iron oxides, which supply active sites for Fe²⁺_{aq}. The Fe₃O₄ phase was detected on the surface of used Fe⁰, and it was not detected on the surface of fresh Fe⁰ (Fig. S10). Therefore it was supposed that the differences of active sites were caused by the differences of Fe species on the surface of Fe⁰. In previous work, it also was found that the TCE degradation rate decreased as the concentration of Fe²⁺_{aq} increased for the acid-washing of Fe⁰, whereas it increased as the concentration of Fe²⁺_{aq} increased for the unwashed Fe⁰ [23]. No significant NO₃⁻ reduction was observed in the used Fe⁰ and the fresh Fe⁰ without Fe²⁺_{aq} (Fig. 4). With the addition of Fe²⁺_{aq} (1.0 mM) to the solution, the NO₃⁻ was quickly reduced in both systems. Therefore, it was

verified the enhanced reactivity of Fe⁰ from the interaction of Fe²⁺_{aq} with the iron oxides. However, they showed different kinetics. In fresh Fe⁰ + Fe²⁺_{aq}, the reaction followed pseudo-first order reaction kinetics ($R^2_{\text{Ct}} = 0.6334$ vs. $R^2_{\text{lnCt}} = 0.8194$), and the decrease of the Fe²⁺_{aq} also exhibited a similar tendency. In contrast, in the used Fe⁰ + Fe²⁺_{aq}, the reaction followed to a zero-order reaction for the first 3 days ($R^2_{\text{Ct}} = 0.9995$ vs. $R^2_{\text{lnCt}} = 0.9984$), and then, the NO₃⁻ removal rate increased significantly. Likewise, the concentration of Fe²⁺_{aq} exhibited an approximately linear decrease for the first 3 days and then a sharp decrease, indicating more iron oxide formation on the Fe⁰ surface at this time (Fig. 4B). Moreover, the NO₃⁻ removal by the fresh Fe⁰ + Fe²⁺_{aq} was faster than the one by the used Fe⁰ + Fe²⁺_{aq} because the surface of the used Fe⁰ had Fe²⁺/Fe³⁺ oxides (Fe₃O₄), whereas the surface of the fresh Fe⁰ mainly had Fe³⁺ oxides. The results indicated that the Fe³⁺ oxides could supply more electron transfer sites for Fe²⁺_{aq} than Fe²⁺/Fe³⁺ oxides, causing a greater enhancement of the Fe⁰ reactivity. In the used Fe⁰ + Fe²⁺_{aq} system, for the first 3 days, the Fe₃O₄ were predominant sites for Fe²⁺_{aq}, but with the reduction of NO₃⁻, more iron oxide production, and more active sites, there was a higher reaction rate. The rate of NO₃⁻ reduction slowed down when the Fe²⁺_{aq} was consumed below the limit of detection in both the fresh Fe⁰ + Fe²⁺_{aq} system and the used Fe⁰ + Fe²⁺_{aq} system. The results also confirmed that the interaction of Fe²⁺_{aq} with iron oxides played an important role in the acceleration of NO₃⁻ reduction by Fe⁰.

3.4. Interface electron transfer and Fe species transformation

In order to investigate different types of iron oxide formation on the surface of Fe⁰ and the role of Fe²⁺_{aq}, the isotopically labelled ⁵⁷Fe²⁺_{aq} instead of natural abundance-level Fe²⁺_{aq} was used in the reduction of NO₃⁻ by Fe⁰ + Fe²⁺_{aq} because the Mossbauer spectra of the used Fe⁰ (Fig. S11) only showed the Fe⁰ sextet [46], although it was covered by iron oxide and Fe₃O₄. The Mossbauer spectra of the fresh Fe⁰ after exposure to ⁵⁷Fe²⁺_{aq} and NO₃⁻ for different times (Fig. S12) showed that a doublet spectrum appeared after 1 day. According to the hyperfine parameters at room temperature (Table 1), such a doublet was the Mossbauer spectra of Fe³⁺ oxides or oxyhydroxides [47–49]. The result indicated that ⁵⁷Fe²⁺_{aq} was transformed into Fe³⁺ oxides on the surface of Fe⁰ with NO₃⁻ reduction in the Fe⁰ + ⁵⁷Fe²⁺_{aq} system. This transformation should be caused by the interaction between ⁵⁷Fe²⁺_{aq} with the surface iron oxides of Fe⁰ during the reduction of NO₃⁻ based on all of the above results. The Fe³⁺ doublet tapered off and transformed into two sextets after 5 days. Both sextets were characteristics of the Fe₃O₄ spectra collected at room temperatures. The outer sextet corresponded to Tet⁵⁷Fe³⁺ ions in the tetrahedral sites. The inner sextet corresponded to the Oct⁵⁷Fe²⁺ and the Oct⁵⁷Fe³⁺ ions present in the octahedral sites, which appeared as one sextet with an average valence state of 2.5 because of very fast electron hopping between the Oct⁵⁷Fe²⁺ and Oct⁵⁷Fe³⁺ ions above the Verwey transition temperature of 121 K [36,48]. The Mossbauer spectra analysis verified that during the reduction of NO₃⁻, the Fe²⁺_{aq} was continuously converted into Fe³⁺ oxides on the surface of Fe⁰ into Fe₃O₄, indicating that the Fe²⁺_{aq} was oxidized into Fe³⁺ by Fe³⁺ oxides on the surface of Fe⁰ and simultaneously reduced into Oct⁵⁷Fe^{2.5+} by Fe²⁺_{aq} or Fe⁰.

Furthermore, in the Mossbauer spectra of the used Fe⁰ after exposure to ⁵⁷Fe²⁺_{aq} and NO₃⁻ (Fig. 5), the doublet Mossbauer spectra of the Fe³⁺ still appeared and exhibited the same transformation process to Fe₃O₄ as those in the fresh Fe⁰. In contrast, the Tet⁵⁷Fe³⁺ sextet appeared after 1 day, and no significant Oct⁵⁷Fe^{2.5+} was observed. The results verified that the electron transfer did not occur between the Tet⁵⁷Fe³⁺ and the Fe⁰ because of pre-existing ⁵⁶Fe₃O₄ on the surface of the used Fe⁰. The electrons coming from Fe⁰ were transferred to NO₃⁻ by Oct⁵⁷Fe^{2.5+} rather than Tet⁵⁷Fe³⁺. The

Fig. 5. Mossbauer spectra of used Fe^0 after exposure to $^{57}\text{Fe}^{2+}_{\text{aq}}$ (1.0 mM) and NO_3^- (1.6 mM) (A) for 1 day, (B) for 3 days, and (C) for 5 days (spectra were collected at room temperature).

Table 1

Mossbauer spectra of fresh Fe^0 /used Fe^0 after exposure to $^{57}\text{Fe}^{2+}_{\text{aq}}$ and NO_3^- for different periods of time.

solid phase	T (day) ^a	IS (mm s^{-1}) ^b	QS (mm s^{-1}) ^c	H (T) ^d	RA (%) ^e	Fe species
Fe^0	1	0	0	33.0	67.6	Fe^0
		0.36	0.75	–	32.4	
	5	0	0	33.1	56.2	Fe^0
		0.61	–0.05	45.4	22.7	$\text{OctFe}^{2.5+}$
		0.29	–0.03	48.6	12.3	TetFe^{3+}
		0.38	0.84	–	6.7	am-Fe(III) ^f
Used Fe^0	0	0.50	2.67	–	2.1	
		–0.11	0	33.0	100	Fe^0
	1	0	0	33.1	61.0	Fe^0
		0.32	–0.06	47.2	9.5	TetFe^{3+}
		0.35	0.85	–	29.5	am-Fe(III)
	3	0	0	33.1	54.3	Fe^0
		0.62	–0.15	45.2	16.9	$\text{OctFe}^{2.5+}$
		0.30	0	48.6	11.5	TetFe^{3+}
		0.44	0.80	–	9.0	am-Fe(III)
		0.72	2.82	–	8.3	
	5	0	0	33.1	52.7	Fe^0
		0.56	–0.09	45.0	20.0	$\text{OctFe}^{2.5+}$
		0.30	–0.03	48.3	13.4	TetFe^{3+}
		0.41	0.84	–	9.5	am-Fe(III)
		0.67	2.83	–	4.4	

^a Reaction time.

^b Isomer shift.

^c Quadrupole splitting.

^d Hyperfine magnetic field.

^e Relative spectrum area.

^f Amorphous Fe^{3+} oxides.

$\text{OctFe}^{2.5+}$ sextet appeared at 3 days and the ratio of the relative spectral areas between the $\text{OctFe}^{2.5+}$ sextet and the TetFe^{3+} sextet increased as time went on (Table 1). The results confirmed that $^{57}\text{Fe}^{2+}_{\text{aq}}$ provided the electrons to transform Fe^{3+} into $\text{OctFe}^{2.5+}$. Therefore the results concluded that the spontaneous electron transfer between the $\text{Fe}^{2+}_{\text{aq}}$ and the surface iron oxides of Fe^0

continued during Fe species transformation and the reduction of NO_3^- .

Based on the redox potentials of $\text{Fe}^{2+}/\text{Fe}^0$ (–0.44 V) and $\text{Fe}^{3+}/\text{Fe}^{2+}$ (0.77 V), the iron oxides coated Fe^0 created galvanic cells wherein Fe^0 served as the cathode, and Fe oxides served as the anode as a result of an electron transfer between Fe species. However, Williams et al. [34] verified that the spontaneous electron

Fig. 6. Results of the cyclic voltammograms using (A) the GC electrode and (B) the Fe^0/GC electrode with a scan rate of 50 mV s^{-1} . The electrochemical cell was filled with a solution containing $0.2 \text{ M Na}_2\text{SO}_4$ and different ions buffered with 28.0 mM MOPS (concentration of $\text{NO}_3^- = 5.0 \text{ mM}$ and $\text{Fe}^{2+}_{\text{aq}} = 5.0 \text{ mM}$).

Fig. 7. The process of the interface electron transfer and Fe species transformation.

transfer between adsorbed Fe^{2+} and structural Fe oxide occurred in the absence of Fe^0 or other chemicals which can create galvanic cells with structural Fe oxide. It means this spontaneous electron transfer was not driven by potential difference. In order to observe the electron transfer process at the water-solid interface, the cyclic voltammetry behaviors of GC and Fe^0/GC electrodes were investigated in a solution containing 0.2 M NaSO_4 and different ions buffered with 28.0 mM MOPS at N_2 atmosphere. As shown in Fig. 6A, no obvious redox peaks were observed at the GC electrode in the NO_3^- system. However, a pair of peaks (an oxidation peak for NO_2^- and a reduction peak for NO_3^-) and a reduction peak for Fe^{3+} appeared in the $\text{NO}_3^- + \text{Fe}^{2+}_{\text{aq}}$ system. The results indicated that the addition of $\text{Fe}^{2+}_{\text{aq}}$ promoted the $\text{NO}_3^-/\text{NO}_2^-$ redox. In the electrolysis cell, the applied potential can be used instead of Fe^0 . The cyclic voltammograms of the Fe^0/GC electrodes exhibited a reduction peak for Fe^{3+} (Fig. 6B). Similarly, no $\text{NO}_3^-/\text{NO}_2^-$ redox peaks were observed in the NO_3^- system, although electron transfer between Fe^{2+} and Fe^{3+} occurred on the surface of Fe^0 . Only when $\text{Fe}^{2+}_{\text{aq}}$ was added to the solution, the $\text{NO}_3^-/\text{NO}_2^-$ redox would be promoted. It indicated that the spontaneous electron transfer between structural Fe^{3+} and $\text{Fe}^{2+}_{\text{aq}}$ is the key to promoting the $\text{NO}_3^-/\text{NO}_2^-$ redox reaction. The process of the interface electron transfer and Fe species transformation in the heterogeneous system of Fe^0 , Fe^{2+} and Fe^{3+} is shown in Fig. 7.

4. Conclusion

Investigation of the mechanism of $\text{Fe}^{2+}_{\text{aq}}$ enhancing Fe^0 reactivity found that both NO_3^- reduction and the decrease in $\text{Fe}^{2+}_{\text{aq}}$ exhibited similar kinetics and were promoted by each other. The $\text{Fe}^{2+}_{\text{aq}}$ and the characteristics and type of minerals on the surface of Fe^0 played an important role in NO_3^- reduction. The isotope specificity of ^{57}Fe Mossbauer spectroscopy found that the $\text{Fe}^{2+}_{\text{aq}}$ was continuously converted into Fe^{3+} oxides on the surface of Fe^0

and then converted into Fe_3O_4 via spontaneous electron transfer between the Fe^{2+} and the pre-existing surface Fe^{3+} oxides. The reduction of NO_3^- produced more surface Fe oxides, supplying more active sites for the $\text{Fe}^{2+}_{\text{aq}}$, resulting in a higher reaction rate. An electrochemistry measurement confirmed that the spontaneous electron transfer between the $\text{Fe}^{2+}_{\text{aq}}$ and surface iron oxides accelerated the interfacial electron transfer between the Fe species and NO_3^- . This finding provides new insight into interface electron transfer and Fe species transformation. It is helpful to further develop Fe-based catalysis technologies and to understand Fe species transformation in nature.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.01.047>.

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