Ligand effects on arsenite removal by zero-valent iron/O₂: Dissolution, corrosion, oxidation and coprecipitation

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ABSTRACT

Ligands may increase the yields of reactive oxygen species (ROS) in zero-valent iron (ZVI)/O₂ systems. To clarify the relationship between the properties of ligands and their effects on the oxidative removal of contaminants, five common ligands (formate, acetate, oxalate, ethylenediaminetetraacetic acid (EDTA), and phosphate) as well as acetylacetone (AA) were investigated with arsenite (As(III)) as the target contaminant at three initial pH values (3.0, 5.0, and 7.0). The addition of these ligands to the ZVI/O₂ system resulted in quite different effects on As(III) removal. EDTA enhanced the oxidation of As(III) to arsenate (As(V)) but inhibited the removal of As(V). Oxalate was the only ligand in this work that accelerated both the removal of As(III) and As(V). By analyzing the ligand effects from the four aspects: dissolution of surface iron (hydr)oxides, corrosion of ZVI, reaction with ROS, and interference with precipitation, the following properties of ligands were believed to be important: ability to provide dissociable protons, complexation ability with iron, and reactivity with ROS. The complexation ability is a double-edged sword. It could enhance the generation of ROS by reducing the reduction potential of the Fe(III)/Fe(II) redox couple, but also could inhibit the removal of arsenic by coprecipitation. The elucidated relationship between the key property parameters of ligands and their effects on the ZVI/O₂ system is helpful for the rational design of effective ZVI/ligand/O₂ systems.

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Introduction

Zero valent iron (ZVI, Fe⁰) has been widely utilized for treatment of various contaminants via reductive pathways in anoxic systems (Dong et al., 2010; Han and Yan, 2016; Mukherjee et al., 2016; Mwakabona et al., 2017; Noubactep, 2010; Xu et al., 2018) or via oxidative pathways in aerated systems (Guan et al., 2015; He et al., 2013; Katsoyiannis et al., 2008; Noradoun and Cheng, 2005; Shimizu et al., 2012; Xu et al., 2016). For the oxidative removal of contaminants, the generation of reactive oxygen species (ROS) in the ZVI/O₂ system is a key issue. However, the yields of ROS in aerated systems are usually too low to be useful for practical application, because ZVI usually exists in a core-shell structure (Guan et al., 2015; Keenan and Sedlak, 2008). The shell is composed of an inner film of magnetite (Fe₃O₄) and an outer film of hematite/maghemite (Fe₂O₃) (Guan et al., 2015; Luo et al., 2010; Suzuki et al., 2012). Electrons can migrate in the inner film, whereas electron transfer is greatly hindered in the outer film (Huang and Zhang, 2005). Therefore, the Fe₂O₃ film is
considered as a surface passivation layer, which accounts for the low activity of aged ZVI. It is reported that some ligands, such as oxalate, nitrioltriacetic acid (NTA), or ethylenediaminetetraacetic acid (EDTA), could enhance the yields of ROS in the ZVI/O2 system (Engelhardt et al., 2007; Keenan and Sedlak, 2008; Lee et al., 2008). The ligand effects were explained as enhanced release of Fe(II) by elimination of the surface passivation layer (Fu et al., 2013; Rivero-Huguet and Marshall, 2009) through complexation of ligands with Fe(III), which accelerates the key reactions for the generation of ROS (Reactions (1) and (2)).

\[
\begin{align*}
{\text{Fe}^0} + {\text{O}_2} + 2{\text{H}}^+ & \rightarrow \text{Fe}^{\text{II}} + \text{H}_2\text{O}_2 \\
\text{Fe}^{\text{II}} + \text{O}_2 & \rightarrow \text{Fe}^{\text{III}} + \text{O}_2^-
\end{align*}
\]

where, Fe(II) and Fe(III) denote all forms of ferrous iron and ferric iron, respectively, including the ligand-bound ferrous iron and ferric iron (Fe(II)L and Fe(III)L) and the free ferrous iron and ferric iron ions in the solution (Fe3+/Fe2+).

The removal of the surface passivation layer comprises two steps: (1) adsorption of ligands onto the surface of passivated ZVI, and (2) reductive or non-reductive dissolution (Pania et al., 1996). The complexation between ligands and Fe(II) or Fe(III) is generally favorable to non-reductive dissolution. Thus, the removal potential of the Fe(III)/Fe(II) redox couple varies with the complexing ligands. Generally, ligands in which oxygen atoms serve as the donor to iron tend to stabilize Fe(III), thus decreasing the reduction potential of the Fe(III)/Fe(II) couple and are consequently favorable to reductive dissolution (Welch et al., 2002).

Besides the complexation effect, the dissociable protons from some ligands have been proved to be an important factor in the dissolution of the surface passivation layer (Pania et al., 1996). In addition to the effects on dissolution of the surface passivation layer, the complexation of ligands could also affect the precipitation of Fe(III): most of the ligands can stabilize Fe(III), preventing it from precipitating, and thus inhibit the coprecipitation removal of contaminants. Therefore, for the removal of oxidizable contaminants, the effects of ligands on the ZVI/O2 systems should be considered from these four aspects: dissolution, corrosion, oxidation, and coprecipitation.

In aquatic environments, there are many types of ligands, possessing quite different properties in terms of proton donating ability, complexation ability, and electron accepting/donating ability. These properties will exert different effects on dissolution, oxidation, and coprecipitation. Although the application of ZVI systems for environmental remediation has been extensively studied for two decades, ligand effects on the oxidation removal of contaminants in the ZVI/O2 systems are still unclear.

Arsenite (As(III)) is a toxic oxyanion in aquatic environments, especially in groundwater. In the normal pH range of surface and ground waters, As(III) exists in the neutral form (H₃AsO₃), which is generally harder than arsenate (As(V)) (H₃AsO₄ and H₂AsO₄⁻) to remove through interfacial interactions. Oxidation is a useful strategy in the treatment of As(III)-containing waters. Therefore, arsenite was chosen as a target contaminant in this work to study the ligands’ effects on the ZVI/O2 systems.

In a previous work (Song et al., 2017), five common aquatic ligands (formate, acetate, oxalate, EDTA and phosphate) as well as acetylacetone (AA) were employed to study the ligand effects on nitrate reduction in anoxic ZVI systems. The six ligands cover a large span: from organic to inorganic, from soft Lewis base to hard Lewis base. Therefore, they are good representatives of ligands in aquatic systems. The objective of the present work is to establish a semi-quantitative relationship between some key property parameters of ligands and their effects on ZVI/O2 systems, which might be helpful for the rational design of effective ZVI/O2/ligand systems.

### 1. Materials and methods

#### 1.1. Materials

All chemicals were obtained from commercial sources and used as received without further purification. Analytical grade NaAsO₂ and Na₃H₂AsO₄·7H₂O bought from Sigma-Aldrich, USA were used to make the As(III) and As(V) stock solutions. The ligands added as sodium formate, sodium acetate, potassium oxalate, disodium hydrogen phosphate, sodium dihydrogen phosphate, disodium dihydrogen ethylenediaminetetraacetate (Na₂EDTA), and AA were of analytical purity grade and purchased from Sinopharm Chemical Reagent Co. Ltd., China. Perchloric acid, sodium hydroxide, 2,2'-bipyridine (BPY), thioacetamide, citric acid monohydrate, trisodium citrate dihydrate, ferrous sulfate, hydrogen peroxide (H₂O₂, 30 wt.%), nitric acid (68 wt.%, guaranteed reagent (GR) grade) and hydrochloric acid (36-38 wt.%, GR grade) were bought from Sinopharm Chemical Reagent Co. Ltd., China. Isopropanol (IPA) were purchased from Nanjing Chemical Regent Co. Ltd., China. Nitro blue tetrazolium chloride (NBT) was purchased from Sigma-Aldrich, USA. KBr₄ was purchased from Shandong Xiya Reagent Co. Ltd., China. N,N-diethyl-p-phenylenediamine (DPD) and peroxidase (POD) from horseradish (150 U/mg) were bought from Sigma-Aldrich Germany and Sigma Switzerland, respectively.

Deionized water with a resistivity of 18.25 MΩ-cm was produced by a water purification system (Shanghai Youpu Industrial Co. Ltd., China). The ZVI was used as received from Sinopharm Chemical Shanghai Reagent Co. Ltd., China. It had a mean diameter of 40 μm and a BET (Brunauer-Emmet-Teller) surface area of 4.64 m²/g (Song et al., 2017). As(III) and As(V) stock solutions (1000 mg/L) were prepared with NaAsO₂ and Na₃H₂AsO₄·7H₂O, respectively. Arsenic-containing ligand solutions (As(III) or As(V) 1000 μg/L, ligand 0.5 mmol/L) were prepared by spiking arsenic and ligand stock solutions into purified water. The initial solution pH values were adjusted with 0.1 mol/L HClO₄ or 0.1 mol/L NaOH. Because buffers can have effects on the transformation of ZVI (He et al., 2018), the ZVI/O₂ systems were not buffered. Instead, the solution pH during the reaction was recorded.
1.2. Batch test for arsenic removal

Experiments were conducted by adding 0.25 g Fe⁰ in 250 mL arsenic solution in closed polyethylene terephthalate bottles and mixing in an overhead shaker (8 r/min). The dissolved oxygen concentration was kept at around 8.7 mg/L by frequent opening of the sample bottles to ensure an aerobic condition. After predetermined time intervals, aliquots were taken out with a syringe for further treatment and chemical analysis. All experiments were conducted at 23 ± 1 °C and were run in duplicate.

1.3. Corrosion experiments

The corrosion of a ZVI working electrode (>99% pure, 1 cm², Shanghai CH Instruments Co. Ltd., China) was used to simulate the corrosion of the ZVI particles in arsenic removal experiments (Mishra and Farrell, 2005). The corrosion solution was prepared by spiking 0.5 mmol/L ligand to a 100 mmol/L NaClO₄ solution. The initial solution pH was adjusted to 5.0. Before being immersed in a corresponding corrosion solution for 1 hr, the ZVI working electrode was polished successively with 0.3 and 0.05 μm alpha alumina powder (CH Instruments Co. Ltd., Shanghai, China) between each corrosion experiment.

1.4. Analytical methods

Measurement of As(III) and total arsenic (As(T)) was conducted with a hydride generation atomic fluorescence spectrometer (AF-640, Beijing Beifen-Ruili Analytic Instrument Co. Ltd., China). Prior to analysis, sample solutions were filtered with a 0.22 μm syringe filter. The selective determination of

![Graph](https://example.com/graph.png)

**Fig. 1** – Effects of ligands on the removal of total arsenic (As(T)) and arsenite (As(III)) as well as the evolution of arsenate (As(V)) in the zero-valent iron (ZVI)/O₂ system. Reaction conditions: ZVI 1.0 g/L, initial pH (pH) 5.0, As(III) 1000 μg/L, and ligand 0.5 mmol/L. EDTA: ethylenediaminetetraacetic acid; AA: acetylacetone.
As(III) was based on a modified method with a citric acid–sodium citrate buffer solution as the current-carrying liquid (0.5 mol/L, pH 5.0) (Hug and Leupin, 2003). Prior to analysis, the sample solutions were diluted stepwise to below 10 μg/L with the buffer solution. A solution composed of 2 wt.% KOH and 20 wt.% KBH₄ was employed as the reductant to selectively reduce As(III) to AsH₃. For the analysis of total arsenic, the sample solutions was firstly mixed with 1 mL of concentrated hydrochloric acid and 1 mL of thiocarbamide solution (5 wt.%) for 30–60 min to reduce As(V) to As(III).

In order to distinguish dissolved iron (Fe₅₀) and total iron (Fe₆₀, the sum of dissolved iron and colloidal iron), sample aliquots of the supernatant were treated with or without filtration by 0.22 μm syringe filters, respectively. The samples were acidified by a drop of nitric acid (2 wt.%, GR grade) and then measured with an atomic absorption spectrophotometer (AA-7000, Shimadzu Co., Japan).

A modified DPD-POD method was employed to measure H₂O₂ by addition of BPY and EDTA to minimize the interference of Fe(II) and Fe(III) (Katsoyiannis et al., 2008). After sampling, the solutions were immediately mixed with 200 μL BPY (25 mmol/L in 1 mmol/L HClO₄) to complex the Fe(II). Subsequently, 200 μL EDTA (50 mmol/L) was added to complex Fe(III), followed by the addition of 400 μL phosphate buffer (pH 6.0, 0.5 mol/L). After 1 min, 20 μL DPD (1 wt.% in 0.1 mol/L H₂SO₄) was added, followed by 10 μL of POD reagent (~150 U/mL). The mixed solution was then recorded with an ultraviolet (UV)-visible spectrophotometer (UV2700, Shimadzu Co., Japan). BPY forms a colored complex with Fe(II). Therefore, Fe(II) could be simultaneously determined by absorbance.

Tafel analysis was performed with an electrochemical workstation (CHI600E, Shanghai CH Instruments Co. Ltd., China). Tafel curves were collected using a three-electrode assembly with a spent ZVI electrode as the working electrode, a saturated calomel electrode as the reference electrode, and a platinum wire as the counter electrode. Before Tafel analysis of each spent ZVI working electrode, its open circuit potential was measured. To minimize polarization effects on ligand concentrations at the anode and cathode surfaces, a solution containing 100 mmol/L NaClO₄ was used. Tafel diagrams were produced by polarizing each ZVI electrode +300 mV with respect to its open circuit potential (from −0.8 to −0.2 V) at a scan rate of 10 mV/sec.

Arsenic species on reacted ZVI particles were analyzed with X-ray photoelectron spectroscopy (XPS). The analysis was conducted with an X-ray photoelectron spectrometer (PHI5000 VersaProbe, Ulvac-Phi Inc., Japan) system using monochromatic Al Kα radiation (1486.6 eV). A nonlinear least-square fitting program (XPS peak software 4.1) was used for peak fitting. All binding energies were referenced to the C1s peak at 284.8 eV.

1.5. Calculation approach for dissociable protons and ligand-bound Fe(II)/Fe(III)

The concentration of dissociable protons was calculated based on the pKₐ values of the ligands (Appendix A Table S1), the solution pH, and the dosage of ligands. The concentration of ligand-bound Fe(II)/Fe(III) was calculated based on the stepwise stability constants for the complexation between iron and ligands (Appendix A Table S2), the solution pH, and the dosage of ligands. The sum of these species met with either charge balance or mass balance. The mathematical calculations were conducted with Matlab. The fraction-pH diagram of iron was obtained by plotting the molar ratio of each iron species to the total iron versus solution pH.

1.6. Calculation approach for the reduction potential of Fe(III)/Fe(II)

The ligand effects on the reduction potential of ligand-bound Fe(III)/Fe(II) (E⁰[Fe(III)L/Fe(II)L]) were calculated by the equation below as described in our previous work (Song et al., 2017).

\[
E^0[Fe(III)L/Fe(II)L] = E^0[Fe(III)/Fe(II)] + \frac{RT}{F} \ln \left( \frac{K_{Fe(III)L}}{K_{Fe(II)L}} \right)
\]

where, \( F \) (C/mol) is the Faraday constant, \( R \) (J/(K·mol)) is the universal gas constant, \( T \) (K) is the absolute temperature, \( K_{Fe(II)L} \) and \( K_{Fe(III)L} \) are the stepwise stability constants for the complexation between Fe(II)/Fe(III) and the ligand, respectively.

Fig. 2 – Effects of ligands on the removal of (a) As(III) and (b) As(V) by ZVI. Reaction conditions: ZVI 1.0 g/L, pH 5.0, As(III) or As(V) 1000 μg/L, and ligand 0.5 mmol/L.
2. Results and discussion

2.1. Effects of ligands on arsenic removal by ZVI

To investigate the ligand effects on arsenic removal, the concentrations of As(III) and As(T) were measured in the supernatants of the ZVI/O2/ligand systems with an initial pH (pHi) of 5.0. The difference between the measured concentrations of As(T) and As(III) was the concentration of the accumulated As(V) in the reaction systems. The tested ligands showed distinctly different effects on As(III) and As(V) removal in the ZVI/O2 systems. EDTA significantly enhanced the oxidation of As(III), but the As(T) in the ZVI/O2/EDTA system was nearly unchanged within 120 min (Fig. 1), indicating that the initially dosed As(III) was oxidized to As(V), but was not removed from the solution. Similar to the case in the ZVI/O2/EDTA system, AA enhanced the oxidation of As(III), but inhibited the removal of As(V). Oxalate enhanced the oxidative conversion of As(III) at the early stage and simultaneously enhanced the uptake of As(V). Formate had negligible effects on both the oxidation of As(III) and the uptake removal of As(V), whereas acetate and phosphate exerted drastically inhibitory effects on both the oxidation of As(III) and the uptake of As(V).

The above effects were further verified by individually spiking As(III) or As(V) into the ZVI/O2/ligand systems at pHi 5.0. Similar ligand effects were observed (Fig. 2). Oxalate was the only ligand in this work that accelerated both the oxidation of As(III) and the removal of As(V).

2.2. Ligand effects on dissolution of iron

As shown in Appendix A Fig. S1, both the oxidation of As(III) and the dissolution of iron were decreased with the increase of solution pH. Higher concentrations of Fetot and Fesol were observed at pHi 3.0 than those at pHi 5.0 and 7.0. Similar phenomena were observed in the presence of ligands (Appendix A Fig. S2). The pseudo-first-order kinetics model was used to describe the oxidation of As(III) and the removal of As(T). The low pseudo-first-order rate constants (\(k_1\)) of As(III) in the ZVI/O2/acetate system at pHi 5.0 were consistent with the low pH change (Fig. 3 and Appendix A Tables S3–S4). These results demonstrate that the ligand effects on As(III) oxidation were pH-dependent (Fig. 3a). In the ZVI/O2 system, the pH of As(III) solutions was increased as the reactions proceeded (Fig. 3b). The final pH (pHf) of the solutions converged to a narrow range of median values from 6.1 (pHi = 3.0) to 7.0 (pHi = 7.0). The pKa values of arsenic acid were 2.0, 6.9, and 11.5. In the pH range of 6.1–7.0, and As(V) exists mainly in the form of H2AsO4\(^-\) and HAsO4\(^{2-}\). Such a speciation might affect the electrostatic interaction between As(V) and iron oxides. Therefore, the removal of As(V) might be also affected by the solution pH, but to a much lesser extent than the oxidation of As(III). This is true in the studied systems, as evidenced by the \(k_1\) values of As(III) and As(T) in Fig. 3a.

At pHi 3.0, all six ligands had dissociable protons of concentration in the range of 0.5–1.5 mmol/L (Appendix A Table S1). At pHi 5.0 and 7.0, only EDTA, AA, and phosphate had dissociable protons, and the concentrations of Fetot and Fesol in the three ZVI/O2/ligand systems were higher than those in the other three systems (Appendix A Fig. S2), suggesting that the dissociable protons played a role in the dissolution of iron.

The contribution of dissociable protons was further investigated by Tafel analysis at pHi 5.0. As shown in Fig. 4a, the presence of AA, EDTA and phosphate dramatically enhanced the corrosion current, and the corrosion currents were positively related to the dissociable protons from the ligands. Ligands without dissociable protons, including formate, acetate and oxalate, had no enhancement effect on the corrosion current (Fig. 4a). The presence of acetate even lowered the corrosion current, which might explain the strongly inhibited removal of arsenic (Figs. 2 and 3).

Ligands with dissociable protons can not only provide additional protons but also be able to form surface complexes with iron, resulting in enhanced dissolution of iron. At pH 5.7–7.7 (the pHf of the ZVI/O2 systems with pHi of 5.0 and 7.0, Appendix A Table S4), the dominant species of iron were Fe(II)
and Fe(OH)$_3$ (Appendix A Fig. S3), i.e., the determined Fe$_{sol}$ and Fe$_{tot}$–Fe$_{sol}$ indicate the concentrations of Fe(II) and colloidal Fe(III), respectively. Fe(II) is mainly formed in the corrosion of Fe$^0$ by dissolved O$_2$ (Reaction (1)) and could be further oxidized to colloidal Fe(III) by O$_2$ in neutral solutions (Reaction (4)). In acid solutions, free protons can also bind to the oxide layer and lead to the dissolution of surface oxides (Reaction (5)). The dissolution of iron oxides was by direct dissolution without redox conversion.

$$\text{Fe(II)}_{(aq)} + \frac{1}{4}\text{O}_2 + \frac{5}{2}\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) + 2\text{H}^+ \quad (4)$$

$$\text{Fe}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Fe(III)} + 3\text{H}_2\text{O} \quad (5)$$

where, Fe$_{(II)}$(aq) and Fe(OH)$_3$(s) denote Fe(II) in the solution and the solid Fe(OH)$_3$.

Reductive dissolution involves electron transfer from ligands to surface oxides and subsequent release of Fe(II) (Panias et al., 1996). In the absence of lattice Fe(II) ions, the generation of Fe(II) from surface oxides is a slow process (Panias et al., 1996). This might be able to explain the limited dissolution of iron at pH 7.0 and the negative pH change in the presence of AA (the dissociable protons were not utilized). At pH 5.0, a sufficient amount of Fe(II) was formed through proton-mediated dissolution of iron, which makes the reductive dissolution operative.

To evaluate the ligand effect on the reductive dissolution, the reduction potential of the Fe(III)L/Fe(II)L couples were calculated (Appendix A Table S5), which increased in the order of EDTA < AA < phosphate < oxalate < acetate. As shown in Fig. 4b, there was a positive correlation between the increased corrosion current (with the control as a reference) and the change of the standard reduction potential ($\Delta E^0 = E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) - E^0(\text{Fe(III)L}/\text{Fe(II)L})$). Therefore, we can conclude that the ligand effect on the dissolution was a composite result of the reduced reduction potential due to complexation with the ligand and the increased number of dissociable protons from the ligand.

### 2.3. Ligand effects on formation of ROS

Ligands have been proposed to enhance the oxidation of Fe(II) (Jones et al., 2015; Keenan and Sedlak, 2008; Noradoun and Cheng, 2005) with a generally accepted pathway as a

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**Fig. 4** – Relationship between (a) the concentration of dissociable protons vs. corrosion current (Corr $i$) and (b) the reduction potential change ($\Delta E^0$) caused by ligands vs. the change in corrosion current ($\Delta$Corr $i$). Reaction conditions: ligand 0.5 mmol/L, pH 5.0, and prior to determination, the iron electrode was immersed into ligand solutions containing 100 mmol/L NaClO$_4$ for 60 min.

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**Fig. 5** – Effects of ligands on the generation of (a) H$_2$O$_2$ and (b) Fe(II) (all forms of ferrous iron) in the ZVI/O$_2$ systems. Reaction conditions: ZVI 1.0 g/L, pH 5.0, and ligand 0.5 mmol/L.
one-electron transfer from Fe(II) to O₂ (Reaction (2)). The 
$E^0(\text{O}_2/\text{O}_2^-)$ was reported to be $-0.33$ V while $E^0(\text{Fe}^{3+}/\text{Fe}^{2+})$ was $0.77$ V (Rybak-akimova, 2010). Taking the $E^0$ values into consideration, Reaction (2) is thermodynamically unfavorable. Although the complexation with the tested ligands decreased the $E^0$ of Fe(III)/Fe(II)L (Appendix A Table S5), Reaction (2) is still thermodynamically unfavorable. However, the formation of O₂$^-$ in the ZVI/O₂ systems was observed in both this study and the literature (Keenan and Sedlak, 2008; Noradoun and Cheng, 2005). The $k_1$ of As(III) oxidation in the ZVI/O₂ system was reduced from 0.0151 to 0.0009 min$^{-1}$ by the addition of 2 mmol/L NBT (a O₂$^-$ scavenger). Besides O₂$^-$, we also observed the formation of H₂O₂ in the ZVI/O₂ system (Fig. 5). There are three possible pathways for the formation of H₂O₂: the corrosion of Fe(II) (Reaction (1)), the disproportionation of O₂$^-$ (Reaction (6)) and the reaction of O₂$^-$ with Fe(II) (Reaction (7)). As shown in Reaction (8), H₂O₂ is the precursor of ·OH.

$$
\begin{align*}
2\text{O}_2^+ + 2\text{H}^+ & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 & (6) \\
\text{Fe(II)} + \text{O}_2^- + 2\text{H}^+ & \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2 & (7) \\
\text{Fe(II)} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe(III)} + \text{OH}^- + \text{OH}^- & (8) \\
\text{As(III)} + \text{H}^+ + \text{O}_2^- & \rightarrow \text{As(IV)} + \text{HO}_2^- & (9) \\
\text{As(III)} + \text{OH}^- & \rightarrow \text{As(IV)} & (10)
\end{align*}
$$

Although the reaction between As(III) and O₂$^-$ (Reaction (9)) has been widely used to explain the oxidation mechanism

Fig. 6 – As 3d X-ray photoelectron spectroscopy (XPS) spectra for the particles collected from ZVI/O₂/ligand systems after reaction for 2 hr. Reaction conditions: ZVI 1.0 g/L, pH 5.0, As(III) 1000 μg/L, and ligand 0.5 mmol/L.
of As(III), we have clarified in a recent work (Chen et al., 2018) that this reaction is thermodynamically unfavorable and the actual reactive species for the oxidation of As(III) was -OH (Reaction (10)). Addition of 100 mmol/L IPA (a OH scavenger) to the ZVI/O2 system reduced the k1 of As(III) oxidation to 36% of the control, indicating the role of ·OH as well as some other oxidants, such as Fe(IV) (Katsosyianis et al., 2008).

A previous study reported that the ligand-enhanced Fenton reaction did not necessarily facilitate As(III) oxidation (Wang et al., 2013). This conclusion is premised on the ligand being present in excess. In our experiments, this was not established since Fe0 was an adequate source of Fe2+ and the dose of ligand was only 0.5 mmol/L. The ligand-enhanced Fenton reaction did have a positive effect on the oxidation of As(III).

\[ \text{Fe(II)} + \cdot \text{OH} \rightarrow \text{Fe(III)} + \text{OH}^- \quad (11) \]

The addition of EDTA significantly increased the formation of H2O2, with a peak concentration of 4.29 μmol/L at 10 min (Fig. 5a). During this period, the concentration of coexisting Fe(II) was low due to the Fenton reaction (Reaction (8)) and oxidation of Fe(II) by the generated ·OH (Reaction (11)). In the presence of AA, the concentration of H2O2 reached a peak value of 0.90 μmol/L at 5 min and then decreased, while the concentration of Fe(II) was steadily increased (Fig. 5). The concentration of H2O2 in the control was comparable to that in the ZVI/O2/AA system, whereas the concentration of Fe(II) in the control was much lower. In the ZVI/O2/oxalate system, the H2O2 concentration was peaked at the very beginning (less than 30 sec) and the Fe(II) concentration was much larger in the stable phase than that in the control (Fig. 5b). In the ZVI/O2/formate and ZVI/O2/acetate systems, the detected Fe(II) concentrations were lower than that in the control, whereas the H2O2 concentrations were similar to the control.

EDTA acted as both a ligand and a target contaminant in the ZVI/O2 system (Noradoun and Cheng, 2005). The presence of such ligands may suppress the oxidation of As(III) because of the competition for ·OH. The rate constants for the reactions of ·OH with the tested ligands are listed in Appendix A Table S5. AA was obviously a powerful competitor with Fe(II) for ·OH (The rate constant of Fe(II) and ·OH is 4.3 × 10^15 L/(mol-sec)) (Buxton et al., 1988), which explained the higher Fe(II) concentration in the ZVI/O2/AA system as compared to that in the control. With a relatively low reaction rate constant with ·OH, oxalate should be less competitive for ·OH with the target As(III), which might explain the effective oxidation of As(III) in the ZVI/O2/oxalate system.

Now that the formation of O2^- was confirmed, the question is how the reaction occurred. It was reported that Fe(II) adsorbed to hematite at pH 7.5 exhibited a reduction potential of ~210 mV (vs. standard hydrogen electrode (SHE)), which is far lower than that of aqueous Fe(II) alone (+233 mV vs. SHE) (Liger et al., 1999). Besides the complexation with ligands, the adsorption to the surface might be helpful for the initially thermodynamically unfavorable reaction to occur.

For the formation of ROS in the ZVI/O2/ligand system, another possibility is O2 activation via oxygen binding to the metal center, which did not involve the production of O2^- (Rybak-akimova, 2010). An example is the four-step activation mechanism in the Fe(II)-EDTA-O2 system (Bernaconi and Baerends, 2009; Jones et al., 2015; Seibig and van Eldik, 1997): (1) the binding of O2 to the Fe(II)-EDTA complex (Reaction (12)), (2) an electron transfer process in [Fe(II)-EDTA(O2)] to form Fe(III)-superoxo species, [Fe(III)-EDTA(O2)] (Reaction (13)), (3) the complexation of [Fe(III)-EDTA(O2)] with another Fe(II)-EDTA to form the peroxy-complex, [EDTA-Fe(III)(O2^-)Fe(III)-EDTA] (Reaction (14)), and (4) fast decomposition of the peroxy-complex to H2O2 (Reaction (15)) or Fe(IV) (Reaction (16)).

\[ \text{Fe(II)-EDTA} + \text{O}_2 \rightarrow [\text{Fe(II)-EDTA}(\text{O}_2^-)] \quad (12) \]
\[ [\text{Fe(II)-EDTA}(\text{O}_2^-)] \rightarrow [\text{Fe(III)-EDTA}(\text{O}_2^-)] \quad (13) \]
\[ [\text{Fe(III)-EDTA}(\text{O}_2^-)] + \text{Fe(II)-EDTA} \rightarrow [\text{EDTA-Fe(III)(O2^-)Fe(III)-EDTA}] \quad (14) \]
\[ [\text{EDTA-Fe(III)(O2^-)Fe(III)-EDTA}] + \text{2H}^+ \rightarrow \text{2Fe(III)-EDTA} + \text{H}_2\text{O}_2 \quad (15) \]
\[ [\text{EDTA-Fe(III)(O2^-)Fe(III)-EDTA}] \rightarrow \text{2Fe(IV)-EDTA} \quad (16) \]

A positive correlation was observed between the concentration of ligand-bound Fe(II) and the k1 of As(III) oxidation (Appendix A Fig. S4), providing further support for the role of complexation in the generation of ROS.

2.4. Ligand effects on Fe(III) precipitation

The oxidation of Fe(II) leads to the production of ferric iron and the subsequent formation of iron hydroxides. Accompanying the precipitation process, arsenic species were removed from the solutions. The complexation of ligands with ferric iron prevented precipitation, and consequently reduced the removal of As(V). As shown in Fig. 6, due to the strong complexation ability of EDTA with ferric ion (Appendix A Table S2), there was no precipitation in the ZVI/O2/EDTA system. As a consequence, no arsenic species was observed in
the XPS spectrum of the EDTA sample. In the other samples, the XPS spectra revealed the presence of both As(III) and As(V) with binding energies at 44.5 and 45.5 eV, respectively. The distribution of arsenic in aqueous and solid phases is shown in Fig. 7. In brief, oxalate enhanced the phase transfer of arsenic from aqueous to solid phases, whereas EDTA, phosphate, and acetate inhibited this transfer. This was consistent with the previous results.

3. Conclusions

To sum up, the ligand effects on the removal of As(III) by ZVI/O₂ are illustrated in Scheme 1. The As(III) removal was comprised of four processes: dissolution, corrosion, oxidation and coprecipitation. The ligand effect on the dissolution process was a composite result of increased dissociable protons from the ligand and a decrease in the reduction potential by ligand complexation. More dissociable protons and a greatly reduced reduction potential were favorable for the dissolution of the surface passivation layer. The corrosion of exposed Fe⁰ from dissolution of the passivation layer led to the formation of ROS. In terms of ROS, the ligands were double-edged swords. The reduced reduction potential of the Fe(III)/Fe(II) couple caused by ligand complexation was favorable for the generation of ROS, whereas the ligands could also compete with the target contaminants for the generated ROS, especially ·OH. The addition of ligands was undoubtedly detrimental to precipitation. The stronger the complexation ability, the lower was the removal of the target contaminants by coprecipitation. Therefore, the selection of ligands for the ZVI/O₂ system depends on the treatment goal. If oxidation is the major demand, strong ligands, such as EDTA and AA, could be good candidates. If the objective is complete removal, moderate ligands, such as oxalate, are suitable ones. The secondary pollution caused by the ligands and their oxidation products is also an issue for discussion. The established relationship between the properties of ligands and the oxidative removal of As(III) provides us a useful tool for screening suitable ligands for water treatment. The knowledge is also helpful for us to better understand the cycling of iron in natural and engineered systems.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jees.2019.05.023.

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