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REVIEW ARTICLE

Redox reactions of iron and manganese oxides in complex systems

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HIGHLIGHTS

- Mechanisms of redox reactions of Fe- and Mn-oxides were discussed.
- Oxidative reactions of Mn- and Fe-oxides in complex systems were reviewed.
- Reductive reaction of Fe(II)/iron oxides in complex systems was examined.
- Future research on examining the redox reactivity in complex systems was suggested.

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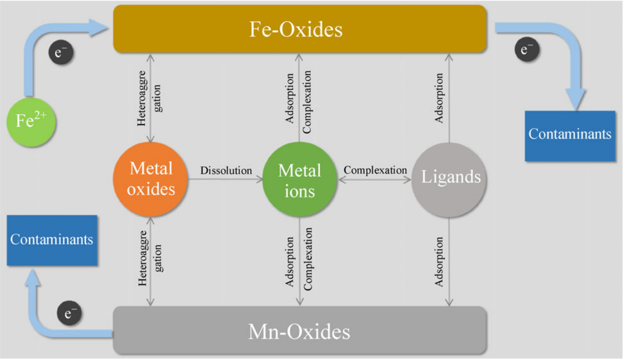
GRAPHIC ABSTRACT



ABSTRACT

Conspectus: Redox reactions of Fe- and Mn-oxides play important roles in the fate and transformation of many contaminants in natural environments. Due to experimental and analytical challenges associated with complex environments, there has been a limited understanding of the reaction kinetics and mechanisms in actual environmental systems, and most of the studies so far have only focused on simple model systems. To bridge the gap between simple model systems and complex environmental systems, it is necessary to increase the complexity of model systems and examine both the involved interaction mechanisms and how the interactions affected contaminant transformation. In this Account, we primarily focused on (1) the oxidative reactivity of Mn- and Fe-oxides and (2) the reductive reactivity of Fe(II)/iron oxides in complex model systems toward contaminant degradation. The effects of common metal ions such as Mn^{2+}, Ca^{2+}, Ni^{2+}, Cr^{3+} and Cu^{2+}, ligands such as small anionic ligands and natural organic matter (NOM), and second metal oxides such as Al, Si and Ti oxides on the redox reactivity of the systems are briefly summarized.

1 Introduction

Iron and manganese are the first and third most abundant transition metals in the earth's crust (Martin, 2005). Redox reactions of Fe- and Mn-oxides play essential roles in the fate and transformation of numerous organic and inorganic contaminants in the environment (Klausen et al., 1995; Zhang et al., 2008; Zhang and Weber, 2013) and the global geochemical cycles of many elements, such as O, N, P and S (Borch et al., 2010; Sunda, 2010). These reactions have been widely accepted as surface reactions, and the change in the oxide surface properties would significantly influence the overall reactivity (Anderson and Benjamin, 1990b; Meng and Letterman, 1993; Taujale et al., 2016; Huang et al., 2019a; Huang et al., 2019b). They might also substantially alter contaminants' solubility, toxicity, and bioavailability. Therefore, the redox reactions of Fe- and Mn-oxides should be considered in many areas such as site remediation and chemical risk assessments.

Fe- and Mn-oxides typically exist in mixtures with other

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metal oxides (e.g., Al- and Si-oxides), metal ions (e.g., Zn^{2+}), and/or ligands (e.g., NOM) in aquatic and soil environments. Despite years of investigation on the redox reactions of Fe- and Mn-oxides, to date, most previous studies have only focused on the roles of single metal oxides (Klausen et al., 1995; Charlet et al., 1998; Zhang and Huang, 2005; Huang et al., 2018). However, the surface and bulk properties of metal oxide mixtures behave largely differently from those of single metal oxides in natural aquatic environments (Anderson and Benjamin, 1990b). For instance, metal oxides might undergo hetero-aggregation and influence the adsorption capacity through altering the number of surface sites and surface charges (Anderson and Benjamin, 1990a,b; Meng and Letterman, 1993; Huang et al., 2019a) and contaminant redox degradation (Taujale and Zhang, 2012; Huang et al., 2019a). Therefore, it is imperative to investigate oxide mixtures containing second metal oxides to enable more accurate prediction of the fate and transformation of numerous contaminants in the environment.

Natural organic matter (NOM) is a complex mixture of organic materials that vary from one source to another. It is ubiquitous in natural environments and has a large impact on the fate and transformation of contaminants (Davis, 1984; Redman et al., 2002). The adsorption of NOM onto Fe- and Mn-oxides can influence their physicochemical properties, e.g., colloidal stability or electrophoretic mobility (Gu et al., 1994). Thus, studies should be carried out to examine the interactions between NOM and metal oxides and to examine how NOM affects the redox reactivity of Fe- and Mn-oxides. This will enable the studied model systems to more accurately resemble actual environmental systems.

In this account, we focus on assessing recent developments and current understanding in the redox reactions of Fe- and Mn-oxides in complex systems, which will provide a bridge to connect the findings from simple model systems with those from natural environmental systems.

2 Oxidative reaction in complex systems

Manganese oxides have high reduction potentials and are able to effectively oxidize a wide range of organic contaminants, including phenols (Stone, 1987), anilines (Laha and Luthy, 1990), and other aromatic compounds (Zhang and Huang, 2003; Zhang and Huang, 2005; Zhang et al., 2008; Huang et al., 2018). Many studies have reported the surface involved reaction kinetics and mechanisms for oxidative degradation of aromatic compounds (ArXH) by single Mn oxides, as shown in Eqs. (1)–(5) (Stone, 1987; Zhang et al., 2008; Huang and Zhang, 2019b).

$$>\mathrm{Mn^{IV}} + \mathrm{ArXH} \rightleftharpoons (\mathrm{Mn^{IV}},\mathrm{ArXH}) \tag{1}$$

$$(>\mathrm{Mn^{IV}},\mathrm{ArXH}) \rightleftharpoons (\mathrm{Mn^{III}},\mathrm{ArX}\cdot) + \mathrm{H^+} \tag{2}$$

$$(>\mathrm{Mn^{III}},\mathrm{ArX}\cdot) \rightleftharpoons \mathrm{Mn^{III}} + \mathrm{ArX}\cdot \tag{3}$$

$$>2\mathrm{Mn^{III}} \rightleftharpoons \mathrm{MnO_2} + >\mathrm{Mn^{II}} \tag{4}$$

$$\mathrm{ArX}\cdot \rightleftharpoons \mathrm{products} \tag{5}$$

It is generally believed that either precursor complex formation (Eq. (1)) or electron transfer (Eq. (2)) is the rate-limiting step in the oxidative reactions of MnO_2. These reactions typically occur on the oxide surface; thus, the physiochemical properties of MnO_2, such as Mn(III) content, oxygen species, and surface area, can dramatically influence its oxidative reactivity (Nico and Zasoski, 2000; Simanova and Peña, 2015; Huang et al., 2018; Wang et al., 2019). Furthermore, the change on the oxide surface properties will likely affect either the precursor complex formation or the electron transfer and, hence, the overall reactivity (Fig. 1).

2.1 Effects of metal ions on the oxidative reactivity

Metal ions, such as Mn^{2+}, Ca^{2+}, Ni^{2+}, Cr^{3+} and Cu^{2+}, could decrease the oxidative reactivity (Klausen et al., 1997; Zhang and Huang, 2003; Barrett and McBride, 2005). (Zhang and Huang, 2003) showed that the inhibitory effect of metal ions deceased in the order: $Mn^{2+} > Zn^{2+} > Ca^{2+}$. This is because the adsorption of these three metal ions on MnO_2 decreased in the same order (Morgan and Stumm, 1964), inhibiting the reactivity. Furthermore, the adsorbed Mn^{2+} can block the reactive Mn (IV) surface sites, also decreasing the reactivity. Besides blocking reactive sites, the adsorbed Mn^{2+} can lower the reduction potential (E) to slow the electron transfer in the oxidation of contaminants (Eq. (6)) (Li et al., 2008; Zhang et al., 2008):

$$E = E_0 - \frac{RT}{nF}\log\frac{[\mathrm{Mn^{2+}}]}{[\mathrm{H^+}]^4} \tag{6}$$

where E_0 is the initial redox potential of manganese oxides; R is the universal gas constant (8.314 J/mol/K), T is the absolute temperature (Kelvin); n is the number of electrons in for the reaction; and F is the Faraday constant (96,485 C/mol).

Besides, some metal ions might even be involved in the redox reaction, such as Cr^{3+}. The inhibitory effect of Cr^{3+} results from the reaction between Cr^{3+} and Mn(IV) to consume Mn(IV), as the simplest case shown in Eq. (7) (Eary and Rai, 1987).

$$3\mathrm{MnO_2} + 2\mathrm{H_2O} + \mathrm{Cr^{3+}} \rightarrow 3\mathrm{Mn^{2+}} + 2\mathrm{HCrO_4^-} \tag{7}$$

However, Wang et al. discovered that Ca^{2+} and Mg^{2+} promoted the oxidation of fulvic acid by birnessite at the

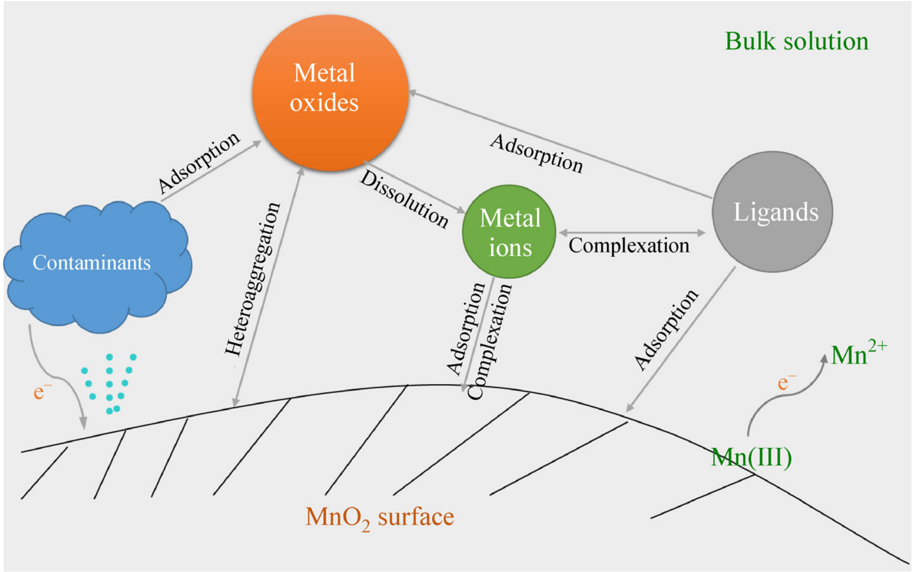


Fig. 1 MnO_2 surface-mediated oxidation of contaminants in complex systems.

early stage, but the mechanism remained unclear (Wang et al., 2019). It should be noted that studies have determined that different reactive sites, such as Mn(III, IV) in MnO_2 sheets, Mn(III,IV) at particle edges, and Mn(III) in interlayers, have different oxidizing abilities (Manceau et al., 1997; Yu et al., 2012). Mn(III) has been confirmed to be more reactive than Mn(IV) in the oxidation of bisphenol A (Huang et al., 2018), Cr^{3+} (Nico and Zasoski, 2000), and ammonia (Anschutz et al., 2005), but less reactive in the oxidation of As(III) (Zhu et al., 2009). Therefore, the interactions between metal ions and various reactive sites on MnO_2 and how they influence the electron transfer warrant further research.

2.2 Effects of ligands on the oxidative reactivity

The effects of anionic ligands on the oxidative reactivity of manganese oxides can be ligand specific. Both inorganic (e.g., phosphate, sulfate, nitrate and chloride) and organic ligands (e.g., small ligands such as oxalic acid, citric acid, malic acid, and pyrophosphate (PP) and NOM) have been revealed to mostly decrease the oxidative reactivity of manganese oxides (Klausen et al., 1997; Ge and Qu, 2003; Zhang et al., 2008; Zhang et al., 2012). The inhibitory effects can be summarized as: (1) the ligands such as sulfate and nitrate compete with the chemicals for the binding sites on MnO_2; and/or (2) the ligands such as oxalic acid and humic acid cause the reductive dissolution of MnO_2 to release Mn^{2+} ions, which is a strong inhibitor, as mentioned in section 2.1 (Klausen et al., 1997; Zhang and Huang, 2003; Lu et al., 2011). HPO_4^{2-} has been reported to have a higher inhibitory effect than other inorganic ligands (Cl^-, NO_3^-, and SO_4^{2-}) because HPO_4^{2-} can firmly adsorb onto the MnO_2 surface (Yao and Millero, 1996; Lu et al., 2011).

The addition of PP has been demonstrated to inhibit the Cr^{3+} oxidation by MnO_2, because PP can solidly complex with Mn(III) to lower the Mn(III) availability (Nico and Zasoski, 2000). However, some researchers observed that PP enhanced the oxidation kinetics of bisphenol A and triclosan (Gao et al., 2018; Huang et al., 2018). This is because the abundance of Mn(III) is key in determining the oxidative reactivity, and PP can stabilize Mn(III) against disproportionation (Eq. (8)) (Huang et al., 2018). Further studies are therefore needed to elucidate the above different effects, such as the oxidative reactivity of Mn(III)-PP toward different chemicals. For instance, Mn(III)-PP has been known to be able to oxidize some chemicals, such as phenols (Jiang et al., 2009; Jiang et al., 2010; Gao et al., 2018), but not others, such as carbamazepine and methyl p-tolyl sulfoxide (Gao et al., 2018).

$$2\mathrm{Mn(III)} + 2H_2O \rightarrow \mathrm{Mn(II)} + MnO_2 + 4H^+ \qquad (8)$$

Humic acid (HA) displayed either promotive or inhibitive effects on the oxidative reactivity of MnO_2. On the one hand, HA exhibited a promotive effect in the degradation of contaminants including methylene blue, nonylhenol, 4-n-nonylphenol, 4-tert-octylphenol, and 17β-estradiol (Xu et al., 2008; Zhu et al., 2010; Lu and Gan, 2013). This is because HA can strongly complex with Mn(II) to decrease the adsorption of Mn^{2+} on MnO_2 surfaces and hence eliminate the large inhibitory effect of the adsorbed Mn^{2+} (Xu et al., 2008; Zhu et al., 2010). On the other hand, HA inhibited the oxidative reactivity of MnO_2 to degrade contaminants, such as 4-chloroaniline, 17β-estradiol and lincosamide, because it blocked the surface reactive sites to prevent the contaminants from being adsorbed and increased the extent of MnO_2 dissolution

(Klausen et al., 1997; Chen et al., 2010; Sun et al., 2016). HA is a complex compound containing various functional groups, which are known to exert different effects on redox reactions (Vindedahl et al., 2016). Therefore, more mechanistic investigation into the effect of the functional groups of HA on the oxidative reactivity of MnO_2 is required to understand these different results.

2.3 Effects of second metal oxides on the oxidative reactivity

Metal oxides have been shown to influence the oxidative reactivity of MnO_2, with different metal oxides exhibiting varying effects and mechanisms. These effects can be summarized as: (1) the interactions between the second metal oxides and MnO_2 (e.g., heteroaggregation, surface complexation/precipitation) mostly inhibited the MnO_2 reactivity; and (2) the second metal oxides might compete with MnO_2 in adsorbing the chemical contaminants (Taujale and Zhang, 2012). For example, the inhibitory effect on the oxidative reactivity of MnO_2 by second metal oxides deceased in the order: $Al_2O_3 > SiO_2 > TiO_2$ (Taujale and Zhang, 2012). This is because both Al_2O_3 and SiO_2 can release Al and Si ions into the aqueous phase due to their dissolution. When examining the relative contribution of the released metal ions and metal oxide particles to the overall inhibitory effect, it was found that the released Al and Si ions had the dominant inhibitory effect (Fig. 2), mainly due to the surface complexation/precipitation of the ions on the surface of MnO_2 (Taujale and Zhang, 2012). TiO_2 only decreased the oxidative reactivity of MnO_2 when a limited amount of triclosan was present, because a strong adsorption of triclosan on TiO_2 inhibited the precursor complex formation between triclosan and the MnO_2.

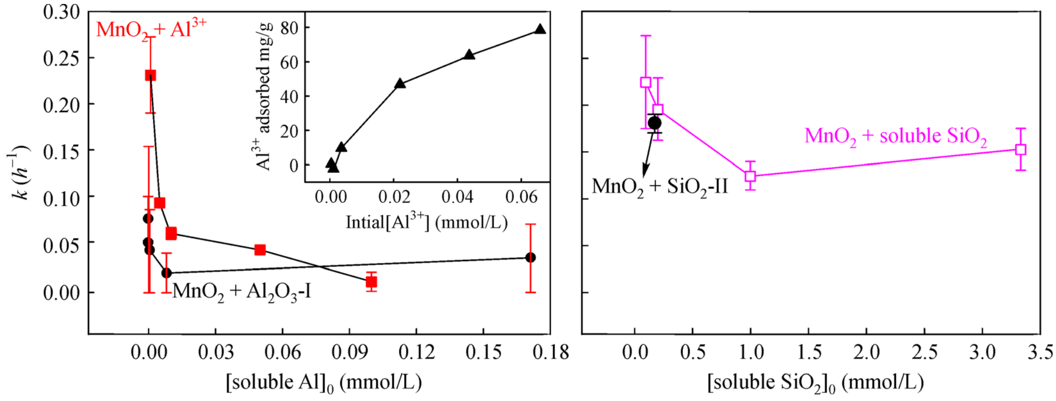
Iron oxides have also been reported to inhibit the oxidative reactivity of MnO_2 (Zhang et al., 2015). The authors also attempted to investigate the relative contribution of (1) soluble Fe^{3+} released from goethite dissolution and (2) aggregation of goethite particles to the overall reactivity. The released Fe^{3+} had limited inhibitory effect because of the poor solubility of iron oxides under a wide range of pH conditions, while the blocking of the surface reactive sites by the heteroaggregation between goethite and MnO_2 (observed based on the sedimentation experiments and TEM images) was the major contributor to the decrease in the oxidative reactivity. The inhibitory effect further increased as the particle size decreased or the goethite loading increased.

Zhang's group then increased the complexity of the model systems and investigated the effect of NOM on the redox reactivity in ternary systems of two types of metal oxides plus NOM (Zhang et al., 2015; Taujale et al., 2016). To differentiate the effects due to NOM from those due to the second metal oxides, the parameter P was introduced (Eq. (9)). A P value of 1 suggests that the NOM does not have any additional effects on the reactivity, while a higher P value indicates higher oxidative reactivity of MnO_2 and vice versa.

$$P = \frac{k_{with\_NOM}}{k_{without\_NOM}} \times 100\% \tag{9}$$

where k_{with_NOM} is the reaction rate constant of the ternary system (metal oxide + MnO_2 + NOM), while $k_{without\_NOM}$ is the reaction rate constant of the binary system (metal oxide + MnO_2).

Using the obtained P values, the authors revealed that higher concentrations of model NOM (Aldrich humic acid, alginate, or pyromellitic acid) in the ternary systems (MnO_2 + goethite + NOM) had larger P values, indicating that the NOM promoted the oxidative reactivity of MnO_2 in the ternary mixtures. This was ascribed to the observation that NOM enhanced the extent of homoaggregation within the iron oxides, which inhibited the extent of heteroaggregation between MnO_2 and iron oxides (Zhang et al., 2015).



(a) (b)

Fig. 2 Effect of (a) soluble Al ions and Al_2O_3 and (b) soluble silicate and SiO_2 particle on the oxidation of triclosan by MnO_2 (Taujale and Zhang, 2012).

The authors also studied another ternary system of $MnO_2 + Al_2O_3 + HA$ and found that the reactivity of $MnO_2 + Al_2O_3 + HA$ was different from that of $MnO_2 +$ Al ions + HA, indicating that Al ions surprisingly did not play a dominant role in influencing the oxidative reactivity in the system of $MnO_2 + Al_2O_3 + HA$. This is drastically different from the binary system of $MnO_2 + Al_2O_3$, as mentioned above, because HA inhibited the dissolution of Al_2O_3 (Zhang et al., 2015). Therefore, the change in the heteroaggregation pattern between Al_2O_3 and MnO_2 (based on sedimentation experiments) upon the addition of HA was of great importance in affecting the oxidative reactivity in the ternary systems. Similar results were also obtained for the ternary systems of $MnO_2 + Al_2O_3 +$ alginate and $MnO_2 + Al_2O_3 +$ pyromellitic acid (Taujale et al., 2016), suggesting that this may be a general phenomenon in similar ternary mixtures.

2.4 Oxidative reactivity of iron oxides in complex systems

Besides MnO_2, iron oxides have been used to oxidize a wide range of contaminants, including phenols, aniline, hydroquinones and fluoroquinolone (LaKind and Stone, 1989; Zhang and Huang, 2007). Compared with MnO_2, iron oxides generally have lower oxidizing ability, with the reduction potentials 0.66–0.67 V vs. 1.23 V for MnO_2 (Eqs. (10) and 11) (LaKind and Stone, 1989).

$$\alpha-\mathrm{FeOOH} + 3\mathrm{H}^+ + \mathrm{e}^- \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{H_2O},\ E^0 = 0.67\mathrm{V} \tag{10}$$

$$\alpha-\mathrm{Fe_2O_3} + 6\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow 2\mathrm{Fe}^{2+} + 3\mathrm{H_2O},\ E^0 = 0.66\mathrm{V} \tag{11}$$

Similar to MnO_2, the oxidation of iron oxides is also considered as surface-related (LaKind and Stone, 1989; Zhang and Huang, 2007; Zhang et al., 2019). Therefore, the addition of metal ions, ligands and second metal oxides can influence the surface properties of iron oxides and thus their reaction kinetics. Sulfate, phosphate and Ca^{2+} at low concentrations ([sulfate] < 0.1 mmol/L, [phosphate] = 0.001–1 mmol/L, and $[Ca^{2+}]$ = 0.01–10 mmol/L) exhibited a negligible effect on the oxidative reactivity of goethite, but decreased the oxidative reactivity at high concentrations ([sulfate]>1 mmol/L) (LaKind and Stone, 1989). Such an inhibitory effect is because these ligands and metal ions might block the surface reactive sites toward the contaminants. This result is different from a later study on the effect of phosphate on the oxidative degradation of anthraquinone-2,6-disulfonate (AH_2DS) by hematite (Liu et al., 2007). Here, phosphate was demonstrated to significantly inhibit the oxidative reactivity of hematite due to its strong complexation with hematite (Liu et al., 2007). In addition, Fe^{2+} has been reported to decrease the oxidative degradation of anthraquinone-2,6-disulfonate (AH_2DS) by hematite through two mechanisms: (1) Fe^{2+} competes with AH_2DS for the surface reactive sites on the hematite surface; and (2) Fe^{2+} as a reaction product decreases the Gibbs free energy of the reaction (Eq. (12)) (Liu et al., 2007).

$$\mathrm{AH_2DS}^{2-} + \mathrm{Fe_2O_3} + 4\mathrm{H}^+ = \mathrm{AQDS}^{2-} + 2\mathrm{Fe}^{2+} + 3\mathrm{H_2O} \tag{12}$$

In a recent work, Zhang et al. (2019) attempted to elucidate the interactions between goethite and Al_2O_3, and to understand how the interactions affected the oxidative reactivity of goethite (Zhang et al., 2019). Not surprisingly, Al_2O_3 exhibited a strong inhibitory effect on the oxidative degradation of hydroquinone by goethite at pH 3. However, unlike the binary system of $MnO_2 + Al_2O_3$ (Taujale and Zhang, 2012), the release of Al ions due to Al_2O_3 dissolution did not affect the reactivity of goethite. Instead, the amount of Fe^{3+} released from the goethite dissolution at pH 3 exhibited a good linear correlation with the obtained reaction rate, indicating that the inhibitory effect was due to the decreasing amount of Fe^{3+} in the presence of Al_2O_3. This difference pointed to the important role of solution conditions such as pH and the types of oxides in affecting the interactions between oxides. It also serves as a reminder to future researchers that when studying complex mixtures, we should always keep the complexity in mind and carefully consider all possible reactions and reaction conditions.

3 Reductive reactions in complex systems

Regarding reductive transformation of contaminants, surface associated Fe(II) has been well documented to be a major reductant and can reduce a wide range of contaminants, including U(VI) (Liger et al., 1999), technetium (Peretyazhko et al., 2009), nitroaromatic compounds (Klausen et al., 1995), CCl_4 (Amonette et al., 2000), polyhalogenated methanes (Pecher et al., 2002), and N-O containing compounds (Li et al., 2019).

Until now, the reasons on how iron oxides significantly enhanced the reductive reactivity of Fe(II) are still not well understood. Previous studies proposed that it might result from the sorbed Fe(II) coordinated with O-donor atoms on the surface of iron oxides, similar to hydroxylated Fe(II) species in aqueous solution (Wehrli et al., 1989). Surface complexation modeling has been employed to examine the formed sorbed Fe(II) species, and $Fe^{III}OFe^{II}OH$ was believed to be the dominant reactive species (Charlet et al., 1998; Liger et al., 1999). However, it has been shown that stable sorbed Fe(II) did not exist because of fast electron transfer between the sorbed Fe(II) and iron oxides (Williams and Scherer, 2004; Larese-Casanova and Scherer, 2007). Moreover, negligible reduction of nitrobenzene was observed when aqueous Fe(II) was removed from the solution, indicating that aqueous Fe(II) was also involved in the reductive reaction (Williams and Scherer, 2004). In addition, Yanina and Rosso (2008) demonstrated a critical role of electron transport through the bulk solid in interfacial redox reactivity (Yanina and Rosso, 2008). Therefore, Gorski and Scherer proposed a revised conceptual model for Fe(II) adsorption onto Fe(III) oxides based on a semiconductor model (Becker et al., 2001; Park and Dempsey, 2005; Barnes et al., 2009; Gorski and Scherer, 2011). In the model, electrons from the sorbed Fe (II) are transferred to the bulk iron oxide particles and effectively doped the iron oxides (considered as semiconductors) with additional electrons, part of which are eventually transferred to reduce the contaminants.

Different factors, such as pH, the amount of Fe(II) sorbed, and surface sorbed Fe(II) species, have been shown to influence the reactivity (Elsner et al., 2004; Zhang and Weber, 2013; Huang et al., 2019a; Huang et al., 2019b). Typically, higher amount of sorbed Fe(II) would result in higher reactivity. Despite the large volume of research that focused on simple model systems containing an Fe(III) mineral and soluble Fe^{2+}, which fails to represent actual environmental conditions, there has been only a few studies investigating the reductive reactivity of Fe^{2+}/iron oxides in complex systems (Fig. 3).

3.1 Effect of metal ions on the reductive reactivity

Metal ions can influence the reductive reactivity of Fe^{2+} complexed with iron oxides. For example, Co^{2+}, Ni^{2+}, and Zn^{2+} exhibited inhibitory effects on the reductive reactivity of Fe^{2+} treated goethite, which was ascribed to the competitive adsorption between these metal ions and Fe^{2+} (Maithreepala and Doong, 2004). However, Cu^{2+} demonstrated a significant enhancement in the reductive reactivity, because Cu(I), reduced from Cu^{2+} by Fe^{2+}, acted as an additional reductant to enhance the reaction rate (Maithreepala and Doong, 2004). In addition, the reductive reactivity of Fe^{2+}/goethite might vary with the amount of Cu^{2+} added. The reactivity increased in the presence of Cu^{2+} with its concentration lower than 0.375 mmol/L, but decreased when the Cu^{2+} concentration was between 0.375 and 1 mmol/L (Tao et al., 2013). The authors believed that the reactivity was related to the density of the sorbed Fe(II) on goethite, and the addition of Cu^{2+} increased it when $[Cu^{2+}]$ was lower than 0.375 mmol/L, while decreased when $[Cu^{2+}]$ was higher than 0.375 mmol/L. However, the mechanism on how the addition of Cu^{2+} influenced the density of sorbed Fe(II) is not clear yet.

3.2 Effect of ligands on the reductive reactivity

Anionic ligands can also influence the reductive reactivity of Fe^{2+}/iron oxides. One of the widely studied ligands is NOM, which exhibited either promotive or inhibitive effects on the reductive reactivity of Fe^{2+}/iron oxides (Colón et al., 2008; Zhang and Weber, 2009; Vindedahl et al., 2016). On the one hand, NOM can enhance the reactivity. (Zhang and Weber, 2009) verified that the reduced Suwannee River NOM and reduced juglone enhanced the reductive degradation of 4-cyano-4’-aminoazobenzene by Fe^{2+}/goethite, because they functioned as electron shuttles and were able to reduce the goethite

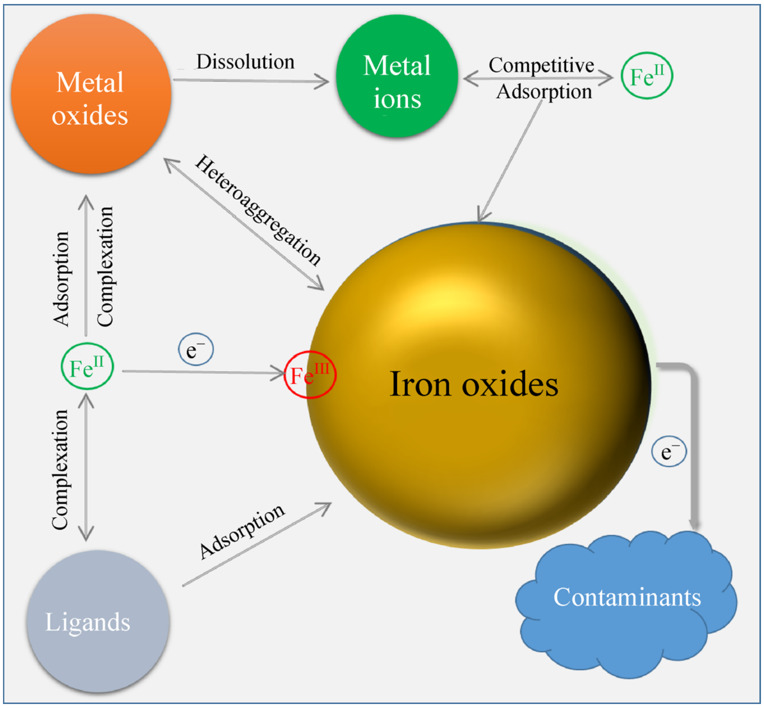


Fig. 3 Reduction of contaminants by Fe(II)/iron oxides in complex systems.

surface to increase the formation of surface sorbed Fe(II).

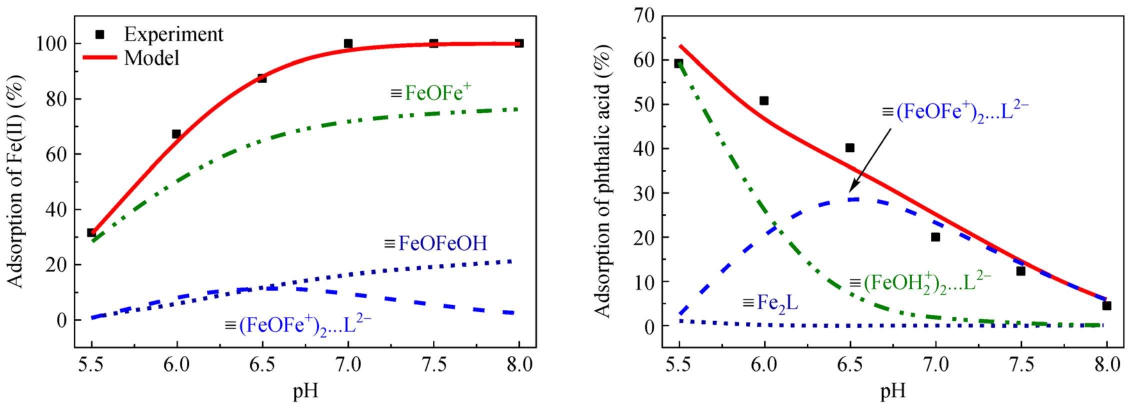
On the other hand, NOM can decrease the reductive reactivity due to multiple reasons (Colón et al., 2008; Vindedahl et al., 2016). First, the reduction rates and capacity of the system having Suwannee river humic acid (SRHA) added after Fe(II) was equilibrated with goethite (G/Fe(II)/SRHA) was lower than that having Fe(II) added after SRHA was equilibrated with goethite (G/SRHA/Fe (II)). This might be ascribed to (1) the oxidation and/or complexation of the surface-sorbed Fe(II) by SRHA; and/or (2) SRHA blocked electron transfer from the surface sorbed Fe(II) to the chemical probes (Colón et al., 2008). Second, compared with (Colón et al., 2008), NOM in the study of (Zhang and Weber, 2009) had been chemically reduced, so the oxidation state of the NOM should be the main reason for the different effects observed in these two studies. Third, the characteristics of NOM can also influence the reactivity. Vindedahl et al. discovered that the increased molecular weight and nitrogen, carbon, and aromatic contents in NOM enhanced the reductive degradation rates, whereas increased carboxyl concentration and oxygen, heteroaliphatic, and aliphatic contents decreased the reactivity. In addition, the authors found that the amount of Fe(II) sorbed on goethite was not affected by NOM and the change in the aggregation state of goethite was not the reason for the reactivity decrease. Thus, they attributed the inhibitory effect of NOM to (1) changes in surface Fe(II) reactive species and (2) blocking of electron transfer to goethite surface (Vindedahl et al., 2016). Given the complexity of NOM effects, future research should focus on NOM of different types, origins, oxidation states, etc.

To better understand the formation of surface sorbed Fe (II) species on iron oxides in the present of ligands and to elucidate how these species affect the reductive reactivity of Fe^{2+}/iron oxides, surface complexation modeling (SCM) has been employed to investigate the formation of surface Fe(II) species in the presence of phthalic acid (Huang et al., 2019b). As shown in Fig. 4, besides the two major binary Fe(II) species ($\equiv FeOFe^{+}$ and $\equiv FeOFeOH$), one additional outer-spheric ternary species ($(\equiv FeOFe^{+})_{2...}L^{2-}$) formed in the presence of phthalic acid, which might partly result in the reactivity decrease. In addition, the decrease in the amount of reactive Fe(II) monohydroxo surface species ($\equiv FeOFeOH$) was another reason for the lower reactivity. However, the above two reasons only accounted for part of the reactivity decrease, thus, the authors proposed two additional mechanisms: (1) phthalic acid might have blocked the more reactive sites on the goethite surface; and (2) phthalic acid might have blocked the electron transfer from Fe(II) to the conduction band of iron oxides and then to the contaminant.

In addition, Latta et al. observed that some anions (PO_4^{3-}, CO_3^{2-}, SiO_4^{4-}, and HA) did not inhibit electron transfer between Fe^{2+} and goethite (Latta et al., 2012). Note that although electron transfer in that study was not completely inhibited, it might still have slowed down, which might have influenced the reductive transformation of various contaminants. In fact, Jones et al. demonstrated that Si and NOM decreased the rate and extent of isotope exchange between Fe^{2+} and iron oxides (Jones et al., 2009). Thus, it is necessary to examine the effect of common anionic ligands on the electron transfer between Fe^{2+} and iron oxides in future studies.

3.3 Effect of second metal oxides on the reductive reactivity

Besides NOM and small anionic ligands, the effect of second metal oxides on the reductive reactivity should also be considered. Along this line, Huang et al. have investigated the effects of SiO_2 and TiO_2 on the reductive reactivity of Fe^{2+}/goethite (Huang et al., 2019a). For SiO_2, it significantly lowered the reductive reactivity of Fe^{2+}/goethite. Then, the authors found that the inhibitory effect by the Si ions (released from SiO_2 dissolution) was quite comparable to that by the SiO_2 particles, suggesting that the aqueous Si ions were the main reason for the overall inhibitory effect. Soluble Si ions might have competed



(a) (b)

Fig. 4 Triple layer modeling results for Fe^{2+} and phthalic acid (L) adsorption onto goethite in the ternary systems (Huang et al., 2019a).

with Fe^{2+} to decrease the amount of Fe(II) sorbed, subsequently leading to the reactivity decrease.

Unlike SiO_2, TiO_2 surprisingly dramatically enhanced the reactivity, which was ascribed to interparticle electron transfer, that is, the electrons from Fe(II) went through the conduction band of TiO_2 to that of goethite before reaching the contaminant (Huang et al., 2019a). The reactivity of Fe^{2+}/goethite + TiO_2 system depended on the types of TiO_2, with the reaction rate decreased in the order: rutile>TiO_2-P25>anatase. This order agreed well with the conduction band energy of TiO_2, suggesting that the conduction band energy of semiconductor minerals might have affected the electron transfer. Then, the authors utilized a dialysis bag to prevent the direct contact between goethite and TiO_2, and found that the promoting effect of TiO_2 disappeared. Based on the above results, interparticle electron transfer was for the first time proposed to occur under dark conditions that enhanced the reductive reactivity. However, additional work is needed to further elucidate the interactions and mechanisms of interparticle electron transfer within different oxide mixtures, especially between iron oxides and titanium dioxides, and how such a new mechanism can be applied to develop new site remediation technologies.

Besides metal oxides, clay minerals in soils and sediments also coexist with iron oxides (Tombácz et al., 2001; Dimirkou et al., 2002). Among them, kaolinite ($Al_2Si_2O_5(OH)_4$)) has been demonstrated to decrease the reductive reactivity, due to the competitive adsorption of Fe^{2+} and the Al/Si ions released from kaolinite dissolution (Strehlau et al., 2017). Al and Si ions can also be incorporated in goethite or on its surface, resulting in the reactivity decrease.

Note that dynamic light scattering (DLS), sedimentation experiments, and electron microscopy (SEM and TEM) have been frequently used to study the size and heteroaggregation of particles. DLS can only be used in dilute suspensions ($<$ 0.2 g/L) for sub-micron particles (Cwiertny et al., 2008; Zhang et al., 2015). For more concentrated suspensions and larger particles, sedimentation experiments have been employed to understand the extents of heteroaggregation of metal oxides (Zhang et al., 2015; Taujale et al., 2016; Huang et al., 2019a). During such experiments, sedimentation of mixed metal oxides was monitored at a certain wavenumber as a function of time with UV-vis spectrophotometry. Here, instead of measuring the adsorption of light, the scattering of light was actually obtained (Huang et al., 2019a); and the faster the sedimentation rate, the larger the formed aggregates in the suspension.

In addition, electron microscopy, such as SEM and TEM, has been used to observe the heteroaggregation and homoaggregation states of mixed metal oxides. Compared with traditional SEM and TEM that are for dry samples only, cryo-TEM/SEM have unique advantages because they are able to provide images of in situ aggregates at specific times. For example, cryo-TEM has been used to examine the aggregation state of goethite in the mixture of goethite and kaolinite (Strehlau et al., 2017). The cryo-TEM image (Fig. 5) surprisingly showed that the goethite was in homoaggregates, independent of the kaolinite loading, even though the surface charges are opposite for goethite (positive) and kaolinite (negative). The phenomenon indicated that the inhibition of the reductive reactivity of Fe(II)/goethite by kaolinite was not because of heteroaggregation in the aqueous phase (Strehlau et al., 2017). However, the reasons why there is no heteroaggregation between goethite and kaolinite are not clear.

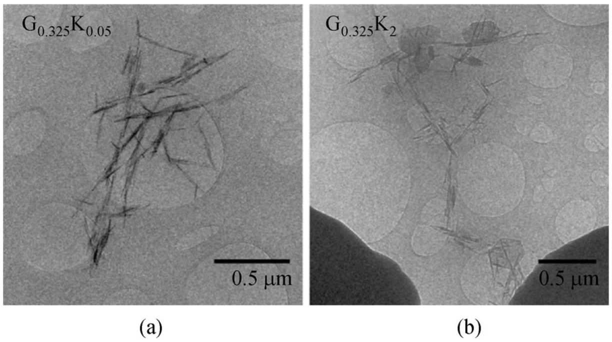


Fig. 5 Cryo-TEM images of (a) 0.325 g/L goethite (G) + 0.05 g/L kaolinite (K) suspension and (b) 0.325 g/L G + 2 g/L K suspension (Strehlau et al., 2017).

3.4 Reductive reactivity in sediments

Metal oxides are an important composition of soil and sediments. Several studies have investigated the reductive reactivity in sediments. Zhang and Weber examined the reductive reactivity of 21 natural sediments and attempted to correlate the sediment physicochemical properties, including BET surface area, cation-exchange capacity, texture, Fe speciation and composition, and organic carbon content, to their reductive reactivity (Zhang and Weber, 2013). Based on the cluster and regression analysis, the authors revealed that surface-associated Fe^{2+} as well as reduced DOC played a deciding role in the reductive reactivity of the anaerobic sediments. Other researchers have also conducted field experiments in a landfill leachate plume of a sandy aquifer to elucidate the contribution of various reductants to the overall reactivity (Rügge et al., 1998). They found that the surface sorbed Fe(II) on iron (hydr)oxides was the dominant reductant, even though DOM had a high concentration. One likely reason is that the DOM in the plume was mostly oxidized, and hence lacking the reducing ability. Despite the above efforts, the relative contribution of Fe^{2+} associated reductants and DOM (and possibly other reductants) to the overall reactivity of actual sediment systems is still mostly unclear, which warrants further research.

4 Future outlook

The knowledge of the redox reactions of Fe- and Mn-oxides in different systems is important to understand biogeochemical processes. Future research focusing on examining their reactivity in complex systems is necessary, as briefly summarized below:

First, the redox reactions of Fe- and Mn-oxides in complex systems are remarkably different from simple model system. To better simulate actual environmental systems, it is necessary to increase the complexity of model systems sequentially (from binary systems to ternary systems, then to more complex systems) to study the redox reactions of organic contaminants with various functional groups and of different inorganic contaminants, which will be important for conducting site-specific chemical exposure assessments.

Second, most of previous studies only focused on δ-MnO_2; this is especially the case in complex systems (Taujale and Zhang, 2012; Zhang et al., 2015; Taujale et al., 2016). However, there are different phase structures of MnO_2, such as α-, β-, γ-, δ-, and λ-MnO_2, and they demonstrated various catalytic and direct oxidative reactivities due to different surface and structural properties (Meng et al., 2014; Huang et al., 2018; Huang and Zhang, 2019a). Therefore, it will be interesting and useful to investigate the effects of metal ions, ligands and second metal oxides on the oxidative reactivity of these MnO_2 of different phase structures.

Third, despite some studies reporting that semiconductor minerals play an essential role in the reductive reactivity of Fe oxides (Taylor et al., 2017; Huang et al., 2019a), how electrons are transferred from these semiconductor minerals to Fe oxides is still not clear. For example, how is the sorbed Fe(II) distributed in complex systems containing iron oxides and other semiconductor minerals? What properties of semiconductors are most influential in affecting the reactivity of Fe(II)/Fe oxides? With further investigation, it is possible to identify the types of semiconductor minerals that can promote the rates of electron transfer in complex systems.

Fourth, besides surface sorbed Fe(II), some iron minerals, such as magnetite and green rust, contain both Fe(II) and Fe(III) and have been demonstrated to reduce a number of contaminants (Génin et al., 2001; Gorski and Scherer, 2009). Many factors have been shown to influence the reactivity, including particle size, the ratio of Fe(II)/Fe(III), and water composition (e.g., pH) (Danielsen and Hayes, 2004; Vikesland et al., 2007; Gorski and Scherer, 2009). However, there are only few studies on the reductive reactivity of these mixed-valent iron minerals in complex systems (Swindle et al., 2015; Sundman et al., 2017). Therefore, investigating the effects of metal ions, ligands and second metal oxides on the reactivity of mixed-valent iron minerals is also necessary to improve site remediation technologies and risk assessments.

Finally, as mentioned in Introduction, numerous contaminants can undergo redox reactions, which can influence their toxicity, solubility and bioavailability in the environment. Many studies on complex systems only focused on the abatement of parent compounds without considering the intermediates or final products, which requires further research.

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