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REVIEW ARTICLE

Interplay of transport processes and interfacial chemistry affecting chromium reduction and reoxidation with iron and manganese

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HIGHLIGHTS

- Cr(VI) can be removed by iron-based adsorption, reduction and precipitation.
- Surface-functionalized iron oxide nanoparticles are promising adsorbents for Cr(VI).
- Surface complexation modeling provides quantitative predicts for Cr(VI) adsorption.
- Cr(III) can be remobilized in the presence of Mn (II, III, IV) at certain conditions.

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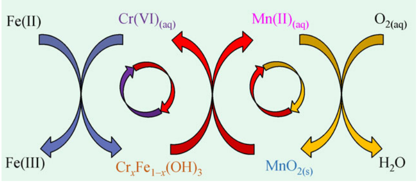
GRAPHIC ABSTRACT



ABSTRACT

Hexavalent chromium (Cr(VI)) is a water-soluble pollutant in soil and groundwater, the mobility, bioavailability, and toxicity of which can be controlled by transforming to less mobile and more environmentally benign Cr(III) by ways of reduction. This review focused on recent advances in identifying the reaction pathways, kinetics, and products of iron-based techniques for Cr(VI) removal. It also examines new information regarding remobilization of Cr(III) in the existence of complexing ligands and manganese (Mn) of different oxidation states. A range of iron-based techniques can remove Cr(VI) from water by adsorption or reduction-coprecipitation processes. However, the success of a chromium treatment or remediation strategy requires the stability of the Cr(III)-containing solids with respect to solubilization or reoxidation in the settings they are generated. Manganese is ubiquitous in aquatic and terrestrial environments, and the redox cycling of manganese may greatly influence the fate, transport, and distribution of chromium. Coupling of redox reactions of chromium, iron, and manganese involves reaction pathways not only in the aqueous phase but also at solid-aqueous interfaces. To provide a quantitative understanding of these processes, it is essential to develop mechanistically based kinetic and transport models. Continued research should be made on iron-based treatment of Cr(VI)-contaminated water and soils and the stability of the subsequently produced Cr(III)-containing solids at environmentally relevant conditions, which will support improved predictions of chromium's environmental fate and transport and aid in decision-making for remediation and treatment of Cr contamination.

1 Introduction

Chromium(VI) (Cr(VI)) is a toxic pollutant that has been observed in private and public water supplies as well as in treated drinking water. It was made famous to public by the movie "Erin Brockovich," where a legal clerk leading a lawsuit against Pacific Gas & Electric (PG&E) for drinking water contamination in California with Cr(VI). The movie ended on a Hollywood high note with a 333 million settlement from PG&E, however, the Cr(VI) contamination for drinking water in United States is still an ongoing battle in real world. United States Environmental Protection Agency (EPA) sets a drinking water standard of 100 μg/L for total chromium. In 2014, California has adopted the first drinking water standard for specific Cr (VI) in the nation, with a maximum contaminant level of 10 μg/L (U.S.EPA., 2014). However, it was invalidated in 2017 due to analytical limitation and the assumption that

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the predominant Cr speciation was less mobile Cr(III) under typical environmental conditions. The chromium contamination in aquatic environments was caused by both anthropogenic activities (e.g., metallurgy, pigment, electroplating and chromite ore processing (Dönmez and Aksu, 2002)) and natural sources (e.g., high chromium concentrations in the mudstones of central Oklahoma aquifer (Parkhurst et al., 1996)). Chromium occurs in soils and natural water primarily in two oxidation states, Cr(III) and Cr(VI). Cr(III) is an essential micronutrient for humans and is found in multivitamins, usually considered stable and insoluble. In comparison, Cr(VI) is acutely toxic, mutagenic, and carcinogenic. Reduction of Cr(VI) to Cr(III) is critical in the in situ remediation of Cr(VI)-contaminated soil and groundwater and ex-situ treatment of groundwater for a drinking water supply. Typical treatment strategies and current removal methods involve reduction of Cr(VI) to Cr(III), subsequent adsorption and separation of the Cr-laden sorbent using filtration or other methods (Jiang et al., 2014).

Many studies investigating Cr(VI) removal from solution has involved iron-based physical and chemical processes. Cr(VI) can adsorb to iron oxides such as amorphous iron oxides, goethite, hematite, ferrihydrite and to iron oxide-coated sands, which are abundant in the earth’s crust (Rosales-Landeros et al., 2013). The rate and capacity of Cr(VI) adsorption onto these iron oxides are highly dependent on the water chemistry conditions and can be negligible in many cases of water supplies. Therefore, the Cr(VI) removal by coagulation/adsorption with the addition of Fe(III) salts in water treatment can be limited even with high doses of coagulant. In contrast, using Fe(II) salts as reductants and subsequent oxidized Fe (III) as coagulants, Cr(VI) has been reported to be removed to low concentration in water (Guan et al., 2011; Barrera-Díaz et al., 2012). Other common iron-based reducing methods include zero valent iron (ZVI) (Lai and Lo, 2008), green rust (Loyaux-Lawniczak et al., 2000) and iron sulfide (Mullet et al., 2007), with the final products of chromium iron hydroxides (Sass and Rai, 1987; Di Palma et al., 2015).

Manganese oxides are naturally present constituents in aquifers that can oxidize Cr(III) to Cr(VI) (Eary and Rai, 1987; Richard and Bourg, 1991; Varadharajan et al., 2017). Field-scale study by McClain et al. showed that the concentration of manganese oxides was a good predictor of Cr(VI) formation in aquifer (McClain et al., 2017). In a field study of Aromas Red Sands aquifer, Gonzalez et al. found that naturally occurring Cr(VI) was attributed to Cr (III) mineral deposits oxidation by manganese oxides from sediment (Gonzalez et al., 2005). The results of the study explained the high Cr(VI) concentration in the drinking water of Santa Cruz, California. The presence of microbial activity may also impact the fate and transport of chromium in biogeochemical cycling. A study by Butler et al. compared the manganese oxides oxidation of chromium iron hydroxides formed in different way, and found that Cr(VI) only formed rapidly from Cr(III)-Fe(III) hydroxides in the absence of microbial activity (Butler et al., 2015). Independent of biochemical processes, the Cr redox transformation and remobilization can also be affected by physical and hydrological conditions in aquifers, where kinetic models based on experiments were further incorporated into a reactive transport model (Liu et al., 2017; Hausladen et al., 2019; McClain et al., 2019)

In this account we seek to review recent developments and the current understanding of Cr treatment approaches and remobilization possibilities. The literature on Cr(VI) removal and Cr(VI) generation in natural environments is tremendous, and we do not intent to provide an exhaustive full review. Rather we hope to highlight the mechanistic linkages of laboratory-derived results to field environments by combining our recent research progress and a selective review of related literature on interactions among Cr, Fe and Mn.

2 Cr(VI) removal by Fe-based approaches

2.1 Cr(VI) reduction by Fe(0), Fe(II) and Fe-containing materials

Many Cr(VI) remediation techniques involve its reduction to Cr(III) by using various reducing agents, among which iron is a particularly promising reductant. For in situ remediation of groundwater, zero valent iron has been shown to effectively remove dissolved Cr(VI) in permeable reactive barriers both in the laboratory and in field tests (Wilkin et al., 2005). However, the rate of reaction is slower at neutral and mildly alkaline conditions due to Fe (0) passivation. Further, the reduction by Fe(0) was unselective and significantly affected by the presence of oxygen (Yoon et al., 2011). In contrast, the rate of Cr(VI) by dissolved Fe(II) is much higher and less affected by oxygen at circumneutral pH (Schlautman and Han, 2001). The rate decreases over the pH range 1.5–4.5 and increases from 5 to 8.7 (Pettine et al., 1998). Cr(VI) can be removed to sub-μg/L concentrations in drinking water by reduction-assisted coagulation with Fe(II). Reduction of Cr(VI) to Cr (III) is coupled with the oxidation of Fe(II) to Fe(III). Humic acid introduced a positive influence on Fe(0) reactivity toward Cr(VI) reduction while having marginal effects on Fe(II) reactivity (Gröhlich et al., 2017; Di Palma et al., 2018) and resulting in the formation of Cr-HA-Fe colloids (Liao et al., 2020). In addition to adsorbing to the iron oxides produced, Cr(III) is mostly structurally incorporated in the Fe(III) oxide by co-precipitation, forming a Fe(III)-Cr(III) (oxy)hydroxide solid solution under circumneutral pH (Eary and Rai, 1988).

In addition to Fe(0) and Fe(II), Cr(VI) can be reduced by Fe-containing solids, including both solid form of Fe(II) and Fe(III)-NOM precipitates (Bishop et al., 2014; Liu et al., 2017; Chen et al., 2019; Liao et al., 2020). For example, Cr(VI) has been reported to be reduced by Fe(II)-Fe(III) hydroxides such as magnetite (Manning et al., 2007), pyrite (Mullet et al., 2007), mackinawite (Mullet et al., 2004), green rust (Loyaux-Lawniczak et al., 2000), biological reduced iron oxide (Jiang et al., 2019) and reduced clays such as montmorillonite, nontronite, illite, vermiculite and kaolinite, which are commonly spread in soils and sediments (Bishop et al., 2014; Liu et al., 2018). A very recent study by Chen et al. found that Cr(VI) could be adsorbed and subsequently reduced to Cr(III) by Fe(III)-NOM precipitates, which were frequently formed in natural and wastewater (Chen et al., 2019). Increased Cr contents in NOM-Fe(III) precipitates could trigger more Cr (VI) reduction.

2.2 Cr(VI) removal by electrocoagulation

While Cr(VI) can be removed by Fe(II) that is introduced to water via chemical addition, iron electrocoagulation (EC) process has received more recent attention by continuously in situ production of Fe(II) in the Cr(VI) contaminated water. EC technology is based on applying an electric voltage to a sacrificial ZVI anode to generate Fe (II) in situ. H^+ generated during Fe(II) oxidation process could be reduced on the cathode, stabilizing pH in the alkaline range (Harif et al., 2012). The generated Fe(II) can be subsequently oxidized by either dissolved oxygen or Cr (VI) to Fe(III), which can then precipitate as Cr(III)-Fe(III) hydroxides or Fe(III) hydroxides. Our group has examined the performance of Cr(VI) removal by iron electrocoagulation relevant to drinking water treatment (Pan et al., 2016). Cr(VI) is chemically reduced to Cr(III) by the Fe(II) generated on iron anode, and X-ray Absorption near Edge Spectroscopy (XANES) of electrocoagulation products indicate that Cr(III) is the predominant Cr speciation in the solid phase. The presence of humic acid inhibited the rate of Cr(VI) removal in electrocoagulation above neutral pH by forming Fe(II)-HA complexes that are more rapidly oxidized by dissolved oxygen than inorganic Fe(II). We used a new model to describe the kinetics of Cr(VI) reduction to Cr(III) in electrocoagulation at conditions of different pH and different oxygen level. The model incorporates Fe(II) generation from the iron anode, Fe(II) oxidation by dissolved oxygen and Cr(VI), surface-mediated Cr(VI) reduction on Fe(III) oxides, and the role of pH and humic acids in affecting the rates. The model could predict Cr(VI) removal in EC very well even when it incorporates natural organic matter as a component into the system (Pan et al., 2017b). Furthermore, iron electrocoagulation lowered Cr(VI) concentrations to levels well below 10 μg/L in the presence of natural organic matter and common groundwater solutes (Pan et al., 2017b).

2.3 Products of Cr(VI) reduction

The reduction of Cr(VI) by iron-based techniques can lead to rapid precipitation of Cr(III)-Fe(III) hydroxide (Di Palma et al., 2015; Pan et al., 2016). Cr(VI) reduction to Cr (III) is coupled with Fe(II) and Fe(0) oxidation to Fe(III). As Cr(III) and Fe(III) have the same charge and similar ionic radii, amorphous hydroxide precipitates of Cr and Fe behave thermodynamically as solid solutions, with a general molecular formula of $Cr_xFe_{1-x}(OH)_3$ (Sass and Rai, 1987; Manning et al., 2007; Dai et al., 2016). In addition, Cr(VI) can be reduced to Cr(III) through microbial reduction of iron (hydr)oxides under anaerobic conditions. Cr(VI) got reduced and immobilized via this coupled biotic-abiotic reaction pathway, finally incorporated into iron oxides as $Cr_xFe_{1-x}(OH)_3$ (Battaglia-Brunet et al., 2004). The chromium solubility in $Cr_xFe_{1-x}(OH)_3$ can be empirically predicted as a function of the Fe/Cr ratio in the solid and the pH of the solution. The solid phases control Cr concentrations in surface environments and underground water to a very low level by rapid precipitation kinetics (Sass and Rai, 1987).

2.4 Cr(VI) adsorption to iron-based nanomaterial

Besides Cr(VI) immobilization by iron-based reduction process, considerable research attention has been diverted to iron oxide-based nanomaterials for Cr(VI) removal via adsorption (Zachara et al., 1987). Iron oxide-based nanomaterial has high surface area and reactivity toward Cr(VI) from contaminated water (e.g., goethite, hydrous ferric oxide, maghemite and magnetite) (Hu et al., 2006; Rosales-Landeros et al., 2013; Bompoti et al., 2019). Adsorption equilibrium was achieved rapidly via electrostatic attraction and ion exchange. Although high adsorption capacities have been reported toward Cr(VI), the aggregation and sedimentation of bare nanoparticles remains a technical hurdle and can significantly affect their surface area and reactivity, subsequently influencing their adsorption behavior.

Surface-functionalized iron oxide nanoparticles are promising adsorbents for Cr(VI) considering their large specific surface areas, higher stability than bare iron oxides nanoparticles as well as ease of separation after chromium removal. The surface of iron oxide nanoparticles can be modified or functionalized with a variety of materials such as humic acid, polymers, macromolecules and fatty acids that can stabilize nanoparticles while retaining or even promoting the ability to remove Cr(VI) (Jiang et al., 2014; Pan et al., 2019b; Xiong et al., 2019). Our group has recently examined the Cr(VI) adsorption onto superparamagnetic magnetite nanoparticles with surface coatings of amine functional group (Pan et al., 2019b). Different from traditional iron oxides, the adsorption of Cr(VI) by trimethyloctadecylammonium (CTAB) functional group coated nanoparticles increased with decreasing pH. In addition, the modification of the magnetite nanoparticle surface enables the particle dispersion in water for adsorption, following with particle separation by a magnetic field. In a different study, the diatomite supported magnetite had a much better adsorption capacity of Cr(VI) compared with the unsupported magnetite (Yuan et al., 2010). Poly acrylic acid (PAA) coated magnetite nanoparticles followed by amino functionalization also revealed high Cr(VI) adsorption capacity as reported by Singh et al. (Singh et al., 2011).

Surface complexation modeling (SCM) can provide a robust reaction-based predictions of Cr(VI) adsorption to iron oxide over varying environmental conditions (Bompoti et al., 2016). Unlike empirical distribution factors, SCM is a powerful approach for interpreting adsorption equilibrium that accounts for electrostatic contributions to adsorption in addition to the inherent chemical energetics of adsorption (Dzombak and Morel, 1990). The SCM based on ferrihydrite surface structure described well enough the Cr(VI) adsorption on ferrihydrite and goethite (Bompoti et al., 2019). The extracted unified parameters applied in SCM can be further implemented in reactive transport modeling in the field. Our group has successfully applied SCM in predicting Cr(VI) adsorption onto magnetite nanoparticles with organic surface coatings (Pan et al., 2019b). With a small number of optimized parameters, the model could predict the trend of the acid-based chemistry and pH-dependence of zeta potentials of the engineered nanoparticles in the absence of Cr(VI). The model was then applied to interpret Cr(VI) adsorption edges in inorganic carbon-free system first and then with air-water equilibrated system (Singh et al., 2011). In recent years, different advanced spectroscopic technologies were combined with SCM for better understanding intrinsic mechanisms and interpreting Cr(VI) adsorption processes, including X-ray photoelectron spectroscopy (XPS), X-ray absorption (XAS) and Fourier transformation infrared (FTIR) (Bompoti et al., 2016; Huang et al., 2016; Xiong et al., 2019).

3 Chromium remobilization in natural environments

Increasing evidence suggests that the reduced Cr in natural aquifers and sediments can be remobilized, and the remobilization is associated with manganese distribution, organic carbon concentrations, evaporated water, and unsaturated zone thickness over geological timescales (Hausladen and Fendorf, 2017; Liu et al., 2017; Hausladen et al., 2018; Hausladen et al., 2019).

3.1 Impacts of ligands on Cr(III) mobilization

Observations of dissolved Cr(III) concentrations above the equilibrium solubility of $Cr(OH)_3$ solids in water indicate the importance of Cr(III) complexation by inorganic or organic molecules (Nakayama et al., 1981; Icopini and Long, 2002) that are ubiquitous in natural water and soils. Organic ligands have been shown to be capable of solubilizing Cr(III) from the Cr(III)-Fe(III) hydroxides solid phase under environmental relevant conditions due to structural similarity of Cr(III) and Fe(III) (Saad et al., 2017). The microbial exudates in water and soils can significantly enhance the release of Cr(III) from remediation products by forming organic-Cr(III) complexes. In addition, chromium could also be significantly liberated by siderophores and organic ligands from chromium-substituted schwertmannite (Xie et al., 2019), chromite and silicate rock (Kraemer et al., 2019). Furthermore, natural organic matter such as humic acid could complex with Cr (III) forming HA-Cr(III) colloids with hydrodynamic diameters around 200 nm, increasing Cr(III) particle stability and its transport through water (Pan et al., 2017b). The high colloidal stability of HA-Cr(III) particles could be attributed to the enhanced electrosteric stabilization effect from adsorbed HA, which decreased particles aggregation based on classical Deriaguin-Landau-Verwey-Overbeek (DLVO) theory.

3.2 Cr(III) reoxidation by Mn oxides

Manganese oxides, produced primarily by Mn(II) enzymatically oxidation via diverse bacteria and fungi, are common in most natural environments (He et al., 2010). Under moderate pH conditions, the manganese oxides appear to be the primary naturally occurring oxidants of Cr (III) (Hausladen and Fendorf, 2017). Chromite ($FeCr_2O_4$) is the primary Cr(III) mineral in ultramafic rocks and serpentine soils. Although $FeCr_2O_4$ was stable and non-reactive to most organic matter and oxidants under near-surface conditions, Oze et al. found significant Cr(VI) release from $FeCr_2O_4$ oxidation by birnessite and oxidation rate was directly related to geochemical interactions between chromite and birnessite (Oze et al., 2007).

Based on our recent study on Cr(III)-Fe(III) hydroxides interaction with MnO_2, Cr(III) oxidation and subsequent Cr(VI) release was significantly observed despite the low solubility of two minerals, indicating the important role of the proximity between the two oxides in the overall reaction process (Pan et al., 2017a). A multichamber reactor was used to simulate the presence of a physical barrier that restrain direct contact of Cr(III)-Fe(III) hydroxides and MnO_2 in separated chambers, but diffusion of dissolved species such as Mn(II) and Cr(III) in aqueous phase was allowed to diffuse across the membrane (Pan et al., 2017a). The overall rate of Cr(VI) production in the multichamber experiments was much lower than that in the completely mixed batch experiments at the same condition because the Mn oxide could only act to take up and oxidize the limited pool of dissolved Cr(III) that was mobilized into the bulk solution (Pan et al., 2017a). $Cr(OH)_3$ was chosen as a target Cr(III)-containing solid for further model development to describe the processes because of its higher Cr solubility at circumneutral pH and easier quantification. The kinetic model was successfully established based on the dissolution of $Cr(OH)_3$(s), the diffusion of dissolved Cr across the membrane and aqueous Cr(III) oxidation by MnO_2, giving indication that the rate of transport of Cr(III) onto manganese oxides and Cr(III) intermediates oxidation by MnO_2 were the rate-controlling factors in Cr(VI) generation (Fig. 1) (Pan et al., 2019a). The extent of physical contact of the Cr(III)-containing minerals and manganese oxides is important in driving oxidation of insoluble Cr(III). Consequently, the net rate of Cr(VI) generation in natural environments can be orders of magnitude lower than observed in well mixed batch experiments in laboratory (Fig. 2). Furthermore, Hausladen et al. modeled Cr(VI) formation from Cr(III)-bearing minerals in soils and sediments by incorporating the physical and heterogeneity of an aquifer into a reactive transport model (Hausladen et al., 2019). Liu et al. investigated the fate and transport of Cr in the hyporheic zone at the US Department of Energy's Hanford Site where there is mixing of groundwater and river water on a daily basis (Liu et al., 2017). A multicomponent reactive transport model that could predict Cr redox transformation and immobilization was established based on coupling biogeochemical processes with hydrological conditions that included the hydraulic conductivity and the thickness of the top alluvial layer.

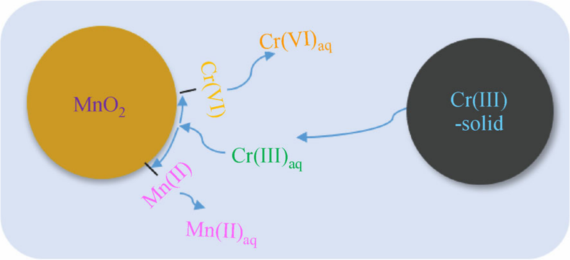

Fig. 1 Reaction pathway of Cr(III)-containing solids oxidation by MnO_2

3.3 Importance of Mn(III) in Cr(III) remobilization

The potential for Cr oxidation in a given environment may depend not only on the total manganese oxide concentration but also on the Mn(III) content. The importance of Mn (III) in natural environment has been traditionally underestimated because Mn(III) is thermodynamically unstable and rapidly disproportionate to MnO_2 and Mn(II). However, soluble Mn(III) can be made stable when complexing with high affinity ligands (Johnson, 2006). Studies at environmentally relevant conditions suggested that ligand-stabilized Mn(III) species may occur as intermediates of Mn redox reaction in the presence of pyrophosphate, siderophores, oxalate and citrate (Wang and Giammar, 2015; Qian et al., 2019). Nico and Zasoski evaluated Cr(III) oxidation by Mn(III) complexes stabilized by pyrophosphate and found that Mn(III) was a crucial oxidant responsible for Cr(VI) production (Nico and Zasoski, 2000). For Mn(III) in solids, Chung et al. compared Cr(III) oxidation by Mn oxides with a series of Mn(III) contents. Hausmannite ($MnO_{1.39}$), which has a relatively high Mn(III) content, reacted much more rapidly and completely with Cr(III) than did either birnessite or pyrolusite (Liu et al., 2019).

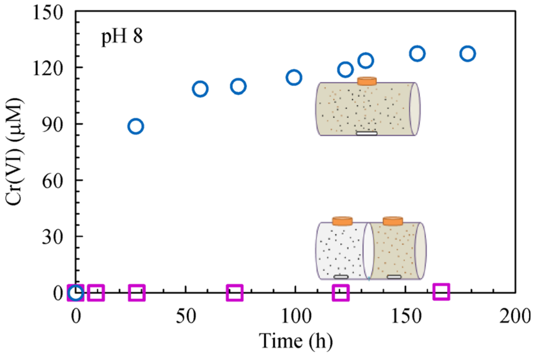

Fig. 2 Comparison of Cr(VI) generation in completely mixed batch experiments and multichamber experiments from $Cr(OH)_3$ oxidation by MnO_2. For multichamber experiments, $Cr(III)_0$ = 1440 μM in the chromium chamber and MnO_2 = 872 mM in MnO_2 chamber. The Cr and Mn concentrations in an individual chamber are twice of that in the completely mixed experiments, which provides overall same Mn and Cr concentrations in two different reactors.

3.4 Cr(III) reoxidation in the presence of Mn(II)

Mn(II) oxidation by dissolved oxygen is thermodynamically favorable under environmental relevant conditions and the reaction can be catalyzed by Mn-oxidizing microorganisms and mineral surfaces. Recent research suggests that Mn(II) may also impact metal geochemical processes directly by Mn redox cycling (Wu et al., 2005; Murray and Tebo, 2007; He et al., 2010; Namgung et al., 2014). Manganese oxidizing bacteria has been first observed to accelerate chromium oxidation by driving Mn cycling in the environment (Wu et al., 2005; Murray and Tebo, 2007). Hastings and Emerson showed that the rate of bacteria oxidized Mn(II) was up to 5 orders of magnitude higher than abiotic reactions (Hastings and Emerson, 1986). The biogenic Mn oxides have an amorphous structure with a high surface area and Cr(III) was catalytically oxidized in the presence of Mn oxides produced by *Pseudomonas putida* (Murray et al., 2005). In addition, Mn(II) oxidation can also be substantially accelerated by its coordination to the surfaces of metal oxides (Diem and Stumm, 1984). The rate of surface-catalyzed Mn(II) oxidation can be comparable to that of microbial Mn(II) oxidation. Moreover, a study by

Namgung et al. has found substantial Cr(VI) release when Mn(II) was spiked into $Cr(OH)_3$ suspensions under oxic condition (Namgung et al., 2014). In their study, dissolved Mn(II) was oxidized rapidly by $Cr(OH)_3$ and precipitated as hausmannite, which was the responsible oxidant for Cr (III). Autocatalytic Mn(II) oxidation for Cr(VI) generation was also observed in our study of Cr(III)-Fe(III) hydroxides in the presence of Mn(II). Significant Cr(VI) generation from $Cr_xFe_{1-x}(OH)_3$ was observed in the presence of Mn(II) and dissolved oxygen at neutral pH.

4 Future outlook

Cr(VI) removal by Fe-based technologies and reoxidation in natural environments involves a complex set of biogeochemical processes across multiple scales. While recent research has made major advances in our understanding of these processes, future work is needed to fill important knowledge gaps.

First, research can extend electrocoagulation experiments to examine their integration into actual treatment process trains. Although Cr(VI) could be rapidly removed from iron-electrocoagulation relevant to drinking water level in well-mixed batch experiments, integration into a treatment process would likely use flow-through reactors, and there is little information about Cr(VI) removal in such reactors. The experiments will include determining the amount of power needed for a given amount of coagulation, and the specification of the reactive transport properties. Successful integration into treatment trains will also require examination of processes for removal of the Cr-containing solids from the suspension. Ideally these will be modular processes (e.g., microfiltration) that can be integrated with electrocoagulation to provide chemical-free treatment processes for small systems and other operations that benefit from low maintenance autonomous processes.

Second, the influence of natural organic matter on Cr (III) oxidation associated with manganese redox cycling can be evaluated. Natural organic matter is ubiquitous in aquatic environments and it can associate with manganese, dissolved iron and iron oxides, affecting the iron and manganese redox chemistry. In future studies it will be valuable to investigate the influence of different types of natural organic matter on $Cr_xFe_{1-x}(OH)_3$ oxidation by MnO_2 from both aquatic chemistry and colloidal perspectives. It would be particularly interesting to test some strong complexing ligands which form complexes with Mn (III), because natural organic matter that may cause reductive dissolution of MnO_2 and subsequently generate organic-Mn(III) complexes or NOM-Mn(III) colloids.

Third, it will be valuable to investigate Cr(VI) generation from $Cr_xFe_{1-x}(OH)_3$ oxidation by MnO_2 in porous media and various field sediments. Our recent work has highlighted the role of solid-solid mixing in Cr(VI) generation from Cr(III)-containing solids oxidation by MnO_2, and the implications for processes in porous media need to be explored. A model has been established to predict Cr(VI) generation in systems with $Cr_xFe_{1-x}(OH)_3$ and MnO_2 via multichamber and well-mixed batch experiments, but there is no mixing of Cr(III)-containing solids and Mn(IV) oxide in a porous media like groundwater sediments and solute transport can be limited to that occurs by diffusion. Integrating the chemical reactions and transport processes at multiple scales into a reactive transport model could provide assessments of the rates and extents of Cr(VI) generation associated with oxidation of Cr(III) by manganese oxides in subsurface environments.

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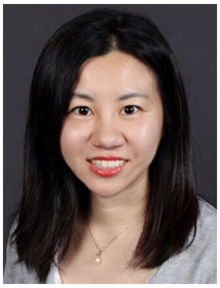

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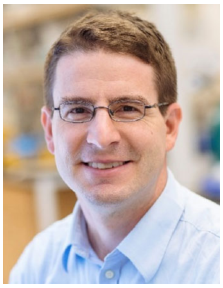

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