Phase Transformation of Cr(VI)-Adsorbed Ferrihydrite at Different pH in The Presence of Mn(II): Fate of Mn(II) and Cr(VI)

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1 **Phase transformation of Cr(VI)-adsorbed ferrihydrite at different**
2 **pH in the presence of Mn(II): Fate of Mn(II) and Cr(VI)**

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8 **ABSTRACT**

9 Ferrihydrite is an important sink for the toxic heavy metal ions, such as
10 chromium(VI). As ferrihydrite is thermodynamically unstable and gradually
11 transforms into hematite and goethite, the stability of Cr(VI)-adsorbed ferrihydrite is
12 environmentally significant. This study investigated the phase transformation of
13 Cr(VI)-adsorbed ferrihydrite at different pH in the presence of aqueous Mn(II), as
14 well as the fate of Mn(II) and Cr(VI) in the transformation process of ferrihydrite.
15 Among the ferrihydrite transformation products, hematite was dominant, and goethite
16 was minor. The pre-adsorbed Cr(VI) inhibited the conversion of ferrihydrite to
17 goethite at initial pH 3.0, whereas little amount of adsorbed Mn(II) favored the
18 formation of goethite at initial pH 7.0. After the aging process, Cr species in solid
19 phase existed primarily as Cr(III) in the presence of Mn(II) at initial pH 7.0 and 11.0.
20 The aqueous Mn concentration was predominantly unchanged at initial pH 3.0,
21 whereas the aqueous Mn(II) was adsorbed onto ferrihydrite or form Mn(OH)₂

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precipitates at initial pH 7.0 and 11.0, promoting the immobilization of Cr(VI). Moreover, the oxidation of Mn(II) occurred at initial pH 7.0 and 11.0, forming Mn(III/IV) (hydr)oxides.

Keywords: Ferrihydrite; Phase transformation; Cr(VI) adsorption and reduction; Mn(II) adsorption and oxidation

1. Introduction

Hexavalent chromium (Cr(VI)), a contaminant often found in ground and surface water, is harmful to human health and environmental safety due to its carcinogenicity and mutagenicity (Costa, 1997). Chromium(VI) is widely used in industries, resulting in a large discharge of Cr(VI)-containing wastewater (Nriagu and Nieboer, 1988; Wu et al., 2018a). The Cr species often exist as Cr(III) and Cr(VI). Between these two forms, Cr(VI) is considered much more toxic than Cr(III) (Saha et al., 2011). Chromium(VI) can move rapidly in aqueous environments due to its high solubility, whereas Cr(III) is less soluble and will precipitate in the pH range of 6-11.5. The fate of Cr in the environment is closely related to its interaction with natural adsorbents, which affects the migration and transformation of Cr (Johnston and Chrysochoou, 2015). Iron (hydr)oxide is one of the most reactive natural adsorbents for Cr(VI) adsorption. Numerous researches have been conducted to study the adsorption of Cr(VI) on iron (hydr)oxide, such as ferrihydrite (Johnston and Chrysochoou, 2012), goethite (Xie et al., 2015), and hematite (Huang et al., 2016). The Cr(VI) adsorption usually increases with the decrease of pH. For example, the adsorption of Cr(VI) by

γ -Fe₂O₃ showed a significant pH dependence, where the decrease of pH value favored the adsorption of Cr(VI) (Wang and Lo, 2009). The mechanisms of Cr(VI) adsorption onto iron (hydr)oxide involved outer-sphere and inner-sphere surface complexation (Mamun et al., 2017).

Ferrihydrite, an environmentally important iron (hydr)oxide, is the first product of Fe(III) hydrolysis (Smith et al., 2012; Boland et al., 2014a). It exists in geological settings, including natural waters, soils, and sediments. The abundance in nature, large specific surface area and high reactivity enable ferrihydrite to sequester many contaminants through adsorption and coprecipitation (Kameda et al., 2017). Typically, ferrihydrite is an important sink for metal(loid) contaminants, due to its strong affinity with metal(loid) ions, such as Cr(VI) (Mamun et al., 2017), As(V) (Das et al., 2015; Paktunc et al., 2008), Sb(V) (Wu et al., 2018b), and U(VI) (Boland et al., 2014b). Although ferrihydrite exhibits a high adsorption capacity for various metal(loid) ions, it is metastable and gradually transforms into secondary minerals, including hematite and goethite (Finck et al., 2019). Hematite is formed by dehydration and reorganization among ferrihydrite particles (Wang et al., 2015a), whereas goethite is formed by ferrihydrite dissolution and reprecipitation (Shen et al., 2012). Depending on the pH and the co-existing substances, different products of ferrihydrite transformation can form (Das, et al., 2011). The conversion of ferrihydrite to more stable minerals will result in the decrease of specific surface area of solid phase, which causes a significant impact on the contaminants originally adsorbed by ferrihydrite.

Manganese (Mn), an important element in terrestrial environments, is often associated with Fe in various geological settings (Alvarez, et al., 2005; Wang et al., 2015b). The presence of Mn(II) affected ferrihydrite transformation (Wang et al., 2015a). On the other hand, the presence of ferrihydrite accelerated the oxidation of Mn(II) by dissolved O₂ (Lan et al., 2017). The interaction between aqueous Mn(II) and ferrihydrite can be affected by the contaminants adsorbed on ferrihydrite. However, little is known about the impacts of Cr(VI) on the interaction between aqueous Mn(II) and ferrihydrite, as well as the fate of Cr(VI) after the conversion of ferrihydrite.

Accordingly, this study is going to investigate: (1) the phase transformation of Cr(VI)-adsorbed ferrihydrite in the presence of aqueous Mn(II), and (2) the fate of Mn(II) and Cr(VI) during the phase transformation of ferrihydrite. The concentrations of aqueous Cr(VI), total Cr, and total Mn were measured during the phase transformation of ferrihydrite. X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) were employed to characterize the solid samples. This study can provide significant information on the stability of Cr(VI)-adsorbed ferrihydrite in the presence of aqueous Mn(II).

2. Materials and methods

2.1. Preparation of ferrihydrite

Ferrihydrite was prepared as the method adopted by Cismasu et al. (2012). Briefly, 0.2 M Fe(NO₃)₃ solution was freshly prepared using 18.2 MΩ•cm Milli-Q

water, and adjusted to pH 7.5 using 1 M NaOH under gentle magnetic stirring. The red brown suspension was centrifuged and washed several times with Milli-Q water to remove residual ions. The precipitates were then freeze-dried, ground into fine powder, stored in a 4 °C refrigerator, and used within 24 h.

2.2. Adsorption experiments

Adsorption experiments were performed in 500 mL conical flasks containing 300 mL aqueous solution with an industrially relevant Cr(VI) concentration of 400 µM (Balel and Kurniawan, 2004). The solution pHs were adjusted to the initial values of 3.0, 7.0, and 11.0 by 0.1~1 M HCl or NaOH solution, to represent acidic, neutral and alkaline conditions. Ferrihydrite was then added into each conical flask to obtain an adsorbent concentration of 3.0 g/L. All conical flasks were covered with a lid, and shaken at 120 ± 5 rpm and 25 ± 1 °C. After 24 h, approximately 3 mL suspensions were drawn out and filtered through a 0.45 µm membrane to determine the aqueous Cr(VI) concentration according to the methods below (Section 2.4).

2.3. Transformation experiments

After the adsorption experiments, 3 mL of 0.1 M or 1.0 M Mn(II) solutions were added into the flasks to obtain 1.0 and 10.0 mM Mn(II), respectively. The pH of solution changed after the addition of Mn(II) (Table S1), and then each suspension was readjusted to their initial pH₀ (3.0, 7.0, and 11.0). No more acids and bases were used to control the pH in the aging process. In order to observe the transformation of ferrihydrite in a relatively short period of time, the transformation experiments were controlled at 60 °C (Wang et al., 2015a; Zhang et al., 2019). Approximately 3 mL

suspensions were withdrawn from the conical flasks at 1, 3, 5, 7, 10, 15, 20 and 30 d of aging for determination of the concentration of Cr(VI), total Cr and total Mn, and the pH was recorded. After 30 d, the solid samples were characterized according to the methods below (Section 2.5). All these experiments were conducted in the presence of air.

In the control experiments, pure ferrihydrite without Cr(VI) and Mn(II) was aged. The overview of experimental conditions for ferrihydrite aging is shown in Table 1. In addition, more control experiments (Table S2 and S3) were carried out for a more comprehensive discussion.

Table 1

Overview of experimental conditions for ferrihydrite aging.

Treatment group No.	pH ₀	Initial Cr(VI) concentration (μM)	Initial Mn(II) concentration (mM)	Volume (mL)	Ferrihydrite concentration (g/L)
1	3.0	0	0	300	3.0
2	3.0	400	0	300	3.0
3	3.0	400	1.0	300	3.0
4	3.0	400	10.0	300	3.0
5	7.0	0	0	300	3.0
6	7.0	400	0	300	3.0
7	7.0	400	1.0	300	3.0
8	7.0	400	10.0	300	3.0
9	11.0	0	0	300	3.0
10	11.0	400	0	300	3.0
11	11.0	400	1.0	300	3.0
12	11.0	400	10.0	300	3.0

2.4. Determination of the concentration of Cr(VI), total Cr, and total Mn

The Cr(VI) concentrations were measured using a UV/visible spectrophotometer (UV2400) and 1,5-diphenylcarbazide was used as the complexing agent (Yuan et al., 2014). The total aqueous concentrations of Mn and Cr were measured using a flame atomic absorbance spectrometer (AAS) (Z-2000, Hitachi, Japan).

2.5. Characterization of the solid samples

The XRD analysis was conducted at ambient conditions using an X-ray powder diffractometer (D8 Advance, Bruker, Germany) equipped with Cu K α radiation. The diffractometer was set at the conditions of 40 kV tube voltage and 40 mA tube current over a range of 10° to 80°. The XRD patterns were collected at a scanning rate of 5°/min and a step size of 0.02° for the samples.

Particle morphologies of the aging samples were examined by a TEM (Tecnai G² F20, FEI, America) conducted at 200 kV. The samples were suspended in absolute ethanol and dispersed via sonication for 30 min, and then dropped on holey Cu grids, followed by air drying before the morphologies testing.

The FTIR analysis was performed on a Fourier Transformed Infrared Spectrometer (Nicolet IS 50, Thermo Fisher Scientific, America). The samples were mixed with KBr in a weight ratio of 1:100, and then ground into fine powder to press into tablets for determination. The measurement conditions were set at 4 cm⁻¹ and 32 scans, and collecting from 400 to 4000 cm⁻¹.

The XPS studies of the samples were conducted using an X-ray photoelectron spectroscopy (Thermo K-Alpha, Thermo Fisher Scientific, America) with Al K α

radiation at a residual pressure of 2×10^{-9} Torr. The C-C component of C 1s peak at 284.8 eV was used to calibrate the sample binding energies data. The XPSPEAK 4.1 software was used to process the XPS spectra.

3. Results and discussion

3.1. Characterization of fresh ferrihydrite

The exact structure of ferrihydrite is still unclear, and many researchers are working on this aspect of research (Manceau et al., 1990; Drits et al., 1993; Campbell et al., 1997; Michel et al., 2007; Manceau, 2009). In this study, the XRD pattern of the fresh synthetic ferrihydrite is shown in Fig. S1(a). Two very broad diffraction peaks at 35° and 62° indicated that this sample is 2-line ferrihydrite (Schwertmann and Cornell, 2000). The morphologies of ferrihydrite are shown in the TEM images of Fig. S1(b). The ferrihydrite is a poorly crystalline iron (hydr)oxide, being consistent with the results reported in the literature (Jiang et al., 2015). Large numbers of pores were present in the fluffy ferrihydrite agglomerates, leading to a high surface area of 341.5 m^2/g (Ding et al., 2018), being consistent with the 200-400 m^2/g for ferrihydrite reported in the literature (Wang et al., 2015c).

3.2. Adsorption of Cr(VI) on ferrihydrite

Figure S2 exhibits the adsorption performance of Cr(VI) by ferrihydrite at pH_0 3.0, 7.0, and 11.0. Almost all Cr(VI) (99.8%) was adsorbed on ferrihydrite at pH_0 3.0. The adsorption efficiency of Cr(VI) decreased slightly to 92.9% when the solution pH_0 increased to 7.0, and only 0.9% Cr(VI) was removed when the solution pH_0 increased to 11.0. The pH dependence of Cr(VI) adsorption is most likely due to

electrostatic interaction. Under the pH range of 3.0-11.0, Cr(VI) exists primarily as oxyanions, including HCrO_4^- at pH 3.0 and CrO_4^{2-} at pH 7.0 and 11.0 based on the values of pKa (Liang et al., 2018; Chagas et al., 2018). The zero point charge (pH_{ZPC}) of ferrihydrite was approximately 8.5 (Cismasu et al., 2013), which indicated that the surface of ferrihydrite carried negative charge at $\text{pH} > 8.5$ and positive charge at $\text{pH} < 8.5$. Therefore, acidic conditions favored the adsorption of Cr(VI) onto ferrihydrite, which was attributed to electrostatic attraction between ferrihydrite and Cr(VI) species. The force of electrostatic attraction decreased when the pH_0 increased to 7.0, and turned into electrostatic repulsion at solution pH_0 11.0.

3.3. Variations of Cr(VI) and Mn concentrations during the aging of Cr(VI)-adsorbed ferrihydrite

At pH_0 3.0, the concentration of aqueous Mn was almost unchanged during the aging of Cr(VI)-adsorbed ferrihydrite (Fig. 1), indicating that the adsorption of Mn was inhibited under such acidic condition (Abdeen et al., 2015; Fu et al., 2019). Negligible Cr(VI) was detected in the aqueous solution, indicating that most Cr(VI) was adsorbed on ferrihydrite or its transformation products at pH_0 3.0. In general, the adsorption of Mn is enhanced when the solution pH increased (Suddai et al., 2018). When the pH_0 was 7.0, the concentration of aqueous Mn decreased gradually throughout the aging process, from initial 10.0 mM to 9.0 mM and from initial 1.0 mM to 0.4 mM after 30 d of aging. The cation bridging of adsorbed Mn on ferrihydrite contributes to a greater Cr(VI) adsorption. After 30 d of aging, the aqueous Cr(VI) concentration decreased from 28.4 μM to 0.7 μM at initial Mn(II)

10.0 mM, and to 2.0 μM at initial Mn(II) 1.0 mM. However, in the treatments without Mn(II) , the concentration of aqueous Cr(VI) increased from 28.4 μM to 45.7 μM during the aging process, indicating the release of Cr(VI) from solid phase into solution. The specific surface area of ferrihydrite was usually higher than that of its transformation products. The release of Cr(VI) may be caused by the reduction of solid phase specific surface area and the reduction of adsorption sites for Cr(VI) during the aging process.

At pH_0 11.0, the aqueous Mn concentration decreased rapidly due to the forming precipitates of Mn(OH)_2 (Eq. 1). The pH dropped rapidly after the addition of Mn(II) , which was due to hydrolysis reactions and the formation of Mn(OH)_2 (Table S1 and Fig. S3). Chromium(VI) can be removed by co-precipitation with Mn(OH)_2 (Watanabe et al., 2006). Therefore, aqueous Cr(VI) concentrations decreased immediately at pH_0 11.0 after 1 d of aging. The higher initial concentration of Mn(II) , the more precipitates of Mn(OH)_2 formed, and more Cr(VI) was immobilized. During the aging process, the oxidation of Mn(II) occurred, forming Mn(III/IV) (hydr)oxide, and ferrihydrite converted to more crystalline and stable iron oxides. Likely due to the oxidation of Mn(OH)_2 and transformation of ferrihydrite, the immobilized Cr(VI) was partially released back into solution, and the aqueous Cr(VI) concentration gradually increased. In the treatment without Mn(II) , the aqueous Cr(VI) remained in high concentration (approximately 396.4 μM). The total aqueous concentration of Cr was also determined via AAS, and it was almost the same as the concentration of aqueous

Cr(VI).

Fig. 1. Variations of Cr(VI) and Mn concentrations during the aging process ([Mn(II)]₀ = 0, 1.0, 10.0 mM).

3.4. Variations of pH during the aging of Cr(VI)-adsorbed ferrihydrite

The variations of pH during the aging process are shown in Fig. S3. In the treatments without Cr(VI) and Mn(II), at pH₀ 3.0 and 7.0 (treatment group No. 1 and No. 5), the pH values of the suspension increased during the aging process, which is likely due to the adsorption of proton from solution onto the ferrihydrite surface (Wang et al., 2015a). While at pH₀ 11.0, the decrease of pH during the aging process (treatment group No. 9) was due to ferrihydrite deprotonation. These results are consistent with those reported by Wang et al. (2015a). In the presence of Cr(VI) and Mn(II), the increase of pH was inhibited at pH₀ 3.0 (treatment group No. 2, 3, and 4).

In the pH₀ 7.0 treatments (No. 6, 7, and 8), the pH dropped 2 units, and remained at around pH 5 for ~ 28 days of the experiment (Fig. S3). In the pH₀ 11 treatments (No. 10, 11, and 12), the pH decline was slightly more gradual, but pH conditions were 1-2 units less than the starting pH (Fig. S3).

3.5. Characterization of aging products

3.5.1. XRD analysis

Figure 2 shows the XRD patterns of the transformation products of ferrihydrite after 30 d of aging under various conditions. From the XRD measurements, it was evident that there were numbers of sharp diffraction peaks in the products after ferrihydrite aging. Most of the observed peaks was assigned to either hematite or goethite. At pH₀ 3.0 (Fig. 2(a)), the characteristic hematite peaks and goethite peaks were found in the secondary mineralization of pure ferrihydrite (treatment group No. 1). In the treatment of Cr(VI)-adsorbed ferrihydrite (No. 2), the relative diffraction peak intensities of goethite decreased distinctly, while the relative diffraction peak intensities of hematite were almost the same as that of treatment group No. 1. In the treatments with Mn(II) (No. 3 and 4), the hematite peak intensities increased slightly. Wang et al. (2015a) reported the low concentrations of Mn(II) favored the phase transformation of ferrihydrite into goethite at pH 4, 5.5, and 7, and proposed that little amount of adsorbed Mn(II) favored the formation of goethite over hematite under acidic and neutral conditions. However, negligible Mn(II) was adsorbed onto ferrihydrite at pH₀ 3.0 in our study (Fig. 1), so the presence of Mn(II) did not show a promotion function for goethite formation at pH₀ 3.0. Besides, the adsorbed Cr(VI) on

ferrihydrite may inhibit the dissolution of ferrihydrite, and then result in the inhibition of goethite formation. The formation of goethite and hematite compete with each other, so the inhibition in the formation of goethite may lead to the transformation of ferrihydrite toward the formation of hematite.

Increasing pH_0 to 7.0 (Fig. 2(b)), in the treatment of pure ferrihydrite (treatment group No. 5), the diffraction peaks of hematite were dominant while the diffraction peaks of goethite were minor. This observation indicated that most of ferrihydrite converted to hematite instead of goethite at pH_0 7.0. The adsorbed Cr(VI) alone show negligible effects on the transformation of ferrihydrite at pH_0 7.0 (treatment group No. 6). In the treatment with Mn(II) (treatment group No. 7 and 8), part of Mn(II) was adsorbed onto ferrihydrite (Fig. 1), promoting the formation of goethite. Moreover, the Mn(III/IV) (hydr)oxides occurred, including manganite ($\gamma\text{-MnOOH}$), hausmannite (Mn_3O_4), and birnessite ($\delta\text{-MnO}_2$), indicating the oxidation of Mn(II). At pH_0 11.0 (Fig. 2(c)), the characteristic peaks of hematite and goethite were detected (treatment group No. 9), indicating that aging ferrihydrite at alkaline condition favored the formation of both hematite and goethite. The inhibition by adsorbed Cr(VI) for the formation of goethite seemed to be negligible at pH_0 11.0 (treatment group No. 10). The Mn(III/IV) (hydr)oxide minerals also occurred under the condition of pH_0 11.0 (treatment group No. 12). No obvious diffraction peaks of Mn oxides were found in treatment group No. 11, which may be due to the low concentration of Mn(II) (1.0 mM). The control experiments containing only Mn(II) and ferrihydrite were also investigated (Table S2 and Fig. S4).

Fig. 2. XRD patterns of the transformation products (The aging temperature is 60 °C, and the experimental conditions of treatment group are shown in Table 1. H: hematite; G: goethite; Ma: manganite; Ha: hausmannite; Bi: birnessite).

3.5.2. TEM analysis

To investigate the particle morphologies of the aging products resulting from ferrihydrite, TEM analysis was carried out. At pH₀ 3.0, the pure ferrihydrite transformed partially into granular hematite and short rod-shaped goethite, and part of ferrihydrite still existed in fluffy agglomerates (Fig. 3(a)). The presence of adsorbed Cr(VI) inhibited the formation of goethite, and no goethite was found from the TEM images (Fig. 3(b)). In the treatment with Mn(II), more hematite particles were

observed in Fig. 3(c), where the remaining ferrihydrite became less. These results further confirmed the above XRD results (Fig. 2(a)).

Increasing pH_0 to 7.0, hematite was dominant in the secondary mineralization of pure ferrihydrite (Fig. 3(d)). The presence of adsorbed Cr(VI) seem to have minor effect on the formation of secondary minerals at pH_0 7.0 (Fig. 3(e)). While the acicular goethite was observed in the treatment with Mn(II) at pH_0 7.0 (Fig. 3(f)). Under the condition of pH_0 11.0, ferrihydrite transformed entirely into secondary minerals. Hematite was dominant in the transformation products resulting from both pure ferrihydrite and Cr-adsorbed ferrihydrite (Fig. 3(g) and (h)). In the treatment group No. 12, fibrous manganite and cubic hausmannite were observed resulting from the oxidation of Mn(II) (Fig. 3(i)). According to the study by Lan et al. (2017), the occurrence of these Mn(III/IV) (hydr)oxide minerals can be explained by the direct electron transfer in the Mn(II)-O₂ complexes, electron transfer in the complexes of Mn(II)-Fe(III)-O₂ and electron transfer in the complexes of Mn(II)-Conduction Band of ferrihydrite-O₂.

Fig. 3. TEM images of the transformation products (treatment group (a) No. 1, (b) No. 2, (c) No. 4, (d) No. 5, (e) No. 6, (f) No. 8, (g) No. 9, (h) No. 10, (i) No. 12). F: ferrihydrite; H: hematite; G: goethite; Ma: manganite; Ha: hausmannite).

3.5.3. FTIR analysis

Figure 4 shows the FTIR spectra of the transformation products. The signature peak at $\sim 3400\text{ cm}^{-1}$ observed for samples in all treatment group is due to OH

301 stretching (Saleh et al., 2017), while the characteristic peak near 1630 cm^{-1} is ascribed
302 to the H-O-H band of water molecules, likely due to the physisorbed water on the
303 secondary minerals (Zhang et al., 2009; Ren et al., 2011). In treatment group No. 1, 7,
304 8, 9, 10, 11, and 12, two OH bending bands at 892 cm^{-1} and 795 cm^{-1} are ascribed to
305 δ -OH and γ -OH, which are the characteristic peaks of goethite (Salama et al., 2015).
306 Hematite also has two significant bands at 471 cm^{-1} and 548 cm^{-1} (Salama et al., 2015).
307 For all treatment groups, hematite was observed. It should be noted that the
308 absorbance peaks at 471 cm^{-1} and 548 cm^{-1} of the transformation products at pH_0 11.0
309 were much higher than those at pH_0 3.0 and 7.0. This was attributed to the fact that
310 more hematite formed at pH_0 11.0. In the presence of Cr(VI), a small peak at 906 cm^{-1}
311 was observed in treatment group No. 2, 3, 4, 6, which is likely associated with Cr(VI)
312 (Zhang et al., 2018). However, in the treatments with Mn(II) at pH_0 7.0 and 11.0 (No.
313 7, 8, 11, and 12), the small peak at 906 cm^{-1} disappeared, which may be due to the
314 reduction of Cr(VI) to Cr(III).

Fig. 4. FTIR spectra of the transformation products (The aging temperature is 60 °C, and the experimental conditions of these treatment groups are shown in Table 1).

3.5.4. XPS analysis

XPS, a surface characterization technique, was used to investigate the surface chemical composition and the oxidation states of the transformation products. As shown in Fig. 5(a), the full-range of XPS spectra showed the presence of Fe, Cr, O, and C on the surface of secondary minerals in treatment group No. 2, 6, 8 and 12, and the presence of Mn on the surface of final transformation products in treatment group No. 8 and 12. Compared with treatment group No. 8, the higher relative intensity of

Mn 2p in treatment group No. 12 was attributed to the complete precipitation of Mn(II) at pH₀ 11.0, which was confirmed by the concentration of aqueous Mn (Fig. 1).

The Fe 2p high resolution spectra is shown in Fig. 5(b), where the binding energies at 724.8 eV and 711.2 eV were associated with Fe 2p_{1/2} and Fe 2p_{3/2}, respectively, attributing to the presence of Fe(III) (Peng et al., 2015). Moreover, a broad satellite peak located at about 719 eV was a characteristic peak of Fe(III) in iron (hydr)oxides (Mallet et al., 2013). The results of Fe 2p spectra showed that Fe existed in the oxidation state of +3 in the transformation products of treatment group No. 2, 6, 8, and 12.

In the O 1s high resolution spectra (Fig. 5(c)), the spectra were satisfactorily divided into three peaks. These peaks at 532.1-532.4 eV, 530.9-531.2 eV, and 529.6-529.9 eV were associated with O in adsorbed H₂O, hydroxyl bonded to metal (M-OH), and metal oxide (M-O), respectively. According to the peak area analysis, M-O accounted for the largest proportion, followed by M-OH, and H₂O was the least. The M-OH on iron (hydr)oxide surface is important for the immobilization of contaminants, including Cr(VI) (Huang et al., 2016), As(III) (Wen et al., 2014), and Zn(II) (Rout et al., 2012). In this study, the presence of M-OH may contribute greatly to the immobilization of Cr(VI).

In the Mn 2p_{3/2} high resolution spectra (Fig. 5d), there were three peaks associated with different oxidation states of Mn. These peaks were located at binding energies of 640.6 eV, 641.6 eV, and 642.8 eV for Mn(II), Mn(III) and Mn(IV), respectively (Jefferson et al., 2015). According to the peak area analysis, Mn species in the solid phase were mainly present in Mn(III) and Mn(IV), indicating that most

Mn(II) in the solid had been oxidized to Mn(III/IV) after the aging process. The dissolved O₂ in solution can contribute to the oxidation of Mn(II). Previous study reported that the oxidation of Mn(II) by dissolved O₂ was promoted by iron (hydr)oxides surfaces under neutral and alkaline conditions, forming Mn(III/IV) (hydr)oxides (Feng et al., 2004; Wang et al., 2015a; Wang et al., 2015b).

As shown in Fig. 5(e), the Cr 2p_{3/2} signals of transformation products in treatment group No. 2, 6, 8, and 12 showed different peaks. The peaks at 578.0 eV and 576.6 eV are assigned to Cr(VI) and Cr(III), respectively (Shen et al., 2013). Without the treatment with Mn(II), a broad and weak peak at about 578.0 eV indicated that Cr species existed mainly as Cr(VI) in the treatment group No. 2 and 6. With the treatment of Mn(II), the spectra of Cr 2p_{3/2} can be deconvoluted into two overlapped peaks associated with Cr(VI) and Cr(III) in the treatment group No. 8 and 12. The new occurring Cr(III) indicated that Cr(VI) was reduced partly into Cr(III). Given the oxidation of Mn(II) in treatment group No. 8 and 12, the reduction of Cr(VI) may be associated with the oxidation of Mn(II). Although Cr(III) can be oxidized by Mn (hydr)oxides under acidic conditions (Landrot et al., 2012), the oxidation of Cr(III) by Mn (hydr)oxides was greatly inhibited at pH > 4 (Fendorf et al., 1992). In addition, James reported that the addition of Mn(II) resulted in the reduction of Cr(VI) at pH > 7.2 (James, 1994), and Mu et al. also reported that Mn(II) promoted the reduction of Cr(VI) (Mu et al., 2018). Therefore, the reduction of Cr(VI) was likely associated with the oxidation of Mn(II) in the treatment group No. 8 and 12, where the initial pH is 7.0 and 11.0, respectively. The control experiments in nitrogen atmosphere were also investigated (Table S3 and Fig. S5).

(a) Full range of XPS spectra

(b) Fe 2p

(c) O 1s

(d) Mn 2p_{3/2}

(e) Cr 2p_{3/2}

Fig. 5. (a) Full-range of XPS spectra, (b) Fe 2p spectra, (c) O 1s spectra of treatment group No. 2, 6, 8, and 12, (d) Mn 2p_{3/2} spectra of treatment group No. 8, 12, and (e) Cr 2p_{3/2} spectra of treatment group No. 2, 6, 8, and 12.

3.6. Mechanisms of Cr(VI)-adsorbed ferrihydrite transformation in the presence of Mn(II)

Based on the discussion above, the potential mechanisms of Cr(VI)-adsorbed ferrihydrite aging in the presence of Mn(II) are proposed (Fig. 6). The Cr(VI) adsorption was enhanced with the decrease of pH. At pH₀ 3.0, almost all Cr(VI) was adsorbed onto ferrihydrite, and hematite was the main transformation products after the aging process, and the Cr(VI) was stably immobilized by ferrihydrite and hematite. At pH₀ 7.0, the adsorption efficiency of Cr(VI) decreased slightly, and hematite and goethite were the main transformation products of Cr(VI)-adsorbed ferrihydrite. Part of Mn(II) was oxidized to Mn(III/IV) (hydr)oxide after 30 d of aging, and Cr(VI) was reduced partly to Cr(III). At pH₀ 11.0, almost no Cr(VI) was adsorbed on ferrihydrite. After addition of Mn(II), Cr(VI) was immobilized with the precipitation of Mn(II), but released partly back into solution during the aging process. After aging for 30 d, the Mn(III/IV) (hydr)oxide formed, and part of Cr(VI) was reduced to Cr(III). Wang et al. (2015a) suggested that the redox transformation between Mn(II) and ferrihydrite may occur to produce trace Fe(II) when Mn(II) has been adsorbed on the ferrihydrite (Eqs. (2) and (3)). In this case, the generated Fe(II) could result in the reduction of Cr(VI) (Eqs. (4) and (5)).

Overall, ferrihydrite may act as an electron shuttle in the redox reactions between Cr(VI) and Mn(II) to mediate the electron transfer process. Similar results were

reported by Cerkez et al. (2015). They observed the redox transformation of Cr(VI) and As(III) on ferrihydrite, where ferrihydrite acts as an electron shuttle for electron transfer. During the aging process, the pH values decreased from initial 7.0 to 4.6, and from initial 11.0 to 8.8. Therefore, the Cr(III) exists mainly as $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, and $\text{Cr}(\text{OH})_3$, and the Cr(VI) exists mainly as HCrO_4^- and CrO_4^{2-} (Kotaś and Stasicka, 2000). The pH_{ZPC} of Mn (hydr)oxides is often lower than that of iron (hydr)oxides, so the surface of Mn (hydr)oxides carries more negative charge than iron (hydr)oxides do in the treatment group No. 7 and 8 at pH_0 7.0 and treatment group No. 11 and 12 at pH_0 11.0. Due to electrostatic interaction, the positive charged $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})_2^+$ are more likely to be adsorbed on Mn oxides, and the negative charged HCrO_4^- and CrO_4^{2-} are more likely to be adsorbed on iron (hydr)oxides. However, it should be noted that in addition to electrostatic interactions, surface complexation and cationic bridging also contribute to the immobilization of Cr species.

Fig. 6. Conceptual schematic diagram of Cr(VI)-adsorbed ferrihydrite aging in the presence of Mn(II).

4. Conclusions

This study examined the phase transformation of Cr(VI)-adsorbed ferrihydrite in the presence of aqueous Mn(II), and the fate of adsorbed Cr(VI) and aqueous Mn(II) during the phase transformation of ferrihydrite. Ferrihydrite was transformed into hematite and goethite, where hematite was dominated in the transformation products. The adsorbed Cr(VI) inhibited the formation of goethite, while the little amount of adsorbed Mn(II) promoted the formation of goethite. In the absence of Mn(II), the immobilization of Cr(VI) was enhanced with the decrease of pH. In the presence of Mn(II), the adsorption of Mn(II) was enhanced with the increase of pH, and the adsorption and precipitation of Mn(II) favored the immobilization of Cr(VI) at pH₀ 7.0 and 11.0. After aging for 30 d at pH₀ 7.0 or 11.0, the Cr species in solid phase existed primarily as Cr(III), and Mn species in solid phase existed primarily as Mn(III/IV). Ferrihydrite may act as an electron shuttle in the redox transformation between Cr(VI) and Mn(II) to mediate the electron transfer process. This study can expand our understanding of the interactions and geochemical processes of chromium, iron, and manganese in subsurface soil/sediments downstream of an industrial Cr(VI) source.

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Figures

Figure 1

Variations of Cr(VI) and Mn concentrations during the aging process ([Mn(II)]₀ = 0, 1.0, 10.0 mM).

Figure 2

XRD patterns of the transformation products (The aging temperature is 60 oC, and the experimental conditions of treatment group are shown in Table 1. H: hematite; G: goethite; Ma: manganite; Ha: hausmannite; Bi: birnessite).

Figure 3

TEM images of the transformation products (treatment group (a) No. 1, (b) No. 2, (c) No. 4, (d) No. 5, (e) No. 6, (f) No. 8, (g) No. 9, (h) No. 10, (i) No. 12). F: ferrihydrite; H: hematite; G: goethite; Ma: manganite; Ha: hausmannite).

Figure 4

FTIR spectra of the transformation products (The aging temperature is 60 oC, and the experimental conditions of these treatment groups are shown in Table 1).

Figure 5

(a) Full-range of XPS spectra, (b) Fe 2p spectra, (c) O 1s spectra of treatment group No. 2, 6, 8, and 12, (d) Mn 2p_{3/2} spectra of treatment group No. 8, 12, and (e) Cr 2p_{3/2} spectra of treatment group No. 2, 6, 8, and 12.

Figure 6

Conceptual schematic diagram of Cr(VI)-adsorbed ferrihydrite aging in the presence of Mn(II).

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