Sorption mechanism of chromate by ferrihydrite and sulfate green rust: comparison by XAFS analysis

*Abdullah Al Mamun[1], Aina Onoguchi[2], Giuseppe Granata[3], Chiharu Tokoro[4]

*[1,2] Graduate School of Creative Science and Engineering, Waseda University, Japan ([1]*mamun@toki.waseda.jp, [2]sept.amour@ruri.waseda.jp), [3,4] Faculty of Science and Engineering, Waseda University, Japan ([3]giuseppe.granata@aoni.waseda.jp, [4]tokoro@waseda.jp)

Abstract

Hexavalent chromium is toxic, carcinogenic and difficult to remove from wastewater due to its high mobility. In this work, we elucidated the sorption mechanism of chromate by ferrihydrite and two types of sulfate green rust; one prepared at pH 8.75 ($GR_{8.75}$) and another one prepared at pH 7.50 ($GR_{7.50}$). We used XAFS analysis to investigate their behaviour by changing the Cr/Fe molar ratio and pH. The $GR_{8.75}$ was found to be 1.7 times more efficient than $GR_{7.50}$ and 6.7 times more efficient than ferrihydrite towards the chromate removal. XAFS indicated that ferrihydrite removed Cr(VI) *via* outer-sphere surface complexation at lower Cr/Fe ratios and *via* inner-sphere surface complexation at higher molar ratios. At higher molar ratios, bidentate binuclear Cr-Fe bonds were dominant and resulted in the expansion of the ferrihydrite structure. For lower molar ratio, both the GRs resulted into the formation of bidentate mononuclear Cr-Fe bonding like $FeCr_2O_4$ even at variable pH. The increase of Fe-Fe edge sharing and double corner sharing coordination numbers confirmed the surface-based redox reaction for $GR_{8.75}$. On the contrary, the significant single corner sharing Fe-Fe coordination *via* oxygen might be the indication of the lateral insertion of Cr into $GR_{7.50}$.

（1 line space）

    Keywords: Chromate, ferrihydrite, green rust, XAFS, pH (5 keywords at maximum)

（2 lines space）

1. Introduction

Hexavalent chromium (Cr(VI)) is well known to be toxic for the ecosystem [1] and more difficult to remove compared to Cr(III). Recently, iron oxides as layered double hydroxides LDH have been found effective and efficient for chromate removal. Among them, sulfate green rust and ferrihydrite are the most studied due to their performances and natural availability in environments contaminated by chromium.

Ferrihydrite (Fh) [$(Fe^{3+})_2O_3.0.5H_2O$] is a widespread hydrous ferric oxy-hydroxide mineral at the Earth's surface, and a likely constituent in extra-terrestrial materials. Due to its nanocrystal and nano porous structure, the hydrous ferric oxide (2 line ferrihydrite) has inbuilt ability to adsorb toxic anions species like chromate, arsenate and selenate [2]. Nevertheless, the information available about its removal mechanism in coprecipitation are very few. On the other hand,

green rust (GR) is a layer double hydroxide Fe(II) and Fe(III) compound that can contain anions like Cl^-, CO_3^{2-}, SO_4^{2-} and water molecules in the interlayer. Due to its efficiency towards the removal of toxic species like chromate and selenate in aqueous media, GR has been recently attracting the researchers' attention. However, the information available about its ability and removal mechanism are little and often conflicting.

In this work, we explore in detail the sorption mechanism of both ferrihydrite and sulfate green rust through an advanced analytical technique as X-ray fine structure absorption (XAFS).

2. Materials and methods

2.1 Preparation of ferrihydrite and GR

All chemicals used in this study were of analytical grade from Wako Chemical Industries (Japan). The Cr(VI) solution

Contact: Abdullah Al Mamun, Doctoral course student, Tokoro laboratory, Waseda university,
Address: 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
E-mail Address: mamun@toki.waseda.jp, phone number: 080-8806-4451

was prepared by dissolving K_2CrO_4 in deionized distilled water while Fh was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ and adjusting the pH in the presence of the chromate solution. The GRs solutions were prepared by dissolving in distilled water pre-defined amounts of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot nH_2O$ and by titrating with 8 M NaOH [3]. All experimental procedures were carried out in a glove box under argon atmosphere. For the investigation of the influence of the preparation pH, two different types of sulfate-GR were prepared by titrating at pH 7.5 ($GR_{7.50}$) and at pH 8.75 ($GR_{8.75}$).

2.2 Batch experiments

The batch experiments were carried out by investigating different Cr/Fe molar ratio. The reaction time was set as 1 hour. In the co-precipitation experiments with ferrihydrite, ferrihydrite was prepared in the presence of Cr(VI) [4]. On the other hand, two types of previously prepared GRs were used in the batch experiments at fixed $Cr/GR_{(T-Fe)}$ ratio.

2.3 XAFS analysis

For X-ray absorption fine structure (XAFS) analysis, both XANES (X-ray Absorption Near-Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) analysis were performed using the beamline BL5S1 in Aichi Synchrotron Radiation Center, Nagoya, Japan. For this purpose, the samples obtained from the co-precipitation experiments were freeze-dried at -45 °C and 10 Pa at least 24 h to avoid crystallization or mineralogical transformation. The precipitates from green rust were vacuum dried within the Ar flushed pass-box within the glove box.

For the analysis, the ionization chamber was filled with N_2 gas (30%) and He gas (70%) to monitor the incident beam. N_2 gas (75%) and Ar (25%) was used used for the transmission beam. The solid samples were coated by a transparent tiny plastic layer, to avoid any influence of the ionization gas in the ionization chamber. The pure ferrihydrite synthesized at pH 5 (Cr/Fe=0), $GR_{8.75}$ and the $GR_{7.50}$ without chromate were used as a reference material for Fe K-edge.

3. Results and Discussion
3.1 Removal performance

A comparison of chromate removal by $GR_{8.75}$, $GR_{7.50}$ and ferrihydrite at different Cr/Fe molar ratio by fixing the pH at 5 as at this pH both sulfate-GR and ferrihydrite showed the best performance in terms of chromate sorption density (figure not shown). Although both GRs were proven efficient towards the removal of chromate below the Japanese wastewater standard, the $GR_{8.75}$ was found 6.7 times more efficient than ferrihydrite and around 1.7 times more efficient

than $GR_{7.50}$ in terms of required amount of iron to obtain the same performance. Accordingly, $GR_{7.50}$ showed 4 times higher removal efficiency than ferrihydrite.

3.2 XAFS analysis with ferrihydrite

Fe K-edge XANES and EXAFS spectra of Cr(VI)-coprecipitated ferrihydrite and fresh ferrihydrite did not show any visible difference. In order to highlight the difference, fourier transformed spectra resembling K^3-weighted EXAFS area fitting was done using goethite (α-FeOOH) [5] to obtain the initial values of the fitting parameters (Fig. 1).

Ferrihydrite usually shows two Fe–Fe shell configurations: one is the edge sharing and the other one is the double-corner sharing. In our case, the interatomic distance was slightly smaller (~0.15 Å) than the previous Fe–Fe second shell distance range of 3.4–3.5 Å. The reason may be researched in the ionic strength adjustment to 0.05 M. Like most of researchers, we obtained two Fe–Fe shell fittings with an interatomic distance of 3.05 ± 0.01 Å (edge sharing) and 3.35 ± 0.003 Å (double-corner sharing).
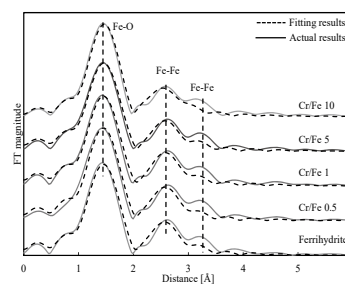

Fig. 1 Fourier-transformed unfiltered spectra and fitting results of Fe K-edge with changing Cr/Fe molar ratio (co-precipitation at pH 5).

The crystal structure of $Fe_2(CrO_4)_3 \cdot 3H_2O$ by Bonin [6] was used to provide the initial fitting parameters for K^3-weighted EXAFS fitting (Fig. 2). The Cr–O distance was ~1.63 Å (data not shown). For high surface coverage at higher Cr/Fe molar ratio below pH 6, the bidentate Cr–Fe relationship is more likely to be established [7]. Our findings suggest that the Cr–Fe surface complexation is close to the bidentate binuclear complex (~3.378 Å) and comprises tetrahedral Cr and octahedral Fe bonding.
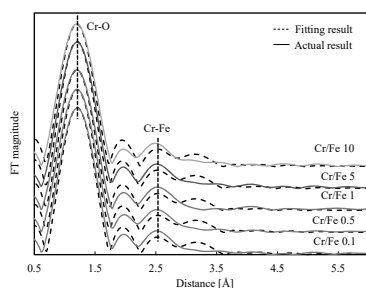
Fig. 2 Fourier-transformed unfiltered spectra and fitting results of Cr K-edge with changing Cr/Fe molar ratio (co-precipitation at pH 5).

Fe–O has an almost octahedral geometry (data not shown). However, for Cr/Fe molar ratio of 0.5, the Fe–O, and Fe–Fe interatomic distance slightly decreased compared to ferrihydrite (Fig. 3). Besides by, increasing the Cr/Fe molar ratio, the interatomic distances gradually increased. This is another notable point regarding the mechanism shift or modification of the local microenvironment between Cr/Fe ratio 0 to 0.5, and this result matches with previously described zeta potential results in which mechanism shift was suggested for Cr/Fe 0.25 in coprecipitation. However, the gradual increase of the interatomic distance between the Fe–O from the Cr/Fe ratio of 0 to a Cr/Fe ratio of 1 suggests that a small amount of tetrahedral Fe^{III} might exist in the ferrihydrite chain and the tetrahedral Fe^{III} might have rearranged to pure octahedral because of the inhibition of a significant amount of chromate.

The Cr–Fe interatomic distance slightly increased from a 0.1 to a 0.5 Cr/Fe molar ratio whilst it decreased above 0.5 (Fig. 3). For the Cr/Fe between 0.1 and 0.5, Cr–Fe might be coordinated via oxygen atoms [6] and the direct coordination increased gradually by decreasing the Cr–Fe interatomic distance at Cr/Fe molar ratio above 0.5. This trend is opposite to Fe-O (Fig. 3). This result suggests that more inner-sphere surface complexation exists for higher Cr/Fe molar ratios.
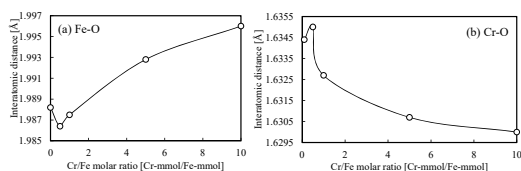

Fig. 3 Inter-atomic distance with changing Cr/Fe molar ratio obtained from EXAFS fitting: (a) Fe K-edge Fe–O inter-atomic distance, (b) Cr K-edge Cr–O inter-atomic distance.

3.2 XAFS analysis with sulfate green rust

XANES results revealed the presence of chromium as Cr(III) irrespective of the pH for both $GR_{8.75}$ and $GR_{7.50}$.

Interestingly, the $GR_{7.50}$ that reacted at pH 5 showed also a minor amount of residual Cr(VI) [8] (figure not shown). Because the surface analysis did not reveal any Cr(VI) on the surface of $GR_{7.50}$, the one detected by XANES must be located in the interlayer. This evidence, along with previous results, is a further confirmation that the Cr(VI) of chromate was preferentially reduced to Cr(III) by $GR_{7.50}$ from the interlayer, upon replacement of the sulfate ion. The fitting of the K^3 weighted EXAFS spectra against ferrihydrite, goethite, magnetite, hematite and GR references (data not shown) confirmed for $GR_{8.75}$ an enhanced formation of magnetite and goethite respectively at pH 9 and 5. As for $GR_{7.50}$, the EXAFS fitting results highlighted a predominant formation of goethite/ferrihydrite along with a 10-15% hematite.

The Fourier-transformed spectra corresponding K^3 weighted EXAFS spectra of Fe-K edge as well as Cr-K edge were fitted to determine the change of interatomic distances and coordination numbers. In order to highlight the differences, the fitting was carried out using goethite (α-FeOOH) and hematite (Fe_2O_3) references to obtain the initial values of the fitting parameters. For all conditions, the Fe K-edge RDF fitting results (Fig. 4) also revealed the presence of Fe-Fe edge sharing and double corner sharing bonds [9] along with Fe-Fe monodentate single corner sharing via oxygen bonding [10]. For $GR_{8.75}$ upon reaction with chromate, the Fe-Fe edge sharing and double corner sharing coordination almost doubled, increasing from 2.45 to 4.48 and from 3.38 to 5.90, respectively. This change is thought to be due to a redox reaction taking place from the surface of GR. In comparison, $GR_{7.50}$ showed a great affinity towards the corner sharing coordination that increased by 6.5 to 10.70 times upon reaction with the chromate, thereby suggesting the lateral insertion of chromate with sulfate replacement.
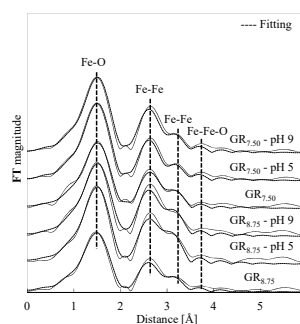

Fig. 4 Fourier-transformed unfiltered spectra and fitting results of Fe K-edge for $GR_{8.75}$ and $GR_{7.50}$ before and after the removal experiments at pH 5 and 9
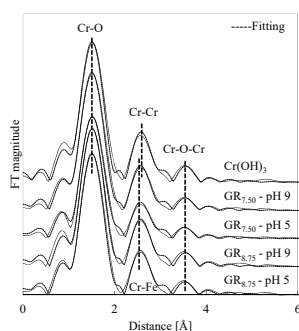
Fig. 5 Fourier-transformed unfiltered spectra and fitting results of Cr K-edge for GR8.75 and $_{GR7.50}$ after the removal experiments at pH 5 and 9 and chromium hydroxide

The Cr K edge Fourier-transformed spectra were fitted with chromium oxides (Cr_2O_3) and iron chromite ($FeCr_2O_4$) (Fig. 5). The Cr-Cr bonding like $Cr(OH)_3$ seemed to change to Cr-Fe bonding with shorter interatomic distances and increased coordination number, thus suggesting the formation of chromite. The Cr-Fe bonding showed a bidentate mononuclear (~2.91Å) geometry instead of a bidentate binuclear (~3.29Å) sharing [11]. Interestingly, that corner sharing Cr-O-Cr (3.94Å) bonding increased significantly for $GR_{7.50}$, thus supporting the previous speculation about the lateral inclusion of chromium into GR.

4. Conclusion

The coprecipitation of chromate with ferrihydrite promoted bidentate-binuclear Cr-Fe coordination whereas bidentate mononuclear Cr-Fe were observed for GRs. Thus, closer Cr-Fe coordination is ensured by the green rust compared to ferrihydrite that will more unlikely to release in the environment.

5. REFERENCES

[1]   Y.M. Tzou, M.K. Wang, R.H. Loeppert, Sorption of phosphate and Cr(VI) by Fe(III) and Cr(III) hydroxides, Arch. Environ. Contam. Toxicol. 44 (2003) 445–453.

[2]   J.F.F. Matthew F. Schultr, Mark M. Benjamin, Adsorption and Desorption of Metals on Ferrihydrite: Reversibility of the Reaction and Sorption Properties of the Regenerated Solid, Environ. Sci. Technol. 21 (1987) 863–869.

[3]   H. Hayashi, K. Kanie, K. Shinoda, A. Muramatsu, S. Suzuki, H. Sasaki, pH-dependence of selenate removal from liquid phase by reductive Fe(II)-Fe(III) hydroxysulfate compound, green rust, Chemosphere. 76 (2009) 638–643.

[4]   F. Futami, C. Tokoro, S. Izawa, S. Owada, Mechanism of As（Ⅴ）Removal in Wastewater Treatment Using Fe（Ⅲ）-Supported Exchange Resins, 9 (2014) 3–9.

[5]   Y. Hexiong, L. Ren, R.T. Downs, G. Costin, Goethite, alfa- FeO(OH), from single-crystal data, Acta Crystallogr. Sect. E Struct. Reports Online. 62 (2006).

[6]   P.A.R.E.A. BONNIN, Structure CristalUne de Fe2(CrO4)3.3H20 alpha, Acta Cryst. 2 (1978) 706–709.

[7]   C.P. Johnston, M. Chrysochoou, Investigation of chromate coordination on ferrihydrite by in situ ATR-FTIR spectroscopy and theoretical frequency calculations, Environ. Sci. Technol. 46 (2012) 5851–5858.

[8]   A.J. Berry, H.S.C. O'Neill, A XANES determination of the oxidation state of chromium in silicate glasses, Am. Mineral. 89 (2004) 790–798.

[9]   A. Al Mamun, M. Morita, M. Matsuoka, C. Tokoro, Sorption mechanisms of chromate with coprecipitated ferrihydrite in aqueous solution, J. Hazard. Mater. 334 (2017) 142–149.

[10]   G.A. Waychunas, B.A. Rea, C.C. Fuller, J.A. Davis, Surface chemistry of ferrihydrite: Part 1.EXAFS studies ongeometrie of coprecipitated and adsorbed arsenate, Geochim. Cosmochim. Acta. 57 (1992) 2251–2269.

[11]   S. Fendorf, M.J. Eick, P. Grossl, D.L. Sparks, Arsenate and Chromate Retention Mechanisms on Goethite. 1. Surface Structure, Environ. Sci. Technol. 31 (1997) 315–320.