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Research paper

Role of pH in green rust preparation and chromate removal from water

Abdullah Al Mamun[a], Aina Onoguchi[a], Giuseppe Granata[b], Chiharu Tokoro[b],*

[a] *Graduate School of Creative Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*
[b] *Faculty of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

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ABSTRACT

The removal of hexavalent chromium from water by sustainable methods still presents challenging aspects. Green rust (GR) is a mixed Fe(II)-Fe(III) layer double hydroxide intercalated with anions and water molecules that was recently found capable of immobilizing low concentrations of chromate. Nevertheless, the influence of pH on GR preparation and chromate removal mechanism has not been fully clarified yet. This work elucidated the influence of pH on GR preparation and chromate removal by sulfate-GR. Two types of GR were prepared at two different pH, namely pH 8.75 ($GR_{8.75}$) and 7.50 ($GR_{7.50}$), and were used in chromate removal experiments at pH 5 and 9. XRD, XPS and XAFS analysis were carried out to assess the change of phase composition, surface oxidation state and crystal structure. Increasing the preparation pH from 7.50 to 8.75 produced a larger inclusion of SO_4^{2-} and Na^+ within the GR interlayer and resulted in a larger crystal lattice and more surface area. $GR_{8.75}$ was 1.7 times more efficient than $GR_{7.50}$ and 6.7 times more efficient than ferrihydrite as Fe required to remove 10 mg/L of chromate from water. While removing chromate, $GR_{7.50}$ released a larger amount of SO_4^{2-} than $GR_{8.75}$ in spite of a lower initial content. At pH 5, $GR_{8.75}$ reduced chromate and oxidized mostly to goethite, whereas magnetite was the main oxidation product at pH 9. In contrast, $GR_{7.50}$ removed chromate and transformed into Cr-intercalated ferrihydrite. XPS results confirmed the larger passivation of $GR_{8.75}$. All results indicated that $GR_{8.75}$ removed chromate mainly *via* surface reduction whilst $GR_{7.50}$ removed it mostly *via* replacement of SO_4^{2-} in the interlayer prior to reduction. EXAFS analysis of solid residues highlighted the presence of bidentate mononuclear $FeCr_2O_4$-like Cr—Fe bonding as well as Cr_2O_3-like Cr—O and Cr—O—Cr bonding under all investigated conditions. The increase of Fe—Fe edge sharing and double corner sharing coordination numbers in the final solid product upon chromate removal by $GR_{8.75}$ suggests a surface-based reaction between GR and chromate. In contrast, for $GR_{7.50}$ upon chromate removal, the increase of single corner sharing Fe—Fe coordination *via* oxygen can be resulted from lateral insertion of chromate into GR interlayer.

1. Introduction

The contamination of soil and surface water by hexavalent chromium (Cr(VI)) is a well-known environmental issue determined by the non-proper discharge of wastewater from various industrial processes such as electroplating, tannery and production of painting pigments (Loyaux-Lawniczak et al., 2000). Because Cr(VI) is carcinogenic and it is difficult-to-treat due to its high mobility, Cr(VI) contamination is a major current concern (Bond and Fendorf, 2003). Kaprara et al. (2015) reported of 95 worldwide conventional tannery sites posing direct or indirect threat to almost 1.6 million of people.

Conventional processes to immobilize Cr(VI) include ion-exchange and/or adsorption on activated carbon (Yanan et al., 2018). However, because the removal efficiency for Cr(VI) is still too low compared to Cr (III) (Wang et al., 2013), alternative methods for removal of Cr(VI) must be developed. Engineered biomasses such as tree-bark (Xavier et al., 2013), leaves (Jadhav et al., 2016), agricultural waste (Namasivayam and Sureshkumar, 2008) and soils (Bolortamir and Egashira, 2008), bio-remedial (Dhal et al., 2013) also exhibit interesting removal properties towards chromate. However, these materials are often geographically localized and seasonal, whereas a sustainable chromate removal requires cost-effective and widely available removing agents. In this view, zero valent iron has been also attracting much attention as a potentially sustainable removing agent for

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Abbreviations: AS, Absorption spectroscopy; EXAFS, Extended X-ray absorption fine structure; ICP-AES, Inductively coupled plasma atomic emission spectroscopy; IC, Ion chromatography; RDF, Radial distribution function; XAFS, X-ray absorption fine structure; XANES, X-ray absorption near edge structure; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction

* Corresponding author.

E-mail addresses: mamun@toki.waseda.jp (A.A. Mamun), sept.amour@ruri.waseda.jp (A. Onoguchi), giuseppe.granata@aoni.waseda.jp (G. Granata), tokoro@waseda.jp (C. Tokoro).

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chromate (Wang et al., 2018 and Zhang et al., 2013). Nevertheless, a method that valorises substances already contained in the wastewater to perform the immobilization would be even more sustainable.

Recently, several forms of iron oxides showed an interesting ability towards the immobilization of chromate, the predominant Cr(VI) species in a wide range of pH. Among them, ferrihydrite [$(Fe^{III})_2O_3{\cdot}0.5H_2O$] has been widely studied but its efficiency is still too low for commercial applications (Mamun et al., 2017).

An interesting alternative to ferrihydrite was found in GR, an iron-based structure composed by Fe(II) and Fe(III) hydroxide units intercalated with water molecules and anions such as chloride, carbonate and sulfate ions (Ayala-Luis et al., 2010a). GR exhibit layer double hydroxide (LDH) structure that can be described by the general formula $[Fe^{II}_{(6\text{-}x)}Fe^{III}_{x}(OH)_{12}]^{x+}[(A)_{x/n}.yH_2O]^{x-}$, where *A* is the anion and *n* is the anion charge. In GR, the Fe(II)/T-Fe ratio ranges between 0.8 and 0.3 (Chaves, 2005; Rogers et al., 2013a, 2013b). Another generalised formula proposed by several researchers is $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}A^{y-}_{x/y}{\cdot}mH_2O$, where M = Fe and *x* ranges from 0.25 to 0.33 (Ayala-Luis et al., 2010b). Due to the Fe(II)/T-Fe ratio lying between 0.66 and 0.75 (Hansen et al., 2001; Ruby et al., 2010), GR exhibit a considerable reducing power that could be conveniently used to reduce oxidized contaminants such as heavy metals (*e.g.* Cr(VI), U(IV), Hg(II)) and organic pollutants (Ahmed et al., 2010).

Among GRs, the ones containing sulfate ions in the interlayer are the most studied (Hayashi et al., 2009; Skovbjerg et al., 2006). This is because the sulfate ion can be naturally found in both engineered and natural geo-environmental systems like seawaters and hydromorphic soils (Christiansen et al., 2009), are easy to prepare and result into more compact precipitates. Moreover, the bio-reduction of ferric species in anoxic water systems could form the GRs mineral counterpart fougerite (Abdelmoula et al., 1998).

Most of research works on the use of GR to remove chromate from water focused on removal performances and kinetics, whereas only a few researches investigated the removal mechanism. Furthermore, the few available information about the mechanism are often conflicting. Discrepancies may arise from the differences in the experimental setup and from the very low stability of GR, which is prone to oxidation. Depending on the operating conditions, the oxidation of GR can result in the formation of different kinds of iron oxides with different oxidation states and structures, from magnetite to ferrihydrite, goethite and hematite (Erbs et al., 1999; Hansen, 1998; Kone et al., 2011; O'Loughlin et al., 2003a, 2003b). Further research is also required to elucidate the final chromium products that forms upon reaction with GR. Although Bond and Fendorf, (2003) speculated about the formation of a product like $Cr_xFe_{1\text{-}x}(OH)_3.nH_2O$, experimental evidences are still required. Furthermore, it is not clear whether sulfate-GR favours the removal through surface sorption (Hayashi et al., 2009) or intercalation (Loyaux-Lawniczak et al., 2000; Skovbjerg et al., 2006). Another interesting point to be elucidated is the relationship between pH and cation intercalation in the interlayer. While Christiansen et al. (2014) confirmed the presence of Na^+ in the interlayer, Guilbaud et al. (2013) reported that the surface of GR is positively charged at pH < 8.3 and negatively charged at pH > 8.3. Therefore, it is necessary to elucidate whether increasing the pH in GR preparation results into a larger inclusion of Na^+ due to charge shift. Ahmed et al. (2010) reported the elongation of GR-sulfate crystal lattice through *a* and *b* plane at pH higher than 8.50. Therefore, the role of pH requires further research because a different pH during GR preparation can result into different structures. In turn, different structures might exhibit different removal mechanisms and performances that is worth investigating.

This work aims to elucidate the influence of pH on GR preparation and chromate removal by sulfate-GR. Based on the evidences reported by Ahmed et al. (2010) showing the change of crystal structure beyond pH 8.50, two types of GR were prepared at two different pH, namely pH 8.75 ($GR_{8.75}$) and 7.50 ($GR_{7.50}$). The behaviour of the as-produced $GR_{8.75}$ and $GR_{7.50}$ was investigated by removal experiments at pH 5 and 9.

2. Materials and methods

2.1. Preparation of removing agents and solutions

All chemicals used in this study were of analytical grade from Wako Chemical Industries (Japan). The Cr(VI) solution was prepared by dissolving K_2CrO_4 in deionized water while the GRs solutions were prepared by dissolving pre-defined amounts of $FeSO_4{\cdot}7H_2O$ and $Fe_2(SO_4)_3{\cdot}nH_2O$. All the experimental procedures were carried out in a glove box under argon atmosphere. For the batch experiments, a gas displacement type acrylic glove box equipped with pass box and oxygen meter (As-One, Japan) was used. A vacuum-type glove box (SUS 304, UNICO, Japan) was used to prepare XPS and XAFS samples.

GR was prepared by co-precipitation method from a mixture of Fe (II)–Fe(III) solution, by titrating with 8 M NaOH as described by Hayashi et al. (2009). For the investigation of the influence of the preparation pH, two different types of sulfate-GR were prepared by titrating at pH 7.50 ± 0.05 ($GR_{7.50}$) and at pH 8.75 ± 0.05 ($GR_{8.75}$). For the preparation of GR, a Fe(II)–Fe(III) solution having a total iron (T-Fe) concentration of 0.4 M and an [Fe(II)]/[T-Fe] ratio of 0.75 was prepared by dissolving $FeSO_4{\cdot}7H_2O$ and $Fe_2(SO_4)_3{\cdot}nH_2O$ in argon-flushed deionized water. The solution was kept under magnetic stirring and argon bubbling by using a glass diffuser for 5 h while continuously monitoring pH (Thermo Scientific) and ORP (Horiba Scientific). Finally, the olive green precipitate GR was collected by centrifuging at 12000 rpm (rotor diameter: 31 cm, centrifugal force was 24,954 *g*) for 10 min (Himac CR21, Hitachi, Japan). Since Fe ions and electrolytes could attach on the surface of GR precipitate, the product was washed by argon-flushed deionized water with vigorous shaking. The paste was collected after a second centrifugation and suspended again in argon-flushed deionized water as a slurry for the batch experiments. The concentrations of Fe, Na^+ and SO_4^{2-} in GR were determined through dissolution in aqua regia and chemical analysis as described in 2.3. The ferrihydrite used in comparison experiment with GR was prepared by the method reported by Cornell and Schwertmann (Cornell and Schwertmann, 2006).

2.2. Batch experiments of chromate removal

The total iron in the GR slurry was measured to ensure the equal inputs in solution. For removal experiment, the concentration of chromate was 0.192 mmol/L (10 mg/L) while total iron in GR was 0.384 mmol/L ($Cr/T\text{-}Fe_{GR}$ molar ratio = 0.5). For the investigation of the role of pH on chromate removal, the pH of the slurry was continuously monitored and kept constant at 5 or 9 through the addition of 0.1 M HNO_3 and 0.1 M KOH. The ORP was also kept constant by flushing argon gas throughout the experiment (1 h). A desired amount of GR suspension was added to 500 mL of Ar-flushed deionized water and then the previously prepared Cr(VI) solution was injected as per the desired $Cr/T\text{-}Fe_{GR}$ ratio.

Samples of the suspension were taken at regular intervals and filtered by using a 0.1 μm membrane filter prior to analysis.

2.3. Analysis

The filtrates from the removal experiments were analysed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, SPS 7800 - Seiko Instruments Inc., Japan) to quantify the residual Cr concentration. The concentration of sulfate was determined by an ion chromatograph with electric conductive detector (ICS 2100, Thermofisher Scientific, USA) equipped with a separation column IonPac AS19 and a guard column IonPac AG19. The analysis was performed by injecting 25 μL of liquid in the column kept at 35 °C.

The concentrations of dissolved Fe(II) and T-Fe were measured by absorption spectrometry (HACH DR 500) upon acid dissolution by 6 M HCl. The Fe(II) analysis was performed with 1–10 Phenanthroline