Removal of chromate from tannery wastewater: the applicability of sulfate-green rust in real coprecipitation processes

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Abstract
Ferrihydrite and green rust (GR) have been identified as promising removing agents for chromate. However, while ferrihydrite efficiency is still too low for practical applications, it is not known whether GR is stable in real wastewater systems. In this work, we investigated the removal of chromate from a real tannery wastewater by using sulfate-GR and ferrihydrite. We studied the effect of pH and Cr/Fe molar ratios on removal performances and elucidated the removal mechanism by XRD analysis. We performed removal experiments from simple chromate-bearing solutions under non-oxidizing Ar atmosphere, and from complex solution under open air atmosphere.

Key words: Chromate, Green rust, Wastewater treatment, Tannery

1. Introduction

Hexavalent chromium (Cr(VI)) is well-known for being carcinogenic and difficult-to-remove from water due to its high mobility¹. For this reason, the improper discharge of chromate is a major concern, especially for industrial processes such as electroplating, tannery and production of painting pigments².

The conventional practice in Cr(VI) removal is based on adsorption and/or ion exchange on cationic resins. However, the non-satisfactory efficiency at low Cr(VI) concentration and the lack of sustainability require for the development of alternative methods. Most of sites identified for Cr(VI) pollution are in fact located in developing countries³, where high costs for wastewater treatment cannot be sustained. More sustainable removing agents were recently obtained from agricultural waste⁴. Nevertheless, despite the lower cost, these materials are often geographically localized and seasonal⁴,⁵.

A promising removing ability for Cr(VI) has been recently identified in iron oxides species like ferrihydrite and green rust⁶,⁷. Ferrihydrite [(Fe³⁺)₂O₃·0.5H₂O] is a hydrous ferric oxyhydroxide that was found able to immobilize chromate from water via surface complexation. However, its removal efficiency seems to be too low for commercial applications and a large production of sludge has to be expected upon chromate removal⁸. Green rust (GR) is a mixed Fe(II)-Fe(III) hydroxide that can be described by the formula [Fe(II)₆₋₄Fe(III)₄(OH)₁₂]⁺⁺[(A)ₙ₋₄yH₂O]⁻, where A is the anion and n is the anion charge. GR exhibits a layered double hydroxide (LDH) structure where Fe hydroxide units are intercalated with water molecules and anions such as chloride, carbonate and sulfate⁹. Given the high Fe(II)/T-Fe ratio, ranging between 0.66 and 0.75¹⁰,¹¹, GR has a considerable reducing power towards potential oxidized contaminants such as chromate, arsenate and organic molecules¹².

Although GR has been proven more efficient than ferrihydrite, all studies were performed in controlled Ar/N₂ atmosphere and from simple synthetic solutions containing only the targeted contaminant. It is not known whether GR would retain its efficiency in complex wastewater systems and under open air atmosphere. As a matter of fact, due to the large portions of Fe(II),
GR might be oxidized before reducing chromate and lose its efficiency.

In this work, we studied the removal of chromate from a tannery wastewater produced at the Bangladesh Small and Cottage Industry Corporation (BSCIC) tannery industrial estate in Bangladesh. The tannery wastewater is a very complex media as processing 1 ton of raw hides requires more than 450 kg of different chemicals and results into 40–70 m$^3$ of wastewater. This wastewater is later discharged with all its pollution load in nearby water bodies, threatening the ecosystem and the human health.

In the present research, the removal of chromate was studied by using sulfate-GR and ferrihydrite. We investigated the effect of pH and Cr/Fe molar ratio and elucidated the removal mechanism by assisting the removal experiments with XRD analysis. In order to confirm the applicability of GR in real processes, we performed removal experiments from simple chromate-bearing solutions under non-oxidizing Ar atmosphere, and from complex solution under open air atmosphere.

2. Experimental

2.1. Site description

The Bangladesh Small and Cottage Industry Corporation (BSCIC) is a tannery industrial estate in Savar, Dhaka (Bangladesh) comprised with 220 from medium to large category tanneries. BSCIC is the biggest tannery estate in Bangladesh and it is located beside the Dhaleshwari River (Fig. 1). The wastewater produced by all tanneries are collected and treated at the central effluent treatment plant (CETP) prior to discharging in the Dhaleshwari River. To prevent pollution of the nearby area, a constant monitoring activity is performed by sampling and analysis of the water outflowing from the CETP. The main physical chemical parameters determined from the wastewater flowing out the CETP are shown in Table 1.

2.2. Standards and reagents

All chemicals used in this study were analytical grade reagents from Wako Chemical Industries (Japan). The Cr(VI) solution was prepared by dissolving K$_2$CrO$_4$ in deionized water. GR was produced by mixing stock solutions of FeSO$_4$·7H$_2$O and Fe$_2$(SO$_4$)$_3$·nH$_2$O while ferrihydrite was prepared by dissolving Fe(NO$_3$)$_3$·9H$_2$O in water. When investigating the use of GR and ferrihydrite from simple Cr-bearing solutions under Ar atmosphere, all experiments were carried out in a gas displacement type acrylic glove box equipped with pass box and oxygen meter (As-One, Japan). When investigating the use of GR from a complex Cr media under air atmosphere, experiments were performed without using any glove box.

The tannery wastewater used in this study was a synthetic solution prepared based on material flow (Fig. 2) and characterization data (Table 2). Since the COD in the wastewater is mostly due to the release of the skin fat during the process, the synthetic solutions was prepared by dissolving fatty acids in water according to the composition shown in Table 3. Accordingly, the DO of the solution was initially fixed to less than 0.1 mg/L by bubbling Ar gas before starting the experiments. The COD was measured using the standard titration method$^{13}$. In order to confirm the GR formation, pH and ORP were continuously recorded.

![Fig. 1](image-url) Area affected by Cr pollution near the Dhaleswari River, Dhaka, Bangladesh.
during the experiments using pH meter (Thermo Scientific) and ORP meter (Horiba Scientific).

2.3 Batch test and analysis

The coprecipitation of ferrihydrite with Cr(VI) was investigated for different Cr/Fe ratios. The experiments were conducted by adjusting the pH of the Cr(VI) solution to 3.5 and keeping the Cr/Fe ratio constant. The pH was then titrated with 0.1 M NaOH solution until the pH reached 9.5. The resulting precipitate was filtered, washed with deionized water, and dried at 100°C for 2 hours. The Cr(III) content in the precipitate was determined by inductively coupled plasma mass spectrometry (ICP-MS).

Table 2: Chemical load for 1 ton raw hides processing (Data from Samina tannery Pvt. Ltd, Dhaka, Bangladesh)

| Process name          | Chemicals name & Chemical inputs (kg/t) | Wastewater discharged (kg/t) | Total discharged (kg/t) | Sectoral average (%) |
|-----------------------|------------------------------------------|-----------------------------|-------------------------|----------------------|
| Soaking               | Degreasing agent = 3, Soda ash = 10, Antibacteria = 2 | 18400                       |                          | 43.4                 |
|                      |                                          |                             |                         |                      |
| Liming                | Sodium sulfide = 40, Lime = 40, Degreasing agent = 2 | 9600                        |                          | 22.7                 |
|                      |                                          |                             |                         |                      |
| Deliming              | Ammonium sulfate = 26                    | 2080                        |                          | 4.9                  |
|                      |                                          |                             |                         |                      |
| Batting               | Batting enzyme = 6.5                     | 10400                       |                          | 24                   |
|                      |                                          |                             |                         |                      |
| Tanning               | Sodium chlorite = 5.2, Cr(III) sulfate = 104, Formic acid = 13, Hypo = 10.4, Sodium formate = 13, Fungicide = 2.6, Magnesium oxide = 13 | 1300                        | 42380                  | 3.1                  |
|                      |                                          |                             |                         |                      |
| Retanning             | Formic acid = 0.6, Cr(III) sulfate = 6, Neutralizing syntans = 6, Aldehyde = 4 | 400                         |                          | 0.8                  |
|                      |                                          |                             |                         |                      |
| Dyeing and fat liquoring | Synthetic fat liquor = 2, Acrylic resin = 10, Other synthetic resin = 20, Syntans = 10, Vegetable extract = 20, Fat liquor = 10–20, Formic acid = 4–8 | 200                         |                          | 0.4                  |

Summary:
- Total Cr input = 14324.98g
- Leather adsorbed = (1.32 • 6894.16) + 371.24 = 7268.04g
- Cr recover by pH adjustment = 651.62g
- Remove by treatment plant = 285.32g
- Discharge to surface water = 420g
molar ratio. In the experiments with GR, the Fe(II)/Fe(III) ratio was set as 2 and used as total Fe input. The pH was continuously monitored during the experiments and adjusted to 5, 7 or 9 (±0.05) by adding 0.1 M HNO₃ and 0.1 M KOH. After 1 hour under stirring, the suspensions were filtered by using a 0.1-μm membrane filter. The filtrates were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using an SPS-7800 atomic emission spectrometer (Seiko Instruments Inc., Chiba, Japan). The solid residues were analyzed by x-rays diffraction (XRD) to determine phase composition and crystal structure upon chromate removal. The x-ray diffractometer (Geiger flex RAD-IX, Rigaku Corp. Japan) was equipped with a copper target (Cu–Kα), a crystal graphite monochromator and a scintillation detector. The X-ray source was operated at 40 kV and 30 mA with step scanning from 2θ values of 2 to 80°, sequential increments of 0.02° and a scan speed of 2°/min. To avoid the oxidation of samples between experiments and analysis, the collected paste samples were mixed with glycerol and transferred to the XRD chamber. A crystal sample holder was used and the derived pattern was not corrected for background diffraction.

3. Results and Discussion

3.1. Pollution load and Cr-material flow analysis in tannery

The tannery process consists of a complex sequence of operations. The main operations in the process are soaking (preliminary washing to rehydrate the skins and remove dirt and excess of salt), liming (removal of hair and fat), deliming (removal of excess of lime used on liming), batting (softening through enzyme baths), tanning-retanning (absorption of chromium into the skins), dyeing and fat liquoring (coloring and fixing the texture), each of them contributing to the overall release of chemicals into wastewater. The sectoral pollution load (Table 2) shows that soaking generates about 44% of the total wastewater volume, whereas more than 70% of total COD is generated through liming and deliming. The COD generated in these two operations arises from the fat released in water. The chromium release in water is almost entirely due to tanning and re-tanning operations, where 15 kg of Cr(III) are used per each tons of raw hides. About 50–70% of the Cr(III) used in tanning and re-tanning is absorbed by the hides while remaining part is discharged in water. The Cr-bearing wastewater from tanning and re-tanning is sent to a chromium recovery section, where 90% of Cr(III) is precipitated at pH to 7.5–8 by dosing NaOH. In contrast, the wastewater generated in pre-tanning and post-tanning is sent directly to the CETP with liquid stream generated in Cr(III) recovery because the chromium concentration is too low to be recovered.

Out of the CETP, the concentration of chromium in water is 10–15 mg/L, accounting for a chromium content of about 2.8% of the total input. The final discharged effluent quality (Table 1) after the CETP also exhibits a low dissolved oxygen (DO <0.2 mg/L), high biochemical oxygen demand at 5 days (BOD₅) and high chemical oxygen demand (COD). The COD and BOD₅ derive mainly from fatty acids and proteins released in liming and from oxidable inorganic species used within the process. The low DO can be considered as a direct consequence of high COD and BOD₅. Indeed, the oxygen naturally-dissolved in water can be consumed by those substances that contribute to COD and BOD₅. In this view, since the oxidation of fatty acids and proteins is a relatively slow process, the low DO in the real wastewater can be considered as an expression of long-term pollution. The residual Cr in the final wastewater is Cr(VI), which is well-known for remaining soluble even in alkaline media.

Due to the improper discharge of a similar wastewater from the Hazaribag tannery area (Bangladesh), the accumulation of Cr(VI) was confirmed in the aquatic fauna of the nearby Buriganga River. Given the 20000 m³ of wastewater flowing out of the CETP per day, the adjacent surface water of the Dhaleshwar River is threatened by the continuous discharge of 210 kg of Cr(VI) per day.

3.2. Removal of chromate by coprecipitated ferrihydrite and GR: comparison

The removal of chromate from water by ferrihydrite and GR was preliminary assessed through coprecipitation experiments from simple Cr-bearing solution under Ar atmosphere. Coprecipitated GR was found to be more effective than ferrihydrite to remove chromate under anaerobic conditions at both pH 5 and 7 (Fig. 3). For GR, increasing pH from 5 to 7 did not determine any

| Table 3  | Synthetic wastewater composition |
|----------|----------------------------------|
| Lauric acid (mg/L) | 34.5 |
| Formic acid (mL/L) | 2.0 |
| Sodium thiosulfate (mg/L) | 20.0 |
| Formaldehyde (mL/L) | 3.0 |
| Sodium sulphide (mg/L) | 11.6 |
| Sodium chloride (mg/L) | 60.0 |
| Cr(VI) (mg/L) | 10.0 |
significant effect on chromate removal. This evidence can be explained considering that pH can affect chromate removal only indirectly, by determining changes in GR structure. Previous works highlighted that increasing the pH beyond 8.3–8.5 produces a decrease of surface charge, \( \text{expansion of GR structure} \), with increase of surface area and larger inclusion of \( \text{Na}^+ \) and \( \text{SO}_4^{2-} \). As a consequence, more chromate could be removed. However, in this work GR was coprecipitated at pH 5 and 7 for a better comparison with ferrihydrite. Under these conditions, neither structural modifications nor changes of surface charge take place. Thus, changing the coprecipitation pH of GR from 5 to 7 did not show any significant influence over Cr(VI) removal.

The higher removal observed for ferrihydrite at pH 5 can be reasonably explained through the higher zeta potential at this pH. Although ferrihydrite at pH 5 adsorbed chromate completely, 3.96 mmol/L of Fe were required to achieve the removal. In contrast, only 0.96 mmol/L Fe were required to remove the same 0.19 mmol/L Cr. The 4 times lower amount of iron required with GR is expected to determine a significantly lower production of sludge upon chromate removal.

### 3.3. XRD analysis

The XRD spectra of coprecipitated ferrihydrite upon chromate removal at pH 5 and pH 7 (Fig. 4) highlighted the typical pattern of ferrihydrite (Fh). This evidence suggests that chromate was removed through a kind of adsorption that does not imply any structural change, namely outer-sphere surface complexation. However, for Cr/Fe 0.5 at pH 5, the XRD spectra exhibited the broadening of the peak at 34°, resulting in a pattern similar to Cr inserted ferrihydrite (Cr-Fh). This evidence was previously described as a change of removal mechanism from outer-sphere to inner-sphere surface complexation.

The XRD spectra of GR upon chromate removal at pH 5 and 7 exhibited a new peak at 30°. The new peak, which suggests the oxidation of GR to Cr-inserted ferrihydrite, was observed at both Cr/Fe molar ratio 0.5 and 0.1 (Fig. 5). This evidence suggests that chromium is inserted in the crystal structure already from low Cr/Fe ratio, possibly during the formation of GR. In other words, while with ferrihydrite the chromate is included only at high Cr concentrations, GR co-precipitates directly with chromium.

### 3.4. Effect of COD

By increasing the COD in water, the residual Cr concentration significantly decreased (Fig. 6). To exclude the possibility that chromate was immobilized by some species contributing to COD, we performed control experiments without GR. The residual Cr concentration in the control experiments was very close to the initial one (10 mg/L), thus confirming that the immobilization was performed by GR. The larger removal of chromate observed by increasing the COD finds
an explanation in the increased concentration of alkaline cations like Na⁺. As reported in our previous work, a higher pH during the GR preparation determines a change of the surface charge from positive to negative⁻²⁰, and results into a larger inclusion of Na⁺ (from NaOH) within GR structure. As a consequence, GR's structure expands, surface area increases, and more chromate can be removed. In this work, an increase of COD according to the wastewater composition determined also an increase of the concentration of Na⁺ due to oxidable species like sodium sulphide and thiosulfate. Accordingly, a more stable and efficient GR might have generated⁻²¹ and more chromate could be removed.

3.5. Cr(VI) removal under open air

The ability of GR to resist oxidation and immobilize chromate from the complex tannery wastewater under open air atmosphere was verified at pH 8.25, which is the one out of the CETP. The Eh(vs SHE) and pH trends during the formation of GR under open air atmosphere and in the presence of chromate are shown in Fig. 7. The points (a), (b) and (c) in Fig. 7 refer to the photos in Fig. 8, taken during the experiments. The trend shown in Fig. 7 is very similar to the one observed under Ar atmosphere (paper under review). Titration at pH 8.25 determined a first potential drop from 300 to about 0 mV within 2–4 minutes and a further drop to −100 mV in the next 10 minutes. At the same time, the colour of the suspension turned first to light reddish and quickly to light-green (Fig. 8a), thus suggesting the formation of GR. The Eh drop observed within 15 minutes was clearly associated with the decrease of the Fe(III)/Fe(II) ratio for the formation of green rust⁻¹². Finally, after 25 minutes the experimental Eh gradually increased and the suspension turned reddish-green, thereby suggesting the oxidation of GR to ferrihydrite. The graph in Fig. 7 highlighted slightly higher values of Eh and a change within a shorter period of time compared to the ones reported in literature⁻²². This difference can be reasonably considered as the consequence of the partial oxidation of Fe²⁺ by the oxygen dissolved in solution under open air atmosphere. The ICP analysis revealed a residual concentration of chromium below the detection limit of our ICP, thus...
highlighting a complete removal of chromate also under open air.

The final solid product upon chromate removal in the presence of COD and under open air atmosphere was analyzed by XRD. The XRD spectra showed the typical pattern of Cr-inserted ferrihydrite, as suggested by the XRD peak shift from 34° to 28° (Fig. 9). In our previous work (currently under review) we proved through XAFS analysis that a close and compact insertion of Cr was possible only without a significant enlargement of the ferrihydrite structure. As a consequence, the Cr-Fe bonding would be stronger and the immobilized Cr would not be easily released in the environment. The Cr-inserted ferrihydrite found under open air atmosphere suggests a similar consideration. Therefore, the formation of a dense Cr-inserted ferrihydrite sludge with good solid-liquid separability and low chromate release tendency has to be expected also upon coprecipitation from complex systems.

4. Conclusions

In this work we studied the removal of chromate from synthetic tannery wastewater produced at the BSCIC tannery estate in Bangladesh. We confirmed that GR can remove chromate more efficiently than ferrihydrite with the formation of a smaller amount of sludge. Although GR is very prone to oxidation, we proved that it can actually resist to the harsh conditions of real wastewater systems and still be more efficient than ferrihydrite. Even in the presence of 265 mg/L of COD and open air atmosphere, GR could form, resist to oxidation and completely remove chromate. The XRD results of this work along with experimental evidences from literature suggest that the final solid product after Cr removal would be a dense sludge with good solid-liquid separability.

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