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Chapter 2.3: Natural Attenuation of Chromium and Manganese from a Bangladesh Tannery Effluent Via Humic Substance Complexation: Field, Laboratory and Modeling Studies

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Chapter 2.3

Natural Attenuation of Chromium and Manganese from a Bangladesh Tannery Effluent Via Humic Substance Complexation: Field, Laboratory and Modeling Studies

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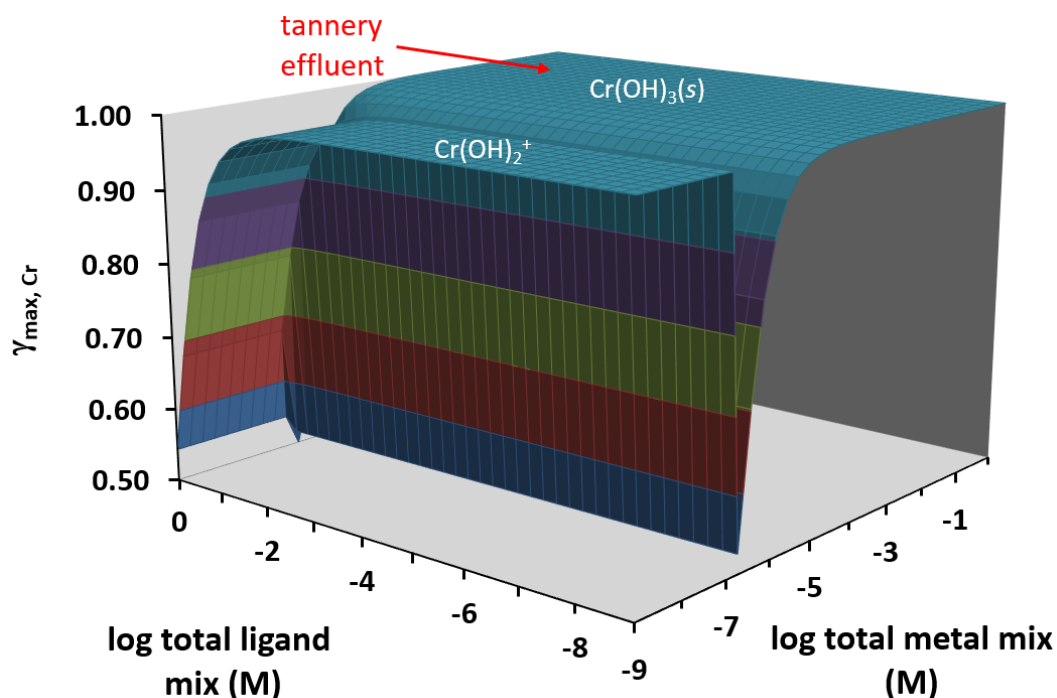
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Abstract

This chapter provides an example of the 3-D TOPOS visualization approach to a real-world application of metal-ligand complexation. It utilizes the Multi TOPOS software, an extension of Complexation TOPOS that includes multi-metal/multi-ligand mixtures. It examines the impact of toxic chromium and manganese in effluents from Bangladesh leather tanneries before completion of a water treatment plant. Effluents were collected from a newly established leather processing district in the Savar suburb of Dhaka, Bangladesh. Trace metal concentrations were determined by both atomic absorption spectroscopy (AAS) and inductively coupled plasma spectroscopy (ICP). Levels of chromium ranged from 0.0188 (\pm 0.0025) to 4220 (\pm 75) mg/L; those of manganese were 0.0130 (\pm 0.0048) to 1.64 (\pm 0.14) mg/L. The concentrations of both metal ions dropped

quickly from the highest value at the discharge point to ever decreasing values with distance from their initial release. Thinking that naturally occurring humic substances might be responsible for the attenuation, we extracted and purified humic acid from the effluent. It was compared with humic acid from rural soils in NE Bangladesh using Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX), and CHN elemental analysis. Purified humic acid from the tannery effluent was combined with Cr^{3+} and Mn^{2+} to assess complexation behavior. Spectral shifts in FTIR and EDX spectra supported the incorporation of metals into humic acid's organic framework. Mathematical modeling was then performed by Multi TOPOS on a system comprised of Cr^{3+} , Mn^{2+} , and a mixture of six organic ligands that mimic humic acid binding sites. At the effluent's ambient pH of 8.5, essentially all of the Cr was precipitated as $\text{Cr}(\text{OH})_3(\text{s})$. Under the same conditions, Mn was bound predominantly to the phthalate (36.7%) and 1,10-phenanthroline (57.9%) components of the humic acid mimic mixture. These results suggest that agglomeration took place between $\text{Cr}(\text{OH})_3(\text{s})$ and colloidal humic acid in the same way that flocculation with $\text{Al}(\text{OH})_3(\text{s})$ does in water treatment plants. Because Mn^{2+} was bound to humic sites, it became incorporated in the coagulated assemblies. The sandy bed of the drainage channel subsequently acted as a filter. Levels of Cr and Mn present in the discharge channel were attenuated to near drinking water standards by the time the receiving river was reached.



2.3.1 Introduction

This chapter examines the impact of toxic chromium and manganese that were present in effluents from a new leather tannery center near Dhaka, Bangladesh before a water treatment plant had been completed. Assessment of the water quality impacts from tanning was undertaken because more than 20,000 people presently live downstream from the site. While the public has complained about odors from the tanning facilities, a deeper concern resides in toxic heavy metals present in the effluent. Most worrisome among these is chromium, a known carcinogen.^{1,2} But manganese pollution also has consequences because it has been linked to the onset of Parkinson-like nerve disorders.³ Interestingly, as the effluent flowed through a man-made drainage channel for about 300 meters of reclaimed sandy river sediments, a significant reduction in solution levels occurred. Because other studies⁴ suggested that humic substances may sequester metal ions in tannery effluents, humic acid was extracted from effluent samples to examine its properties. The attenuation of the heavy metal contents we observed is consistent with the sandy soils of the drainage channel filtering out a suspension of chromium hydroxide flocs that agglomerated colloidal humic acids with complexed manganese. This chapter documents the heavy metal content of the tannery effluent, the removal gradients that were determined through field studies, characterization of extracted humic substances, and computer modeling of the complexation processes and precipitation behind their attenuation.

Historically, tanneries were situated amidst the densely populated Hazaribagh District of Dhaka, neighborhoods of low-income residents (Figure 2.3.1). Karim *et al.*⁵ estimated that these tanneries released 0.35 tons of chromium daily into a 25-ha lagoon. They found that chromium seriously contaminated the sediments of the lagoon and that it was predominantly present as insoluble chromium salts. Beginning in 2003, after much pressure from the public about exposure to tannery waste, the leather industry agreed to establish a combined leather manufacturing complex near Savar, away from the urban center. The complex would include a Central Effluent Treatment Plant (CETP). The new tannery complex is now located on a reclaimed tract along the Dhaleshwari River about 13 km WNW of Dhaka (Figure 2.3.2). During our sampling events of 2016-17, three tanneries at the northern end of the complex were discharging their waste through a drainage channel directly to the river, not through the CETP that was still undergoing completion.

Figure 2.3.1. Historic photo of urban waste channel in the Hazaribagh District of Dhaka. (Photo: Daniel Lanteigne. Creative Commons BY-NC-ND.)

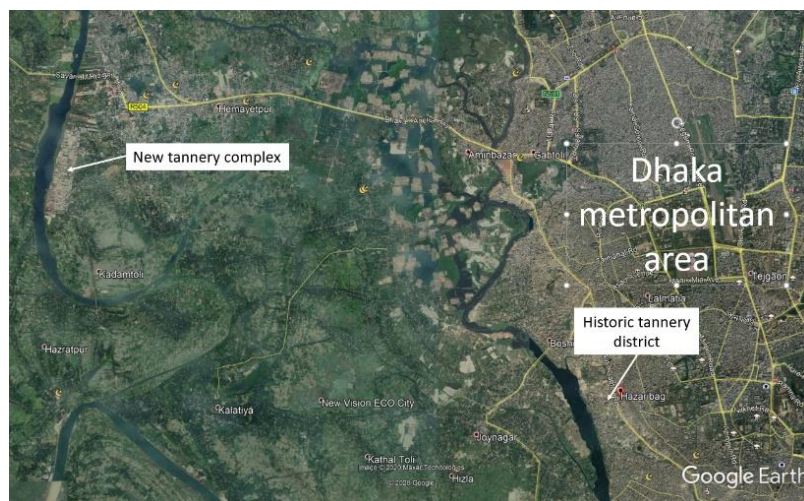


Figure 2.3.2. Location of the new tannery complex 13 km WNW of the Dhaka urban center.

The observed heavy metals – chromium and manganese – come from the tanning process that is most commonly practiced in Bangladesh. Known as chrome tanning⁶, it employs chromium(III) hydroxide sulfate as a collagen fiber cross-linking agent in the crucial procedural step. The finished leather product contains 3 – 5% chromium. In fact, about a quarter of the world's chromium production is consumed by the leather goods industry in this application.⁷ Not all of the chromium, however, gets incorporated into the leather and ends up in the facility's effluent.⁸ Manganese(II) acetate or manganese(II) oxide is associated with the liming and hair removal steps in the tanning process.⁹

The chromium and manganese content of the tannery effluent was mediated by humic acids that were present in the process water used at the tanning facility. The drainage channel bed, having been reclaimed with some

sandy fill material, did not exhibit humic content. Humics are a mixture of relatively high molecular weight, light brown- to black-colored organic species that result from the partial decomposition of plant matter.¹⁰ They offer a rich array of complexing moieties. Among their structural features are sites that can participate in chelated complexes. Their complexation capacity is associated with sites analogous to phthalate, salicylate, benzoate, catechol, methylamine and 1,10-phenanthroline. Because the humic acid fraction is insoluble at the pH of the effluent, it was present as a colloidal suspension. The colloidal particles also offer a surface to which metal hydroxide salts can be sorbed. For example, Wang *et al.*⁴ showed that chromium and manganese were associated with the colloidal particles. The tannery humic particles were subsequently “sand-bed filtered” as the effluent flowed through the drainage channel.

Once the presence and removal of the two heavy metals had been confirmed, we performed a computer simulation of the uptake of metal ions by a multi-ligand mixture that mimics humic acid complexation sites. Using a composition grid that covered a wide range of possible metal ion concentrations as its x -axis and a wide range of possible ligand mixture concentrations as the y -axis, a series of 3-D trend surfaces were generated to demonstrate how Cr^{3+} and Mn^{2+} behave in this mixture of ligands. The results suggest that Cr^{3+} is mostly present as sorbed $\text{Cr}(\text{OH})_3(\text{s})$ or bridged complexes while Mn^{2+} was preferentially bound to phthalate and 1,10-phenanthroline sites.

2.3.2 Materials and methods

Chemicals and reagents. The reagents used in this study were analytical grade and used without further purification. Deionized water was used as the solvent to prepare solutions used in this work. The specific reagents were: glacial acetic acid, CH_3COOH (99.8%) (Merck, Germany); sodium hydroxide, NaOH (Merck, Germany); ethanol, CH_3OH (99.0%) (Merck, India); isoamyl alcohol (99.0%) (Merck, Germany); humic acid (Merck, India); hydrochloric acid (98%) (Merck, Germany); chromium(III) hydroxide sulfate (Merck, India); manganese sulfate (Merck, India); acetone (Sigma-Aldrich); sodium deuteroxide (NaOD) (Sigma-Aldrich); deuterium hydroxide (D_2O) (Sigma-Aldrich); dimethyl sulfoxide- d_6 (99.9%) (DMSO-d_6) (Merck, Germany).

Instruments. Analysis of the samples was performed using the following instruments: atomic absorption spectrometer (AAS) - Shimadzu, AA 7000, Japan; inductively-couple plasma – optical emission spectroscopy (ICP-OES) - Shimadzu ICPE 9820, Japan; energy-dispersive X-ray spectroscopy (EDX) - Philips, Expert Pro, Holland; CHN Elemental Analyzer - Perkin Elmer 2400 series 2 CHNS/O Analyzer, USA; and Fourier transform infrared spectrophotometer (FTIR) - Shimadzu FTIR-8400, Japan.

Study area. Replicate tannery effluent samples were collected on three dates in late 2016 and early 2017. These were taken from a drainage channel that was established at the north end of the tannery complex prior to facilities hooking up to the Central Effluent Treatment Plant. They represent the collective release from three facilities – Bay Tanneries, Fancy Tanneries and Sathi Tanneries. Four sample locations were distributed along the drainage channel (Figure 2.3.3): Site 1 - upwelling from a wastewater manhole of the line that connects to the CETP (Figure 2.3.4a); Site 2 - 100 m downstream (Figure 2.3.4b); Site 3 - 200 m downstream (Figure 2.3.4c); and Site 4 - the mouth of the ditch outfall at the riverside (Figure 2.3.4d). Because of facility-imposed restrictions, samples were collected with an acid-washed ceramic mug and 1-liter PETE (polyethylene terephthalate ester) containers. Once at the laboratories, samples were transferred to sealed polyethylene containers.

Figure 2.3.3. Detailed view of the tannery complex with sampling locations noted on inset.





Figure 2.3.4. Sampling locations. a) Site 1; b) Site 2; c) Site 3; d) Site 4.

At each sampling site, two containers of effluent were collected - one used for determining chromium and manganese, and the other for the humic acid extraction process. The containers with trace metal samples were immediately preserved with 1 mL of concentrated HNO_3 (65%) to bring the pH below 2. This minimized precipitation and adsorption of metal ions on the container's walls. To prevent the likelihood of hydrolysis, microbial degradation and oxidation, samples were refrigerated at 4°C until processed.

2.3.3 Elemental analysis

Atomic absorption spectroscopy (AAS). Tannery effluent samples were analyzed for their chromium and manganese content with a Thermo Scientific model ICE 3000 atomic absorption spectrometer. This analysis was restricted to Cr and Mn because specific elemental lamps were needed. It does, however, give better limits of detection than the other techniques that were employed. In each case, triplicate measurements were aspirated into the instrument.

Inductively-coupled plasma – optical emission spectroscopy (ICP-OES).

The same tannery effluent samples were analyzed by Shimadzu ICPE 9820 inductively-coupled plasma – optical emission spectroscopy (ICP-OES). This is an atomic emission technique where the signal emanates from within an argon plasma. Because emission lines are emitted by all elemental species within the sample, the presence of more than just Cr and Mn could be accomplished with detection limits near 10 ppb.

Energy-dispersive X-ray spectroscopy (EDX). Elemental abundances were determined for two sources of humic substances – tannery water and Bangladesh haor district humic acid. The analyses were performed on a Philips Expert Pro energy dispersive x-ray spectrometer. The tannery humic substances were extracted, purified and acid washed as described below.

2.3.4 Humic substance preparation

Extraction and purification of humic acid (HA) from tannery wastewater.

Because humic substances were implicated in the attenuation of heavy metals in tannery effluents, the humic content of the effluent was extracted and purified. Its presence was visibly evident in the chocolate brown color of the samples. The turbulence of the samples is consistent with its presence as a colloidal suspension at the ambient pH of 8.5. In order to extract the humic acid from tannery wastewater, two steps were involved.

First, 100 mL of wastewater sample were placed in an Erlenmeyer flask with a magnetic stirrer as 5 mL of glacial acetic acid were added. Next, 15 mL of isoamyl alcohol were blended in. The mixture was placed on a rotary shaker and left overnight at 150 rpm. The mixture was transferred to a 250-mL separatory funnel and allowed to stand until two layers formed. The humic acid accumulated in the upper layer (Figure 2.3.5a). Second, the contents of the separatory funnel were filtered through a sintered-glass filter funnel under vacuum. The suspended humic acid was retained in the funnel on a paper filter (Whatman 10370002, Grade GF 6). The filter paper was transferred to another funnel and washed initially with 95% ethanol followed by distilled water adjusted to pH 2 with HCl (Figure 2.3.5b) to remove any hyalomelanic acid present. The final isolate was air dried. The average yield was 0.346 g of humic acid per 100 mL of tannery effluent.

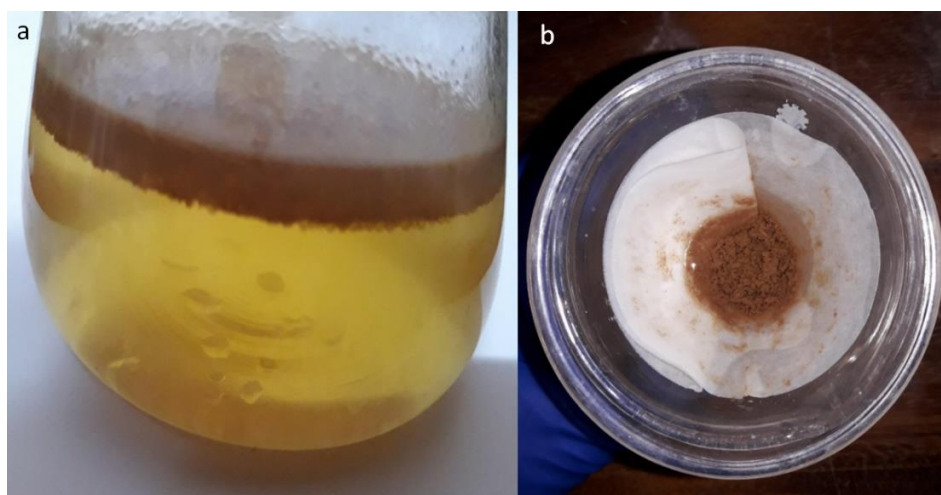


Figure 2.3.5. Extraction of humic acid. a) humic suspension accumulated in the upper isoamyl alcohol layer; b) humic substances in wash funnel.

Extraction and purification of HA from soil. Initially, each 100 g soil sample was washed with a 1.0 M HCl solution. Then 1.0 M NaOH was added to extract any base-soluble humic acids. Conical flasks containing the sample suspended in the NaOH solution were placed in a rotatory shaker overnight at 150 rpm. The shaker solutions were centrifuged at 3500 rpm and the supernatant, containing dissolved humic acid, was removed. The supernatant's pH was adjusted to between 1 and 2 with HCl. This re-protonates humic acid molecules, displacing any complexed metals, and causes them to be insoluble. The solution sat undisturbed for sufficient time to allow the humic acid to agglomerate into gelatinous clusters (Figure 2.3.6). The precipitate was collected on a paper filter (Whatman 10370002, Grade GF 6) and washed with distilled water to remove impurities.

Figure 2.3.6. Gelatinous humic acid clusters settle as a precipitate.



Preparation of Synthetic Metal Ion-HA Complexes. In order to support the hypothesis that the chromium and manganese in the tannery effluent were associated with humic acid, the extracted humic acids were combined with solutions of the two heavy metal ions. This began by dissolving 0.998 g of HA in 200 mL of distilled water. To keep the humic acid soluble, the pH was maintained around 10.5 with additions of 1.0 M NaOH. The solution was stirred for 4 h, then centrifuged for 15 min at 3500 rpm.

Mn-HA mixture. Manganese sulfate monohydrate, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (3.3804 g), was dissolved in 20 mL of water and added dropwise into 200 mL of the humic acid solution under vigorous stirring and continuous control of pH between 8 and 9 with additional 1.0 M NaOH. The solution was diluted to 500 mL, stirred for 14 h and then centrifuged for 15 min at 3500 rpm to separate the brownish Mn-HA product from the supernatant. The product was washed with distilled water to remove sulphate spectator ions. Finally, the precipitates were dried in an oven at 95°C and stored in a desiccator under vacuum.

Cr-HA mixture. 14.446 g of chromium(III) hydroxide sulfate, $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$, were dissolved in 20 mL of water and added dropwise into 200 mL of the humic acid (0.998 g) solution using the same procedure as above. The Cr-HA product was greyish blue in color when collected as a precipitate (Figure 2.3.7).

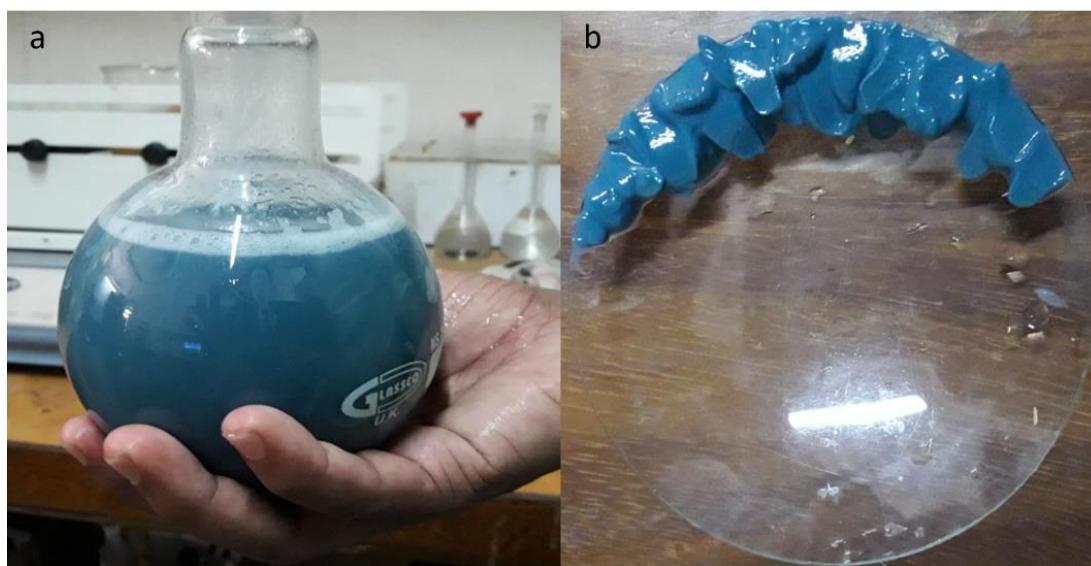


Figure 2.3.7. Cr-HA product. a) in suspension; b) as an isolated precipitate.

2.3.5 Spectroscopic characterization of HA and its metal products

Fourier transform infrared (FTIR) analysis. The infrared spectra of humic acid and its metal products were recorded on an FTIR spectrometer over the region of $4000 - 400 \text{ cm}^{-1}$. A small portion of each sample was placed in a glass vial and oven dried at 95°C to assure no moisture was present. The presence of any water in a sample will obscure many important bands beneath its broad and strong -OH band. The chunks of dried metal-HA products were so hard that it was necessary to grind them in a mortar and pestle to obtain a fine powder. Pure HA samples required no grinding as they were already in a powdered state after completely drying. A 0.5-mg sample of dried HA or metal-HA product was mixed and ground together with 100 mg of KBr until it became a homogenous mixture. The powder was compressed into a pellet and then placed in the path of the IR beam for measurements.

Energy-dispersive X-ray spectroscopy (EDX). The completely air-dried samples were placed onto a conducting carbon strip. A very thin platinum layer (a few nanometers thick) was sputtered onto the sample to ensure good conductivity in the sample surface. The loaded strip was then mounted in a chamber that was evacuated to $\sim 10^{-3}$ to 10^{-4} torr. Each sample was positioned in the main scanning electron microscope (SEM) chamber to view its surface. The microscope was operated at an accelerating voltage of 10.0 kV. The instrument's X-ray detector was interfaced to a computer such that X-ray emission spectra could subsequently be generated either on the screen or in a hard-copy format.

CHN Elemental analysis. Principal elemental analysis was conducted in a Perkin Elmer 2400 Series 2 CHNS/O Analyzer which quantifies the carbon, hydrogen and nitrogen contents of a sample. Overall, 3 mg of sample were used for each run and analyses were conducted in triplicates.

2.3.6. Experimental Results and Discussion

Analysis of tannery wastewater

Manganese and chromium in tannery waste by AAS. The concentrations of Cr and Mn in tannery effluent, collected at different distances from the discharge

point, were determined by AAS and are shown in Figure 2.3.8. Four replicate measurements were made of each solution. Values ranged from 0.0188 (\pm 0.0025) to 4220 (\pm 75) mg/L for chromium and from 0.0130 (\pm 0.0048) to 1.64 (\pm 0.14) mg/L for manganese. The results clearly demonstrate that the concentrations of chromium and manganese quickly dropped as the tannery effluent flowed through the discharge channel. Note that the high initial number is associated with Site 1, the direct discharge point, before there is an opportunity for any channel filtration. Note also that the levels of Cr are more than three orders of magnitude higher than Mn, an indication of the relative importance of chromium in the final tanning stage. The manganese is used in early stages of the process and in much lower quantities.

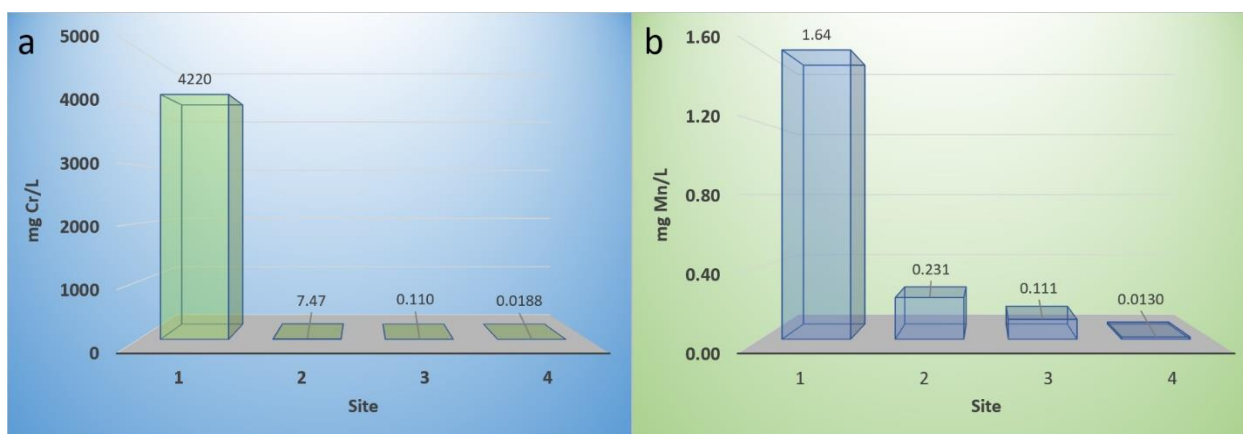


Figure 2.3.8. Cr and Mn in tannery wastewater by AAS.

Elemental analysis in tannery water by ICP-OES. The ICP-OES analyses offered an opportunity to obtain a second, independent analysis of the two elements of concern. The ICP-OES data for Cr and Mn exhibited the same pattern as the AAS results (Figure 2.3.9). Both heavy metals were at their highest levels at Site 1 (direct tannery effluent) and fell off with distance toward the receiving river. The ICP-OES value for Cr was slightly higher than by AAS, while Mn showed lower levels. These differences could be due to the chemistry that happens during the atomization step. With AAS, the flame combustion in the burner head can lead to the formation of oxo-species. On the other hand, ICP-OES embeds the analyte stream within an inert argon atmosphere. This would lead to pyrolysis of the humic components and eliminate most possibilities for oxo-species formation.

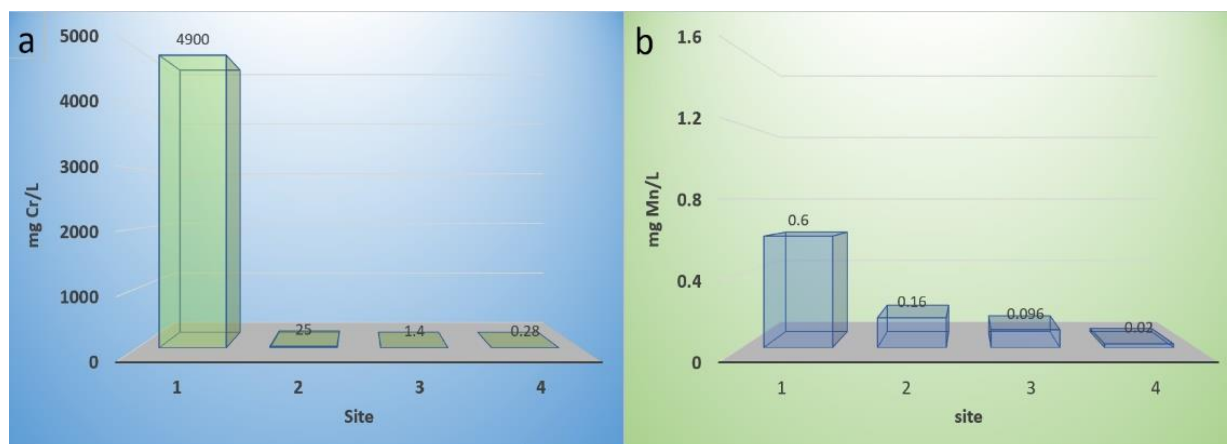


Figure 2.3.9. Cr and Mn in tannery wastewater by ICP-OES.

The use of ICP-OES had an added benefit of looking at the levels of other elements in the effluent samples. The three additional elements that were seen at high levels in the direct tannery effluent at Site 1 were sulfur (5300 mg/L), sodium (4900 mg/L) and magnesium (2900 mg/L). The presence of sulfur is expected as the chrome tanning process uses chromium(III) hydroxide sulfate, $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$, as a principal tanning reagent. There is also sulfur in unhairing agents (*e.g.*, sodium sulfide and sodium hydrosulfite) and pickling agents (sulfuric acid). The sodium originates from the initial salt curing of hides to prevent putrefaction before they can be processed as well as in the unhairing salts noted above and in pickling brines. Magnesium sulfate is used as a filler in the production of high-quality leather.

A number of other metal ions were measured by ICP-OES, namely aluminum (7.2 mg/L), iron (6 mg/L), platinum (2.2 mg/L), lead (2.0 mg/L), nickel (1.9 mg/L), indium (1.7 mg/L), and vanadium (1.4 mg/L). These levels are all three to four orders of magnitude less than the concentration of humic acid. At pH 8.5, these metals would not be present as bare ions anyway. Iron and aluminum will be largely present as colloidal hydroxide precipitates and the others largely as hydroxy complexes.¹¹ Their presence is at such low levels they should not impact the range of complexation sites available to either chromium or manganese. Thus, they were not included in the subsequent modeling that was conducted.

Characterization of extracted humic acid and its metal products

Fourier transform infrared spectroscopy (FTIR) of humic acids. The FTIR spectra of both tannery and soil humic acids (Figure 2.3.10) provide insights into some of their structural character. The vertical offset between the two spectra was occasioned by a difference in sample size within the IR beam. This also accounts for the peak broadening seen in the soil humic acid trace. A broad absorption peak appears between 3700 and 3100 cm^{-1} that is associated with -OH and -NH stretching. The sharp set of peaks centered at 2926 cm^{-1} are due to aliphatic -CH stretching. Because the sample spectra were recorded with the beam passing through air, there is a CO_2 peak near 2300 cm^{-1} . From 1800 to 1600 cm^{-1} there is a complicated set of peaks that relate to functional groups with either O or N atoms involved. At 1651 cm^{-1} there is the -C=O stretch from -COOH groups. N-containing aromatic heterocycles and the -C=O stretching vibration in -COOH give rise to spectral features in the $1600\text{-}1400\text{ cm}^{-1}$ range. An important peak for confirming metal complexation is located at 1223 cm^{-1} . It represents the -CO stretch in COOH groups. This is the primary site type to which Cr^{3+} will bind as it forms complexes. A broad band from 750 to 450 cm^{-1} correlates to aromatic ring absorptions. Overall, these results suggest that both humic acids contain carboxylic and phenolic -OH groups embedded in an aromatic framework with some N-containing heterocycles. The humic acid extracted from the tannery effluent was essentially no different from that found in a typical soil sample that was obtained at the distant haor location.

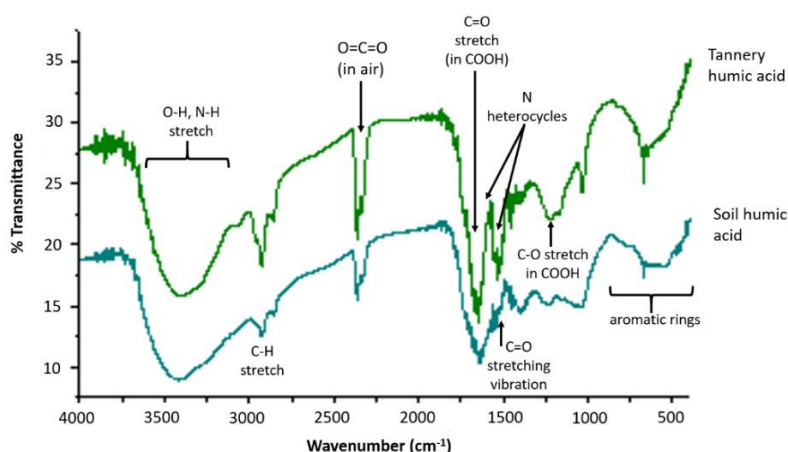


Figure 2.3.10. FTIR spectra of tannery-and soil-derived humic acids.

CHN analysis of extracted humic acid. The elemental composition of humic substances, as well as their properties, vary according to the source of the organic matter and its place of formation. The elemental analysis is important as it provides information about the general composition of the organic framework for the humic acid. The CHN elemental composition of tannery humic acids revealed 46.29% C, 6.72% H and 8.22% N. Much of the balance is attributed to oxygen. The presence of N lends supports to more complexation sites within the structure.

FTIR spectra of tannery humic acid with added chromium. A chromium solution was added to the extracted tannery humic acid to test for complexation interactions. If Cr formed complexes with humic acid, their formation should change aspects of the IR spectra, especially those associated with -COOH, -OH, and N-containing groups. The IR spectra of tannery humic acid before and after the addition of chromium are compared in Figure 2.3.11.

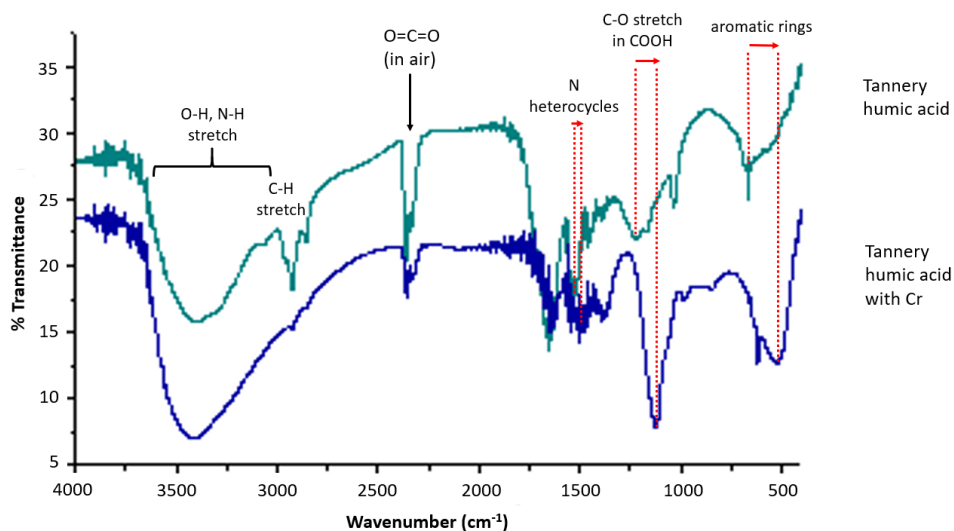


Figure 2.3.11. FTIR spectra for tannery humic acid before and after Cr addition.

Previous researchers have noted that when Cr complexes with humic acid, peaks shift to lower frequencies.¹² Three such shifts are highlighted in Figure 2.3.11. Near 1500 cm^{-1} a shift is seen in an adsorption peak associated with N-containing heterocycles. A larger shift occurs at around 1200 cm^{-1} that corresponds to an absorption band for the -C-O stretch in -COOH groups. The third, and largest shift of more than 100 cm^{-1} , is seen where the aromatic

absorption feature is offset from 623 to 507 cm^{-1} . Not only is there a shift in the peak locations, but also a noticeable increase in the relative size of the peaks. This is especially true with the absorption at 1118 cm^{-1} which descends to a transmittance value of about 7%. It is twice as deep as the peak at 1651 cm^{-1} when Cr is present, but only half as deep in the tannery humic acid alone.

FTIR spectra of tannery humic acid with added manganese. The same arguments hold for manganese. To support our hypothesis, Mn must also form stable complexes with tannery humic acid. The spectra for tannery HA before and after addition of Mn is shown in Figure 2.3.12. The two main differences between the two traces are highlighted. First, the same peak shift is seen for the -C-O stretch of -COOH. As was true with Cr, besides the shift, there is also an increase in the magnitude of the absorption peak versus other spectral elements. Second, there is a trio of very prominent absorption peaks that occurs below 750 cm^{-1} . These peaks are attributable to Mn-O bridging between two complexation sites involving N-heterocycles. Chu *et al.*¹³ showed $[\text{Mn}(\mu\text{-O})]_2$ bridges giving rise to IR bands similar to these for a variety of natural ligands such as would occur in humic acid. These absorb very strongly; the peaks at 623 and 507 cm^{-1} essentially attenuate the entire IR beam to result in transmittance values near 0%.

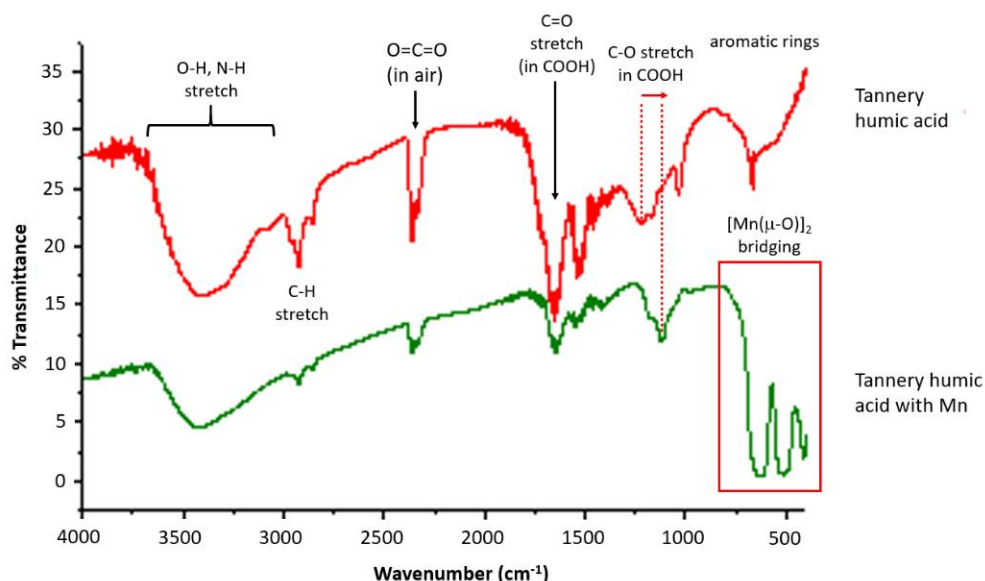


Figure 2.3.12. FTIR spectra for tannery humic acid before and after Mn addition.

Energy dispersive X-ray (EDX) spectra of metal-HA products. After washing excess metal solutions from the isolated Cr and Mn products of tannery humic acid, the EDX spectra of the two complexes were collected to show the incorporation of the metals into the HA structure.

The spectrum for the chromium product is presented as Figure 2.3.13. The chromium in the HA complex gives rise to an emission peak near 5.5 keV and a small companion peak near 6.0 keV. The large oxygen peak at 0.5 keV supports the presence of possible complexation sites within the HA framework. When mass% calculations were performed for peak areas by the EDX software, 30.22% was attributable to chromium. This reflects its much higher atomic weight (compared to C, O, Na and S) plus its greater emission efficiency.

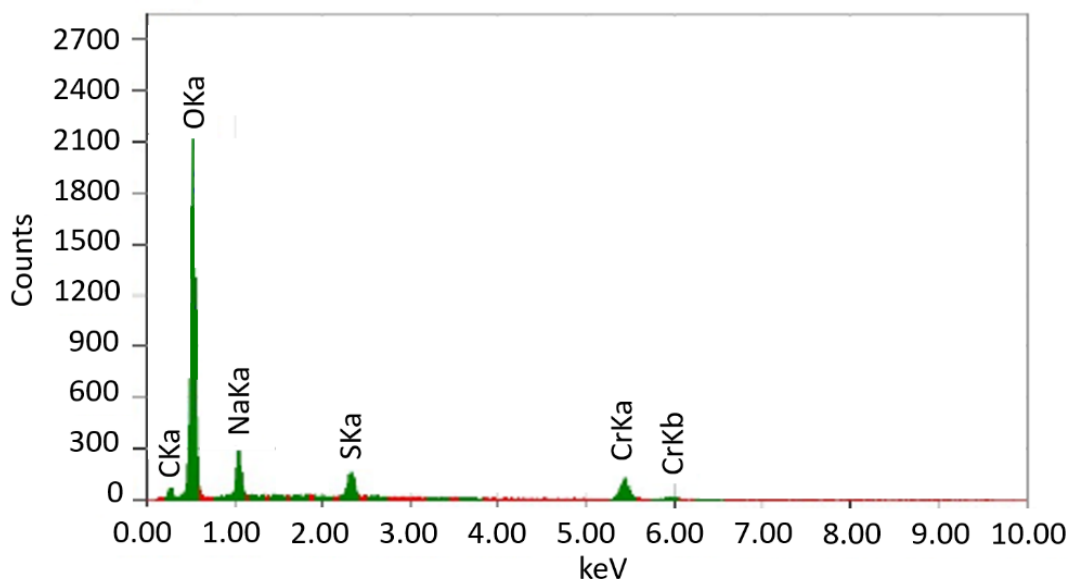


Figure 2.3.13. EDX spectrum for the chromium-tannery humic acid product.

The EDX spectrum for manganese is shown in Figure 2.3.14. Despite using a much smaller sample for the EDX spectrum of the Mn-HA product, there is a large emission peak for Mn at 5.9 keV with its companion peak at 6.5 keV. The EDX software assigned 84.04% of the normalized peak mass% to manganese.

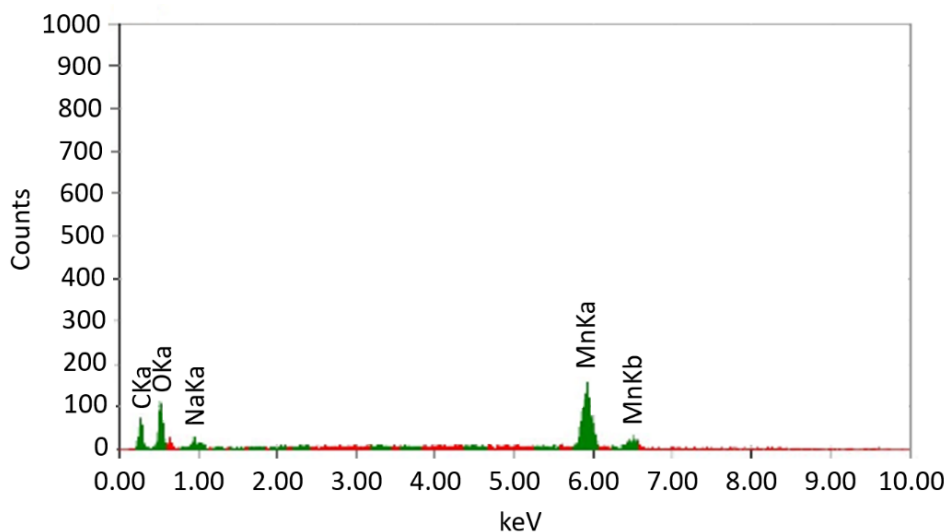


Figure 2.3.14. EDX spectrum for the manganese complex of tannery humic acid.

2.3.7. Modeling

The removal of chromium and manganese by humic substances has been described as complexation, but this is probably a simplification regarding the nature of the interactions. Both chromium and manganese often interact with organic matter via oxygen bridging structures. None the less, it is useful to briefly model what occurs in a mixture of traditional ligands with these two metals assuming simple complexation occurs. The metal ions will preferentially first be found residing on the sites with the highest formation constants.¹⁴ As the stronger complexing sites become saturated, then sites with lower formation constants will begin to be incorporated into the system. Once complexed to the humic acid, the metal ions are resistant to detaching and re-entraining in the effluent flow.

Complexation in humic acid is usually attributed to several categories of sites within its organic backbone. The best sites are those that embed a phthalic acid moiety into the structure. This gives the possibility of forming stable 7-member chelate rings with the transition metal cation. Next, there are salicylic acid regions where there is a carboxylic acid group with an adjacent phenolic group. This permits a 6-member chelate ring to form. Third, with catechol groups, two adjacent phenolic groups can form 5-member chelates. Lastly, there are individual benzoic acid groups. Evidence for heterocyclic nitrogen also

increases the complexing capacity for a humic substance. A section of humic acid that resembles 1,10-phenanthroline will form a 5-member chelate. Isolated N atoms can also act as monodentate ligands, probably as either a primary or secondary amine. A separate file within this chapter details the chemical model described here.

The binding of Cr^{3+} and Mn^{2+} to a mixture of ligands mimicking humic acid was modelled via a Microsoft Excel Visual Basic workbook containing the Multi TOPOS software. The results are displayed as trend surfaces above a composition grid such that a wide range of conditions are encompassed. The x -axis denotes the total metal concentration of the system on a logarithmic scale from 10^{-9} to 1 M. The y -axis represents the total ligand mixture on a similar logarithmic scale.

Formation constants for Cr^{3+} and Mn^{2+} are not easily found in the literature. Both form such stable oxyanions that their interactions with other substances probably occur through oxygen-bridge structures. The model system used here relies upon discrete, small molecular ligands that are commonly used in laboratory studies. Even then, it was necessary to estimate nearly all formation constants for Cr^{3+} and many for Mn^{2+} . Oxalic acid was used as an analog for the phthalic acid moieties as no phthalate complex constants were obtained. Estimates for Cr^{3+} constants were based on the relative complexing strength of Cr^{3+} vs. Mn^{2+} for other ligands where constants for both were found. Only 1:1 complexes were included in the model because it is unlikely that multiple sites on a rigid humic acid framework could fold into the geometry required for higher stoichiometries. Furthermore, while the humic acid was present as a gel-like colloid, we refer to the sites with molar concentrations, *i.e.*, moles of sites available per liter of solution. One large molecule of humic acid will contain many complexation sites dispersed throughout its backbone. An assumption when interpreting the model's results is that the individual binding sites act essentially independent of one another. Many studies have considered humic acid to be a polyelectrolyte.¹⁵

The system presented below contains six organic ligands plus hydroxide as complexing agents for the metal ions. Distribution of sites was made roughly according to proposed humic acid structures in the literature. For the surfaces shown below, the percentages for each site type were: 5% oxalic acid, 10% salicylic acid, 20% catechol, 30% benzoic acid, 5% 1,10-phenanthroline, and 30%

methylamine. A pH of 8.5 was used, a mid-range value for the field samples that were collected from the tanneries. The metal mixture, determined from the effluent sample at Site 1, had 99.986% chromium and 0.013% manganese. The hydroxy species included were those listed in Smith and Martell's *Critical Stability Constants*.¹⁶ For Cr^{3+} these were CrOH^{2+} , $\text{Cr}(\text{OH})_2^+$, $\text{Cr}_2(\text{OH})_2^{4+}$, $\text{Cr}_4(\text{OH})_4^{8+}$, and $\text{Cr}_4(\text{OH})_6^{6+}$. For Mn^{2+} , the hydroxy species were MnOH^+ , $\text{Mn}(\text{OH})_4^{2-}$, $\text{Mn}_2\text{OH}^{3+}$ and $\text{Mn}_2\text{OH}^{3+}$. Given the pH of the effluent and the high level of Cr^{3+} , the possibility of $\text{Cr}(\text{OH})_3(\text{s})$ was also included.

The fate of Cr^{3+} in the model system is completely controlled by hydroxide. Essentially, the organic ligands never have a chance to grab much Cr^{3+} because it is either in the $\text{Cr}(\text{OH})_2^+$ complex or has precipitated out as $\text{Cr}(\text{OH})_3(\text{s})$. This is evident in the species predominance surfaces shown as Figure 2.3.15 where γ_{max} is assigned to the species with the largest fractional presence. The grid point associated with the tannery effluent is shown with a red X on the surface. It is far into the $\text{Cr}(\text{OH})_3(\text{s})$ region. Because the two predominance regions show little variation over the entire range of ligand mixture values on the y-axis, it means they are basically independent of the ligand concentrations. No changes in proportions of ligands would have made any difference at this pH. At the effluent pH = 8.5, the saturation boundary occurs at a $\log[\text{total metal}]$ value around -6.75.

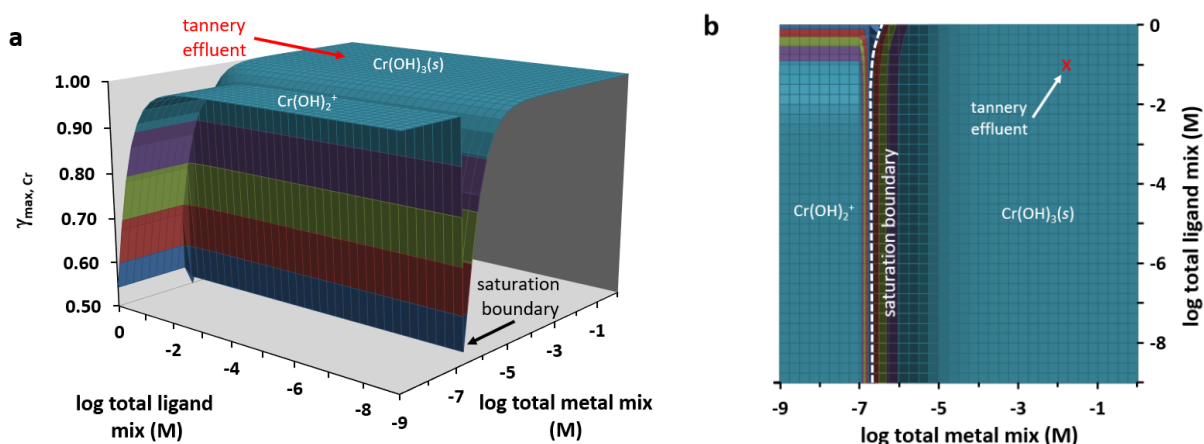


Figure 2.3.15. Species predominance surfaces for chromium(III) in the mixed metal – mixed ligand system at pH 8.5. a) wire-frame surface; b) contour map.

The saturation boundary for $\text{Cr}(\text{OH})_3(\text{s})$ is strongly related to pH. When the pH is dropped to 7.5, the saturation boundary moves one log unit from $\log [\text{total metal}] = -6.75$ to $\log [\text{total metal}] = -5.75$ (Figure 2.3.16). At low metal and high

ligand mixture levels, the predominant form of chromium is its complex with oxalic acid (CrOxal^+), almost 68% at its highest point. Second in prominence is the complex of Cr^{3+} with 1,10-phenanthroline at about 31%.

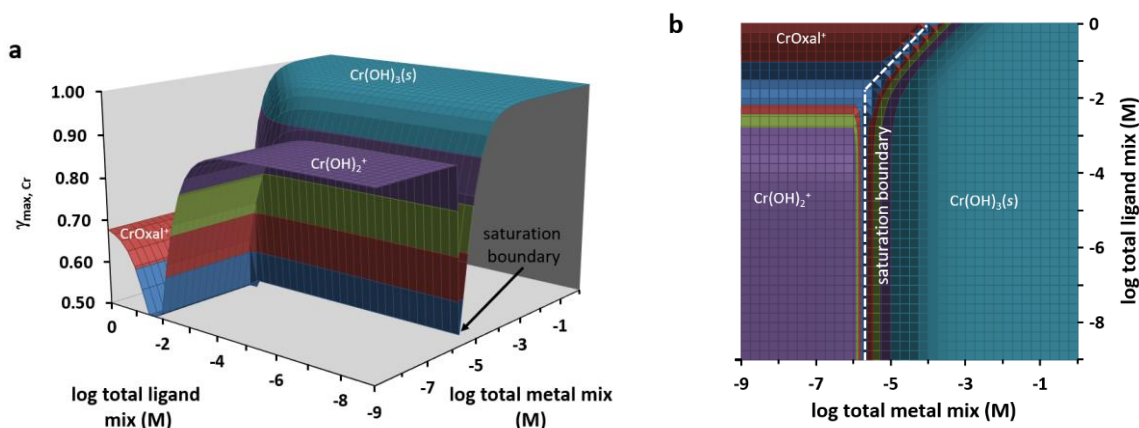


Figure 2.3.16. Species predominance surfaces for chromium(III) in the mixed metal – mixed ligand system at pH 7.5. a) wire-frame surface; b) contour map.

The angle at which the boundary bends to the right increases as pH is dropped, bringing successively larger segments of the composition grid into soluble forms. If the pH is lowered to about 5.5, the chromium(III) content of the effluent is in mobilized forms, not $\text{Cr(OH)}_3(s)$, and could be carried into the receiving river. This would not be a good situation for residents living downstream from the tanneries. Also note, some components in the ligand mixture can begin to compete with -OH groups.

The story with manganese is just the opposite. Its predominance surfaces (Figure 2.3.17) show horizontal divisions, an indication that Mn species are primarily dominated by the nature of the ligand mixture. Inspection of the model results indicates that, at the tannery effluent grid-point, the predominant form of Mn(II) is the complex with 1,10-phenanthroline, Mn(phen)^{2+} , with a gamma value of 0.579. This is exactly what is anticipated for ligand mixtures, *i.e.*, the metal ion preferentially attaches to the ligand with the highest formation constant. The formation constant for the Mn(phen)^{2+} complex is 1.26×10^4 . Despite 1,10-phenanthroline being present at only 5%, its large formation constant, K_f , more than makes up for this. Second in prominence is the complex of manganese with oxalate ion, Mn(oxal)^0 . It has the second largest K_f at 7.94×10^3 and a gamma of 0.367. The slight bend at the right-hand edge of the contour map is caused by growing importance of weaker complexes under excess metal conditions. In this

case, the stronger ligands are completely saturated with metal ions, so some of the weaker complexes begin to form. The independence of Mn(II) speciation from pH was shown by running the model at pHs of 7.5 and 9.0. There was no appreciable difference in the surface appearance in either case.

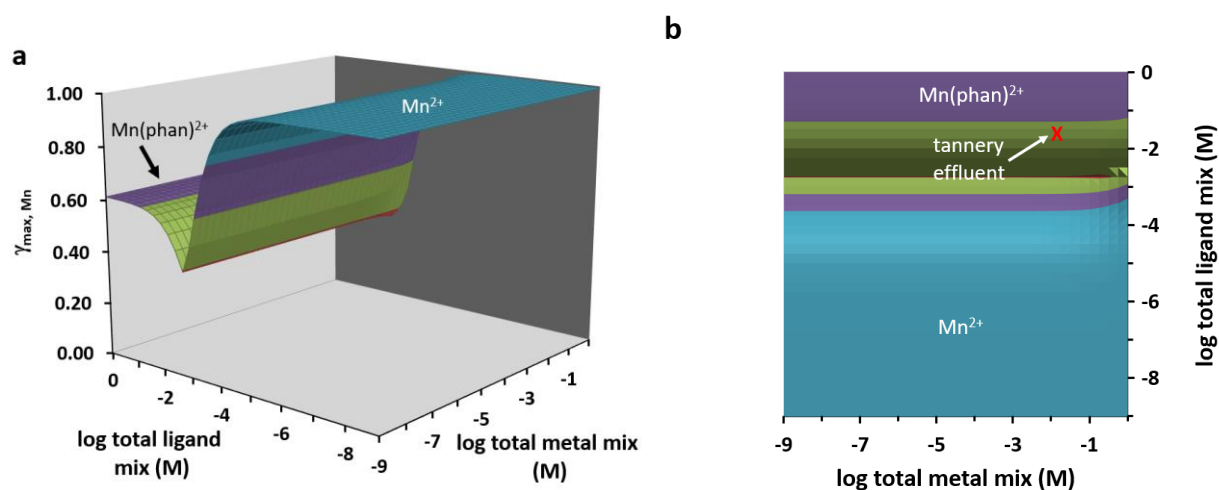


Figure 2.3.17. Species predominance surface for manganese(II) in the mixed metal – mixed ligand system at pH 8.5. a) wire-frame surface; b) contour map.

The composition grid modeled above includes a wide range of metal and ligand mix values. The tannery effluent corresponds to only a single point on this grid. At Site 1, the emerging effluent had a total chromium concentration of 0.0829 M while that of manganese was 1.09×10^{-5} M. Added together, this gives a “total metal mix” concentration of 0.0829 M or a log “total metal mix” value of -1.08. The humic substance concentration of the effluent was 0.346 g per 100 mL. Using a literature suggested value of 0.500 equivalents per 100 g yields a “total ligand mix” value of 0.173 M or a log “total ligand mix” of -1.76. Thus, the predominant speciation of the metal ions of interest is given by the grid point at (-1.08, -1.76). As mentioned above, this point has been marked with a red “X” on the surfaces of Figures 2.3.15 and 2.3.17. The tannery effluent’s composition reveals that chromium(III) is essentially all in the $\text{Cr(OH)}_3(s)$ form while manganese(II) is complexed with 1,10-phenanthroline (57.9%) and oxalate (36.7%).

2.3.8. Conclusions

This work set out to assess the potential impact of releasing toxic chromium and manganese in tannery effluents into Bangladesh's Dhaleshwari River near Savar, Dhaka. The levels of both metals rapidly dropped off with distance from the initial release point. Laboratory studies were conducted to understand the structure and composition of the humic acids present in this specific tannery effluent. To the best of our knowledge, this was the first time humic acids were extracted from any tannery wastewater. The extracted and purified humic acid was combined with both Cr^{3+} and Mn^{2+} to evaluate complexation behavior. Most previous complexation studies with humic acids were based on soil-derived organic materials.

The tannery humic acid contained aromatic, carboxylic acid, carbonyl, alcoholic and ether-like functional groups. From FTIR studies, the tannery humic acids had similar functional groups to HAs from swampy soils in rural haor areas. The elemental analysis did show a slightly higher N/C ratio for the tannery HA. Investigation of the complexing ability of humic acids revealed that tannery HA had a higher affinity for Mn than Cr.

A better idea of how humic acid was attenuating Cr and Mn emerged after modeling Cr^{3+} and Mn^{2+} in a mixture of ligands that simulate the types of binding sites on the humic acid framework. Given the pH of 8-9 at which the effluent is released from the facility, the model revealed that the chromium is essentially present as $\text{Cr}(\text{OH})_3(s)$, 99.9999046%. Just like an $\text{Al}(\text{OH})_3$ floc is used in the clarifying of drinking water to agglomerate clay particles and natural organic matter¹⁷, the $\text{Cr}(\text{OH})_3$ "floc" coagulated the colloidal HA particles. Again, analogously to drinking water treatment, the chromium floc is sand-bed filtered in the discharge channel.

Manganese is removed via a different mechanism. Because its hydroxy species are non-competitive compared to the HA complexation sites, the Mn ends up complexed to the HA's strongest binding sites, *i.e.*, those that mimic phthalate (as oxalate) and 1,10-phenanthroline. The model showed that under the tannery effluent conditions, 57.9% was $\text{Mn}(\text{phen})^{2+}$, 36.7% was $\text{Mn}(\text{oxal})^0$, and 5.2% was Mn^{2+} . As the agglomerated $\text{HA/Cr}(\text{OH})_3$ is retained with sand filtration, so too, is 94.6% of HA-attached Mn.

By virtue of the tanning process conditions and the serendipitous discharge into a sandy drainage channel, the leather-making facilities stumbled onto a natural wastewater treatment system. By the time the effluent reached the end of the drainage channel, the levels of Cr (0.28 mg/L) and Mn (0.02 mg/L) discharged into the Dhaleshwari River are near the drinking water standards - 0.05 mg/L for Cr and 0.1 for Mn.¹⁸ After the discharge mixes with bulk river water and is diluted, it will be far below analytical detection limits.

The standard method of removing dissolved toxic metals is by precipitation with lime, $\text{Ca}(\text{OH})_2$ followed by filtration.¹⁹ The pH conditions of the tannery effluent discharge fortuitously mimicked this process. It would be interesting to revisit the effluent discharge site and investigate the sandy drainage channel to ascertain that the Cr and Mn have indeed accumulated there. Unfortunately, that will not be possible as the entire tannery district is now connected to a modern, traditional wastewater treatment facility and the drainage channel back-filled. Earlier work by Karim *et al.*⁵ on the old Hazaribagh District of Dhaka found the same disposition of chromium in the lagoon, namely, it was concentrated as insoluble Cr(III) salts in the lagoon sediment.

A recent paper by Rahman *et al.*²⁰ suggests that the now-completed Central Effluent Treatment Plant is not doing as well at controlling chromium release to the river. They found surrounding water bodies near the plant contained up to 3.54 mg/L of chromium, far above the maximum drinking water standard. This is more than three orders of magnitude higher than at the mouth of the drainage channel that we monitored. It is true, however, that the effluent treatment plant is handling effluents from dozens of tanneries. The effluent source tracked in this paper was confined to just the first three facilities.

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