



8/8/2019

Chromium Contamination in Tannery Effluent

Toxicology and Potential Interventions

CIVE 480B Final Report

Executive Summary

Leather tanning has been practiced by humans for thousands of years. Animal hides are subject to putrefaction and when wet, and are tough and useless for practical purposes when dried. The process of tanning replaces the water molecules in collagen, the main protein in animal skin, with new molecules. Prior to the Industrial Revolution, vegetable tanning was primarily how leather was tanned. Animal hides are soaked in a vegetable tannin bath, which is usually made from tree bark extracts. In 1859, two technologists invented the process of mineral tanning. This process is very similar, but usually uses chromium ions instead of vegetable tannins to displace and replace water molecules in the collagen. Chrome tanning is quicker, easier, and results in leather that is softer and suppler than vegetable-tanned leather. Currently the leather tanning industry is valued at 100 billion USD, and 80-90% of leather is chrome-tanned.

Chromium mainly exists in nature in two oxidation states – chromium (III) and chromium (VI). Chromium (III) is what is used in chrome tanning, but chromium (VI) can also be present in the watershed through errors in the salt manufacturing and oxidation by natural compounds. Chromium (VI) is much more toxic, causing a plethora of both acute and chronic toxic effects. These effects include dermal and respiratory damage to tannery workers, and gastrointestinal effects from chromium entering drinking water.

Three potential interventions were developed to prevent chromium in tanning effluent from being present in drinking water. One intervention is to halt or limit the use chromium tanning by using synthetic leathers and alternative tanning methods. The second intervention is to treat the chromium effluent as it leaves the leather manufacturing facilities. The third and final intervention is to upgrade existing water treatment methods to better remove chromium and heavy metals using a process called electrocoagulation.

Analysis of the three interventions revealed that the first intervention – to use synthetic leathers and alternative tanning practices – best met the original objectives. It is recommended that this option is pursued, and that companies conduct more research into synthetic leathers that have similar, if not better, properties than chrome-tanned leather.

All these interventions have their own limitations and challenges; however, one must be pursued in order to ensure that people around the globe no longer unintentionally consume dangerous levels of toxic chromium.

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List of Abbreviations

| | |
|-------------|---------------------------------|
| DWTP | Drinking Water Treatment Plant |
| EPA | Environmental Protection Agency |

Abstract

The practice of leather tanning has been completed by humans for thousands of years. Until the discovery of chrome tanning in 1859, all leather was tanned using vegetable tanning. Vegetable tanning is a process in which untanned hides are repeatedly soaked in baths of vegetable tannins to displace and replace water molecules in animal hides. This process takes a few months to complete and produces workable leather. Chrome tanning operates on the same principle as vegetable tanning, in which chromium (III) displaces and replaces water molecules in animal hides. After chrome tanning was discovered, it quickly captured much of the market share of the leather tanning industry due to its ability to produce stronger and suppler leather, and being able to be completed in a day. Today, chrome tanning makes up 80-90% of the tanned leather industry. If not managed properly, chromium (III) contaminated effluent can enter the watershed, where some may oxidize to chromium's more toxic form, chromium (VI). This chromium is later consumed by humans in drinking water. Some possible interventions to reduce the amount of chromium that enters drinking water are: halting or limiting chromium use, water treatment of tannery effluent at tanneries, and upgrading water treatment plants to more effectively remove chromium. A common limitation of all interventions is cost; each intervention will require significant monetary investment but must be completed to ensure the global population will no longer consume dangerous levels of chromium.

1.0 Introduction

Leather tanning has been performed by humans for thousands of years to give practical use to animal hides [1]. Untreated hides are prone to microbial degradation and putrefaction when wet, and are stiff and useless when dried. At present, there are two main types of leather tanning: vegetable tanning and chrome tanning. Vegetable tanning involves the soaking of the animal hides in vegetable tannin baths, which are usually created from tree bark. Vegetable tanning was the main tanning process for thousands of years, up until the Industrial Revolution. In 1859, technologists Friedrich Knapp and Hylten Cavalin invented the process of chrome tanning. Chrome tanning uses baths filled with ions from chromium salts. Chrome tanning is currently the most common method of leather tanning, with 80-90% of leather being tanned using this method [2].

Unfortunately, chrome tanning has many negative effects on both human health and the environment. The discharge of chromium-rich wastewater can cause ecosystem damage, material loss, and the loss of agricultural land [3]. If chromium eventually enters drinking water after travelling through the watershed, it can be ingested by humans. Human exposure to chromium can cause a plethora of negative health effects, including vomiting, hemorrhage, developmental effects, and cancer [4].

Three possible interventions have been developed with the main goal of preventing chromium from tannery effluent from being present in drinking water. To design these interventions, a list of secondary objectives was developed:

- minimize environmental impact of the leather production,
- minimize other health impacts, including respiratory and dermal,
- minimize the cost to produce the leather,
- minimally disrupt the global leather industry, and
- be feasible in both developed and developing countries.

2.0 Background

To fully understand the scope of the problem, it is important to understand the background of chrome tanning. This background includes chromium's industrial function, chromium's chemistry, current drinking water treatment effects, chromium's toxicology, and the life cycle of chromium.

2.1 Industrial Function

In order to make the hide resistant to hydrolysis, the process of tanning modifies the molecular structure of the hide. The main protein that makes up animal hide is collagen (see Figure 1). In animal skin, collagen tends to align and wrap around each other, creating long and tough fibres that have high tensile strength and give skin its structure and elasticity.



Figure 1: Collagen fibers in animal skin [5]

The process of tanning removes the water molecules from the collagen and replaces them with new molecules, which could be vegetable tannins, chromium ions, or another alternative tanning agent. This removal prevents hydrolysis, which is the separation of chemical bonds caused by water. The tanned leather lasts much longer and will not harden or degrade.

The traditional tanning process, vegetable tanning, uses vegetable tannins to enter the hide and displace water molecules in the collagen. This method usually requires several soakings in the vegetable tannin bath, a time period of a few months, and the work of highly-skilled tradespeople to complete. This complexity and time required eventually led to the creation of mineral tanning, which most commonly uses chromium to complete a very similar process. During chrome tanning, the hides are first placed in an acidic bath to open space between the collagen fibres. Then, they are placed in a chromium salt bath in which the water molecules are displaced and replaced with chrome ions. This replacement is largely driven by a reaction between trivalent chromium ions and collagen carboxyls. Chromium, compared to other metals used for tanning, has the unique ability to form stable, covalent bonds with these carboxyl groups. These bonds can also form between one chromium ion and multiple carboxyl groups, which is believed to be the origin of leather's high hydrothermal stability, or the temperature at which the leather begins to shrink in water (see Figure 2).

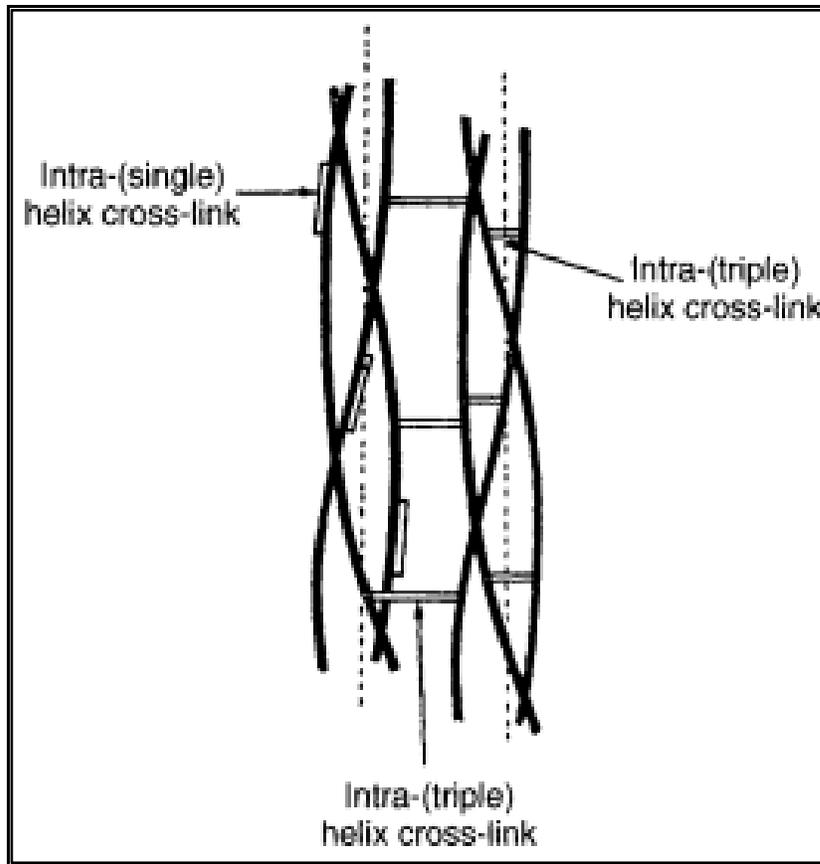


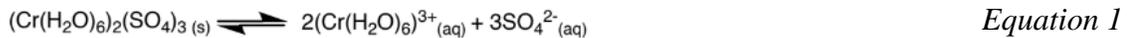
Figure 2: Covalent complexes formed between chromium and collagen carboxyls [6]

Chrome tanning also has the benefits of a more long-lasting colour and softer, suppler leather [1]. Because of its many harmful effects, there are regulatory guidelines for total chromium content, which are created and enforced by associations such as the Environmental Protection Agency (EPA) [7]. However, many countries, such as China and India, have weak environmental regulations that result in chromium-rich effluent entering watersheds. Unfortunately, these are also two of the highest producing countries for leather in the world, alongside countries such as Italy, Brazil, and Bangladesh. Globally, the tanning industry is estimated to earn a global trade value of US\$100 billion per year [8]. This number makes sense considering the quantity of leather produced, as the country that manufactures the most leather, China, was estimated to have produced over 4000 million square feet of bovine, buffalo, sheep, and goat leather in 2006 alone. Currently, there are roughly 480,000 tons of chromium tannins produced per year [2]. From estimates completed by the government of Bangladesh, approximately 80 cubic metres of effluent is created every day by each tanning facility [9]. In addition, in India alone the tanning industry employs 3.09 million people. This number is expected to double by 2022 [10]. It is clear from these high numbers that the leather industry is very important in today's society, and even with the new emergence of fake and synthetic leathers, the sudden stoppage of the industry would have a massive impact on the livelihoods of thousands of workers and the economies of many developing countries.

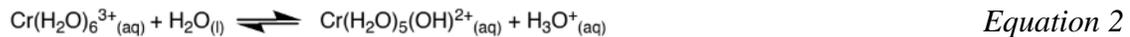
2.2 Chromium Chemistry

Chromium exists in nature mainly as either trivalent or hexavalent chromium, shown symbolically as Cr (III) and Cr (VI) respectively. Additionally, there are several compounds present in both the watershed and drinking water treatment that can oxidize chromium (III) to chromium (VI) and reduce chromium (VI) back down to chromium (III). The oxidation state of chromium used in leather tanning is chromium (III) in the form of a chromium salt, usually chromium sulfate. However, errors in the salt manufacturing process can also result in hexavalent chromium being present in chromium tanning baths.

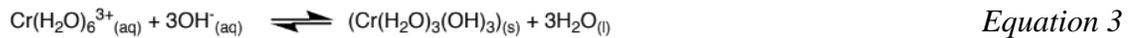
There are many different reactions that chromium commonly undergoes. Firstly, chromium sulfate is soluble in water and undergoes dissolution into chromium (III) and sulfate ions, as shown in Equation 1.



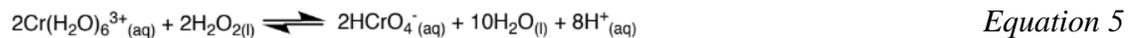
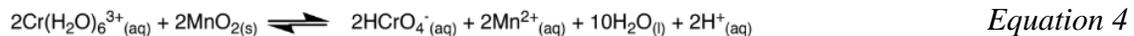
These hydrated chromium (III) ions are how chromium enters the watershed from leather production [11]. Trivalent chromium is fairly acidic in water, losing a hydrogen atom to water molecules, as shown in Equation 2 [12].



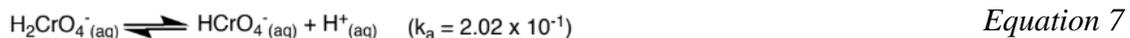
Trivalent chromium can also precipitate quite easily in the presence of hydroxide ions (see Equation 3).

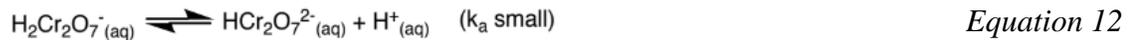
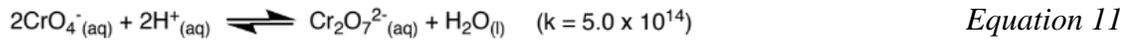


The most common form of this precipitate in neutral water is $\text{Cr}(\text{OH})_3$. The chromium (III) compounds that exist once this equilibrium is established can very easily be oxidized to chromium (VI) by a number of agents including manganese dioxide, hydrogen peroxide, and hypochloric acid, which is present in drinking water treatment (see Equation 4, Equation 5, and Equation 6) [13].



Hexavalent chromium is much more toxic and hazardous to the environment, so this oxidation is very detrimental and should be avoided. These redox reactions can often produce chromic acid, which, depending on the pH of solution and other factors, can exist predominantly as chromate ions, dichromate ions, chromic acid, or dichromic acid (see Equation 7, Equation 8, Equation 9, Equation 10, Equation 11, and Equation 12).





Lastly, chromium is very rarely present as an elemental metal in nature and therefore was not included in this summary of reactions. A summary of all these main chemical reactions for chromium is shown in Figure 3.

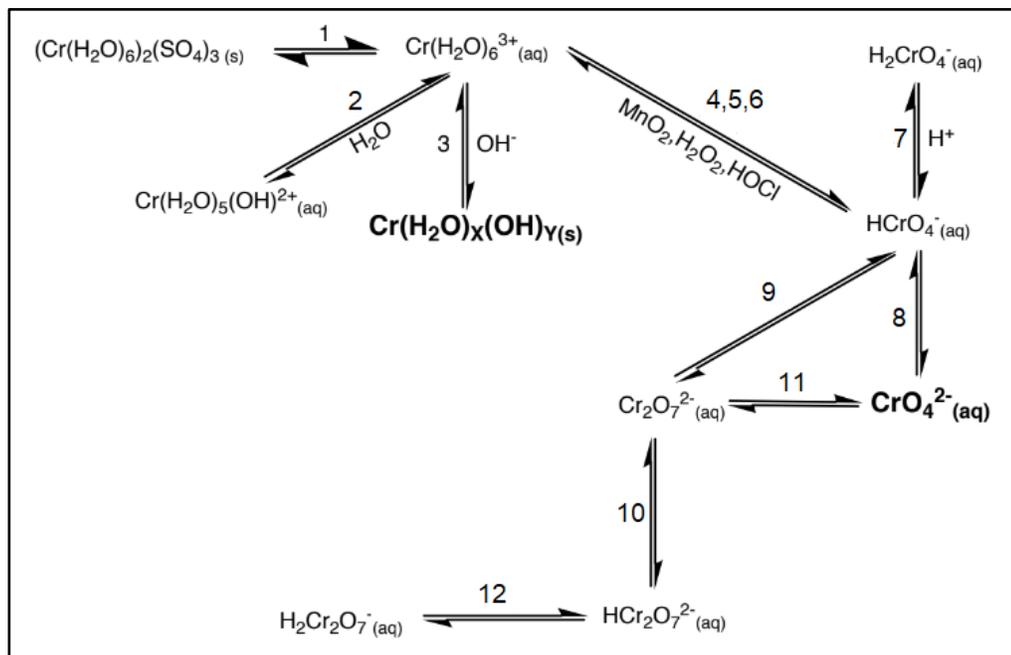


Figure 3: Chemical Flowchart for Chromium in the Watershed

2.3 Effect of Conventional Drinking Water Treatment Practices

The processes of coagulation, flocculation, and sedimentation together form the main mechanism for the removal of heavy metals from drinking water. During coagulation, a coagulant, most commonly aluminum sulfate (alum), is added to the water, which then undergoes fast mixing for a short period of time. This mixing, in combination with the addition of the coagulant, destabilizes the surface charges on the contaminant particles. The addition of a coagulant neutralizes the negatively charged contaminants and causes them to attract to one another through van der Waals forces. Coagulation via alum dosing has been shown to not produce an acceptable reduction in chromium concentration [14]. Although this chemical coagulant tends to be ineffective, there are several other forms of coagulants that are shown to be more effective [15].

Once particles have been destabilized through coagulation, flocculation can occur. During the flocculation stage, water is slowly mixed for a longer period than coagulation. To encourage the formation of flocs, the water undergoes a slow mix period, which aims to maximize collisions of destabilized particles. The formation of larger flocs drastically increases the settling velocity of particles and therefore decreases the amount of time particles take to settle out of the water according to Stokes' law.

Once particles have been formed into flocs during the flocculation stage, they settle to the bottom of the tank and create a sludge. Any increase in the surface area of the bottom of the settling tank will increase the speed at which particles will settle out of the water. This process does not rely on any chemical processes and uses only gravitational forces to settle flocs from the water.

This sludge would then be cleaned out; however, filtration either by granular or membrane filtration would then be required. Filtration is the process in which water is passed through a porous medium, usually granular or a membrane media. Filtration aims to attach particles to the medium they are being filtered through by attraction to filter media particles. This can happen for a number of reasons, including electrostatic forces, hydrodynamic forces, inertia, etc. Filtration can be performed without the use of granular media, by membrane filtration or capacitive deionization. Membrane filtration operates on the same principle as granular media filtration while capacitive deionization separates anions and cations via the creation of an electric potential between a cathode and anode. Filtration of chromium contaminated waters through reverse osmosis or nanofilters has been proven as an effective method of removing both trivalent and hexavalent chromium from water [16]. Capacitive deionization has also been shown to significantly reduce trivalent chromium concentrations, even in the presence of other heavy metal ions [17].

In the disinfection stage of the treatment process there is typically a disinfection agent added to treat a variety of contaminants. This stage involves pathogens being inactivated, removed and/or destroyed via boiling, radiation, or chemical oxidation. The most common disinfection method is chlorination. Chlorination has been shown to oxidize chromium (III) into the metal's more dangerous oxidation state, chromium (VI) [18]. A pH of 9 has been shown to be the least favorable conditions for this reaction to occur. This pH level falls within Canadian guidelines for finished drinking water [19].

2.4 Chromium Toxicology

In general, compounds containing hexavalent chromium have been found to be more hazardous than compounds containing trivalent chromium. Additionally, hexavalent chromium compounds are much more readily absorbed into the body than trivalent chromium compounds [20]. Chromium (III) compounds are generally not very toxic. There is a lack of information regarding certain aspects of its toxicity, and the information that does exist states that its effects are limited to mutagenicity, some acute toxicity, and respiratory hazards [21]. In fact, chromium (III) is an essential element in a healthy human diet in very low concentrations [22]. The main chronic effects associated with human exposure to chromium (VI) compounds such as chromate and chromic acid

are carcinogenicity, mutagenicity, and endocrine activity. Acute effects include coughing, shortness of breath, skin burns, vomiting, and hemorrhage. Additionally, it has been determined that many chromium compounds are very persistent in the environment [21]. Lastly, most of the chromium compounds studied have been shown to cause endocrine activity and be aquatically toxic.

Hexavalent chromium compounds can be absorbed through the gastrointestinal tract, lungs, and skin [23]. After hexavalent chromium enters the gastrointestinal tract, it is reduced to trivalent chromium and is then excreted in the form of urine approximately one week after ingestion. Although most chromium is removed from the body within a week, it is possible for small amounts of chromium that enters the body through any means to stay in human cells for several years [24]. The general public is predominantly exposed to hexavalent chromium through the gastrointestinal tract, while workplace exposure happens more frequently through skin contact and inhalation [25]. The most common exposure pathway relating to tannery wastes is chromium entering the watershed and eventually contaminating drinking water and being ingested by humans.

Several groups are much more affected by chromium contamination in drinking water than others. Women and children are more generally sensitive to chromium toxicity due to their lower body mass. Additionally, many tanneries operate in countries that do not have strong environmental protections or drinking water treatment, so low income tannery workers and people who live in the surrounding rural communities are more likely to be affected. Table 1 shows the summarized research of the toxicities of several main chromium compounds. There are several data gaps in the hazard table, mostly for acute toxicity and endocrine activity of chromium (III) compounds. Without this missing information, it is difficult to conclude for certain that hexavalent chromium is more acutely toxic than trivalent chromium. Additionally, there is no quantitative data on the potency of the compounds. Comparing compound toxicity qualitatively is much more difficult than using actual indications of relative hazards. Lastly, there are also data gaps regarding the carcinogenicity of trivalent chromium compounds and the mutagenicity of hexavalent chromium compounds. This missing information makes comparing the carcinogenicity and mutagenicity of the different chromium oxidation states very difficult.

Table 1: Hazard Table for Major Chromium (III) and Chromium (VI) Compounds

| Compound (Name & CAS RN) | Carcinogenicity, Mutagenicity & Reproductive Toxicity | Developmental Toxicity & Endocrine Activity | Acute Toxicity, Sensitization, Irritation, & Other | Persistence & Bioaccumulation | Aquatic Toxicity & Other Ecotoxicity | Physical Hazard |
|--|--|--|---|--|---|---|
| Chromic Acid, 7738-94-5 | found to be carcinogenic | endocrine activity present | acute toxicity, sensitization and irritation found | found to be very persistent | a lot of ecotoxicity and aquatic toxicity | large health hazards, respiratory and cardiovascular systems at risk |
| Chromate, 13907-45-4 | high-medium carcinogenic and reproductive toxicity | affects endocrine activity | acute toxicity | very persistent | a lot of ecotoxicity and aquatic toxicity | health hazards include genotoxicity, reproductive toxicity and acute mammalian toxicity |
| Chromium (III) Hydroxide, 1308-14-1 | minimal reproductive toxicity | minimal endocrine activity | some sensitization is found in research | medium-low persistency | can lead to aquatic toxicity once left in environment | health hazards include respiratory and gastrointestinal toxicity |
| Chromium Hydroxide Sulfate, 12336-95-7 | mutagenicity and reproductive toxicity found | minimal endocrine activity | - | medium-low persistency | can lead to aquatic toxicity once left in environment | health hazards include respiratory and reproductive hazards |
| Chromium(III) Sulfate, 10101-53-8 | some mutagenicity found | - | sensitization and acute toxicity found | persistent | aquatic toxicity present | health hazards include potential for DNA damage and cancer |
| Chromium(III) Potassium Sulfate (chrome alum), 81827-72-7 | mutagenicity and reproductive toxicity found | minimal endocrine activity | sensitization and acute toxicity found | very persistent | aquatic toxicity present | health hazards include respiratory damage, skin and urinary system damage |

3.0 Life Cycle of Chromium in Leather Tanning

Figure 4 shows a complete visual representation of the life cycle of chromium as it relates to leather tanning. The boundaries for this life cycle include that the mining of chromium and the manufacturing of chromium salts are not included, because the main concern is chromium from leather tanning ending up in drinking water, and what happens to the chromium before it becomes a salt in the tannery is out of the scope. Also, the interventions are developed to prevent chromium from entering drinking water, so the life cycle of chromium beyond the drinking water treatment plant (DWTP) is also out of the scope.

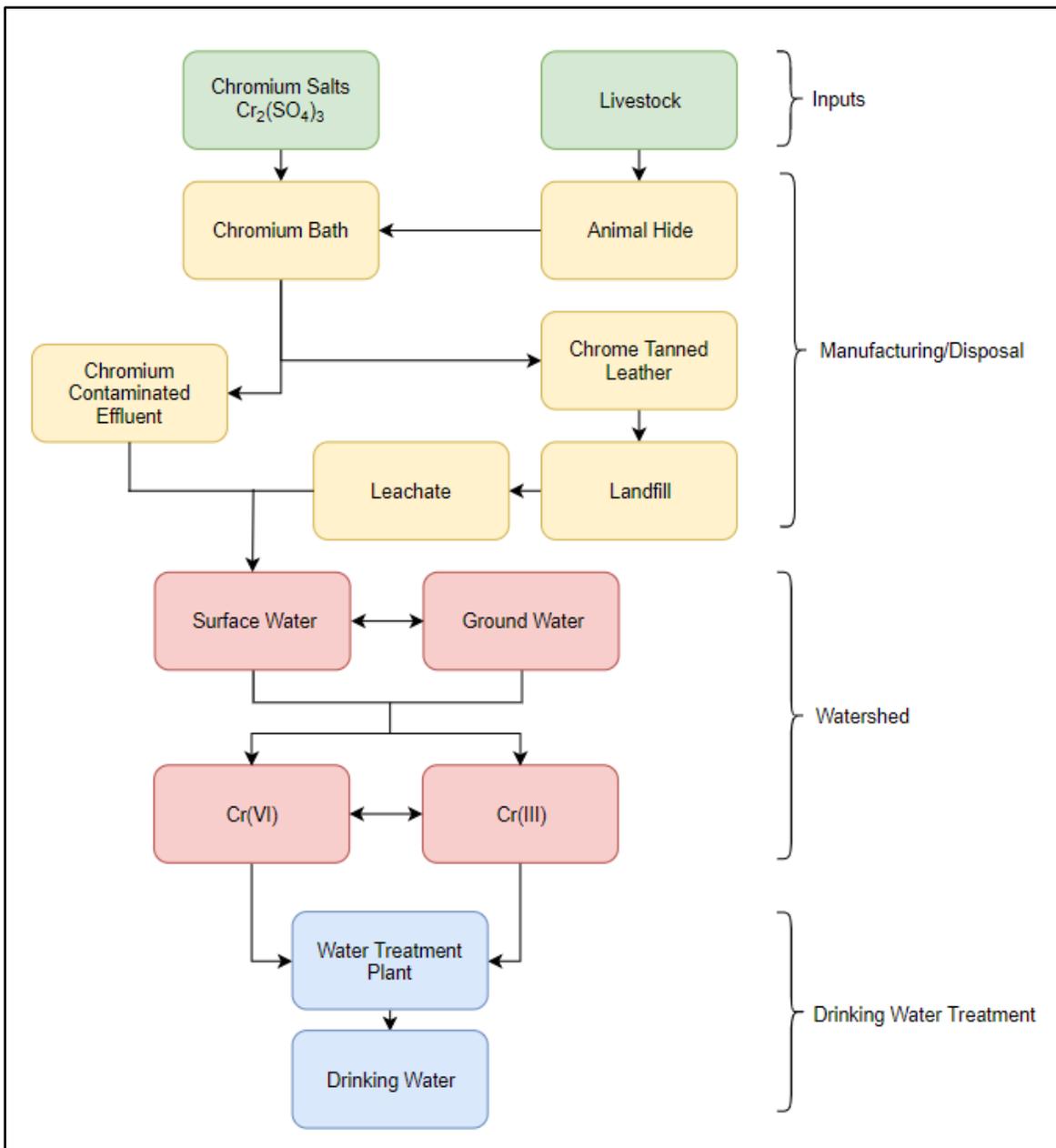


Figure 4: Life Cycle of Chromium in Chrome Tanning

Chromium originates as the mineral chromite found in the earth and is primarily mined in South Africa, Kazakhstan, India, and the United States [26]. From chromite ore it is manufactured into the chromium (III) salts that are used for chrome tanning. These salts are mixed with water to create a bath which is used to soak the hides, remove water molecules from the collagen, and tan the leather. Chromium contaminated effluent from tanned leather may enter the environment through the chromium-rich effluent or leachate from landfills that contain disposed leathers. Once chromium enters the surface or ground water, there are several interactions that can take place that result in redox reactions. Firstly, chromium can react with ferrous iron in the soil [27]. Iron can be found in several oxidation states in the environment. If chromium (VI) contacts iron (II) and certain conditions are met, the chromium (VI) can be reduced to chromium (III), which then precipitates in the soil and is effectively immobilized. Chromium (VI) can be reduced in the environment by several compounds including free chlorine and manganese oxide. Chromium-rich surface and groundwater can end up entering DWTP's, where it is treated to drinking water quality. This drinking water treatment process is not always effective at removing chromium, which is a serious health concern considering its high toxicity.

Three main intervention points were identified using this life cycle. The first intervention point is at the inputs of the system – prevent or reduce the use of chromium salts or animal hides. This intervention point is beneficial, because it is relatively simple to implement and it prevents chromium from ever entering the watershed. The second intervention point is as the chromium effluent leaves the tannery. This intervention point is favorable because it prevents the chromium from entering the environment. Lastly, the final intervention point is at the drinking water treatment plant. This point is also beneficial, as it would ensure with high certainty that chromium would not be contained in the drinking water, since it is being treated just before consumption. Clearly, each of these intervention points has its own benefits and limitations, which is useful for developing interventions of varying scope and scale.

4.0 Interventions

Three possible interventions have been developed: halting or limiting chromium use through alternative leather practices, removing chromium from the effluent before it leaves the tannery, and removing chromium at the drinking water treatment plant using electrocoagulation.

4.1 Halt or Limit Chromium Use

The first intervention is to halt or limit the use of chromium in leather tanning. This limitation can be accomplished in two ways. Firstly, alternative tanning agents, such as mixed-metal tanning, can be used to reduce the chromium used in the tanning process. Three alternate tanning agents were considered: henna-aluminum, tara-aluminum, and chrome-zinc-silica. The second method is to increase the use and reliance on synthetic leathers, such as coffee leather and recycled rubber.

4.1.1 Alternative Tanning Agents

Henna-aluminum and tara-aluminum tanning both use a combination of plant tannins and aluminum ions to displace and replace the water molecules in collagen. This process is slightly slower than chromium tanning, and can be completed in 2-3 days [28]. The optimized process for plant-aluminum tanning results in leather with a maximum

shrinkage temperature of approximately 97°C, compared to the 100+°C shrinkage temperature of chrome-tanned leather. Maintaining this high shrinkage temperature is important for the feasibility of alternate leathers because shrinkage damages and ruins leather products. Chrome-zinc-silica tanning uses a combination of three metals to reduce the concentration of chromium that in the effluent leaving the tannery. This process uses only 25 percent of the chromium compared to chromium tanning. For tanneries to switch to using mixed metal tanning methods, there would need to be minimal change to the tanning infrastructure that currently exists as the only change needed is the contents of the tanning baths. For this reason, this intervention is the least expensive of those developed.

Replacing chromium as a tanning agent has some limitations. Firstly, 80-90% of leather that is tanned currently is tanned using chromium [2]. Leather tanned using these alternative tanning agents also has issues of its own, such as excess aluminum affecting the aesthetics of drinking water. Leather tanned using these new methods is not produced as quickly as chrome tanned leather. Because of this drawback, current tanning infrastructure could not meet the demand if all tanneries switched to mixed metal tanning and additional infrastructure would need to be built.

4.1.2 Alternative Leathers

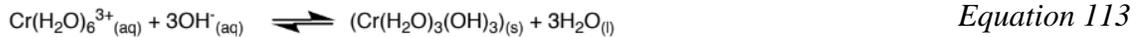
Secondly, alternatives to animal leather can be used. There are many alternatives to leather that feel and look like leather but contain no chromium and have minimal health and environmental impacts. These include alternatives such as Pinatex, which is made from the fibers of the leaves of pineapples that are collected as byproducts during harvests. Another alternative is Mylo, which is produced from mushroom roots and is very similar to leather. Lastly, many companies use agave plant fibers, which is a similar alternative to Pinatex. All of these alternatives are also biodegradable and there is no risk of harmful chemicals or heavy metals leaching into the ground after being discarded. There are also lots of other alternatives for leather such recycled rubber belts, cork bags, and other vegan leathers derived from items such as coffee grounds and wood.

Alternative leathers are not without their own limitations. Many are made out of plastics, rubbers, and fossil fuels that take long periods of time to decompose. Additionally, many faux leathers consist of synthetic polymers which can end up in drinking water with the possibility of by-products and health effects. However, these potential by-products and effects are currently not well-researched. Synthetic leathers also tend to not have similar properties to chrome-tanned leather, which results in issues with shrinking, ripping and fading. This reduced performance further results in a shorter lifespan, resulting in synthetic leathers ending up in landfills a lot faster than chrome-tanned leather.

Furthermore, the current leather industry employs roughly 2.5 million people [29], most of which being in third world countries such as India. Should the switch to alternatives be widely accepted, there could be very negative impacts on the large number of people in the leather tanning industry. Lastly, another limitation is the global acceptance to alternative leathers. There are many cultures that rely on leathers heavily, and use leather as a cultural or status symbol. In these places, it would require a significant cultural shift in how people view leather for them to adopt the use of synthetic brands.

4.2 Treatment at Leather Tannery

The second intervention that can be made in the chrome tanning process is the treatment of chromium contaminated effluent at tanneries directly after its use. Treatment of chromium contaminated effluent would happen in three steps. The first step would be to reduce any chromium that has been oxidized to chromium (VI) back to chromium (III). This process would use a reducing agent such as manganese dioxide or perchloric acid. The chromium, now all in its trivalent state, would be precipitated out by the addition of a base to form chromium hydroxide (see Equation 113).



The effluent, now free of chromium, would be released into the environment or a wastewater system if available. The easiest way to deal with environmental contaminants is to deal with them directly at the source, and this intervention takes advantage of that fact.

One study completed using aluminum oxide hydroxide revealed that more than 99% removal of Cr(III) was achieved at the optimized test properties of pH, adsorbent dose, and contact time [30].

This intervention does have some limitations. Treating chrome tanning effluent directly at the tannery would not have any effect on the environmental impacts of the tanned leather itself, such as chromium that could leach out of the tanned leather in landfills and into groundwater [31]. Common reducing agents for chromium such as manganese dioxide or perchloric acid also have their own environmental and human health impacts, and would need to be removed from the wastewater as well. Manganese dioxide, for example, is acutely toxic if swallowed or inhaled, has high acute and chronic aquatic toxicity, and is suspected of having reproductive toxicity as well as being carcinogenic [32]. Most of the chrome tanning that is completed happens in low-income rural areas of developing countries such as India and Morocco. These areas are an attractive area to operate a tannery due to their relaxed environmental protection laws. Installing water treatment plants at every tannery would be very expensive, and it is unlikely that they could be implemented in the low resource areas that most tanning occurs unless proper environmental protection laws are put in place and enforced.

4.3 Removal at Water Treatment Plant

The third and final intervention is upgrading existing water treatment infrastructure to be better suited to the removal of both chromium (III) and chromium (VI). Water treatment using alum as a coagulant has proven to be ineffective at removing chromium from contaminated wastewater, removing only 15-28% [33]. In addition to this, disinfection of wastewaters using chlorine can oxidize chromium (III) to chromium (VI). Water treatment plants can be upgraded to better remove chromium by the use of electro-coagulation. Electrocoagulation uses electric cells to destabilize surface charges on particles in the water. This method has shown to be better suited to remove heavy metal contaminants, in one study reducing chromium (VI) concentration from 140 mg/L to <5

mg/L at the optimized current [15]. Electrocoagulation also is still effective at removing common wastewater contaminants such as suspended solids and emulsified oils. A further benefit of using electrocoagulation versus coagulation via alum dosing is that the method produces no coagulation by-products.

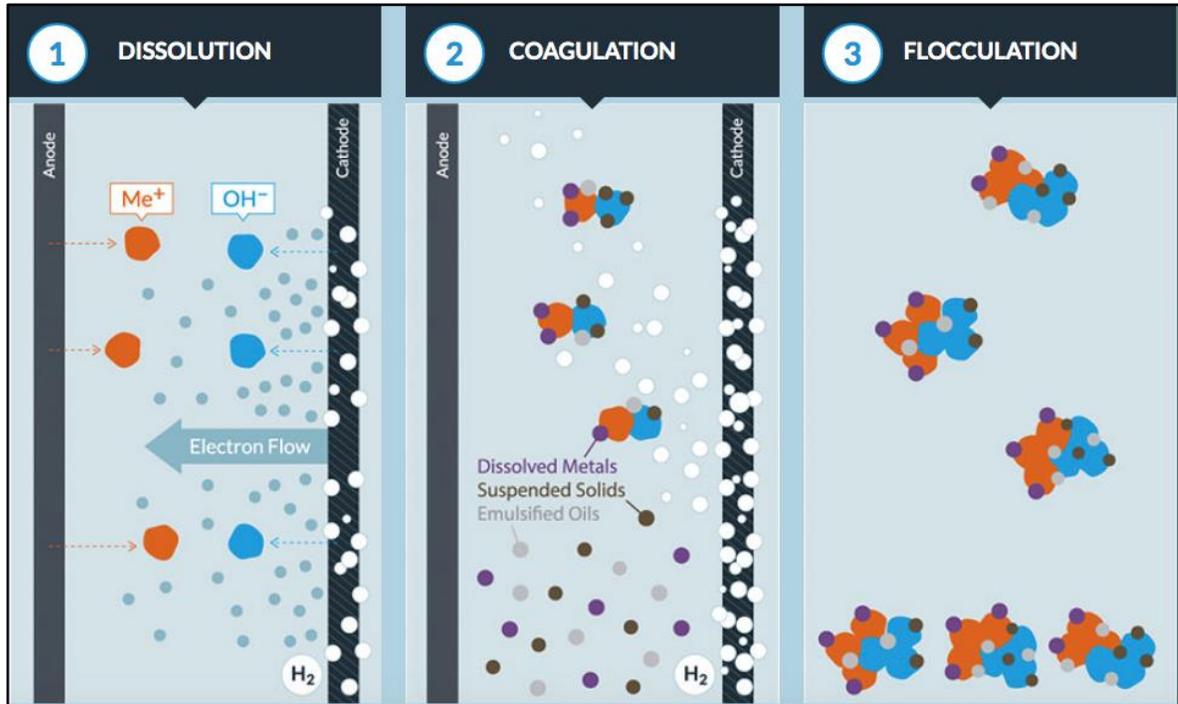


Figure 5: Electrocoagulation Process

Electrocoagulation happens in three steps.

1. Water hydrolyzes into hydrogen gas and hydroxide ions. A metal is then added, which forms a bond with the hydroxide ions.
2. The electrons, now flowing from cathode to anode, destabilize the surface charges on contaminants that exist in the wastewater
3. Particles no longer repel each other due to destabilized surface charges, and flocs will form. These flocs greatly increase the settling velocity of particles which will then settle out of the solution'

This intervention does have some limitations. Firstly, upgrading existing water treatment infrastructure will have no impact on the environmental effects of chromium-rich effluent that never reaches wastewater collection systems. This limitation is important to note because in the low resource contexts where much of the world's chrome tanning occurs, much of the effluent is released directly into the environment. Additionally, this intervention also does nothing to mitigate the environmental impacts of chromium in the tanned leather that makes its way into groundwater in the form of landfill leachate. It would also be difficult to implement in developing countries due to its high cost and the fact that many developing countries do not have advanced drinking water treatment infrastructure.

5.0 Discussion and Recommendations

All three interventions accomplish the initial objectives to varying degrees, and were ranked using the following criteria (see Table 2) and a weighted objectives chart (see Table 3).

| Rating | Description |
|--------|-------------------------------|
| 5 | Fully meets objective |
| 4 | Meets objective well |
| 3 | Meets objective minimally |
| 2 | Does little to meet objective |
| 1 | Does not address objective |

Table 2: Weighting Criteria

| Objective | Weight | IV1 | Value | IV2 | Value | IV3 | Value |
|---|--------|------|-------|------|-------|------|-------|
| Remove or limit the amount of chromium that ends up in drinking water | 0.4 | 4 | 1.6 | 5 | 2 | 4 | 1.6 |
| Minimize environmental impact | 0.1 | 3 | 0.3 | 5 | 0.5 | 3 | 0.3 |
| Minimize other health impacts | 0.1 | 4 | 0.4 | 4 | 0.4 | 3 | 0.3 |
| Minimize the cost to produce the leather | 0.1 | 4 | 0.4 | 1 | 0.1 | 2 | 0.2 |
| Minimally disrupt the global leather Industry | 0.1 | 1 | 0.1 | 3 | 0.3 | 5 | 0.5 |
| Feasible in both developed and developing countries | 0.2 | 4 | 0.8 | 1 | 0.2 | 2 | 0.4 |
| | Result | IV1: | 3.6 | IV2: | 3.5 | IV3: | 3.3 |

Table 3: Weighted Objectives Chart

The first intervention, halting or limiting chromium use in in leather tanning, is the best method to accomplish the objectives outlined in the weighted objectives chart. The use of alternative tanning agents like henna-aluminum and tara-aluminum can eliminate chromium altogether from the tanning process and therefore accomplish the first objective very well. If chrome-zinc-silica tanning is used, some chromium may still enter surface or ground waters; however, the amount of chromium that is used in this process is much lower than that of regular chrome tanning. This reduction in chromium entering the environment will help minimize environmental and other health impacts. This intervention is also the most feasible in developing countries as the tanning infrastructure already exists and all that would need to be changed is the contents of the bath used for the tanning process. The use of alternate tanning agents would cause minimal disruption to the leather industry.

The second intervention, treating chromium-rich effluent directly at leather tanneries, is the also met most of the objectives very well. If leather tanneries build small treatment plants and operate them correctly, almost no chromium will leach into the environment, as all contaminated effluent would be dealt with directly at its source. Unfortunately, this intervention is also likely the most expensive of the three interventions considered. Building a miniature water treatment plant at every tannery would be prohibitively expensive for most tanneries that operate in developing countries, and would likely not be implemented unless it was mandated to do so by local governments.

The third and final intervention, the removal of chromium at water treatment plant, is the lowest rated out of the three possible interventions for several reasons. Upgrading existing water treatment infrastructure to be better suited to the removal of chromium can be an effective way

of limiting the chromium that ends up in drinking water if and only if the chromium-contaminated effluents are disposed of into a wastewater system that is centrally treated. In the low resource context in which many tanneries exist, this central wastewater collection system does not exist and this intervention would therefore have little impact in many areas that tanning occurs. This intervention would, however, be an effective method of preventing chromium from entering drinking water in developed countries or other areas where central wastewater collection systems exist. This intervention would come at minimal cost to leather tanneries, and be subsidized by local governments. This intervention therefore would do little to disrupt the industry as a whole.

The final recommendation, based on the weighted objectives chart and the analysis completed, is to pursue the first intervention and try to halt or reduce chromium use in leather tanning. Scientists and researchers should complete much more research into both synthetic leathers and alternative tanning practices to determine their effectiveness, to improve their leather properties such as shrinkage temperature, and to work toward expanding their production capability. These steps are very important in moving toward full implementation of chromium-free leather tanning and the increased reliance on synthetic leathers.

6.0 Conclusion

The presence of chromium in its hexavalent form in drinking water presents a significant health risks. Possible interventions to reduce the human health risk posed by chromium-contaminated drinking water include: halting or limiting chromium use, water treatment of tannery effluent at tanneries, and upgrading water treatment plants to more effectively remove chromium.

The common factor for all interventions is cost; for chromium to be adequately removed from the watershed or prevented from entering the watershed, sufficient funding is needed. An analysis of all interventions revealed that the first intervention, halting chromium use in leather tanning, best met the original objectives due to its effectiveness in removing chromium from drinking water, its minimal environmental impact, and its ability to disrupt and replace the entire chrome tanning industry. Researchers must pursue studies into both synthetic leathers and alternative tanning practices to optimize them and work toward full-scale implementation of one or more alternative. Despite the cost that this work will involve, this intervention must be pursued to ensure that millions of people around the globe stop consuming dangerous levels of toxic hexavalent chromium.

7.0 References

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