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Application and investigation of chemical precipitation method for chromium removal and its recovery in one of the leather industries in Ethiopia.

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Application and investigation of chemical precipitation method for chromium removal and its recovery in one of the leather industries in Ethiopia.

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Acronyms

| | |
|---------------------------|---|
| APHA | American public health Association |
| EEPA | Ethiopian Environmental Protection Authority |
| GTZ | German Agency for Technical cooperation |
| UNIDO | United Nations Industrial Development Organization. |
| USEPA | United States Environmental Protection Authority |
| UNEP | United Nations environmental programme |
| FAAS | Flame Atomic Absorption Spectroscopy |
| TN | Total Nitrogen |
| TP | Total phosphorus |
| Cr | Chromium |
| mg/L | Milligram per liter |
| BOD | Biological Oxygen Demand |
| COD | Chemical Oxygen Demand |
| DO | Dissolved Oxygen |
| $\text{NH}_4^+ \text{-N}$ | Ammonium-Nitrogen |
| $\text{NO}_3^- \text{-N}$ | Nitrate-Nitrogen |
| TS | Total solid |
| TSS | Total suspended solid |
| TDS | Total dissolved solid |
| EM | Engineering Manual |
| BCS | Basic Chromium Sulfate |
| SE | Standard Error |
| μL | Micro liter |
| Mn | Manganese |
| DIW | Deionized water |
| UV | Ultra violet |
| g | Gram |
| Kg | Kilo gram |
| mg | Milligram |
| mL | Milliliter |

Abstract

Most tanneries in Ethiopia (90%) do not treat and very few (10%) partially treat their effluent before discharging it into the receiving water bodies, therefore, untreated leather effluent causes tremendous pollution of water resources in the country, especially due to its high organic loading and chromium content. Thus, proper treatment to eliminate or reduce the problem has to be devised. The purpose of this study performed at Addis Ababa Tannery Sh.Co. was to develop an alternative technical process for removing and recovering trivalent chromium from tannery wastewater via chemical precipitation. Chromium(III) salts are the most widely used chemicals for tanning processes, but 60-70% of total chromium salts reacts with the hides. In the other word, about 30-40% of the chromium amount remains in the solids and liquid wastes (especially spent tanning solutions). Therefore, the removal and recovery of the chromium content of these wastewaters is necessary for environmental protection and economic reasons. To this purpose, three precipitating agents; calcium hydroxide, sodium hydroxide and magnesium oxide were used. The effects of pH, stirring time, settling rate and sludge volume were studied in batch experiments. Flame atomic absorption spectroscopy (FAAS) method was used to determine Cr concentration. The results NaOH(99.973%), Ca(OH)₂(99.97%) and MgO(99.98%) showed that removal efficiencies at optimum pH values were not significant. However, there is significant difference in sludge characteristics with sludge volume of NaOH (590 mL), Ca(OH)₂(412 mL) and MgO(85 mL). The optimum pH is 9.8-10.3 with removal efficiency of 99.98% and the good sludge with high settling rate and lower volume was obtained by MgO precipitating agent. Hence the MgO is a good precipitating agent for removal and recovery of chromium from tanning wastewater. The basic chromium sulfate (BCS) recovered at pH 2.8 is suitable for tanning mixed with fresh BCS from the market.

Key words: Chromium, removal, recovery, chemical precipitation, tannery wastewater

Chapter one

Introduction

1.1 Background and justification

Industrial wastewater in Ethiopia has become the most vital problem because of the high growth rate and enormous discharge quantity to the environment (Zinabu and Zerihun, 2002). Many industries discharge harmful wastes into the rivers and land, in which pollutants are characterized by long persistence compounds (remaining active for a long period of time) and reversing their effects is almost impossible. These industries are at the infant stage and cannot afford enormous investment in pollution remediation equipments, as their profit margin is very small. The discharge of the untreated effluent to the surrounding water bodies and land cause Environmental and health problems to the surrounding inhabitants (EPA, 1997). Accelerated water quality change, due to industrial pollution, is one of the major environmental concerns through out the world (Zinabu and Zerihun, 2002).

Chromium solutions are widely used in many industrial processes such as chrome plating; wood preserving, textile dyeing, pigmenting, Cr chemical production, pulp and paper industries and tanning. The wastewater resulting from these processes contains high amount of chromium metal, which is harmful for environment and human health (Patterson, 1985; Zayed & Terry, 2003). Tanning process using chromium compounds is one of the most common methods for processing of hides (Sreeram & Ramasami, 2003). In this process about 60-70% of chromium reacts with the hides. In the other words, about 30-40% of the Cr remains in the solid and liquid wastes (especially spent tanning solutions) (Esmaaeili *et al.*, 2005).

Hence, the wastewater of tanning process is an important source adding Cr pollutant to the environment. In addition, the cost of the chromium metal is also high and it is possible to be recovered from the wastewater (Fabiani *et al.*, 1997; Ludvic, 2000; Kocaoba and Akin, 2002). Hafez *et al.* (2002) and Chaudry *et al.* (1998) reported that the Cr ions concentration in the tanning wastewater varies from 2500 to 8000 mg/L and 1300 to 2500 mg/L, respectively. Several methods have been used for removing toxic metal ions from aqueous solutions. These include chemical precipitation, ion exchange, reverse osmosis, membrane processes,

evaporation, solvent extraction, and adsorption (Patterson, 1985; Fabiani *et al.*, 1997; Ludvic, 2000). Of these, chemical precipitation is the common method for this purpose. Many factors affect the process of chemical precipitation including the type of precipitating agent, pH, and rate of precipitation, sludge volume, time of mixing and complexing agents (Patterson, 1985; Kocaoba and Akin, 2002; Tsugita and Ellis, 1981).

Chromium salts are undesirable for two reasons. Firstly, they can have a poisoning effect on the microorganisms used for sewage treatment (EPA 600/8-80-042c). Secondly they are precipitated as chromium hydroxide at neutral and near neutral pH's, meaning that they persist into the sludge from the sewage treatment plants. This gives a build-up of chromium(III) hydroxide in the sludge, which is undesirable as sludge is commonly used as a fertilizer. However, chromium is an essential trace element and there is no evidence of leaching of chromium in any form from sludges under normal conditions. As recently as 1994, the American courts prohibited the setting of limits on chromium(III) discharges as no detrimental effects had been demonstrated. Since world supply of chromium is limited the tanning liquor lost can be made alkaline and the chromium hydroxide separated is recovered by re-acidification for reuse (website: nzic.org.nz/chem_processes/animal/5c.pdf).

The chromium sulfate produced is suitable as a tanning solution. Leather production requires the use of large quantities of water. Through the use of modern equipment efforts are being made to reduce this volume. By use of the methods described above, the levels of undesirable chemicals in the water discharged from the tanneries can be reduced to the levels, which are acceptable to drainage authorities and if necessary acceptable for discharge into surface waters. As with all pollution control, the costs are high, and significant volumes are involved. However, the technology now exists for these problems to be controlled (website: nzic.org.nz/chem_processes/animal/5c.pdf). The purpose of this research is to compare pH, rate of precipitation, sludge volume and time of mixing when using the three precipitation agents (lime, sodium hydroxide and magnesium oxide) in the Cr precipitation of the tannery wastewater.

1.2 Statement of the problem

Tannery effluents contain large amount of chromium. Chromium discharges from tannery effluent in Ethiopia are above the permissible standards and it is one of the most toxic metals to plants, animals and microorganisms (EEPA, 2001). Even in low concentrations, it has a toxic effect upon aquatic biota such as fish, thus disrupting the food chain for fish life, cause soil salinity in irrigated farmland and possibly inhibiting photosynthesis in aquatic organisms in river (Tadesse Alemu, 2010).

However, treatment of tannery chromium-rich effluents by primary treatment systems such as; biological, oxidation or physico-chemical processes still leaves chromium levels in the treated wastewater above the legal discharge limit for surface waters (Alves *et al.*, 1993 and Assaye Ketema, 2009). So chromium has to be removed before discharged in to the rivers. Several methods have been used for removing toxic metal ions from aqueous solutions. These include chemical precipitation, ion exchange, reverse osmosis, membrane processes, evaporation, solvent extraction, and adsorption (Hintermeyer *et al.*, 2008). Of these, chemical precipitation is the usual way for this purpose (Esmaeili, 2005).

1.3 Objectives of the study

1.3.1 General objective

The main objective of this study is application and investigation of chemical precipitation method for chromium removal and its recovery in one of the leather industries in Ethiopia.

1.3.2 Specific objectives

- i) To characterize the wastewater effluent of Addis Ababa Tannery Sh.Co for selected parameters (see table 3.2 for the details).
- ii) To compare the efficiency of lime, sodium hydroxide and magnesium oxide in the precipitation process for the removal of chromium from tannery effluent.
- iii) To recover BCS or chromium from chromium hydroxide sludge for re-use.
- iv) To recommend the best chromium precipitating agent for tannery wastewater chemical treatment systems.

Chapter two

Literature review

2.1 The chemistry of chromium and its compounds

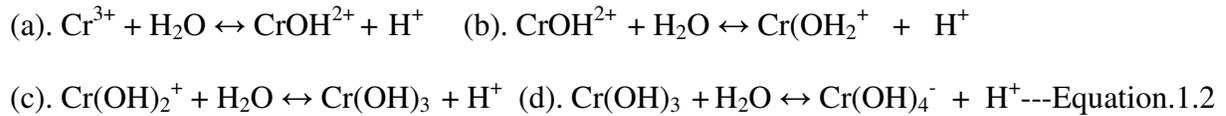
Understanding of the chemistry and geochemistry of chromium is important in developing remediation systems that can deal with industrial pollution. Chromium metal was discovered in 1797 by the French chemist, Louis, Nicolas Vauquelin. And it was named chromium because of many different characteristics colors of its compounds (Greek word “chroma” meaning color) (Motzer *et al.*, 2005).

Chromium is a steel-gray, lustrous, hard metal. Like other transition metals, chromium has variable oxidation states. The most common oxidation states of chromium are 0, +2, +3 and +6 with +3 being the most stable. But only three oxidation states are found in nature; these are:

Cr(0) which occur in metallic form, Cr(III) in chromic compounds and Cr(VI) occurs as soluble chromate(CrO_4^{2-}) and dichromate($\text{Cr}_2\text{O}_7^{2-}$) compounds. Pure Cr metal is extremely susceptible to combining with atmospheric oxygen. Therefore, it is almost impossible to have pure Cr in an oxygen-containing atmosphere because chromium is passivated by oxygen, forming a thin protective oxide surface layer that prevents oxidation of the underlying metal (Motzer *et al.*, 2005; Mohan *et al.*, 2006).

Chromium can be combined with various nonmetals (oxygen, fluorine, and chlorine, etc.). And polyatomic anions such as nitrate, sulfate, etc, forming relatively stable, soluble and insoluble compounds. More common are Cr(III) compounds such as chromium tribromide (insoluble), chromium nitrate (soluble), chromic hydroxide (insoluble) and chromic oxide (insoluble). Chemicals made from sodium dichromate include chromic acid, Cr(III) oxide, and potassium dichromate. Most chromium compounds are brightly colored and these colors are reflected in synonyms for there respective compounds. For example, basic chromium sulfate is known as chrome tan, Cr(III) oxide is known as chrome green, barium chromate is known as baryta yellow or lemon chrome, etc (Agaje Bedemo, 2007).

Under standard conditions, in the Cr-O-H₂O system, the Cr(III) stability zone occurs over a wide Eh (measure of the tendency of a medium to be oxidizing or reducing) and pH field under both reducing to oxidizing and acid to alkaline conditions. In aqueous environment under low Eh conditions, the main Cr(III) species are the Cr(III) cations: Cr³⁺ and CrOH²⁺ (Motzer *et al.*, 2005). In the Cr-O-H₂O system, under standard conditions, the governing reactions are



Under standard conditions, Cr-O-H₂O system, the Cr(VI) stability zone occurs over a much narrower range than the Cr(III) stability field. At pH < 6.5, HCrO₄⁻ dominates at low concentrations (<0.03 mol/L), but at concentrations greater than 0.001 mol/L, HCrO₄⁻ ions begin to change to Cr₂O₇²⁻ which becomes the dominant entity at concentrations greater than 0.03 mol/L (Mohan *et al.*, 2006).

2.2 Sources of chromium

Chromium contamination is primarily owing to its use in numerous industrial processes such as metallurgy, refractory and chemical manufacturing involving numerous commercial processes like leather tanning, electroplating, manufacturing of dyes, paints and paper milling, mining (ore refining) and wool preservation (Kumar, 2006). And human caused one has recently been the focus of much scientific discussion, regulatory concern and legal posturing. However, relatively high concentrations of naturally occurring dissolved Cr have been observed, usually observed with the very soluble chromates. Thus both anthropogenic and natural sources of chromium can lead to locally elevated concentrations in soils and waters. Common to all chromium contamination sites are the questions that continue to arise regarding water supply. As with most environmental challenges, questions of science compete with emotional and political responses and financial interests. Chromium from anthropogenic sources is commonly released as Cr bearing liquid or solid wastes such as chromate by-products, ferrochromium slag, or chromium plating wastes. Such wastes can contain any combination of Cr(III) or Cr(VI) with various solubility (Motzer *et al.*, 2005).

The nature and behavior of various forms of chromium found in wastewaters can be quite variable. The presence, form and concentration of Cr in discharged effluents depend mainly on the Cr compounds utilized in the industrial process, on the pH, and on the presence of other

organic and inorganic processes. Chemicals containing Cr(VI) are principally used for metal plating (which uses chromic acid, H_2CrO_4 , as dyes paint pigments and leather tanning. Thus, Cr(VI) will dominate in wastewater from the metallurgical industry, metal finishing industry (Cr hard plating), refractory industry and production or application of pigments (chromate color pigments and corrosion inhibition pigments) (Agaje Bedemo, 2007).

Chromium(III) found mainly in wastewaters of tannery, textile (printing, dyeing) and decorative plating industries. However, there is exception to these generalities owing to several factors. For example, in wastewater where Cr(III) is most expected form, the redox reactions occurring in sludge because of presence of oxidized impurities can increase the concentration of Cr(VI). Chromium(VI) can be transported great distances in groundwater owing in part to its high solubility. But, if the transported Cr(VI) enters an area with relatively low Eh (in the presence of organic matter, Fe(II) and dissolved sulfides especially where pH is low) it may be transformed by reduction to, and precipitated as, Cr(III). Chromium(III) generally is not transported great distances by ground water because of its low solubility. However, Cr(III) can be transformed to the more soluble Cr(VI) if the redox conditions along the transport path way change from reducing to oxidizing. Under natural conditions, Cr(III) has been found to be oxidized to Cr(VI) by Mn (Agaje Bedemo, 2007).

2.3 Advantages of chromium

Since its discovery chromium has become a very important industrial metal because of its many application in ferrous and non-ferrous alloy metal fabrication, and in the chemical industry. Chromium compounds are used in a wide variety of industrial and manufacturing applications including steel alloy fabrications, where they enhance corrosion and heat resistance and in plated product fabrication where they are used for metal decoration or increased wear resistance. They are also used in nonferrous alloy metal fabrication to impart special qualities to the alloys; in production and processing of insoluble salts, as chemical intermediates; in the textile industry for dyeing, silk treating, in the leather industry for tanning to obtain leather of desirable quality; in the manufacture of green varnishes inks, paints and glazes; as catalyst for halogenation, alkylation and catalytic cracking of hydrocarbons; as fuel and propellant additives; and in ceramics (Mohan *et al.*, 2006 & Sumathi *et al.*,2004).

Table 2.1. Uses and color of different forms of chromium,

| Form | Appearance (co lour) | Uses |
|---------|-------------------------|--|
| Cr(0) | Metallic grey / silvery | Stainless steel production, Alloy production, etc. |
| Cr(III) | Green | Alloy manufacturing, brick lining, chrome plating, tanning, and textiles, copying machine toner. |
| Cr(VI) | Red, orange or yellow | Chrome plating, Leather tanning, textiles and machine toner. |

Source: Agaje Bedemo, 2007

2.4 Toxicity and health effect of chromium

The presence of heavy metals in the environment is a major concern because of their toxicity to many life forms. Heavy metals like mercury, lead, cadmium copper, chromium and nickel are toxic even in extremely minute quantities (Selvaraj *et al.*, 2003). Since the majority of heavy metals do not degrade in to harmless end products, their concentrations must be reduced to acceptable levels prior to discharge of industrial effluents. Otherwise, they could pose threats to public health and affect the aesthetic quality of potable water.

According to the World Health Organization (WHO), the metals of most immediate concern are aluminium, chromium manganese, iron, cobalt, nickel, copper, zinc, cadmium, and mercury and lead (Baig *et al.*, 2003). Chromium contamination of soil and ground water is one of the significant environmental problems today (Salimi *et al.*, 2006)). Chromium is believed to be the second common inorganic contaminant after lead. The toxicity of chromium does not reside solely with the elemental form but varies greatly among a wide variety of chromium compounds. Oxidation state and solubility are crucial factors in this regard (Salimi *et al.*, 2006).

Chromium occurs in the environment primarily in two valence states, the oxidized hexavalent chromium, Cr(VI), and the less oxidized trivalent chromium, Cr(III). Under common

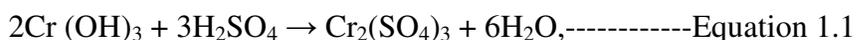
environmental conditions of pH and Eh, Cr(III) compounds are slightly soluble in water, whereas Cr(VI) compounds are quite soluble. Chromium(III) is considered to be essential to mammals for glucose, lipid, and protein metabolism and hence is an essential dietary element (Salimi *et al.*, 2006). On the other hand, Cr(VI) is much more toxic and mobile in ground water than the relatively immobile Cr(III) and possesses mutagenic and carcinogenic activity (Sarin and Pant, 2006; Nomanbhay and Palanisamy, 2005).

In humans, Cr(VI) exposure causes marked irritation of the respiratory track and ulceration and perforation of the nasal septum in workers in the chromate producing and using industries (Ageje Bedemo, 2007). Ingestion of 1.0 to 5.0 g of Cr(VI) as chromate results in severe acute gastrointestinal disorders, hemorrhagic diathesis, convulsions and death may occur following cardiovascular shock (Motzer *et al.*, 2005). The maximum levels in drinking water are 5 mg/L for trivalent and 0.05 mg/L for hexavalent chromium. But, there is still uncertainty regarding what daily dose of Cr(VI) is considered toxic and what ingestion concentration of Cr(VI) is acceptable (Acar and Malkoc, 2004; Aliabadi *et al.*, 2006).

2.5 Recovery of chromium for tanning

Oxidation of chromium containing wastewater under basic conditions is considered to be suitable for the recovery of chromium as chromate which can be converted to other use full products. For this purpose three oxidants hydrogen peroxide, sodium hypochlorite and calcium hypochlorite can be employed independently in oxidizing chromium(III) containing wastewater to soluble chromate (CrO_4^{2-}) under alkaline conditions. Hydrogen peroxide is potentially a suitable oxidant as it could recover chromate up to 98% from synthetic Cr^{3+} solution and 88% from tanning drums (Aliawan *et al.*, 2003).

Because of the limited world supply of chromium, it is necessary to develop means by which chromium tanning materials are recycled. This can be achieved by saving and re-using the chromium tanning liquors. The tanning liquor lost can be made alkaline and the chromium hydroxide separated and recovered by re-acidification. The basic chromium sulfate (BCS) so produced is suitable as a tanning solution



(**Web site:** Nzic.org.nz/chem.Processes/animal/5c.pdf.)

The basicity and concentration of recovered chromium generally ranges from 30-33% and 100 mL of recovered chrome liquor is generally equivalent to 20-25 g of BCS available in the market. Under the indirect reuse method the recovered chromium in the form of solution is collected and used in normal chrome tanning operation, generally in the ratio 70% market BCS to 30% recovered chromium (Rajamani, 1995).

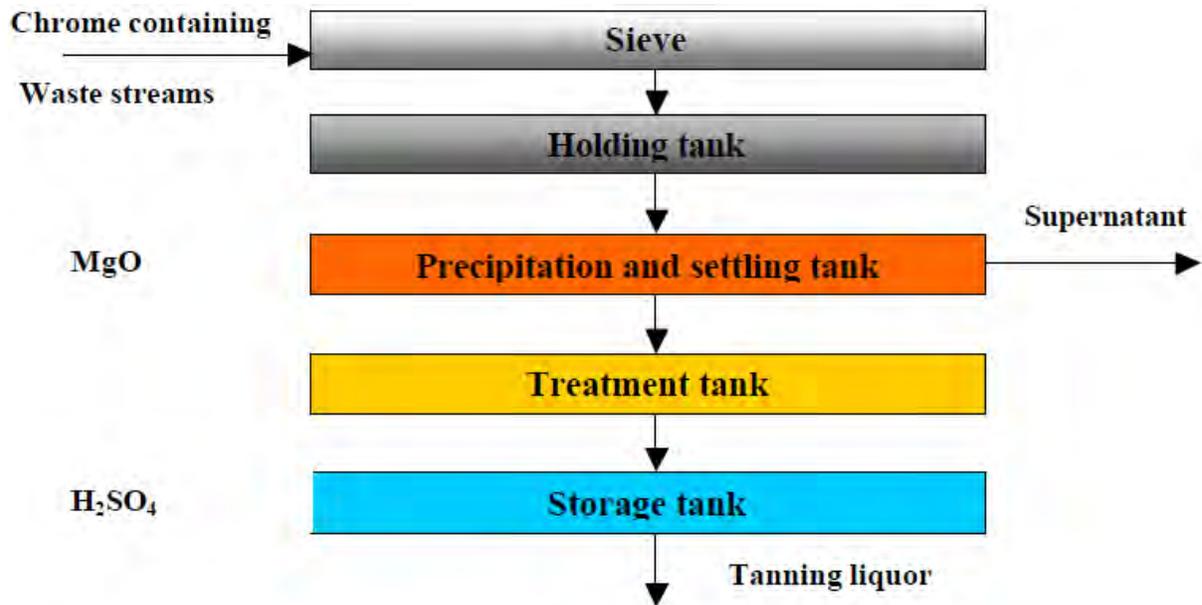


Figure 2.1. Simple flow diagram of chrome recovery by precipitation with magnesium oxide and acidification.

Under standard conditions, the pH value should normally not exceed 10.0 because chromium hydroxide rediscovers at a higher pH. When precipitating of floats from high-exhaustion tanning, it is sometimes useful to raise the pH over 10.0. The filter cake should have a dry substance content of at least 25-30%. The filter cake is dissolved by concentrated sulfuric acid while stirring until pH 2.5-2.8 is reached (Ludvik, 2000). In conventional chrome tanning, the chrome oxide content in the recovered liquor is usually 100-150 g Cr₂O₃/L. When recovering chrome from high-exhausted tanning floats, the chrome oxide concentration in the liquor will normally be lower. The effect of pH on the tanning reaction is associated with the pH influence on chrome species. It is known that a chrome complex solution of 33% basicity has pH 2.8 and contains mostly binuclear species ((Ludvik, 2000).

Most commercial chrome tanning chemicals or raw materials are used in powder form. It contains about 25% Cr₂O₃ of 33% basicity (Hussein *et al.*, 1995; Egli, 2003; Fifield and Haines, 1997). Basic chrome sulfate liquor is also used which is prepared by reducing the Na / K dichromate in the presence of H₂SO₄ (Andrzej and Jan, 1997; Shanker *et al.*, 2005). Experience in India has shown that leather tanned with 70% fresh chrome and 30% recovered chrome has more or less the same quality as leather tanned with 100% fresh chrome (Rajamani, 1995). Given that only 25-30% of the chrome offer is recoverable, adverse effects on leather quality need not be feared provided chrome recovery was properly carried out. A model for chrome distribution between leather and spent floats has been described with respect to indirect chrome reuse by recovery (Covington, 1995).

It follows from this model that approximately 29% of the chrome offer can be reused and saved by means of a recovery technique using precipitation when conventional tanning is applied and only 2.4% of the chrome offer is discharged. In the case of a high-exhaustion tanning, approximately 9% of the chrome offer can be reused and saved, while discharging only 0.7% (Ludvik, 2000).). Corresponding data related to the chrome tanning/re-tanning efficiencies of 68% and 90% are presented in the table 2.2 below.

Table 2.2. Chrome distribution between leather and spent floats with respect to indirect chrome reuse

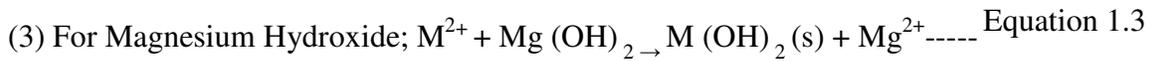
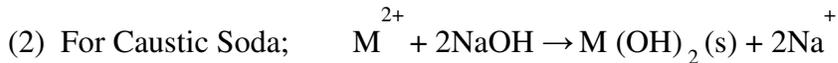
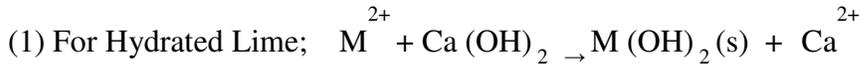
| | Distribution % | |
|----------------------------|----------------|----------------|
| | Efficiency 68% | Efficiency 90% |
| Offer | | |
| -total | 100 | 100 |
| -tanning | 83 | 83 |
| -retanning | 17 | 17 |
| Leather | | |
| -total | 68.3 | 90.0 |
| -tanning | 56.4 | 74.7 |
| -retanning | 11.9 | 15.3 |
| Spent tanning float | | |
| -recoverable | 23.3 | 7.3 |
| -unrecoverable | 1.5 | 0.5 |
| -total | 24.8 | 7.8 |
| Residual water recoverable | | |
| -sammying | 1.5 | 0.5 |
| -draining | 0.3 | 0.1 |
| Spent retanning float | | |
| -recoverable | 4.2 | 1.3 |
| -unrecoverable | 0.9 | 0.2 |
| Recovered | | |
| -tanning | 23.3 | 7.3 |
| -sammying/draining | 1.8 | 0.6 |
| -retanning | 4.2 | 1.3 |
| -total | 29.3 | 9.2 |
| Total | | |
| -to reuse | 29.3 | 9.2 |
| -to discharge | 2.4 | 0.7 |

Source: Ludvik 2000

2.6 Hydroxide precipitation

In hydroxide precipitation, soluble heavy metal ions are converted to relatively insoluble metal-hydroxide precipitates by adding an alkali-precipitating agent. The most common hydroxide precipitating agents are: caustic soda (NaOH), hydrated lime (Ca(OH)₂),

magnesium hydroxide (Mg(OH)₂). Precipitation reactions are given below, where M²⁺ is the soluble metal cation being removed. Chemical equations, for simplicity, show metals and other ions in their uncomplexed state.



(EM publication/eng-manuals, 2001).

The solubilities of the metal-hydroxide precipitates vary, depending on the metal ion being precipitated, the pH of the water, and, to a limited extent, the precipitating agent used. The extent of precipitation depends on a number of factors, namely:

- The solubility product constant (K_{sp}) of the metal-hydroxide.
- The equilibrium (stability) constants (K_f) of the metal-hydroxyl constants.
- The stability constants of ligands or chelating agents (e.g., EDTA, citrate, tartrate, gluconic acid, cyanide, or NH₃) that may be present (EM publication/eng-manuals, 2001).

Ease of automatic pH control, well proven and accepted in industry, relatively simple operation and relatively low cost of precipitant are the advantages of hydroxide precipitation. The disadvantage is that hydroxide precipitates tend to resolubilize if the solution pH is changed. Hydroxide sludge quantities can be substantial and are generally difficult to dewater because of their amorphous particle structure. Little metal hydroxide precipitation occurs at pH<6 (EM publication/eng-manuals, 2001).

Treating waste streams containing metals with lime is the most common way that industrial wastes are treated. It is widely used because lime is pumpable, has low cost, and is effective. A major disadvantage of the lime process is that large amounts of sludge are formed (EPA, 1987). Caustic soda NaOH (or caustic) is commonly used to precipitate heavy metals and to neutralize strong acids. It is used almost exclusively in a solution form of 50% or less. It is approximately 100 times more soluble in water than lime (at 25°C). Caustic soda precipitation processes are set up on the basis of waste type, volume, and raw waste pH level and variability. The disadvantage is high volume of sludge is formed (EM publication/eng-manuals, 2001).

An alternative to lime and caustic soda for hydroxide precipitation is magnesium oxide (MgO). The slurry must be mildly agitated during storage because of its low solubility (EPA, 1987). Performance among the three hydroxide precipitation methods does not vary significantly. The minimum metal-hydroxide solubilities attained by each method are approximately the same. However, as earlier discussed, sludge characteristics can vary tremendously. Hydroxide precipitation can decrease several metals (e.g., chromium, nickel, cadmium, copper, and zinc) in solution to concentrations that are less than 1.0 mg/L. Solubility product constant (K_{sp}) at 25 °C is as follows: Ca(OH)_2 , $7.9 \times 10^{-6} \text{ (mol/L)}^3$; Mg(OH)_2 , $1.5 \times 10^{-11} \text{ (mol/L)}^3$, NaOH almost completely soluble and Cr(OH)_3 , $6.7 \times 10^{-31} \text{ (mol/L)}^4$.

Table 2.3. Comparison of hydroxide reagent properties

| Property | sodium hydroxide, NaOH | Calcium hydroxide, Ca(OH)_2 | Magnesium hydroxide, Mg(OH)_2 |
|---|------------------------|--------------------------------------|--|
| Molecular weight (g/mol) | 40 | 74.1 | 58.3 |
| Hydroxide content (%) | 42.5 | 45.9 | 58.3 |
| Heat of solution (kg-cal/mole) | 9.94 | 2.79 | 0.0 |
| Solubility (g/dL H_2O) | 42.0 | 0.185 | 0.0009 |
| Reactive pH maximum | 14.0 | 12.5 | 9.0 |
| Weight equivalency | 1.47 | 1.27 | 1.0 |
| Freezing point (°C) | 16.0 | 0.0 | 0.0 |
| Solids content of sludge (%) | 30.0 | 35.0 | 55.0 |
| Sludge density (kg/m ³) | 1300 | 1400 | 1600–1750 |
| Filtration time (h) | 7–8 | 7–9 | 1.5–2.0 |
| Sludge volume (m ³) | 5.0 | 4.2 | 2.2 |

Source: EM publication/eng-manuals, 2001.

Metal ions effectively removed via hydroxide precipitation include cadmium, copper, trivalent chromium, iron, manganese, nickel, lead, and zinc (Anderson, 1994); EPA, 1987; EPA 600/2-77-049; EPA 625/8-80-003 and EPA 600/8-80-042c). Anderson (1994) is especially good for summarizing how well the precipitation methods perform for mixed-metal solutions and solutions containing various complexing and chelating agents.

2.7 Ethiopian leather industry

Tanning industry is one of the oldest industries of the world and the problem of treatment and disposal of the wastes is probably as old as the industry itself (Karabay, 2008). Ethiopia is relatively well endowed in its livestock base in the continent with a share of 15.7% in cattle and 9% percent in sheep and goats. However, being one of the poorest countries in the region, it has the lowest off-take rate. Annual production is only 21 percent of the country's livestock population. The fact that production of hides and skins heavily relies on the demand for meat makes the rate of expansion of the leather sector dependent on the rate of growth of the economy (Andualem Ayalew, 2005).

Though Ethiopia has a large livestock population indicating its leather production potential, its leather sector significantly lags behind many countries that are less endowed. But now the leather sector is expanding and obtaining vast amount of foreign exchange by exporting semi processed or finished leather products. Most tanning firms are operating at much below full capacity due to mainly lack of demand, lack of raw material inputs and absence of effective marketing networks between households who supplied the great proportion of raw materials throughout the country and factory gate points. One of the major advantages that could give a competitive edge to the leather sector is its large livestock base (Andualem Ayalew, 2005)

Table 2.4. Livestock bases of Ethiopia and others (in millions)

| Economic zone | Cattle | Sheep | Goats | Livestock |
|----------------------|--------|-------|-------|-----------|
| World | 1323 | 1056 | 705 | 3117 |
| Developing countries | 1007 | 678 | 681 | 2366 |
| Developed countries | 331 | 391 | 29 | 751 |
| Africa | 223 | 234 | 206 | 669 |
| Ethiopia | 35 | 22 | 17 | 74 |

Source: FAO, Production Year Book

Addis Ababa Tannery Sh.Co was established in 1925, and is Ethiopia's oldest tannery. The tannery is located in kolfe-keranio subcity, approximately 10 kilometers from Addis Ababa town center on the Ambo road. Addis Ababa Tannery Sh. Co has an attainable processing capacity of approximately 1,350,000 kg of hides and skins per annum, and is currently producing at the level of approximately 951,277 kg per annum, representing capacity utilization of approximately 70%. Most Ethiopian leather industries do not treat their waste before they discharge it out. As the cost of implementing and running the treatment plant is high, most solid waste, wastewater, air pollution, soil protection and health industries do not bother about the environment. The releases potentially contain toxic, persistent or harmful substances, which can directly affect the aquatic environment and even the surroundings (Andualem Ayalew, 2005).

Currently, there are more than 20 tanning industries operating in Ethiopia and only 10% of the existing tanning industries treat their wastewater to any degree, while the majority (90%) discharge their wastewater into nearby bodies, streams and open land without any kind of treatment (EEPA, 2001; Seyoum Leta *et al.*, 2003). Out of the existing tanneries in the country, 14 are located at Modjo along the rivers. And only two, Colba and Ethiopia share company, treat their waste to certain level and the rest 12 discharges their wastewater in to river (Assaye ketema, 2009).

2.8 Leather tanning

Leather tanning is the process of converting raw hides or skins in to leather. Hides and skins have the ability to absorb tanning acid and other chemical substances. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep and pigs. Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum or other chemical agents. The common tanning agents used in most leather industries are trivalent chromium and vegetable tannins extracted from specific tree barks. Alum, syntans (man-made chemicals), formaldehyde, glutaraldehyde and other vegetable extracts (Addis Mekonen, 2006).

Tanning is a process, which means the addition of tanning agent (chromium salts, aluminum, zirconium, etc. or vegetable extracts of mimosa or quebracho tree, etc). It is possible to stabilize the skin structure by forming transversal bonds among its fibers. The tanning agent blocks carboxylic groups, in the case of mineral tanning agents, or the amine groups, in the case of vegetable tanning agents, and joins the proteinic colloid, thus increasing the cross linking of collagen fibers (Hussein *et al.*, 1995). This way, the leather is turned in to a durable material in respect of physical and biological degradation (Hussein *et al.*, 1995). The complete tanning process, including finishing treatments, lends the leather to have characteristics of resistance, smoothness, softness, colour, etc. required for its industrial production (Roshan, 2002).

2.8.1 Vegetable tanning

Heavy leather and sole leathers are produced by the vegetable tanning process, the oldest of any process use in the leather tanning industry. The hides are first trimmed and soaked to remove salt and other solids and to restore moisture lost during curing (Quevauviller *et al.*, 1995). Following the soaking, the hides are fleshed to remove the excess tissue, to impart uniform thickness and to remove muscles or fat adhering to the hide. Hides are then dehaired to ensure that the grain is clean and the hair follicles are free of hair roots. Liming is the most common method of hair removal, but thermal, oxidative, and chemical methods also exist (Addis Mekonnen, 2006).

The normal procedure for liming is to use a series of pits or drums containing lime liquors (calcium hydroxide) and sharpening agents. Following liming, the hides are dehaired by scraping or by machine. Deliming is then performed to make the skins receptive to the vegetable tanning. Bating, an enzymatic action for the removal of unwanted hide components after liming is performed to impart softness, stretch, and flexibility to the leather (Sudersanan *et al.*, 1988).

2.8.2 Chrome tanning

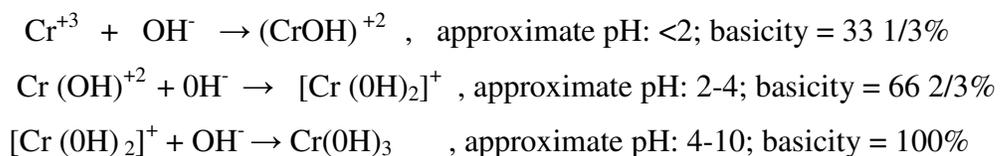
Chrome tanning is the most common type of tanning in the world. Chrome tanned leathers are characterized by top handling quality, high hydrothermal stability and excellent user properties (Quevauviller *et al.*, 1995). Chrome-tanned leather tends to be softer and more pliable than vegetable tanned leather, has higher thermal stability, is very stable in water, and takes less

time to produce than vegetable tanned leather. Almost all leather made from lighter-weight cattle hides and from the skin of sheep, lambs, goats and pigs is chrome tanned. The primary steps of the process (soaking, fleshing, liming/dehairing, deliming, bating, and pickling), the drying / finishing steps are essentially the same as in vegetable tanning. However, in chrome tanning, the additional process of retanning, dyeing, fat liquoring are usually performed to produce usable leathers and preliminary degreasing step may be necessary when using animal skins, such as sheepskin. Chrome tanning in the United States is performed using a one-bath process that is based on the reaction between the hide and trivalent chromium salt, usually BCS (Addis Mekonnen, 2006). In the typical one bath process, the hides are in a pickled state at a pH 3 or lower, the chrome tanning materials are introduced, and the pH is raised. Following tanning, the chrome-tanned leather is piled down, wrung and graded for the thickness and quality, split in to flesh and grain layers, and shaved to the desired thickness (Addis Mekonen, 2006).

2.8.2.1 Chemistry of chrome tanning

Chrome tanning was discovered in 1858 by Knapp. The first commercial chrome tanned leather was produced in 1884 by Augustus Schultz of New York. The chemistry of chrome tanning is complex, since it involves several reactions occurring simultaneously. These reactions are controlled by temperature, pH, and the chemicals used in the process of chrome tanning. These factors greatly influence the quality of the final leather.

Basicity; commercially available chrome salts have a valency of +3. These salts are soluble in strong acids and usually precipitate as chromium hydroxide or hydrated chromium oxide at pH values above 4. The trivalent chromium attracts the negatively charged hydroxyl (OH⁻) ions. The term basicity is defined as the percentage of the total primary valences of the chromium atoms present in the solution that are occupied by the hydroxyl groups. Therefore, if the chromium atom contains one hydroxyl group, then the chromium complex is 33 1/3% basic. If the chromium atom contains two hydroxyl groups, then the complex is 66 2/3% basic and so on. The following reactions further clarify the concept of basicity:



As basicity refers to the association of hydroxyl ions with the chromium, the term acidity refers to the acid portion of the salt the sum of the percentages of the basicity and acidity for a given salt in solution, by definition, equals 100. The chromium salts used in the tanning industries usually have basicity values between 33% and 45% (Thorstensen, 1993).

2.9 Tannery operations, sources and characteristics of tannery wastewater

2.9.1 Tannery operations

The conversion of animal hide and skin in to useful articles may be man's oldest technology. Untreated skins have limited value, because when wet they are susceptible to bacteria attack and so they putrefy, but if they are dried they become inflexible and useless for purpose such as clothing. Those effects are eliminated by tanning process by which putrefyable biological material is converted into a stable material which is resistance to microbial attack and has enhanced to wet and dry heat (Anthony, 1997).

Tanning consists of a series of successive operations converting rawhide and skin into leather. The raw material in the production of leather is a byproduct of the meat industry. Tanners recover the hides and skin from the slaughter houses and transform them into a stable material that can be used in the manufacture of a wide range of products. Leather is an intermediate industrial product with numerous applications in down stream sector. It can be cut and assembled into shoes, clothing, leather good furniture and other items of daily use. In addition the produced products have distinct properties, which include stability, appearance water and abrasion resistance, temperature resistance and elasticity, to help increase the shelf life (COTANCE, 2002).

The production process in a tannery can be split into four main categories, namely beam house, tanning (tan-yard), post tanning, and finishing operation. The beam house operation consists of a sequence of processes. Soaking is the first stage where the hide and skin are soaked. In order to remove salt, restore the moisture content of the hide and skin and remove any foreign material such as dirt and manure. Dehairing, liming and fleshing subsequently follows the soaking step which helps to remove the hair, open up the collagen structure by removing interstitial material and remove access tissue from the interior of the and skin respectively. Tanning (tan-yard) operation is where the tanning agents stabilize the collagen fiber so that the hide and skin would be no longer susceptible to putrefaction. In order to do so, the hide and

skin pass through different processes in tanning operation. Those operations include deliming, bating, pickling and tanning. Bating and pickling condition the skin and hide to receive the tanning agent, whereas the tanning process stabilize the material and impart basic properties of the skin and hide (infogate, 2002; [http; // www.gtz.de/gate/gateid.afp](http://www.gtz.de/gate/gateid.afp)).

Post tanning sometimes also called retanning operation involves neutralization followed by retanning, dyeing and fat liquoring. Neutralization and retanning are used to improve the feel and handle of leather, where as dyeing and fat liquoring provide special property to the leather (i.e. water resistance, abrasion resistance, flame retardancy and anti-electrostatic properties); replenish oil to the hide and skin and to give the leather different colors. Furthermore; the fat liquoring help to lubricate the leather to achieve product specific characteristics and to reestablish the fat content in the previous procedures. After dyeing the leather from post tanning operations, the finishing operation follows. The over all objective of finishing operation is to attain final product specification by enhancing the appearance of the end providing the performance characteristics with respect to color, gloss, handle etc. (web site: infogate, 2002; [http; // www.gtz.de/gate/gateid.afp](http://www.gtz.de/gate/gateid.afp)).

2.9.2 Sources and characteristics of the wastewater

The tannery process is almost wholly a wet process that consumes high amount of water, estimated to be 34-56 m³ of water per tone of hide or skin processed, where out of the total water consumed, 85% is discharged as a wastewater (Teodorescu and Gaidau, 2007).

Table 2.5. Water consumption in individual tannery processing operations.

| Operation | Water consumption (m ³ /tone of raw hide and skin) |
|---------------------|---|
| Soaking | 7-9 |
| Liming | 9-15 |
| Deliming and bating | 7-11 |
| Tanning | 3-5 |
| Post tanning | 7-13 |
| Finishing | 1-3 |
| Total | 34-56 |

Source: Ludvick, 2000.

The characteristics of the wastewater vary considerably from tannery to tannery depending on the size of the tannery, chemicals used for the specific processes, amount of water used and type of the final product produced from the tannery. According to Seyoum Leta *et al.* (2003), a composite tannery wastewater has BOD₅ (1900-4800 mg/L), COD (7900-15200 mg/L), sulfide (325-930 mg/L), and total chromium (12-64 mg/L). Another study in Pakistan also indicated BOD₅ (84018620 mg/L), COD (1320-54000 mg/L), SS (220-1610 mg/L), TN (236-350 mg/L), sulfate (800-6480 mg/L), chromium (41-133 mg/L), (Haydar *et al.*, 2007). The variations of effluent characteristics also occur through each working day in a tannery. According to Cristina *et al.* (2007), average COD and pH analyzed in one day were 2010 mg/L, and 6.98, respectively. Whereas 2068 mg/L and 7.93 respectively in another day. Table 2.6 summarizes the pollution load discharged from individual tannery processing operations.

Table 2.6. Summary of pollution load discharged in effluents from individual tannery processing operations (Kg/tonne of hide and skin).

| Pollution | Soaking | Liming | Deliming and bating | Tanning | Post tanning | Total |
|--------------------|----------------|---------------|--------------------------------|----------------|-------------------------|--------------|
| SS | 11 - 17 | 53 - 97 | 8 – 12 | 5 - 10 | 6 - 11 | 83 - 149 |
| COD | 22 - 33 | 79 - 122 | 13 – 20 | 7 - 11 | 24 - 40 | 145 - 231 |
| BOD ₅ | 7 - 11 | 28 - 45 | 5 – 9 | 2 - 4 | 8 - 15 | 50 - 86 |
| Sulfate | 1 - 2 | 1 - 2 | 10 – 26 | 30 - 55 | 10 - 25 | 52 - 110 |
| Sulfide | | 3.9 - 8.7 | 0.1 - 0.3 | | | 4 – 9 |
| TKN | 1 - 2 | 6 - 8 | 3 – 5 | 0.6 - 0.9 | 1 - 2 | 12 - 18 |
| NH ₃ -N | 0.6 - 0.9 | 0.4 - 0.5 | 2.6 - 3.9 | 0.6 - 0.9 | 0.3 - 0.5 | 4 – 6 |
| Chromium | | | | 2 - 5 | 1 - 2 | 3 – 7 |

Source: Ludvick, 2000

2.9.3 Environmental challenge of the tannery wastewater

It could be agreed that the leather industry performs an environmentally important activity by giving a new life to the left over of the meat industry. The transformation of this by-product is, however, potentially pollution intensive and tanning is widely perceived as a consumer of natural resources. Among various environmental pollutants of wastewater released from

different industries, tannery waste is the major challenging and devastating pollutant (Assaye Ketema, 2009). Leather industry is one of the most harmful to the environment for being responsible for extreme pollution of water resources. The quantities and qualities of emission and waste produced by tanneries depend on the type of leather processed, the source of hides and skins and the technique applied (COTANCE, 2002).

The leather industry throughout the world has been identified closely with the generation of air, liquid and solid waste pollution. This has created a negative public image. Tanneries are therefore expected to invest in waste disposal and effluent treatment plants. In industrialized countries environmental protection legislation obliges industries to invest heavily in pollution reduction and control (Boehnk *et al.*, 2002).

2.10. Tannery wastewater treatment system

Today due to increased pollution as well as elevated public awareness and consequent demand for protection of the world's water resource different types of treatment techniques that remove organic matter and nutrients from wastewater have been developed (Nicholas, 1996; UNEP, 1999; USEPA, 2004; Linda and Peter, 1999). Treatment of tannery effluent is a challenge because it is a mixture of biogenic matter of hides, inorganic chemicals and a large variety of organic pollutant with large molecular weights and complex structures (ESCAP, 1982; Elke *et al.*, 1996; Thoresten and Martin, 1997).

Wastewater channeling is important, that is traditionally, the baths from different process stages were drained by opening the drum valves and leaving the bath to drain to the ground to be subsequently gathered in collection boxes where the different wastewaters were mixed, thus making their reuse impossible. In order to avoid this drawback, the drain systems of the tanning drums have been modified by installing some curved channels equipped with flexible outlet in order to separate the wastewater of the tanning drums (Egli, 2003).

The new channels are equipped with a flexible hose to be connected to different outlets, according to the destination of the wastewater of the tanning drum (to be recycled or to be sent to the treatment plant for industrial wastewater). Likewise, the way to discharge the pickling-tanning bath has been optimized for its total treatment and reuse, ensuring that the entire bath is

drained and avoiding, as much as possible, sweeping suspended matter. In this sense, emphasis was put on the definition of the drum rotating speed during draining, the valve opening and the type of channeling for bath collection. Finally, the tanning wastewater is led to a channel where fine leather particles sediment is located (Egli, 2003; Merry and Franson, 1998).

2.10.1. Chromium removal methods

There are a number of different techniques of chromium remediation methods such as adsorption, chemical precipitation, solvent extraction, electrolytic extraction and ion exchange. Since the biogeochemical properties of Cr and the associated matrix can affect the efficiency of many treatment strategies, an understanding of these properties is essential for choosing an effective treatment method. Once the properties of Cr, the associated matrix and treatment environments are understood, remedial alternatives for Cr can be addressed. The common chemical processes can be biologically mediated either directly through metabolic processes or indirectly as microorganisms change their geochemical environment. Chromium(VI) is far more mobile than Cr(III) and more difficult to remove from water (Motzer *et al.*, 2005; Sumathi *et al.*, 2004 and ChamCarthy *et al.*, 2001)

2.10.1.1. Biological treatment system

In biological treatment, microorganisms convert the organic wastes into stable compounds. Typical biological treatment processes make use of trickling filters, activated sludge, sequencing batch reactor (SBR) and wetland as polishing system (Assaye Ketema, 2009).

According to Ramsar Convention (1997: 2) wetlands are areas of marsh, fen, peat land or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed six meters. They are also important water bodies' in-terms of ecological balance because they provide breeding areas for different types of flora and fauna and act as active and natural treatment system, which in-turn gives rise to improvement of water quality. In many cases, however, the reasoning behind this use was disposal, rather than treatment and the wetlands simply served as convenient recipient that was closer than the nearest river or other waterways (Vymazal, 1998).

Phytoremediation technique focuses mainly on the functioning of constructed wetlands for wastewater treatment, in particular surface-flow and infiltration wetlands. In general, constructed wetlands can be designed to remove more than 90% of BOD, COD (Verhoeven *et al.*, 1999). According to the report of Assaye Ketema (2009), on a study made at Modjo tannery constructed wetland, the chromium removal efficiencies of different plants was as follows: maximum by *Schenoplectus corymbosus* (98%), followed by *Cyperus alopecuroides* (97.8%), and the minimum by *Cyperus papyrus* (95%). Constructed wetlands have the following advantages: (i) they attract wildlife like birds, mammals, amphibians, and variety of dragonflies and other insects make the wetland home (Martha, 2003). (ii) they are cost effective and technically feasible approach for treating wastewater (Reddy, 2004).

Higher plants (aquatic macrophytes) which are commonly found floating or submerged in ponds and tropical part of the world have been widely tried for exploration of their uptake and accumulation potential of toxic wastes, particularly heavy metals such as lead, cadmium, mercury, chromium and arsenic. Research outcome has shown that aquatic macrophytes such as water hyacinth (*Eichornia crassipes*), duckweeds, water lettuce (*Pistia stratiotes*), and cat-tails (*Typha species*) are natural scavengers of toxic metals (Chatterji, 2007).

Limitations of constructed wetland: generally they require land areas than do conventional wastewater treatment system; performance may be less consistent than in conventional treatment. Wetland treatment efficiencies may vary seasonally in response to changing environmental conditions including rainfall and drought. There might be also chromium toxicity. Wetland treatment cannot be relied upon if effluent quality must meet stringent discharge standards at all times. Because of this limitations physico-chemical treatment systems are preferred especially for small tanneries (Assaye Ketema, 2009).

2.10.1.2 Physico-chemical treatment system

Physico-chemical methods, such as adsorption, coagulation-flocculation and advanced oxidation, are used for wastewater treatments. Oxidative degradation by chlorine and ozone are the most common chemical processes for color removal, but chlorination has the disadvantage of producing organochloride byproducts (Sarasa *et al.*, 1998). Although photo catalytic oxidation with hydrogen peroxide (H_2O_2) would be more attractive from an economic point of

view, photo catalytic processes are limited to post-treatment units because of the low penetration of UV radiation in highly colored wastewaters (Vandevivere *et al.*, 1998; Yang *et al.*, 1998).

All the processes, which can be used for removal of both organic matter and nitrogen, are simple in principle; however, they are expensive (high operating and maintenance cost, and consumption of chemicals) and also produced harmful products (Delpozo and Diez, 2003). The most important processes to remove the Cr(III) ion from the tanning wastewater are: precipitation, reverse osmosis and adsorption (Hinter Meyer *et al.*, 2008).

2.10.1.2.1 Ion exchange

Varying parameters such as chromate concentration and contact time carried out the removal of chromate ions in trace concentration from tannery wastewater effluent using ion exchange technique. A maximum of 99% removal efficiency in the batch ion exchange process could be achieved over an equilibrium contact time of 20 min. Even in the presence of high concentration of competing ions high removal efficiency of chromate ions could be achieved. Obviously, this shows that the selectivity of the resin towards the chromate uptake. The ion-exchange technique was found to be appealing for the removal of trace concentration of chromate when in the background there is high concentration of chloride and sulphate co-ions present in the tannery wastewater (Kabir and Ogbeide, 2008). Major disadvantage of ion exchange process is high cost of resins (Hintermeyer *et al.*, 2008).

2.10.1.2.2 Reverse osmosis

Reverse osmosis is a process in which a semi permeable membrane is used to retain species of low molecular weight and a pressure is applied as driving force to revert the solvent natural tendency of passing from a more diluted solution to another more concentrated one. The phase that passes through the membrane is named "permeate" and contains water with very small amount of dissolved salts. Meanwhile, the phase that does not pass through the membrane is called "concentrate" and has almost the totality of dissolved salts (Cheryan, 1998). The semi permeable membrane is a thin film that is constructed by different materials and it is assembled in order to support a high transmembrane pressure. Important removals of chromium(III)

dissolved in tanning wastewaters were obtained with a polyamide semipermeable membrane (Pérez Padilla and Tavani, 1999; Galán *et al.*, 1991).

2.10.1.2.3 Adsorption

Adsorption is the process of the accumulation of a liquid or gas (adsorbate) on the surface of a solid (adsorbent). When the adsorption is used for the removal of substances dissolved in a liquid medium, acceptable results are obtained with solid adsorbents of high specific surface. The soluble substance is accumulated on the solid surface from the liquid that surrounds it. Thus, a change in the concentration of some system components is originated by effect of such mass transfer between both phases. During the treatment of the tanning wastewater, the chromium(III) is transported from the liquid medium to the solid surface through the respective interface. Reagent addition is not necessary to perform the adsorption. Chromium(III) adsorption was made only at laboratory scale up to the present time. Acceptable results could be achieved with several adsorbents: synthetic zeolite in its sodic form (Barros *et al.*, 2003), activated carbon (Leyva-Ramos *et al.*, 1995) and smectite (natural clay) (Volzone and Tavani, 1995). Major disadvantages of adsorption processes are the regeneration of the spent adsorbent and subsequent treatment of the backwash water (Hintermeyer *et al.*, 2008).

2.10.1.2.4. Chemical precipitation

The chromium(III) precipitation is frequently carried out in tanneries. Substances used habitually to promote the precipitation are: calcium hydroxide, sodium hydroxide, magnesium oxide or calcium magnesium carbonate. Addition of the alkaline substance to the liquid effluent with stirring at required pH is necessary. With this methodology, a supernatant free of chromium(III) (with abundant calcium/sodium or magnesium chloride) and a precipitate of chromium(III) hydroxide (containing diverse impurities) are obtained. The added alkali determines the formation of reaction products that affect the later chromium(III) reuse. When the precipitation is carried out with calcium hydroxide (or carbonate), the sulfate present in the tanning wastewater is combined with the alkaline cation to form calcium sulfate. The anion of the organic acid (formic, acetic or lactic) used as chromium(III) complexing agent, also reacts with the alkali. Both reaction products together with fats and denaturalized proteins, substances

released from the skin in significant amounts during the tannage process, are the main impurities that co precipitate with chromium (Rutkowski *et al.*, 1998; Toprak, 1994).

Calcium salts are harmful for the leather (Christner, 1993), while fats and denaturalized proteins difficult the tannage process (Heidemann, 1991). An adequate selection of operative variables (ratio alkali–effluent and reaction time) allows controlling the calcium co-precipitation. The effluent ultrafiltration before alkali addition was the alternative used to decrease the presence of fats and denaturalized proteins in the chromium(III) precipitate (Fabiani *et al.*, 1996). The alkaline substance is not recovered at the precipitation end, so it is necessary to have a continuous provision of such raw material. In order to select the alkaline substance, it is useful to take into account the cost as the easiness for its obtention, storage and manipulation. The calcium (magnesium or sodium) carbonate has these conditions although its reaction with the chromium(III) occurs less directly than with hydroxide or oxide. Of the three alkalis, the calcium carbonate requires larger attention in the selection of operative variables for the precipitation process (Hintermeyer *et al.*, 2008).

Chapter three

Experimental

3.1 Materials and Methods

3.1.1 Instrumentation

Determination of chromium amount was carried out using Flame Atomic Absorption Spectroscopy (FAAS) (Buck Scientific Model 210 VGP, East Norwalk, USA) equipped with deuterium arc background corrector, nebulizer and hollow cathode lamp corresponding to metal of interest, in this case chromium, using air-Acetylene flame. The operating conditions of AAS employed for chromium determination are given in Table 3.1.

Table 3.1 Instrumental operating conditions for flame atomic absorption spectrometer

| Element | Wavelength (nm) | Detection limit (mg/L) | Slit width (nm) | Lamp energy (eV) |
|---------|-----------------|------------------------|-----------------|------------------|
| Cr | 357.9 | 0.05 | 0.7 | 3.7 |

3.1.2 Preparation of standard solutions for atomic absorption spectrometry

To determine the concentration of chromium in the influent (raw waste), effluent (supernatant) and filtrate of digested basic chromium sulfate, three series of working standard chromium solutions of concentration 0.5, 1.0 and 1.5 mg/l were prepared in 50 mL volumetric flasks from 1 mL of standard stock solutions that contain 1000 mg/L of chromium by diluting with de-ionized water to 100 mL of 10 mg/L of chromium and their absorbances were 0.000742, 0.001481 and 0.002248 respectively.

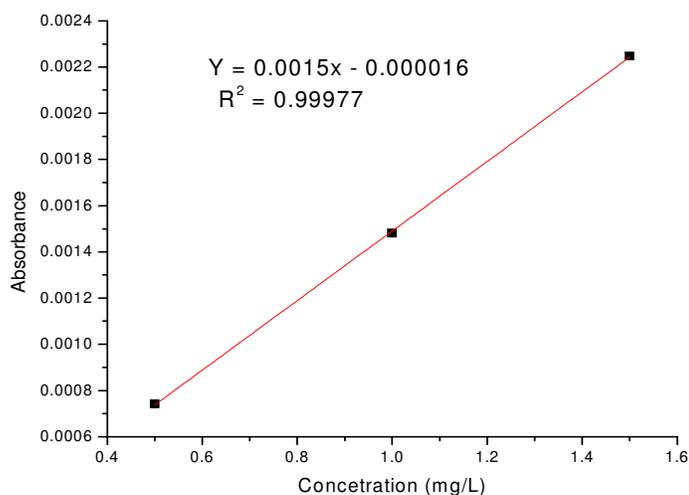


Figure 3.1. Linear calibration curve to determine Cr concentration

The standards were run in flame absorption spectrometer and a three point linear calibration curves were established for each determination. Then, sample solutions were aspirated into the AAS instrument and direct readings of total Cr concentrations were recorded. Three replicate determinations were carried out for each sample. The blanks, de-ionized water and nitric acid solution were run in AAS for Cr determination. The amount of chromium precipitated was calculated from the difference between the amount before and after treatment or precipitation.

3.1.3 Apparatus and Chemicals

The chemicals used in this study were solutions of lime 12%, sodium hydroxide 15% and magnesium oxide 10% and raw wastewater from tanning process (Esmaeilli *et al.*, 2005). All chemicals used are of analytical reagent grade. Analytical digital balance was used to weigh the chemicals and dry sludge of basic chromium sulfate. Measuring cylinders and micropipettes (Dragonmed, Shanghai, China 0-1000 μ L) were used for measuring different volumes of influent chrome liquor, supernatant, acid reagents and standard solutions. Volumetric flasks (50 mL, 100 mL and 1000 mL) were used for the dilution of the sample solution and preparation of standards. Flame Atomic Absorption Spectrophotometer (Buck Scientific Model 210 VGP AAS, East Norwalk, USA) using deuterium arc background corrector with air-acetylene flame was used for the determination of concentration of chromium metal.

3.1.4 Description of the study area

The Addis Ababa tannery Sh.Co through processes of producing leather generates wastewater which directly channeled without treatment to the river where Gefersa and Leku rivers meet. A.A city is located b/n $8^{\circ} 55' - 9^{\circ} 06' N$ latitude and $38^{\circ} 05' - 39^{\circ} 05' E$ longitude. An elevation 2800m (Entoto)-2200m (Akaki) with an average elevation of 2400m a. s. l. above sea level, total area 540 km² (EEPA, 2004). The study site is found in south of Addis Ababa.

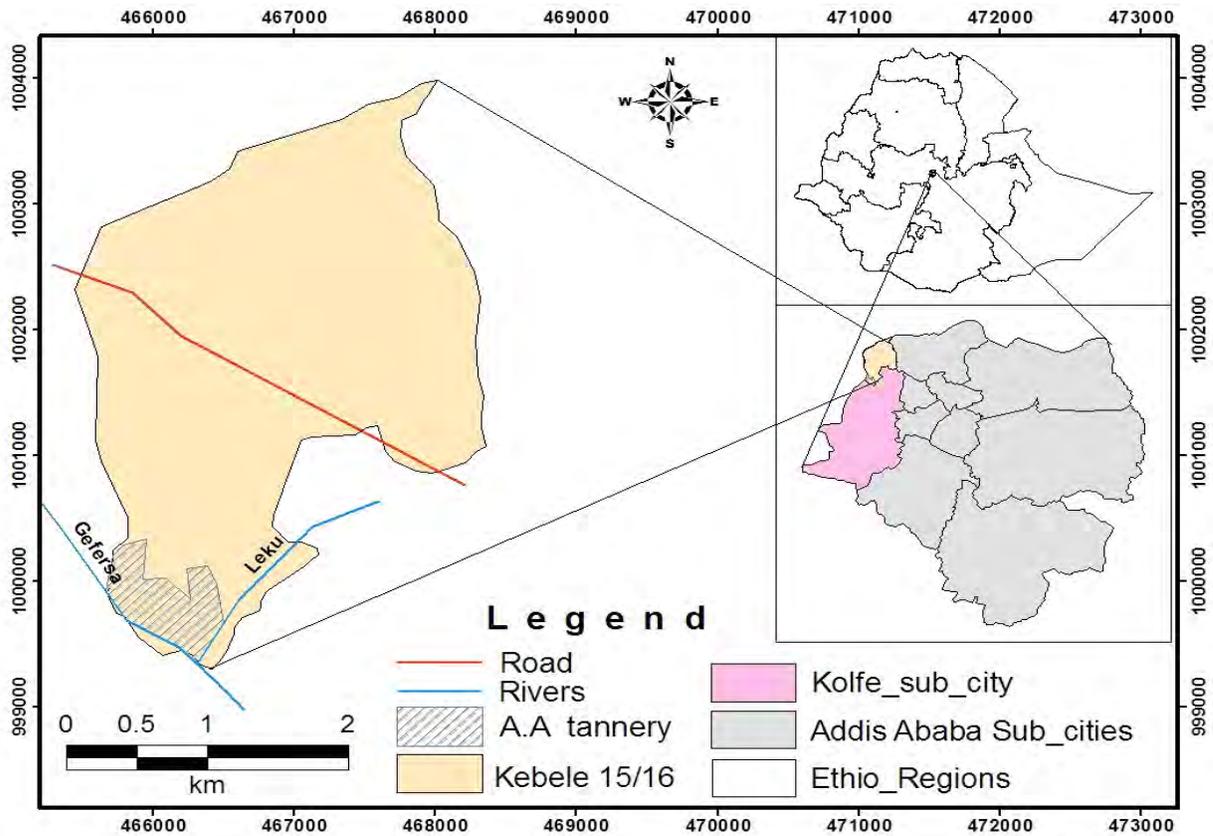


Figure 3.2 Map of the study area (Kolfe-Keranio subcity, Addis Ababa)

3.1.5 Sampling techniques and procedure

Composite samples from the general waste and chrome liquor sample from the drum were taken from the wastewater of Addis Ababa Tannery Sh. Co at Colfe-Keranio sub-city. Waste water samples were collected using plastic bottles three times. Since the process of tanning is batch, after finishing the process (12 h), spot samples were collected and transported to laboratory for the determination of the most important parameters as quickly as possible.

These parameters included were Cr concentration, pH, total solids, dissolved solids, suspended solids, color, TN, NH₃-N, TP, BOD₅, COD, sulfate and sulfide concentration (APHA, 1992).

To determine the effect of each parameter six beakers were used for each stage and 500 mL of wastewater was added to each beaker after screening using sieve. The precipitation agents were added to each sample separately and pH was controlled between 5.9 to 10.3 using nitric acid. In order to mix solution, samples were taken to the beakers and mixed for one minute in 90 rpm as the first step. In the next step samples were mixed for 20 min with the speed of 30 rpm. After these 20 minutes of stirring using magnetic stirrer and hot plate, in the last stage, after 4 h settling time, samples were taken from the supernatant. Supernatant solution was then filtered and chromium concentration was determined. The effects of each factor on the three precipitating agents were measured by fixing the effect of the other variables. For instance settling rate, sludge volume and the shape of the precipitation for all precipitating agents were measured when pH is fixed on the optimum level. In order to determine settling rate and sludge volumes, samples were poured into scaled cylinders and after 5 h the height of supernatant or sludge volume were read. Atomic absorption spectroscopy method was used for measuring chromium concentration in wastewater before and after settling process (Esmaeilli *et al.*, 2005).

3.1.6 Experimental procedure design

3.1.6.1 Pre-experiment design

Three samples were collected at different times from chrome effluent (from the drum) in five days time interval and were preserved using 2% concentrated HNO₃ (70%). Finally equal volumes of the samples were mixed in volumetric flask and prepared for digestion and then total Cr before treatment was determined. Since 500 mL of wastewater was to be treated in each 6 beakers for each of the three precipitating agents or chemicals, MgO, NaOH and Ca(OH)₂, a total of 500 mL x 18 = 9000 mL was preserved by diluting 180 mL of conc. HNO₃ to 9000 mL in a big plastic container.

3.1.6.2 Actual laboratory experiments

Experiment 1. Characterization of Addis Ababa tannery wastewater

Wastewater characterization was done for the physico-chemical water quality parameters; pH, BOD₅, COD, TN, NH₃ nitrogen, sulfate, sulfide, conductivity and total chromium. The parameters; COD, TN, sulfate, sulfide, nitrate, ammonia nitrogen were measured by spectrophotometer (DR/2010, HACH, USA) according to HACH instructions, pH with pH meter, and conductivity with conductivity meter.

Calculations

1. Concentrations of S²⁻, SO₄²⁻, COD, NO₃⁻-N, NH₃-N, total N, total P, and total Cr was calculated using the dilution formula $C_1V_1 = C_2V_2$ -----Equation 1.4

2. $BOD_5 = \frac{D1 - D2}{P}$, when dilution water is not seeded. -----Equation 1.5

where D1 = DO of diluted sample immediately after preparation, mg/L.

D₂ = DO of diluted sample after 5 day incubation at 20 °C

P = decimal volumetric fraction of sample used.

3. $TS, TDS = \frac{A - B}{a} \times 1000 \times 1000$ -----Equation 1.6

where unit is mg/L, A = g weight of dish + dried sample

B = g weight of dish, a = mL of aliquot effluent.

4. Percentage of Cr removal or R (%) = $\frac{C_i - C_f}{C_i} \times 100$ -----Equation 1.7

Where C_i is the initial concentration and

C_f is the final concentration of supernatant.

5. Moisture content = wet wt.-dry wt/wet wt, solid content = dry wt/wet wt. -- Equation 1.8

6. Cr recovery (%) = $\frac{\text{Chrome recovered}}{\text{Chrome offered}} \times 100$ -----Equation 1.9

Table 3.2 A summary of procedures adapted from standard methods for the examination of water and wastewater, 20th edition, 1998.

| Parameters | Instruments | Apparatus | Reagents, chemicals | Method | Range | Selected program |
|---------------------------------|---|---|--|---|--|--|
| pH | pH meter | | | | | |
| Conductivity | Conductivity meter | | | | | |
| S ²⁻ | Spectrophotometer | Sample cell, pipette, tips | DIW, sulfide 1 reagent, sulfide 2 reagent | Methylene blue method | 5-800 µg/L | 690 sulfide |
| SO ₄ ²⁻ | Spectrophotometer | Sample cell, beaker | Sulfaver 4 reagent powder pillow, Sample | Sulfaver 4 method | 2-70 mg/L | 680 sulfate |
| COD | Spectrophotometer, COD reactor/digester | Digestion reagent vials (Cells), pipettes | DIW, sample | Reactor Digestion method | 3-150, 20-150 and 200-15,0000 mg/L COD | 435 COD HR(high range/high range plus) |
| BOD ₅ | Magnetic stirrer and hotplate Incubator | Pipette, cylinder c. flask, v. flask, beakers, incubation bottle, burette | Phosphate buffer soln., soln. of MgSO ₄ , CaCl ₂ , FeCl ₃ , MnSO ₄ , azide reagent, starch | 5_Day BOD Test titration method, azide modification | | |
| NO ₃ ⁻ -N | Spectrophotometer | Sample cell, beaker | Sample, Nitraver 5 reagent powder pillow | Cadmium reduction method | 0.3-30 mg/L (HR) | 355N, Nitrate HR |
| NH ₃ - N | Spectrophotometer | Graduated cylinder, sample cell, pipets | Sample, DIW, mineral stablizer, polyvinyl alcohol, nessler reagent | Nessler method | 0.02-2.50 mg/l | 380N, Ammonia, Ness. |
| Total N | COD reactor, adapter, spectrophotometre | funnel, digestion reagent vials | Tot. N, persulfate, HR total N hydroxide digsn. Reagent vials, DIW, TNR A, B, C | Persulfate digestion method | 10-150 mg/L (HR) | 350 N, total TNT |
| Total P | COD reactor, spectrophotometer | Pipette, Tesvial TT rack, funnel | Potas. per sulfate powder pillow, NaOH stand. soln., phosver 3 powder | Phosver 3 with acid persulfate digestion method | 0.06-3.50 mg/L or 0.02-1.10 mg/L | 536 P total/AH PV TNT |
| Total Cr | Atomic absorption spectrometre | Volum.Flask, micropipet | Composite sample | AA Spectroscopy | | |
| Total Cr | Atomic absorption spectrometre | Volum.Flask, micropipet | Chrome liquor sample | AA Spectroscopy | | |
| TS, TDS, TSS | Centrifuge, hot plate, electric balance, oven drier | Crucible, beakers descicator | Tannery wastewater | Centrifugation, Filtration | | |

Source: standard methods for the examination of water and wastewater

Experiment 2. Determination of total Cr in the original chrome liquor sample and in the composite sample

All the samples were brought to the laboratory using plastic bottles and preserved with 2% of HNO₃. The chrome samples collected from the tanning drum after tanning operation were colored (dark blue), whereas the composite samples were simply muddy or reddish in color. To decolorize the chrome samples and to eliminate interfering matrixes, the samples were digested by acidifying with concentrated HNO₃ (70%). After 50 ml of the sample was digested for a total of 1 hour a clear solution was obtained and the digestion procedure was adapted from Addis Mekonnen, 2006.

The method was used to determine total Cr in the original chrome liquor and the composite samples. In this case 50 mL of the sample was taken into a 250 mL beaker and 5 mL of HNO₃ was added to each sample and covered with watch glass. Then the samples were digested for 45 minutes using magnetic stirrer with hot plate, Cole-Parmer instrument Company, Model 04803-02, USA, at a temperature of 150 °C. It was cooled and further heated to 15 minutes after adding additional amount of 5 mL of HNO₃. The samples were then cooled, filtered and diluted to 50 mL and stored in a refrigerator until analysis (Addis Mekonnen, 2006).

Experiment 3. Removal of Cr using precipitating agents and determination of Cr in the Supernatant

15% NaOH, 12% Ca(OH)₂ and 10% MgO solutions (w/w) were prepared in separate beakers of 250 mL for each. After removing suspended particles and fat mechanically and using sieve, 500 mL of wastewater was added to each of the other six 500 mL beakers. Precipitating agents were added separately and the required pH was controlled using concentrated HNO₃ by adding

5 mL, 4 mL, 3 mL, 2 mL, 1 mL and 0 mL to beaker 1, 2, 3, 4, 5 and beaker 6, respectively and further adjustment was done by adding the acid drop by drop arbitrarily for the precipitating agents (NaOH and Ca(OH)₂). But for MgO, 2 mL, 1 mL and 0 mL conc. HNO₃ and the pH of the rest two were adjusted by adding more bases drop by drop. Mixing in 90 rpm for one minute and then in 30 rpm for 20 minutes. After 4 h settling time supernatant was decanted, filtered, diluted to 50 mL with deionized water in triplicate and stored in a refrigerator until analysis in AAS (Esmaeilli *et al.*, 2005).

The chromium content of chromium hydroxide sludge, Cr(OH)₃, was calculated as follows:
Cr content of the sludge = Cr conc. before treatment - Cr conc. after treatment. The removal efficiency at the different pH values was calculated as follows:

$$\% \text{ of Cr removal} = \frac{C_i - C_f}{C_i} \times 100 \text{ -----Equation 1.7}$$

where C_i is the initial concentration and C_f is the final or supernatant concentration. Sludge volume, supernatant volume, and rate of precipitation were measured.

Experiment 4. Recovery of BCS or Cr from Cr(OH)₃ sludge using conc. H₂SO₄

10% MgO solution was added to the 500 mL wastewater in a beaker and then stirred until pH 8. About 3 mL of concentrated H₂SO₄ was added drop by drop slowly to 50 mL sludge slurry, Cr(OH)₃, with stirring until the colour of the solution is dark blue at pH 2.8 (Rajamani, 1995). About 50 mL of recovered basic chromium sulfate solution was evaporated in sunlight and the dry sludge or basic chromium sulfate (BCS) was obtained. Some 300 mg of the sludge was digested to determine concentration of Cr recovered. The simplified chemical reaction for BCS recovery is $\text{Cr(OH)}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ -----Equation 1.1

3.1.6.3 Digestion procedure of the solid sludge (basic chromium sulfate) for Chromium determination

EPA Method 3050B (EPA, 1996a) is a very strong acid digestion method designed to dissolve almost all elements in sediments, soils, and sludge that could become environmentally available. For this test, approximately 300 mg of the sample or the air dried sludge (basic chromium sulfate) was placed in a 50 mL Griffin beaker. 5 mL of an 8 M HNO₃ solution was

added to the beaker; the beaker was then covered with a watch glass, and the unit was heated to 95 °C in a hot plate. Successive additions of concentrated HNO₃ and heating were performed until no reaction with the sample was noted. The sample was then allowed to digest for two hours at 95°C. The sample was removed and allowed to cool. After cooling, 1.5 mL of 30% H₂O₂ was added to the sample and the temperature was increased to 95 °C. Successive additions of H₂O₂ and heating were performed until no further reaction was noticed. The sample was allowed to digest for 2 hours at 95 °C. After cooling, the solution was filtered through a filter paper to remove the insoluble particles prior to analysis and 0.05 mL of the filtrate was diluted to a final volume of 50 mL with DI water in triplicate for Cr analysis. The concentration of chromium was determined by atomic absorption spectrophotometer (AAS) (Lindberg and Deutsch, 2006).

3.2 Statistical data analysis

Statistical analysis was performed using SPSS program (SPSS; Version 16.0, USA). The data was analyzed through one-way analysis of variance (ANOVA) at 95% confidence level to compare the performance efficiency of each precipitating agents at different pH for the removal of Chromium. The ANOVA was used for statistical analysis because it uses the F statistics to compare whether the difference between sample means of chromium at different pH are significant, if the opposite then, it is not significant.

Chapter four

Results and Discussion

4.1. General information

Determination of chromium in environmental and biological samples has received considerable attention owing to its importance as essential element, to recycle for environmental protection and economic reasons and also to its toxicity even at low concentrations. Because of the different sensitivity and bioavailability of Cr(III) and Cr(VI), determination of total Cr concentration may not give full information about possible hazards. In this case monitoring of concentration of separate Cr species is necessary. According to Addis Mekonnen (2006) Addis Ababa Tannery wastewater concentration of total Cr, Cr(III) and Cr(VI), (mean \pm SD), in mg/L in the composite were 372.334 ± 89.923 , 372.303 ± 89.920 and 0.031 ± 0.003 , but in this study total Cr in the composite is 139.00 ± 2.65 which is nearly equal to Cr(III) concentration. The difference might be due to the difference in the sampling point or the discharging load or the amount of raw materials used.

From the report of Addis Mekonnen it is understood that the amount of Cr(III) in the composite waste from the discharging point is close to the amount of the total Cr obtained. The level of chromium(VI) in the sample has no significant effect on the Cr(III) concentration and its treatment or removal, therefore, this implies that amount of Cr(VI) in the chrome waste of the tanning drum is almost nil or insignificant, thus in this study the concentration of chromium(VI) is disregarded. The high Cr(III) concentration is due to the chrome salts or Cr(III) salts used as a raw material for the tanning process. Addis Ababa Tannery has no wastewater treatment plants; it discharges its waste into the water system or into a river where Leku and Gefersa rivers meet. The amount of chromium in the waste from the tanning drum and at the discharge point depends on the absence or presence of treatment plant and the amount of Cr that is offered during tanning process.

4.2. Wastewater characterization

The first objective of this study was to characterize wastewater for selected parameters. To achieve this objective characterization was done using HACH method for BOD₅. COD and other organic parameters were analyzed by standard method (APHA, 1998); pH and conductivity were measured by portable pH meter on site and conductivity meter, respectively. The wastewater from raw hide and skin processing at Addis Ababa leather industry contains trivalent chromium and organic matter. The different characteristics of the wastewater prior to its treatment reveals the composition of the wastewater was variable that results from the various operations and the different chemicals used which released different types of wastes at different stages. For example Cr concentration before treatment ranges from 5001 mg/L to 5023 mg/L, on average 5010.33 ± 6.57 in the chrome waste and 134 mg/L to 143 mg/L, on average 139.00 ± 2.65 for the general or composite waste at the discharge point.

The average chromium concentrations in the raw chrome wastewater of the tanning operation and in the composite were 5010.33 ± 6.57 mg/L and 139.00 ± 2.65 mg/L, respectively. The results of this study showed that the wastewater of tannery process or tannery industry is one of the most important sources of environmental pollutants as the concentration of chromium and other pollutants is very high in the wastewater as reported by Song *et al.* (2000) and Ro and Ganter (1998).

The result obtained in this study which is the mean composition of the tannery waste wastewater is summarized in table 4.1 below.

Table 4.1 The Mean \pm SE composition of Addis Ababa Tannery wastewater in mg/L

| Parameters | Mean \pm SE | Minimum | Maximum |
|---|-----------------------|---------|---------|
| pH | 7.33 \pm 0.36 | 6.90 | 8.05 |
| Conductivity | 18.46 \pm 0.60 | 17.51 | 19.57 |
| BOD ₅ | 2795.67 \pm 234.82 | 2340 | 3122 |
| COD | 7552.67 \pm 1295.45 | 5000 | 9213 |
| NH ₄ ⁺ _N | 236 \pm 62.40 | 135 | 350 |
| NO ₃ ⁻ _N | 343.33 \pm 8.82 | 330 | 360 |
| TN | 634.33 \pm 46.19 | 560 | 719 |
| TP | 16.00 \pm 2.65 | 12 | 21 |
| S ²⁻ (sulfide ion) | 139.33 \pm 7.97 | 129 | 155 |
| SO ₄ ²⁻ (sulfate ion) | 3345.33 \pm 473.06 | 2500 | 4136 |
| Total Cr (composite) | 139.00 \pm 2.65 | 134 | 143 |
| Total Cr (chrome waste) | 5010.33 \pm 6.57 | 5001 | 5023 |
| TS | 11341.67 \pm 465.49 | 10473 | 12066 |
| TSS | 3463.00 \pm 675.15 | 2596 | 4793 |
| TSD | 7878.67 \pm 826.91 | 6693 | 9470 |

*conductivity in ms, pH is unit less and all other parameters in mg/L.

4.3 Factors that affect chemical precipitation of the tannery wastewater for Cr(III) removal

The second objective of this study is to evaluate the efficiency of the precipitating agents (NaOH, Ca(OH)₂ and MgO) for chromium removal by chemical precipitation process. To achieve this objective factors that affect the chemical precipitation of Cr(III) are considered and the effect of these factors which are pH, mixing time, settling rate, sludge volume for each precipitating agent and also the type of precipitating agent itself on the precipitation process are tested and results are obtained as described below.

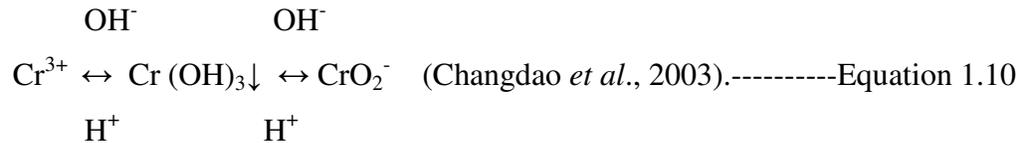
4.3.1 Effect of pH when using NaOH as precipitating agent

In order to get the optimum pHs for Cr(III) removal using NaOH base, chrome waste of the measured initial concentration 5010 mg/L, 15% of NaOH solution and concentration HNO₃ (70%) to control the pH were used in the six beakers. After about 20 minutes of stirring time and then 4 hours settling time the following results were obtained as indicated in table 4.2 below.

Table 4.2 The efficiency of NaOH for Cr(III) precipitation at different pH

| pH | Influent Cr conc., mg/L | Supernatant Cr conc.(mg/L) mean ± SE | Sludge volume, mL | % removal |
|------|----------------------------|--|----------------------|--------------|
| 5.9 | 5010.33 ± 6.57 | 187.62 ± 0.23 | ND | 96.26 |
| 6.9 | 5010.33 ± 6.57 | 178.95 ± 0.39 | 465 | 96.43 |
| 8.6 | 5010.33 ± 6.57 | 1.35 ± 0.15 | 590 | 99.97 |
| 9.1 | 5010.33 ± 6.57 | 2.53 ± 0.49 | 585 | 99.95 |
| 9.8 | 5010.33 ± 6.57 | 4.00 ± 0.53 | 590 | 99.92 |
| 10.3 | 5010.33 ± 6.57 | 4.57 ± 0.11 | 590 | 99.91 |

The pH value is the main and important factor that controls the chemical precipitation of chromium and the chromium hydroxide, Cr(OH)₃, produced is amphoteric which will be dissolved when the liquor pH is below 5.5 or over 12 according to Equation 1.10 below.



The pH values were measured after equal amount of the basic solution is added in each six beakers. The experimental result revealed that the minimum percentage removal (96.26%) is obtained at lowest pH 5.9 and the maximum percentage removal (99.97%) at pH 8.6. According to the result of this study the optimum pH was 8.6-9.1 for Cr(III) removal using NaOH as precipitating agent. The corresponding Cr concentration of the supernatant at pH 8.6

was 1.35 mg/L which is below the EEPA standard or limit (2 mg/L). Generally, the statistical analysis of one way ANOVA showed there is a significant difference ($p < 0.05$) in the mean concentrations of chromium between each pH values but there is no significant difference ($p > 0.05$) between pH 9.8 and pH 10.3 in removing Cr (III) in the wastewater.

However, for those pH values chromium concentration was above the limit that is at pH 9.8 (4 mg/L) and at pH 10.3 (4.57 mg/L) this is because at higher pH peptizing or redissolution of the precipitate, $\text{Cr}(\text{OH})_3$ has occurred that increases the Cr concentration of the supernatant this is due to amphoteric nature of the chromium hydroxide which is soluble in both acidic and basic media (EM publication/eng-manuals, 2001). The precipitate, $\text{Cr}(\text{OH})_3$ from using NaOH has the most stability in the pH range of 8.6-9.1. This is almost in agreement with the result of Esmaili *et al.* (2005) which was 8.5-9.5 range. The gelatinous nature of the sludge at that particular pH might affect the exact sludge detection.

4.3.2 Effect of pH when using $\text{Ca}(\text{OH})_2$ as precipitating agent

The chromium removal efficiency of $\text{Ca}(\text{OH})_2$ precipitating agent at different pH values was examined by studying the percentage reduction of chromium in the wastewater before and after treatment. Wastewater analysis showed that the average chromium concentration of the influent or chrome waste was 5010.33 ± 6.57 mg/L. This variability of chromium in the influent comes from different sources of the wastewater released due to the different operations in the industry. In this case chrome waste of initial concentration 5010.33 ± 6.57 mg/L, 12% of $\text{Ca}(\text{OH})_2$ solution and (70%) concentrated HNO_3 were taken for each six beakers. The pH values were adjusted by adding the acid drop by drop and after 20 minutes of stirring time and 4 hours settling time the following results were obtained as indicated in Table 4.3 below.

Table 4.3 The efficiency of Ca(OH)₂ for Cr(III) precipitation at different pH values

| pH | Influent Cr conc., mg/L | Supernatant Cr conc.(mg/L) Mean ± SE | Sludge volume, mL | % removal |
|-----------|------------------------------------|---|------------------------------|----------------------|
| 5.9 | 5010.33 ± 6.57 | 237.28 ± 0.10 | 242 | 95.26 |
| 6.9 | 5010.33 ± 6.57 | 195.58 ± 0.33 | 201 | 96.10 |
| 8.6 | 5010.33 ± 6.57 | 2.17 ± 0.37 | 185 | 99.956 |
| 9.1 | 5010.33 ± 6.57 | 2.05 ± 0.25 | 410 | 99.959 |
| 9.8 | 5010.33 ± 6.57 | 1.70 ± 0.20 | 395 | 99.966 |
| 10.3 | 5010.33 ± 6.57 | 1.5 ± 0.10 | 412 | 99.970 |

From the above table the maximum chromium removal efficiency was observed at pH 10.3 (99.97%) and the minimum Cr removal was observed at pH 5.9 (95.26%). This is because at lower pH Cr precipitation is low. Statistical analysis showed that no significant difference ($p > 0.05$) between pH values below 8.6. But there is an increasing of Cr removal efficiency as pH increases gradually. The Cr concentration of 2.05 mg/L at pH 9.1, 1.7 mg/L at pH 9.8 and 1.5 mg/L at pH 10.3 were below EEPA standard limit (2 mg/L) and there is a slight increase at pH 8.6 which is 2.17 mg/L. But If the target is to minimize the sludge volume pH 8.6 is taken as optimum or best which was the smallest of all (185 mL). The optimum condition or pH for chromium removal was in the wide pH range of 8.6-10.3 as indicated in the table above. This is because the solubility of Ca(OH)₂ is low with a small solubility product constant of $K_{SP} = 7.9 \times 10^{-6}$ at 25 °C (EM publication/eng-manuals, 2001).

Above pH 8.6 there was a slight decrease of Cr concentration of the supernatant and there was no sludge or hydroxide dissolution until pH 10.3 when using Ca(OH)₂ or even though increasing pH results in peptizing adsorption of chromium(III) ions from the supernatant by the insoluble calcium sulfate, CaSO₄ was produced. The reason for amount of sludge disordering might be the acidity of the reaction mixture or pH, the gelatinous nature or the undetectability of the slight increase or decrease in amount of sludge in the measuring cylinder.

4.3.3 Effect of pH when using MgO as precipitating agent

The chromium removal efficiency of MgO as precipitating agent at different pH values was examined by calculating the percentage of Cr reduction in the wastewater or chrome liquor. The concentration of Cr in the influent or initial chrome waste was 5010.33 ± 6.57 mg/L, 10% MgO solution (Esmaeili *et al.*, 2005) and concentrated HNO₃ (70%) was used to control pH in the first four beakers, but for the last two beakers higher pH is achieved by adding more dose of MgO suspension. The pH values in each beaker were measured after addition of equal amount of the base drop by drop. After 20 minutes of stirring time and then 4 hours of settling time the following result was obtained as indicated in the Table 4.4 below.

Table 4.4 The efficiency of MgO for chromium(III) removal at different pH values

| pH | Influent conc., mg/L | Supernatant Cr con., mg/L Mean \pm SE | Sludge volume, mL | % removal |
|-----------|-----------------------------|---|--------------------------|------------------|
| 5.9 | 5010.33 ± 6.57 | 972.53 ± 1.94 | 95 | 80.59 |
| 6.9 | 5010.33 ± 6.57 | 834.13 ± 0.71 | 88 | 83.35 |
| 8.6 | 5010.33 ± 6.57 | 318.73 ± 3.29 | 90 | 93.64 |
| 9.1 | 5010.33 ± 6.57 | 15.32 ± 0.02 | 80 | 99.69 |
| 9.8 | 5010.33 ± 6.57 | 1.52 ± 0.16 | 85 | 99.97 |
| 10.3 | 5010.33 ± 6.57 | 1.00 ± 0.00 | 85 | 99.98 |

From the above table the maximum Cr removal was observed at pH 10.3 (99.98%) and the minimum Cr removal at pH 5.9 (80.59%). The optimum conditions for Cr concentration were in the pH range of 9.8-10.3 that is at pH 9.8 (99.97%) and pH 10.3 (99.98%) where the Cr concentrations were 1.5 mg/L and 1.00 mg/L, respectively which are below the EEPA limit (2 mg/L). This result is different from the report of Esmaeili *et al.* (2005) in which the optimum pH range was 8-9. This deviation might be due to the additional base added to control the pH or the reason that the optimum pH occurs at higher pH values might be due to very low reactivity and small solubility product constant ($K_{sp} = 1.5 \times 10^{-11}$) of the weak base,

$\text{Mg}(\text{OH})_2$, that furnishes OH^- ions very much slightly than the other two bases, however its hydroxide content (58.3%) per formula unit is higher than NaOH (42.5%) and that of $\text{Ca}(\text{OH})_2$ (45.9%) (EM publication/eng-manuals, 2001).

Statistical analysis also showed that generally there is significance difference between each pH values ($p < 0.05$). But, there is no significant difference ($p > 0.05$) between pH values 9.8 (99.97%) and pH 10.3 (99.98%). However, still there is an increase in chromium removal efficiency as pH value increases.

4.4 Effect of sludge volume

After 20 minutes of stirring time, the mixture was poured into 600 mL measuring cylinders labeled as 1 to 6. After 5 hours of settling time the volume of the sludge in each six measuring cylinders were measured and the average sludge volume produced by the three precipitating agents was calculated to be 568 mL for NaOH , 308 mL for $\text{Ca}(\text{OH})_2$ and 87 mL for MgO and the ratio of average sludge volume, $V_{\text{MgO}} : V_{\text{Ca}(\text{OH})_2} : V_{\text{NaOH}}$ was 1 : 3.5 : 6.5 as indicated in Figure 4.1 below.

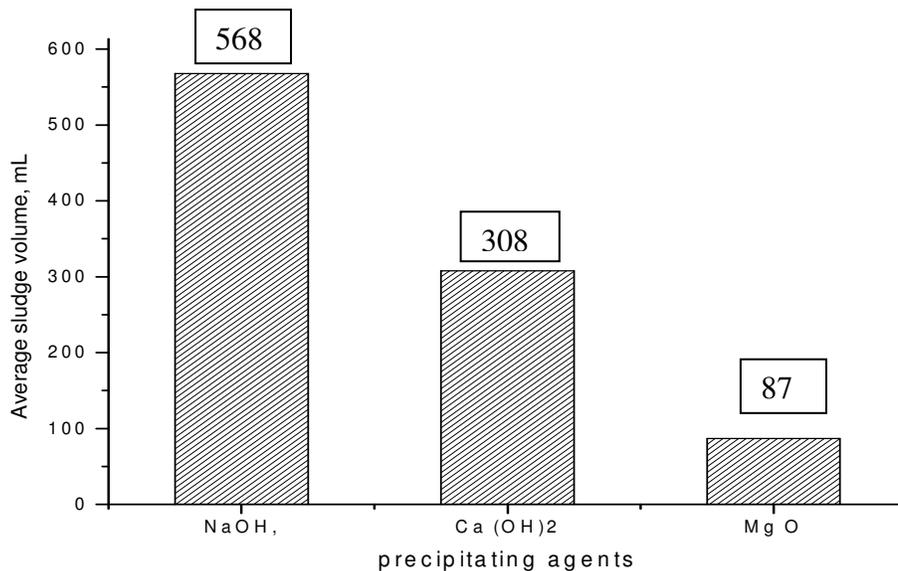


Figure 4.1 Average sludge volume produced by the three precipitating agents

Sludge volumes at optimum pH were measured as 590 mL, 412 mL and 85 mL for each precipitating agents , NaOH, Ca(OH)₂ and MgO, respectively .This is also compared in the figure 4.2 below.

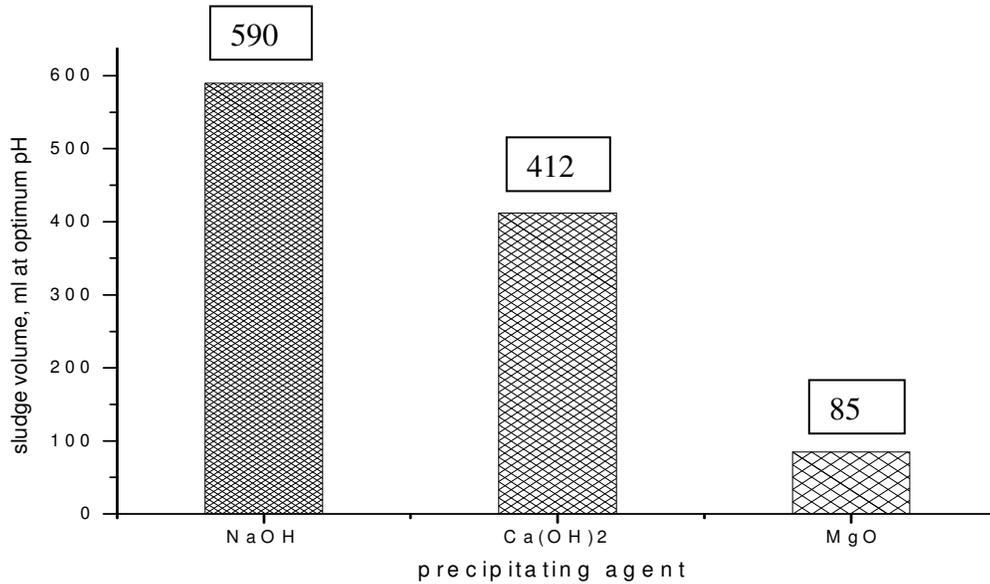


Figure 4.2 Sludge volume produced by the three precipitating agents at optimum pH

Sludge volume produced by MgO is much less than sludge volume produced by Ca(OH)₂ and NaOH in the two figures above and the ratio of sludge volume at optimum pH values was $V_{MgO} : V_{Ca(OH)_2} : V_{NaOH}$ was 1 : 4.8 : 6.9. This result is not in agreement with the result obtained by Esmaeili *et al.* (2005) in which the ratio was 1 : 2.5 : 3.3. As Figure 4.1 and Figure 4.2 showed sludge volume of chromium hydroxide, Cr(OH)₃ resulted from MgO is also much smaller than the volume when using NaOH and Ca(OH)₂. This is important, because it does not only help to reduce the volume of treatment plants but also recovering chromium from such sludge is much easier than sludges with huge volume. This is confirmed by Panswad *et al.* (1995) and Esmaeili *et al.* (2005).

The statistical analysis showed the mean difference is significant at 0.05 level which means that there is a significant difference ($p < 0.05$) among the three precipitating agents. The sludge volume for NaOH at pH 5.9 was not detectable because at lower pH values Cr cannot be precipitated significantly. The reason for the smaller volume of sludge by MgO is due to a grainy, dense and easily settleable precipitate forming. Whereas the sludge formed by NaOH

and $\text{Ca}(\text{OH})_2$ are gelatinous and dewatering is also difficult. This is in agreement with the report of Esmaeili *et al.* (2005), Panswad *et al.* (1995) and Hemming *et al.* (1978). Therefore, the result obtained in this study showed that MgO is the most suitable precipitating agent for removing and recovering chromium from tanning wastewater.

4.5 Effect of settling rate

Settling rate can be measured in terms of sludge volume per unit time or the volume of supernatant per unit time. In this case the later was measured by pouring out the reaction mixture into 600 mL measuring cylinder after 20 minutes of stirring time, because it was generally easily detectable in all the six beakers in the three cases. The height or volume of supernatant was measured in one hour time gap for each precipitating agent at optimum pH. The result obtained was indicated in the Figure 4.3 below.

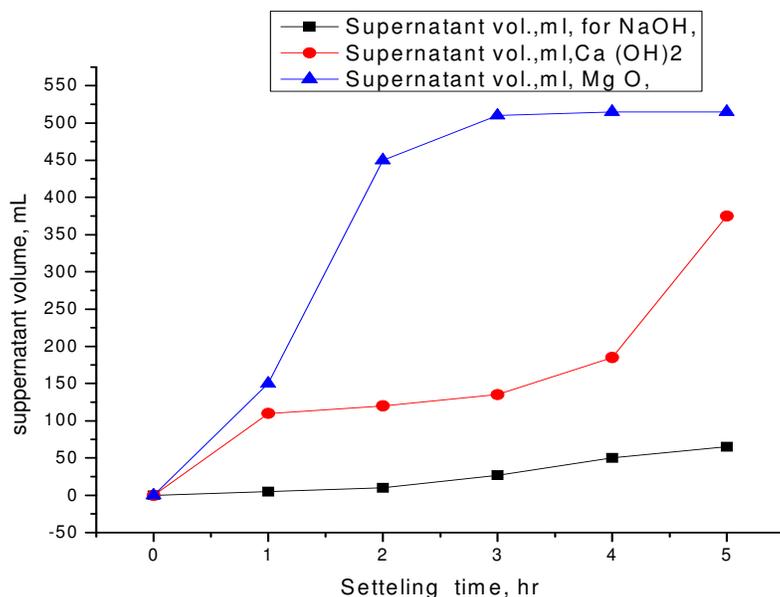


Figure 4.3 Precipitation settling rate for the three precipitating agents

Settling rate or supernatant volume per unit time of the process for magnesium oxide, MgO , was much more than the rate for the other two agents, for example, for the first 1 hour at optimum conditions or pH values settling rate was 5 mL/h, 110 mL/h and 150 mL/h for NaOH,

Ca(OH)₂ and MgO, respectively. The supernatant volume increases gradually for NaOH, it increases rapidly initially and then gradually for Ca(OH)₂ and increases rapidly for the first 2 hrs and then remains constant at the end for MgO. Furthermore, a grainy, dense, easily settleable precipitate can also be formed when MgO is used as a precipitator. Whereas precipitate formed from NaOH was very gelatinous and the settling rate was low. Also settling rate of Ca(OH)₂ is low with undesirable sludge volume, but faster than NaOH. This is in agreement with the report of Esmaeili *et al.* (2005).

4.6 Effect of mixing time

Chrome liquor wastewater of 500 mL with chromium concentration 5010.33 ± 6.57 mg/L, 15% NaOH solution, 10% MgO solution and 12% Ca(OH)₂ solution were used in separate beakers with stirring and the pH of system was measured at 5 minutes interval, the results obtained are indicated in Figure 4.4 below.

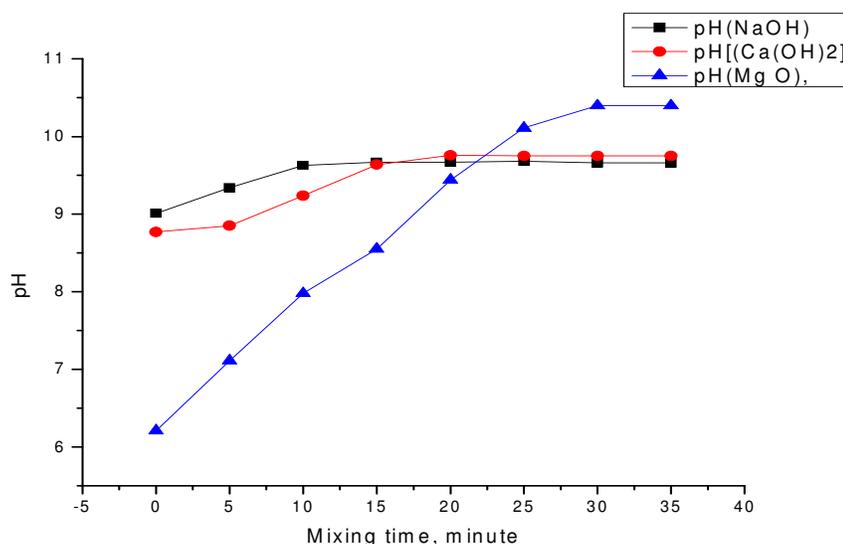


Figure 4.4 Variation of pH vs mixing time for the three precipitating agents (rate of mixing 90 rpm in the hot plate)

Optimum time of rapid mixing for the three precipitating agents is shown in Figure 4.4 above. The time needed for rapid mixing of NaOH is shorter than others because of its high solubility whereas that of Mg(OH)₂ was longer than the other two precipitation agents. The pH value for NaOH and Ca(OH)₂ is gradually increasing and finally remains constant which occur earlier

for NaOH with 100% solubility than Ca(OH)₂. But pH value of MgO continues to increase gradually because of slow reactivity and the solubility product constant for Mg(OH)₂ is small ($K_{sp} = 1.5 \times 10^{-11} \text{ (mol/L)}^3$) or its solubility rate is smaller than that of Ca(OH)₂ ($K_{sp} = 7.9 \times 10^6 \text{ (mol/L)}^3$) and the hydroxide content of NaOH, Ca(OH)₂ and Mg(OH)₂ are 42.5%, 45.9%, and 58.3%, respectively (EM publication/eng-manuals, 2001). The high hydroxide content of magnesium hydroxide could be brought by continuous stirring. Generally as mixing time increases, pH increases thereby decreasing chromium concentration in the supernatant.

4.7 The comparison of the effect of pH on Cr concentration of supernatant for the three precipitating agents

From the wastewater analysis after treatment in each six beakers for the three precipitating agents at different pH values, the Cr concentration of the supernatant was measured by atomic absorption spectrometer (AAS). The concentration values are indicated in Table 4.2, 4.3 and 4.4 above and the graphs are indicated Figure 4.5 below.

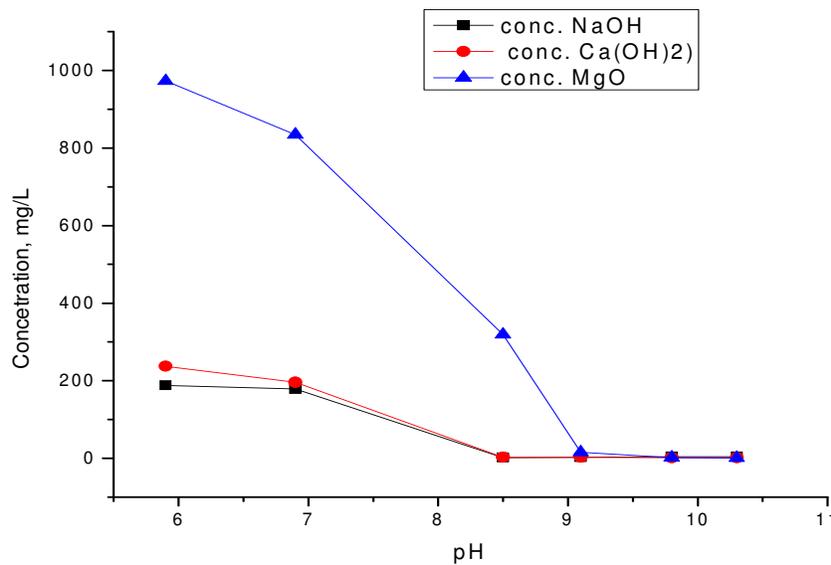


Figure 4.5 Chromium concentration in the supernatant solution vs pH for the three precipitating agents (after 4h settling)

As indicated in the graphs above the minimum solution of Cr is presented at pH 8.6 (1.35 mg/L) when using NaOH as a precipitating agent which is the optimum pH for NaOH and at

this pH the resulting chromium hydroxide, $\text{Cr}(\text{OH})_3$, has the most stability. However adding more NaOH or as stirring time increases, pH increases and this results in peptizing or redissolving. When using $\text{Ca}(\text{OH})_2$ increasing pH decreased the chromium concentration. This discrepancy between NaOH and $\text{Ca}(\text{OH})_2$ is that the difference between the ability of the chemicals for dissolving in water. This ability for NaOH is 100% and according to the result in this study, the $\text{Cr}(\text{OH})_3$ formed is almost stable in pH range of 8.6-9.1.

In contrast since the solubility of $\text{Ca}(\text{OH})_2$ is lower than NaOH base, pH increases gradually. However, in the case of $\text{Ca}(\text{OH})_2$ adsorption causes chromium ions take apart from the supernatant (Esmacili *et al.*, 2005). Since the reactivity and solubility of $\text{Mg}(\text{OH})_2$ is low at lower pHs Cr concentration is high. The optimum pH for $\text{Ca}(\text{OH})_2$ is in the pH range of 9.1-10.3 and for MgO is in the range of 9.8-10.3. The optimum conditions for the three precipitating agents are compared as indicated in the table 4.5 below.

Table 4.5 Chromium removal efficiency at optimum pH for the three precipitating agents

| Precipitating agents | Optimum pH range | Influent Cr conc., mg/L | Supernatant Cr conc., mg/L | Sludge volume, mL | Max. % of Cr removal |
|-----------------------------|-------------------------|--------------------------------|-----------------------------------|--------------------------|-----------------------------|
| NaOH | 8.6-9.1 | 5010.33 ± 6.57 | 1.35 ± 0.15 | 590 | 99.973 |
| $\text{Ca}(\text{OH})_2$ | 8.6-10.3 | 5010.33 ± 6.57 | 1.5 ± 0.10 | 412 | 99.970 |
| MgO | 9.8-10.3 | 5010.33 ± 6.57 | 1.0 ± 0.00 | 85 | 99.98 |

When the maximum percentage chromium removal efficiency for the three precipitating agents is compared the efficiency of MgO at pH 10.3 (99.98%) is the highest and the best of all, this is for two reasons, one is Cr concentration of supernatant is smaller than the other two and its sludge volume is almost half of sludge volume of $\text{Ca}(\text{OH})_2$ and very much smaller than that of NaOH sludge. This smaller sludge volume of MgO occupies fewer disposal site or land. If the sludge is to be treated the size of the treatment plant would be small and also for recovery purposes small volume of sludge is important. The performance among the three hydroxide precipitation does not vary significantly ($P > 0.05$) at optimum conditions. However, the sludge characteristics vary tremendously as observed in table 4.5 above. The minimum metal

hydroxide, Cr(OH)₃, solubility obtained by each method are approximately the same, that is the solubility product constant, K_{sp}, of Cr(OH)₃ is 6.7 x 10⁻³¹ (mol/L)⁴.

4.8 Chromium recovery efficiency of the best precipitating agent (MgO)

After preparing 10% magnesium oxide (MgO) suspension or slurry it was slowly added to the 500 mL chrome wastewater taken from the tanning drum with stirring operated until pH 8 is reached. After allowing a 4 hour settling time, about 50 mL of chrome slurry or Cr(OH)₃ sludge was taken. After adding about 3 mL of concentrated H₂SO₄ with stirring until pH 2.8, basic chrome sulfate solution was produced and according to Rajamani (1995) the required basicity at this pH is 33%. The formula of basic chromium sulfate produced vary at different pHs, for example BCS with formula Cr₄(OH)₆(SO₄)₃ is produced in the pH range 3.0-4.0 (Barbootia *et al*, 2010). It is known that a chrome complex solution of 33% basicity has pH 2.8 and contains mostly binuclear species and about 25% Cr₂O₃ containing chrome tannin products are suitable for tanning (Ludvik, 2000).

The percentage of solid content and liquid content of the tested duplicate sample were determined after evaporation in air (Sun-dry) and the concentration value of chromium was calculated on a dry sludge weight basis and on wet sludge weight basis.

Table 4.6 Percentage of solid content and liquid content of the BCS sludge

| Sample number | Liquid content (%) | Solid content (%) |
|---------------|--------------------|-------------------|
| Beaker 1 | 33.9 | 64.1 |
| Beaker 2 | 30.3 | 69.3 |
| Average | 32.3 | 66.7 |

*Efficiency (%) = actual yield/expected yield X 100, *moisture content = wet wt.-dry wt/wet wt, solid content = dry wt/wet wt

After digestion of the 300 mg of dry sludge (BCS) using HNO₃ as described in the methodology (3050B acid digestion of sludge). The concentration of chromium was determined in triplicate using AAS and the results were 398 mg/L, 399 mg/L and 402 mg/L with an average value of 399.6 mg/L and by subtracting the average blank concentration 300

mg/L the net concentration of chromium was 99.6 mg/L which is 0.996 g for the 10 mL of filtered sample which is equivalent to the 0.3 g of the solid sample digested. Thus, the concentration of chromium on dry weight basis was 0.996 mg/0.3 g or 3.32 mg of Cr/g of dry weight and the concentration on wet weight basis was 0.996 mg/0.46 g or 2.17 mg of Cr/g of wet weight and of course the concentration on wet weight basis is lower than dry weight basis by 2.5%.

The masses of the two samples on dry weight basis in beaker 1, beaker 2 and their average were 7.53 g, 8.23 g and 7.88 g, respectively and the average weight of the total basic chromium sulfate suspension was approximately 12 g. Recovered chrome liquor or basic chromium sulfate solution of 100 mL is generally equivalent to 25 g of BCS (Rajamani, 1995), but in this study from 50 mL BCS solution, 7.88 g of BCS was recovered which is less than the expected value of about 12 g proportionally.

Addis Ababa Tannery Sh. Co uses a raw material or input of goat skin 2500-3500 kg, animal hide of 1200-2200 kg with an average value of 3000 kg skin and 1700 kg hide. The industry uses a basified chrome of 3% on pelt weight basis, which means 3% of 3000 kg (90 kg BCS) and 3% of 1700 kg hide (51 kg BCS). These 90 kg and 51 kg BCS is considered as 100% chrome offered. The amount of water used is 50% on pelt weight basis for tanning process that means 50% of 3000 kg skin (1500 kg of water) and 50% of 1700 kg hide (850 kg of water) using density of water 1000 kg/m^3 this is equivalent to 1.5 m^3 (1500 liters) for skin and 0.85 m^3 (850 liters) for hide. The amount of basic chromium sulfate (BCS) recovered or determined from 500 mL chrome waste treated with MgO at pH 8 was approximately 8 g.

Directly proportionally if 1.5 m^3 chrome wastewater were to be treated for recovery 24000 g (24 kg) BCS could be recovered for skin out of 90kg BCS offered and 13600gm (13.6 kg of BCS) could be recovered from 51 kg of chrome offered. Thus chrome recovery efficiency from spent tanning float for both skin and hide was 26.7% as calculated using Equation 1.9 $\% R = \text{BCS recovered} / \text{BCS offered} \times 100$. This is almost in agreement with chrome recovery efficiency of 23.3% for conventional chrome tanning with tanning efficiency of 68% in which 56.4% is fixed in the leather and 24.8 % in the spent tanning float out of which 23.3% is

recoverable and 1.5% not recoverable. The rest 1.8% is in the recoverable residual water sampling and draining (Ludvik, 2000).

With respect to the spent tanning float it is possible to separate or remove almost all Cr(III) ions as Cr(OH)_3 sludge from the wastewater and could be recovered and used directly for tanning. If treatment is done properly at the required pH of about 2.8 using concentrated H_2SO_4 the recovered BCS with about 33% basicity accounts almost 30% that can be added to 70% fresh basic chromium sulfate from the market which is suitable for tanning (Voice *et al*, 1988)

Chapter five

Conclusions and recommendations

5.1. Conclusions

Based on the results obtained, the following points are concluded

1. The pollution load of the selected parameters was above the discharge limit set by environmental protection authority for instant: chrome waste Cr(5010.33 mg/L), composite Cr(139 mg/L), BOD₅ (2795.67 mg/L), COD (7552.67 mg/L), TN (634.33 mg/L), S²⁻ (139.33 mg/L), TS (11341.67 mg/L), TSS (3463.00 mg/L), etc.

Limits: Cr(2 mg/L), BOD(200 mg/L), COD(500 mg/L), TN (60 mg/l), S²⁻ (1 mg/L) and TSS(50 mg/l).

2. Because of seasonal variation, Cr toxicity tolerance and harvesting problems, recovering and recycling are important even for those tanneries with available land which can use the best biological treatment or constructed wetland treatment system.

3. Recovery efficiency at optimum pH: NaOH(99.973%), Ca(OH)₂(99.97%) and MgO(99.98%) was not significant. However, there is significant difference in sludge characteristics NaOH (590 mL), Ca(OH)₂(412 mL) and MgO(85 mL). It is concluded from our results that the optimum pH for the precipitating chromium from tannery wastewater is 9.8-10.3 with removal efficiency of 99.98% and the good sludge with high settling rate and lower volume was obtained when using MgO as the precipitating agent. Hence the MgO is a good precipitating agent for removal and recovery of chromium from tanning wastewater. It is also concluded that magnesium oxide is much more desirable than lime and sodium hydroxide for removing and recovering chromium from tannery wastewater.

4. If treatment of the tannery wastewater or chrome waste is done properly using MgO at the required pH 8 and recovery using concentrated H₂SO₄ at about pH 2.8, the basic chromium sulfate (BCS) so produced accounts almost 30% and is suitable for tanning mixed with 70% fresh basic chromium sulfate from the market.

5. The pH is the dominant factor that affects chemical precipitation in tannery wastewater treatments.

5.2. Recommendations

In tannery wastewater treatment the following should be done.

1. Magnesium oxide (MgO) as found to be the best precipitating agent for chromium removal may be applied in Ethiopian Tanneries.
2. Magnesium oxide (MgO) as an alternative to Ca(OH)_2 may also be applied for basic chromium sulfate(BCS) or chromium recovery in Ethiopian Tanneries.

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Annexes

Annex 1: EEPA Tanning and leather finishing discharge limit values for receiving water bodies

| Parameter | Limit value |
|--|--|
| Temperature | 40 °C |
| pH | 6 – 9 |
| BOD ₅ at 20°C | 90% removal or 200 mg/l, whichever is less |
| COD | 500 mg/l |
| Suspended solids | 50 mg/l |
| Total ammonia (as N) | 30 mg/l |
| Total nitrogen (as N) | 80% removal or 60 mg/l, whichever is less |
| Total phosphorus (as P) | 80% removal or 10 mg/l, whichever is less |
| Oils, fats, and grease | 15 mg/l |
| Mineral oils at oil trap or interceptors | 20 mg/l |
| Chromium (as total Cr) | 2 mg/l |
| Chromium (as Cr VI) | 0.1 mg/l |
| Chlorides (as Cl) | 1000 mg/l |
| Sulphides (as S) | 1 mg/l |
| Phenols | 1 |

Annex 2: Multiple Comparisons, Dependent Variable: MgO, LSD

| (I) BASES (J) BASES | | Mean Difference (I-J) | Std. Error | Sig. | 95% Confidence Interval | |
|---------------------|------|--------------------------|------------|------|-------------------------------|-------------|
| | | | | | Lower Bound | Upper Bound |
| 1.00 | 2.00 | 138.4000 | 2.24763 | .000 | 133.5028 | 143.2972 |
| | 3.00 | 653.8000 | 2.24763 | .000 | 648.9028 | 658.6972 |
| | 4.00 | 957.2167 | 2.24763 | .000 | 952.3195 | 962.1138 |
| | 5.00 | 971.0167 | 2.24763 | .000 | 966.1195 | 975.9138 |
| | 6.00 | 971.5333 | 2.24763 | .000 | 966.6362 | 976.4305 |
| 2.00 | 1.00 | -138.4000 | 2.24763 | .000 | -143.2972 | -133.5028 |
| | 3.00 | 515.4000 | 2.24763 | .000 | 510.5028 | 520.2972 |
| | 4.00 | 818.8167 | 2.24763 | .000 | 813.9195 | 823.7138 |
| | 5.00 | 832.6167 | 2.24763 | .000 | 827.7195 | 837.5138 |
| | 6.00 | 833.1333 | 2.24763 | .000 | 828.2362 | 838.0305 |
| 3.00 | 1.00 | -653.8000 | 2.24763 | .000 | -658.6972 | -648.9028 |
| | 2.00 | -515.4000 | 2.24763 | .000 | -520.2972 | -510.5028 |
| | 4.00 | 303.4167 | 2.24763 | .000 | 298.5195 | 308.3138 |
| | 5.00 | 317.2167 | 2.24763 | .000 | 312.3195 | 322.1138 |
| | 6.00 | 317.7333 | 2.24763 | .000 | 312.8362 | 322.6305 |
| 4.00 | 1.00 | -957.2167 | 2.24763 | .000 | -962.1138 | -952.3195 |
| | 2.00 | -818.8167 | 2.24763 | .000 | -823.7138 | -813.9195 |
| | 3.00 | -303.4167 | 2.24763 | .000 | -308.3138 | -298.5195 |
| | 5.00 | 13.8000 | 2.24763 | .000 | 8.9028 | 18.6972 |
| | 6.00 | 14.3167 | 2.24763 | .000 | 9.4195 | 19.2138 |
| 5.00 | 1.00 | -971.0167 | 2.24763 | .000 | -975.9138 | -966.1195 |
| | 2.00 | -832.6167 | 2.24763 | .000 | -837.5138 | -827.7195 |
| | 3.00 | -317.2167 | 2.24763 | .000 | -322.1138 | -312.3195 |
| | 4.00 | -13.8000 | 2.24763 | .000 | -18.6972 | -8.9028 |
| | 6.00 | .5167 | 2.24763 | .822 | -4.3805 | 5.4138 |
| 6.00 | 1.00 | -971.5333 | 2.24763 | .000 | -976.4305 | -966.6362 |
| | 2.00 | -833.1333 | 2.24763 | .000 | -838.0305 | -828.2362 |
| | 3.00 | -317.7333 | 2.24763 | .000 | -322.6305 | -312.8362 |
| | 4.00 | -14.3167 | 2.24763 | .000 | -19.2138 | -9.4195 |
| | 5.00 | -.5167 | 2.24763 | .822 | -5.4138 | 4.3805 |

* The mean difference is significant at the 0.05 level. *1(pH=5.9), 2(pH=6.9), 3(pH=8.6) 4(pH=9.1), 5(pH=9.8), 6 (pH=10.3).

Annex 3: Test results of ANOVA for Cr removal with level of significant 0.05

| | | Sum of Squares | df | Mean Square | F | Sig. |
|---------------------------|----------------|----------------|----|-------------|-----------|------|
| NaOH | Between Groups | 129977.816 | 5 | 25995.563 | 67594.097 | .000 |
| | Within Groups | 4.615 | 12 | 0.385 | | |
| Ca(OH)₂ | Between Groups | 971.526 | 5 | 194.305 | 1050.298 | .000 |
| | Within Groups | 2.220 | 12 | .185 | | |
| MgO | Between Groups | 2933560.461 | 5 | 586712.092 | 77425.349 | .000 |
| | Within Groups | 90.933 | 12 | 7.578 | | |

Annex 4: Variation of pH with mixing time

| | | | | | | | | | |
|---------------------|--------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| NaOH | Mixing time,(min.) | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
| | pH | 12.60 | 12.90 | 12.95 | 12.99 | 13.00 | 13.02 | 13.02 | 13.02 |
| Ca(OH) ₂ | Mixing time(min.) | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
| | pH | 5.80 | 10.11 | 10.48 | 10.61 | 10.66 | 10.72 | 10.71 | 10.71 |
| MgO | Mixing time(min.) | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
| | pH | 6.10 | 6.57 | 7.10 | 7.76 | 7.97 | 8.10 | 8.19 | 8.24 |

Annex 6: Block diagram for flame atomic absorption spectrometer

