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## Chemical precipitation method for chromium removal and its recovery from tannery wastewater in Ethiopia

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### ABSTRACT

Most of the tanneries in Ethiopia (90%) do not treat and very few (10%) partially treat their effluent before discharging it into the receiving water bodies. The untreated tannery effluent causes tremendous pollution of water resources in the country, especially due to its high organic loading and chromium content. Chromium(III) salts are the most widely used chemicals for tanning processes, but only about 60-70% of total chromium salts reacts with the hides and about 30-40% of the chromium remain 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. The purpose of this study was to develop an alternative process for removing and recovering trivalent chromium from tannery wastewater via chemical precipitation with sodium hydroxide (NaOH), calcium hydroxide (Ca(OH)<sub>2</sub>) and magnesium oxide (MgO). The effects of pH, stirring time, settling rate and sludge volume were studied in batch experiments. Flame atomic absorption spectrometry was used to determine Cr concentration. The results showed that removal efficiencies of the precipitating agents NaOH (99.97%), Ca(OH)<sub>2</sub> (99.97%) and MgO (99.98%) at optimum pH values were not significantly different. However, there was a significant difference in sludge volume of NaOH (590 mL), Ca(OH)<sub>2</sub> (412 mL) and MgO (85 mL). The optimum pH of 9.8-10.3 with removal efficiency of 99.98% and the good sludge with high settling rate and lower volume was obtained using MgO precipitating agent. Hence the MgO was found to be 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.

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**Capsule Summary:** Chromium removal and its recovery by chemical precipitation from tannery wastewater from leather industry in Addis Ababa, Ethiopia were evaluated by flame atomic absorption spectrometry.

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## INTRODUCTION

Industrial wastewater in Ethiopia has become the most vital problem because of the high growth rate and enormous discharge of wastewaters to the environment (Gebre-Mariam and Desta, 2002; Belay, 2010; Gebre et al., 2016). 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 causes environmental and health problems to the surrounding inhabitants (Gebre-Mariam and Desta, 2002; Belay, 2010; Gebre et al., 2016). Accelerated water quality change, due to industrial pollution, is one of the major environmental concerns throughout the world (Gebre-Mariam and Desta, 2002; Belay, 2010; Siddiquee et al., 2012; Adeel et al. 2012).

Chromium solutions are widely used in many industrial processes such as chrome plating; wood preserving, textile dyeing, pigmenting, chemical production, pulp and paper industries and tanning. The wastewater resulting from these processes contains high amount of chromium, which is harmful for environment and human health (Zayed and Terry, 2003; Belay, 2010; Siddiquee et al., 2012; Adeel et al. 2012; Bedemo et al., 2016). Tanning process using chromium compounds is one of the most common methods for processing of hides (Sreeram and Ramasami, 2003; Belay, 2010; Adeel et al. 2012; Bedemo et al., 2016). In this process about 60-70% of chromium reacts with the hides. In the other words, about 30-40% of the chromium remains in the solid and liquid wastes (especially spent tanning solutions) (Esmaeili et al., 2005).

Hence, the wastewater of tanning process is an important source in adding chromium pollutant to the environment. In addition, the cost of the chromium metal is also high and it is possible to recover chromium from the wastewater (Fabiani et al., 1996; Ludvic, 2000). Kocaoba and Akin (2002) and Hafez et al. (2002) have reported that the chromium concentration in the tanning wastewater varies from 1300 to 2500 and 2500 to 8000 (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 (Fabiani et al., 1996; Ludvic, 2000; Belay, 2010; Adeel et al. 2012; Gebre et al., 2016; Bedemo et al., 2016). 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 (Kocaoba and Akin, 2002; Barbooti et al., 2010; Mottalib et al., 2015; Terfie and Asfaw, 2015).

Chromium salts are undesirable for two reasons. Firstly, they can have a poisoning effect on the microorganisms used for sewage treatment (EEPA, 2001; Beghetto et al., 20130; The New Zealand Institute of Chemistry, 2016). 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 can be recovered by reacidification for reuse (Beghetto et al., 2013; The New Zealand Institute of Chemistry, 2016).

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 (Beghetto, et al., 2013; The New Zealand Institute of Chemistry, 2016). The purpose of this research is to compare pH, rate of precipitation, sludge volume and time of mixing when using the three precipitating agents (lime, sodium hydroxide and magnesium oxide) for the chromium precipitation of the tannery wastewater.

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 (Terfie and Asfaw, 2015; Amanial, 2016). 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) Barbooti et al., 2010; Amenu, 2015). Therefore chromium has to be removed before it is 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 (Kocaoba and Akin, 2002; Esmaeili, 2005; Barbooti et al., 2010; Mottalib et al., 2015; Terfie and Asfaw, 2015).

The main objective of this study is (i) to investigate the chemical precipitation method for chromium removal and its recovery from the tannery wastewater in the leather industries in Ethiopia, (ii) to characterize the wastewater effluent of Addis Ababa Tannery Share Company for selected parameters, (iii) to compare the efficiency of lime, sodium hydroxide and magnesium oxide in the precipitation process for the removal of chromium from tannery effluent, and (iv) to recover basic chromium sulfate or chromium from chromium hydroxide sludge for reuse.

## MATERIAL AND METHODS

### 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. All the 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  $\mu$ 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.

### Instrumentation

Determination of chromium was carried out using Flame Atomic Absorption Spectrometer (Buck Scientific Model 210 VGP, East Norwalk, USA) equipped with deuterium arc background corrector using air-acetylene flame.

### Preparation of standard solutions for atomic absorption spectrometry

To determine the concentration of chromium in the influent (raw wastewater), effluent (supernatant) and filtrate of digested basic chromium sulfate, four series of working standard chromium solutions of concentration 0.5, 1.0, 1.5 and 2.0 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 deionized water to 100 mL which gives 10 mg/L of chromium and their absorbance's were measured. The standards were run in flame atomic absorption spectrometer and a four point linear calibration curves were established for each determination. Then, sample solutions were aspirated into the atomic absorption spectrometer and direct readings of total chromium concentrations were recorded. Three replicate determinations were carried out for each sample. The blanks were also run before chromium determination. The amount of chromium precipitated was calculated from the difference between the amount before and after treatment or precipitation.

### Sampling of tannery waste water

The Addis Ababa Tannery Share Company during the processes of producing leather generates wastewater which is directly channeled without treatment to the river where Gefersa and Leku rivers meet. Composite samples from the general waste and chrome liquor sample from the drum were taken from the wastewater of Addis Ababa Tannery Share Company at Colfe-Keranio sub-city. Waste water samples were collected using 10 L 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.

The parameters determined were Cr concentration, pH, total solids, dissolved solids, suspended solids, color, TN,  $\text{NH}_3\text{-N}$ , TP,  $\text{BOD}_5$ , 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 precipitating agents were added to each sample separately and pH was controlled in the range 5.9–10.3 using nitric acid. In order to mix solution, samples were taken to the beakers and mixed for 1 min by stirring at 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 min 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 amount of the precipitate for all the 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 spectrometry was used for measuring chromium concentration in wastewater before and after settling process.

### Pre-experiment design

Three samples were collected at different times from chrome effluent (from the drum) with the interval of five days and were preserved using 2%  $\text{HNO}_3$ . 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  $\text{Ca}(\text{OH})_2$ , a total of 500 mL  $\times$  18 = 9000 mL was preserved by diluting 180 mL of conc.  $\text{HNO}_3$  to 9000 mL in a large plastic container.

### Characterization of Addis Ababa tannery wastewater

Wastewater characterization was done for the physico-chemical water quality parameters; pH,  $\text{BOD}_5$ , COD, TN,  $\text{NH}_3$  nitrogen, sulfate, sulfide, conductivity and total chromium.

**Table 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	18.5 $\pm$ 0.60	17.5	19.6
BOD <sub>5</sub>	2796 $\pm$ 235	2340	3122
COD	7553 $\pm$ 1295	5000	9213
NH <sub>4</sub> <sup>+</sup> -N	236 $\pm$ 62	135	350
NO <sub>3</sub> <sup>-</sup> -N	343 $\pm$ 8.8	330	360
TN	634 $\pm$ 46	560	719
TP	16.0 $\pm$ 2.6	12	21
S <sup>2-</sup>	139 $\pm$ 8	129	155
SO <sub>4</sub> <sup>2-</sup>	3345 $\pm$ 473	2500	4136
Total Cr (composite)	139 $\pm$ 3	134	143
Total Cr (chrome waste)	5010 $\pm$ 7	5001	5023
TS	11342 $\pm$ 465	10473	12066
TSS	3463 $\pm$ 675	2596	4793
TSD	7879 $\pm$ 827	6693	9470

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

**Table 2:** The efficiency of NaOH for Cr(III) precipitation at different pH

pH	Effluent Cr conc. (mg/L)	Supernatant Cr conc. (mg/L) Mean $\pm$ SE	Minimum Cr conc. (mg/L)	Maximum Cr conc. (mg/L)	Sludge volume (mL)	% removal
5.9	5010 $\pm$ 6.6	188 $\pm$ 0.23	187	188	ND	96.3
6.9	5010 $\pm$ 6.6	179 $\pm$ 0.39	178	178	465	96.4
8.6	5010 $\pm$ 6.6	1.35 $\pm$ 0.15	1.05	1.50	590	99.9
9.1	5010 $\pm$ 6.6	2.53 $\pm$ 0.49	1.55	3.05	585	99.9
9.8	5010 $\pm$ 6.6	4.00 $\pm$ 0.53	3.05	4.90	590	99.9
10.3	5010 $\pm$ 6.6	4.57 $\pm$ 0.11	4.35	4.70	590	99.9

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.

#### Determination of total chromium in the chrome liquor sample and in the composite sample

All the samples were brought to the laboratory using plastic bottles and preserved with 2% of HNO<sub>3</sub>. 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 matrices, the samples were digested by acidifying with concentrated HNO<sub>3</sub> (70%). After 50 mL of the sample was digested for a total of 1 hour a clear solution was obtained.

Atomic absorption spectrometry 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 HNO<sub>3</sub> was added to each sample and covered with watch glass. Then the samples were digested for 45 min using magnetic stirrer with hot plate at a temperature of 150 °C. It was cooled and further heated to 15 min after adding additional amount of 5 mL of HNO<sub>3</sub>. The samples were then cooled, filtered and diluted to 50 mL and stored in a refrigerator until analysis.

#### Removal of chromium using precipitating agents and determination in the supernatant

Precipitating agents 15% NaOH, 12% Ca(OH)<sub>2</sub> and 10% MgO solutions (w/w) were prepared in separate beakers (250 mL). 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 HNO<sub>3</sub> by adding 5, 4, 3, 2, 1 and 0 mL to beaker 1, 2, 3, 4, 5 and 6, respectively and further adjustment was done by adding the acid drop by drop

arbitrarily for the precipitating agents (NaOH and Ca(OH)<sub>2</sub>). But for MgO, 2, 1 and 0 mL conc. HNO<sub>3</sub> and the pH of the rest two were adjusted by adding more bases drop by drop. Mixing at 90 rpm for one min and then at 30 rpm for 20 min. 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.

The chromium content of chromium hydroxide sludge, Cr(OH)<sub>3</sub>, 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 shown in Eq. 1.

$$Cr\ removal\ (\%) = \left\{ \frac{C_i - C_f}{C_i} \right\} \cdot 100 \quad (1)$$

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.

### Recovery of basic chromium sulfate, Cr(OH)<sub>3</sub> sludge

A 10% MgO solution was added to the 500 mL wastewater in a beaker and then stirred until pH 8. About 3 mL of concentrated H<sub>2</sub>SO<sub>4</sub> was added drop by drop slowly to 50 mL sludge slurry, Cr(OH)<sub>3</sub>, with stirring until the color of the solution is dark blue at pH 2.8. About 50 mL of recovered basic chromium sulfate solution was evaporated in sunlight and the dry sludge or basic chromium sulfate (BCS) was obtained. A known amount (300 mg) of the sludge was digested to determine concentration of Cr recovered.

### Digestion procedure for the solid sludge for chromium determination

Acid digestion of the solid sludge (basic chromium sulfate) was done by the USEPA method 3050B (USEPA, 1996). For this test, approximately 300 mg of the sample or the air dried sludge (basic chromium sulfate) was placed in a 50 mL beaker. A 5 mL of 8 M HNO<sub>3</sub> 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 HNO<sub>3</sub> 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% H<sub>2</sub>O<sub>2</sub> was added to the sample and the temperature was increased to 95 °C. Successive additions of H<sub>2</sub>O<sub>2</sub> 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 deionized water in triplicate for Cr analysis. The concentration of chromium was determined by atomic absorption spectrometry.

### Statistical data analysis

Statistical analysis was performed using SPSS program (SPSS; Version 20.0, 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 or not.

## RESULTS AND DISCUSSION

### 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 due to its toxicity even at low concentrations. Total chromium in the composite was found to be 139±3 mg/L. The high chromium 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 chromium that is offered during tanning process.

### Wastewater characterization

The first objective of this study was to characterize wastewater for the selected parameters. To achieve this objective characterization was done using HACH method for BOD<sub>5</sub>. COD and other organic parameters were analyzed by standard method (APHA, 1992); 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 revealed that 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 chromium concentration before treatment ranges from 5001 to 5023 (mg/L), on average 5010±6.6 mg/L in the chrome waste and 134 to 143 (mg/L), on average 139±2.7 mg/L 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±6.6 and 139±2.7 (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. The results obtained in this study which is

**Table 3:** The efficiency of Ca(OH)<sub>2</sub> for Cr(III) precipitation at different pH values

pH	Effluent Cr conc. (mg/L)	Supernatant Cr conc. (mg/L) Mean ± SE	Minimum	Maximum	Sludge volume (mL)	% removal
5.9	5010±6.6	237±0.10	237	237	242	95.3
6.9	5010±6.6	196±0.33	195	196	201	96.1
8.6	5010±6.6	2.17±0.37	1.75	2.90	185	99.9
9.1	5010±6.6	2.05±0.25	1.55	2.35	410	99.9
9.8	5010±6.6	1.70±0.20	1.45	2.10	395	99.9
10.3	5010±6.6	1.50±0.10	1.00	2.01	412	99.9

**Table 4:** The efficiency of MgO for chromium(III) removal at different pH values

pH	Effluent Cr conc. (mg/L)	Supernatant Cr conc. (mg/L) Mean ± SE	Minimum Cr conc. (mg/L)	Maximum Cr conc. (mg/L)	Sludge volume (mL)	% removal
5.9	5010±6.6	973±1.9	970	976	95	80.59
6.9	5010±6.6	834±0.71	833	835	88	83.35
8.6	5010±6.6	319±3.3	312	324	90	93.64
9.1	5010±6.6	15.3±0.02	15.3	15.4	80	99.69
9.8	5010±6.6	1.52±0.16	1.20	1.70	85	99.97
10.3	5010±6.6	1.00±0.00	1.00	1.00	85	99.98

the mean composition of the tannery waste wastewater are summarized in Table 1.

#### Factors that affect chemical precipitation of the tannery wastewater for chromium removal

The second objective of this study is to evaluate the efficiency of the precipitating agents (NaOH, Ca(OH)<sub>2</sub> 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.

#### 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 chromium concentration 5010 mg/L, 15% of NaOH solution and concentrated HNO<sub>3</sub> (70%) were used to control the pH. After about 20 min of stirring time and then 4 hours settling time, the following results were obtained as indicated in Table 2.

The pH value is the important factor that controls the chemical precipitation of chromium and the chromium

hydroxide, Cr(OH)<sub>3</sub>, produced is amphoteric, which will be dissolved when the liquor pH is below 5.5 or above 12 (Changdao et al., 2003).

The pH values were measured after equal amount of the basic solution is added in each of the 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 chromium 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, Cr(OH)<sub>3</sub> has occurred that increases the chromium concentration of the supernatant this is due to amphoteric nature of the chromium hydroxide which is soluble in both acidic and basic

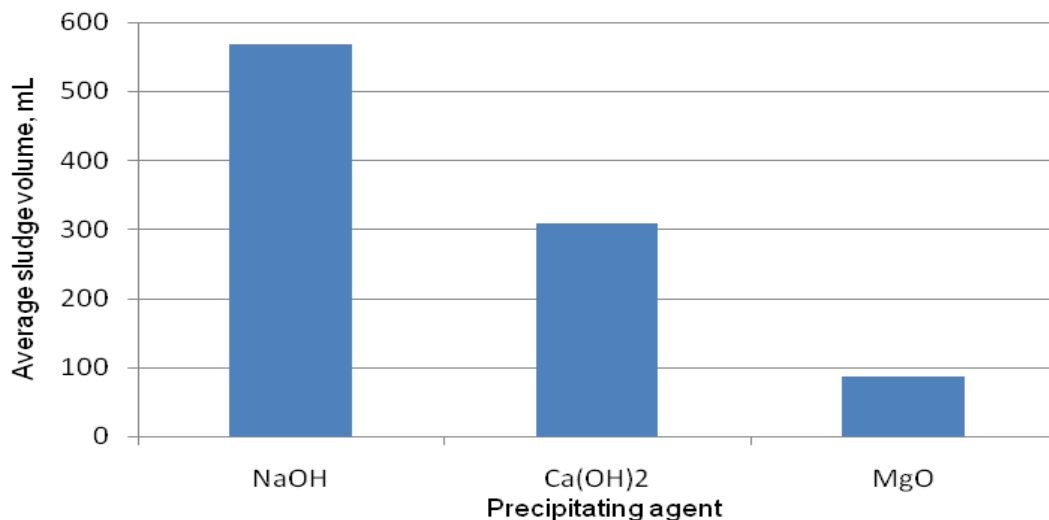


Fig. 1: Average sludge volume produced by the three precipitating agents

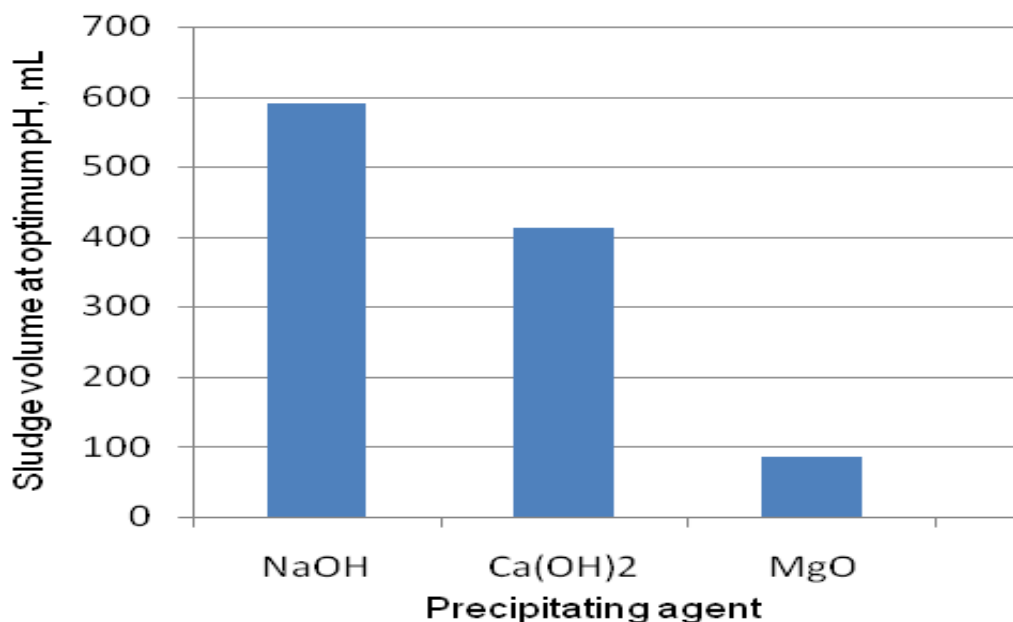


Fig. 2: Sludge volume produced by the three precipitating agents at optimum pH

media. 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.

#### 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 the treatment. Wastewater analysis showed that the average chromium concentration of the influent or

chrome waste was  $5010 \pm 6.6$  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  $5010 \pm 6.6$  mg/L, 12% of  $\text{Ca}(\text{OH})_2$  solution and concentrated  $\text{HNO}_3$  (70%) were taken for each six beakers. The pH values were adjusted by adding the acid drop by drop and after 20 min of stirring time and 4 hours settling time the following results were obtained as indicated in Table 3.

From Table 3, the maximum chromium removal efficiency was observed at pH 10.3 (99.97%) and the minimum chromium removal was observed at pH 5.9 (95.26%). This is because at lower pH chromium 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 chromium removal efficiency as pH increases gradually. The chromium 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  $\text{Ca}(\text{OH})_2$  is low with a small solubility product constant of  $K_{\text{sp}} = 7.9 \times 10^{-6}$  at 25 °C.

Above pH 8.6 there was a slight decrease of chromium concentration of the supernatant and there was no sludge or hydroxide dissolution until pH 10.3 when using  $\text{Ca}(\text{OH})_2$  or even though increasing pH results in peptizing adsorption of chromium(III) ions from the supernatant by the insoluble calcium sulfate,  $\text{CaSO}_4$  was produced. The reason for amount of sludge disordering might be the acidity of the reaction mixture or pH and the gelatinous nature of the sludge.

#### Effect of pH 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 chromium reduction in the wastewater or chrome liquor. The concentration of chromium in the influent or initial chrome waste was  $5010 \pm 6.6$  mg/L, 10% MgO solution (Esmaeili et al., 2005) and concentrated  $\text{HNO}_3$  (70%) was used to control pH in the first four beakers, but for the last two beakers higher pH was 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. The results obtained after 20 min of stirring time and then 4 hours of settling time are given in Table 4.

From the above table the maximum chromium removal was observed at pH 10.3 (99.98%) and the minimum chromium removal at pH 5.9 (80.59%). The optimum conditions for chromium 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 chromium 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 ( $K_{\text{sp}} = 1.5 \times 10^{-11}$ ) of the weak base,  $\text{Mg}(\text{OH})_2$ , that furnishes  $\text{OH}^-$  ions very much less 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%). Statistical analysis also showed that generally there is significance difference between each pH values ( $p < 0.05$ ). However, there is no significant difference ( $p > 0.05$ ) in the chromium removal 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.

#### Amount of sludge volume

After 20 min 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 of the 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, MgO :  $\text{Ca}(\text{OH})_2$  : NaOH was 1 : 3.5 : 6.5 as shown in Figure 1. Sludge volumes at optimum pH were measured as 590 mL, 412 mL and 85 mL for each precipitating agents: NaOH,  $\text{Ca}(\text{OH})_2$  and MgO, respectively. This is also compared in Figure 2.

Sludge volume produced by MgO is much less than sludge volume produced by  $\text{Ca}(\text{OH})_2$  and NaOH as shown in Figure 1 and 2 and the ratio of sludge volume at optimum pH values is MgO :  $\text{Ca}(\text{OH})_2$  : 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. Figure 1 and Figure 2 show sludge volume of chromium hydroxide,  $\text{Cr}(\text{OH})_3$  resulted from MgO is also much smaller than the volume when using NaOH and  $\text{Ca}(\text{OH})_2$ . This is important, because it 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 Esmaeili et al. (2005). The statistical analysis showed the mean difference is significant at  $p = 0.05$  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 chromium 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). Therefore, the result obtained in this study showed that MgO is the most suitable precipitating agent for removing and recovering chromium from tanning wastewater.

#### 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 min 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 is shown in Figure 3.

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 per hour, 110 mL per hour and 150 mL per hour for NaOH, Ca(OH)<sub>2</sub> and MgO, respectively. The supernatant volume increases gradually for NaOH, it increases rapidly initially and then gradually for Ca(OH)<sub>2</sub> and increases rapidly for the first 2 hours and then remains constant at the end for MgO. Furthermore, a grainy, dense, easily settled 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)<sub>2</sub> is low with undesirable sludge volume, but faster than NaOH. This is in agreement with the report of Esmaeili et al. (2005).

### Effect of mixing time

Chrome liquor wastewater of 500 mL with chromium concentration 5010±6.6 mg/L, 15% NaOH solution, 10% MgO solution and 12% Ca(OH)<sub>2</sub> solution were used in separate beakers with stirring and the pH of system was measured at 5 min interval, the results obtained are shown in Figure 4.

Optimum time of rapid mixing for the three precipitating agents is shown in Figure 4. The time needed for rapid mixing of NaOH is shorter than others because of its high solubility whereas that of Mg(OH)<sub>2</sub> was longer than the other two precipitation agents. The pH value for NaOH and Ca(OH)<sub>2</sub> is gradually increasing and finally remains constant which occur earlier for NaOH with 100% solubility than Ca(OH)<sub>2</sub>. But pH value of MgO continues to increase gradually because of slow reactivity and the solubility product constant for Mg(OH)<sub>2</sub> is small ( $K_{sp} = 1.5 \times 10^{-11}$  (mol/L)<sup>3</sup>) or its solubility is smaller than that of Ca(OH)<sub>2</sub> ( $K_{sp} = 7.9 \times 10^{-6}$  (mol/L)<sup>3</sup>) and the hydroxide content of NaOH, Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub> are 42.5%, 45.9%, and 58.3%, respectively. 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.

### Effect of pH on precipitating agents

From the wastewater analysis after treatment in each of the six beakers for the three precipitating agents at different pH values, the chromium concentration of the supernatant was measured by atomic absorption spectrometer. The concentration values are indicated in Table 2, 3 and 4 and the graphs are shown in Figure 5. As shown in Figure 5, the minimum concentration of chromium 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, Cr(OH)<sub>3</sub>, has the most stability. However adding more NaOH or as stirring time increases, pH increases and this results in peptizing or redissolving. When using Ca(OH)<sub>2</sub> increasing pH decreased the chromium concentration. This discrepancy between NaOH and Ca(OH)<sub>2</sub> 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 Cr(OH)<sub>3</sub> formed is almost stable in pH range of 8.6-9.1.

In contrast since the solubility of Ca(OH)<sub>2</sub> is lower than NaOH base, pH increases gradually. However, in the case of Ca(OH)<sub>2</sub> adsorption causes chromium ions take apart from the supernatant (Esmaeili et al., 2005). Since the reactivity and solubility of Mg(OH)<sub>2</sub> is low at lower pHs chromium concentration is high. The optimum pH for Ca(OH)<sub>2</sub> 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 Table 5.

When the maximum percentage of 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 chromium concentration of supernatant is smaller than the other two and its sludge volume is almost half of sludge volume of Ca(OH)<sub>2</sub> 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 5. The minimum metal hydroxide, Cr(OH)<sub>3</sub>, solubility obtained by each method are approximately the same, that is the solubility product constant,  $K_{sp}$ , of Cr(OH)<sub>3</sub> is  $6.7 \times 10^{-31}$  (mol/L)<sup>4</sup>.

### Chromium recovery efficiency of 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)<sub>3</sub> sludge was taken. After adding about 3 mL of concentrated H<sub>2</sub>SO<sub>4</sub> with stirring until pH 2.8, basic chrome sulfate solution was produced. The formula of basic chromium sulfate produced vary at different pHs, for example BCS with formula Cr<sub>4</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>3</sub> is produced in the pH range 3.0-4.0 (Barbooti 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% Cr<sub>2</sub>O<sub>3</sub> 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. The results are given in Table 6.

After digestion of the 300 mg of dry sludge (BCS) using HNO<sub>3</sub>, 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

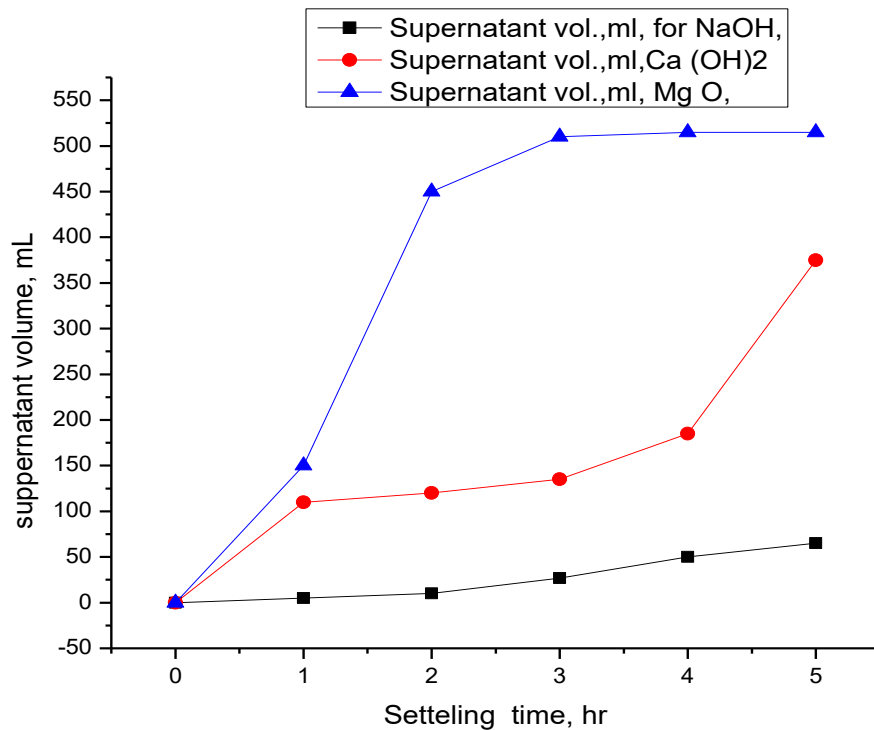


Fig. 3: Precipitation settling rate for the three precipitating agents

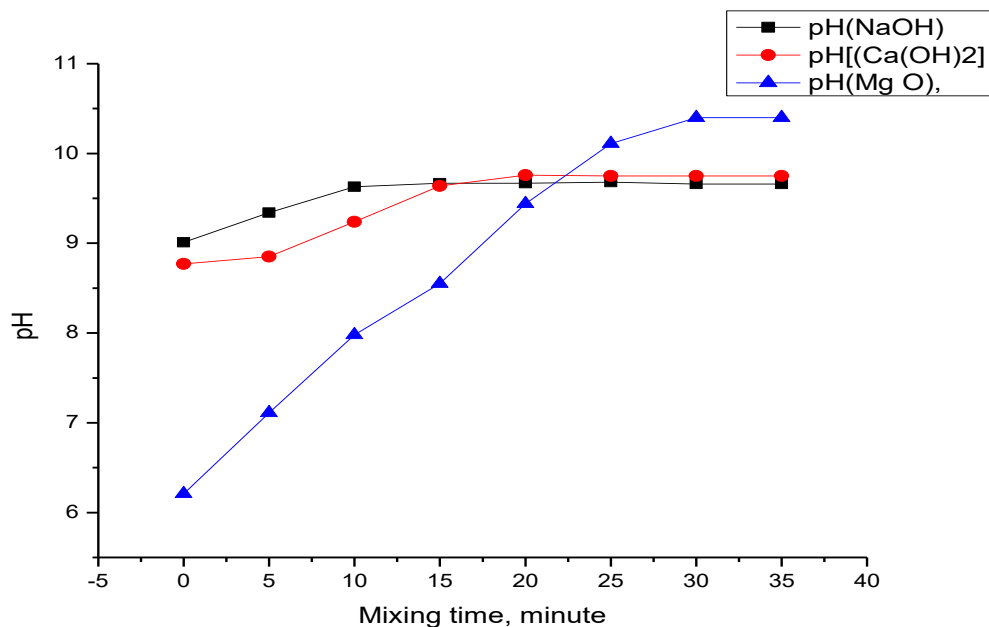
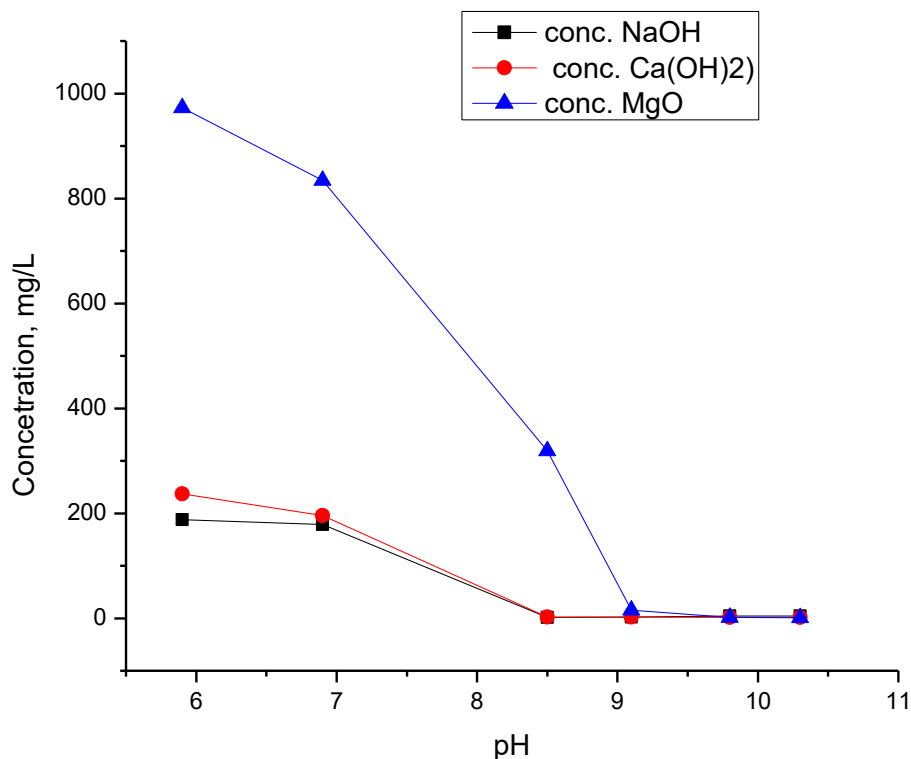


Fig. 4: Variation of pH vs mixing time for the three precipitating agents (rate of mixing 90 rpm in the hot plate)

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



**Fig. 5:** Chromium concentration in the supernatant solution vs pH for the three precipitating agents (after 4 hours settling)

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, 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 Share Company 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<sup>3</sup> this is equivalent to 1.5 m<sup>3</sup> (1500 liters) for skin and 0.85 m<sup>3</sup> (850 liters) for hide. The amount of basic chromium sulfate (BCS) recovered or determined from 500 mL chrome waste treated with MgO at pH 9.8 was approximately 8 g. Directly proportionally if 1.5 m<sup>3</sup> chrome wastewater were to be treated for recovery 24000 g (24 kg)

BCS could be recovered for skin out of 90 kg BCS offered and 13600 g (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% (% R = BCS recovered/BCS offered x 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 sammying 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)<sub>3</sub> 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<sub>2</sub>SO<sub>4</sub> 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). So far results revealed that the precipitation methods is efficient for the removal of chromium from tannery wastewater and could be used for wastewater contains chromium ions. Under the current scenario of environmental pollution (Abbas et al., 2018; Ahamd et al., 2017; Arshad et

**Table 5:** Chromium removal efficiency at optimum pH for the three precipitating agents

Precipitating agents	Optimum pH range	Effluent Cr conc. (mg/L)	Supernatant Cr conc. (mg/L)	Sludge volume (mL)	Max. % of Cr removal
NaOH	8.6-9.1	5010±7	1.35±0.15	590	99.97
Ca(OH) <sub>2</sub>	8.6-10.3	5010±7	1.5±0.10	412	99.97
MgO	9.8-10.3	5010±7	1.0±0.00	85	99.98

**Table 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.

al., 2018; Aslam et al., 2018; Bhatti et al., 2017a; Bhatti et al., 2017b; Bhatti et al., 2016; Bibi et al., 2017; Bilal et al., 2016a; Hussain et al., 2017; Iqbal, 2016), there is need to adopt efficient methods like precipitation to clean the environment contaminated with chromium and other heavy metals (Arris et al., 2016; Chen and Ray, 2001; Gupta and Ali, 2004; Liu et al., 2016; Monser and Adhoum, 2002; Ngah and Hanafiah, 2008; Rengaraj et al., 2001; Sharma and Malaviya, 2016; Srivastava et al., 2016). This methods is efficient for the removal of metal ions from wastewater and these findings are in line with previous studies employed for the removal of metals ions using precipitation method (Barakat, 2011; Chen et al., 2009; Gjengedal and Steinnes, 1990; Lazrus et al., 1970; McDonald et al., 1996; Papadopoulos et al., 2004).

## CONCLUSIONS

The pollution load of the selected parameters: chrome waste Cr (5010 mg/L), composite Cr (139 mg/L), BOD<sub>5</sub> (2796 mg/L), COD (7553 mg/L), TN (634 mg/L), S<sup>2-</sup> (139 mg/L), TS (11342 mg/L) and TSS (3463 mg/L) was above the discharge limit set by environmental protection authority: Cr (2 mg/L), BOD (200 mg/L), COD (500 mg/L), TN (60 mg/L), S<sup>2-</sup> (1 mg/L) and TSS (50 mg/L). There is no significant difference in recovery efficiency at optimum pH: NaOH (99.97%), Ca(OH)<sub>2</sub> (99.97%) and MgO (99.98%). However, there is significant difference in sludge volume: NaOH (590 mL), Ca(OH)<sub>2</sub> (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. If treatment of the tannery wastewater or chrome waste is done properly using MgO at the required pH

9.8 and recovery using concentrated H<sub>2</sub>SO<sub>4</sub> at about pH 2.8, the basic chromium sulfate so produced accounts almost 30% and is suitable for tanning mixed with 70% fresh basic chromium sulfate from the market.

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