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Removal of Chromium from Metal Finishing Wastewater by Lime Coagulation

Getachew Meka[1], Alemayehu Abebaw [2] and Mekibib Dawit [3]

[1]*Ambo University, Graduate School of Environmental Science, Ambo, Ethiopia*
[2]*Ambo University, Chemistry Department, P. O. Box 19, Ambo, Ethiopia*
[3]*Addis Ababa University, Environmental Science Department, P.O.Box1176, Addis Ababa*

Abstract

This study is carried out to assess the levels of total chromium in the chrome plating wastewater and its removal by chemical precipitation using lime water suspensions. The wastewater produced from chrome electroplating is huge and complex which far exceed the assimilative capacity of nature and lead to an irreversible health and ecological consequence. Wastewater samples are collected from Homicho Ammunition Engineering Industry. The physicochemical analysis and heavy metal concentrations determined for different parameters using FAAS and titration. The average results obtained are: total dissolved solids (20,848.20 ± 0.35 mg/L), total suspended solids 889.55 ± 0.43 mg/L, electrical conductivity (182.26 ± 0.11 mS/cm) , pH (2.64 ± 0.01), Cr^{+6} (196,960 ± 0.70 mg/L), Cr^{+3} (117,20 ± 0.55 mg/L), total Cr (2,155,33 ± 428.99 mg/L), Fe (3,514.50 ± 21.55 mg/L), Pb (1,070.75 ± 3.35 mg/L) and Cu (1,239.16 ± 18.74 mg/L). The samples collected starting from 2002 to 2012 were analyzed separately and the results were found to be significantly different ($p<0.05$) for each parameter. The stored wastewater treated through chemical precipitation by reducing Cr^{+6} with ferrous sulfate in acidic media, (pH 2 to 3.5) to trivalent chromium. Chemical precipitation process was found to be efficient in the removal of chromium from the effluent at different pH (73.68% at pH 7.5; 82.60% at pH 8 and 99.98% at pH 8.5).The treatment of chromium is pH dependent. The percentage removal achieved for the other metals is Cu 89.71%, Fe 94.82%, and Pb 98.27% at pH 8.5 respectively. The best removal for chromium is 99.98% at pH 8.5 leaving 0.16 mg/L in the filtrate which is below permissible limits as per the Ethiopian Environmental protection guidelines. Therefore, this method of removal was found to be cost effective and environmentally friendly.

Key words: Chromium removal; total chromium; lime precipitation; wastewater; Flame Atomic Absorption Spectrophotometer (FAAS)

Introduction

Metal plating encompasses a broad range of processes that are performed on manufactured parts to decorate objects, for corrosion inhibition, to improve solder ability, to improve wearablity, to reduce friction and to alter conductivity of the surface of the article, thus plated metal lend its properties not possessed in its “unfinished state” (Murphy, 1996 and USEPA, 1995). Industrial wastewater often contains considerable amount of heavy metals that would endanger public health and the environment if discharged without adequate treatment. Technology of chromium wastewater neutralization is, in most cases, based on detoxification of waste, which involves reduction of Cr^{+6} to Cr^{+3}(Huber J., 1994). Then precipitation of chromium (+3) hydroxide can be done using ferrous sulfate or calcium hydroxide. Finally, the dewatered precipitate and the sludge obtained would be stored in specially prepared graves.

In Ethiopia, the generation of industrial waste, including hazardous waste, is increasing rapidly. This is as a result of industrialization, urbanization, and the implementation of a new economic policy. While the Ethiopian economy grew by 1.9% in the period 1980 to 1990 in real terms the toxic load generated per unit of industrial output increased by 1.8% which is higher as compared to the Sub-Saharan Africa average of 1.3% (UNIDO, 2001).

Homicho Ammunition Industry (HAEI) has been practicing chrome plating fully since 2005 to present, for corrosion prevention and steel products surface improving purpose. However, the wastes generated from the chromium industry have not ever been treated and simply stored in steel and plastic barrels near the work environment. These contaminants must be removed from the wastewaters before discharge as they are considered persistent, bio-accumulative and toxic substances. The chrome plating wastewater is highly toxic in nature because of the presence of metals such as chromium, copper, lead, and iron.

In HAEI, chrome electroplating industry generates waste effluents amounting to around 500 liter in five years (starting from year 2005 to 2012), or around 300 liter/year (Personal communication). Poor storage and improper disposal of these hazardous wastes may cause irreparable environmental damages in the long term (USEPA, 1995). In addition, it can cause a great health and psychological impact, to the workers as well as the surrounding community. An increase in the level of heavy metals in the environment indicates presence of a serious threat to human health, living resources and ecological systems (Sastre *et al.*, 2002). This study is, therefore, aimed at development of removal techniques for chromium through reduction of the soluble and mobile hexavalent chromium compounds to the less toxic, less mobile and stable ones, which are minimally soluble precipitates.

Materials and Methods

Description of the study area

HAEI is located in the Western Shoa, Oromia Regional State. It is about 140 km far from Addis Ababa, the capital city of Ethiopia, 25 km from Ambo town to the western and 10 km in northern part of Guder. Geographically, it is located at a latitude and longitude of 9^0 02' N and 37^0 44' E respectively and elevation of 1816.3 m a.s.l.

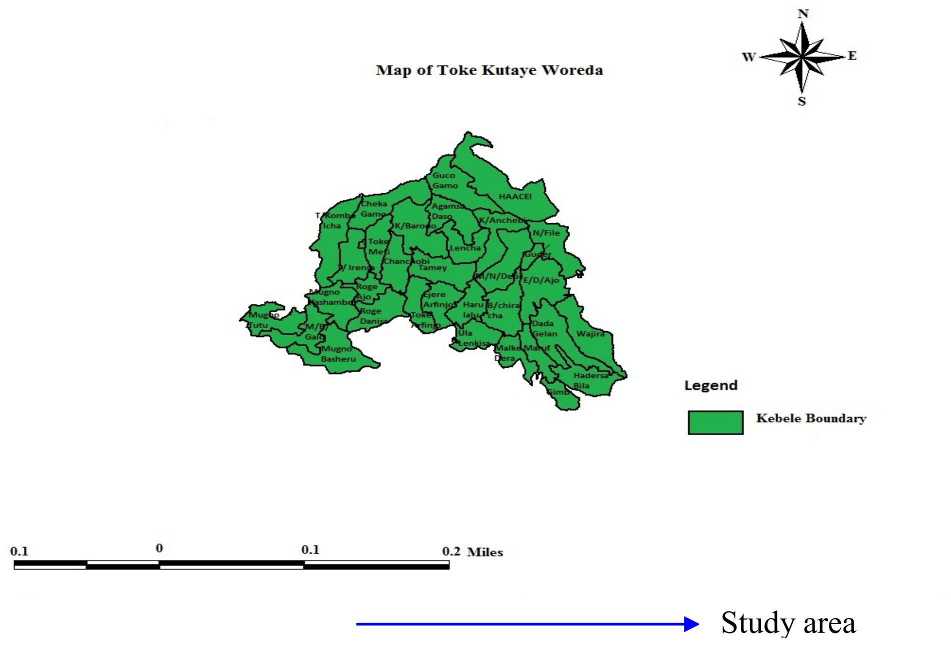

Fig.1. Map of the study area

Experimental Materials

Glassware and Apparatus

Volumetric flasks 20, 25, 100 and 1000 mL for preparation of standards and sample dilutions; pipettes and micropipettes (1 to 5 mL and 50 µL); burettes; Flame Atomic Absorption Spectrophotometer (SL 194, Double beam AAS, ELICO, India) equipped with deuterium background correction for the determination of Cr, Fe, Cu and Pb metals.

Chemicals

All the chemicals used in the study are of pure analytical grade (purity greater than 99.5%) and prepared in deionized water.

Sampling and Sample Collection

The type of samples collected may depend on suspected waste types and characteristics; size and accessibility of waste containers, impoundments and other media; target analytes; health and safety requirements (Huibregtse *et al.,* 2003). The volume of a sample should be sufficient to perform all required laboratory analyses. However, because chromium waste samples are generally of high concentration, sample volumes need to be kept to a minimum (to minimize disposal costs).The samples were coded according to their age; the oldest sample as S_1, the next sample S_2, S_3 and S_4. A total of four representative samples amounting to 500 mL from each stored wastewater were taken by agitating with compressed air from the barrels and one synthetic wastewater containing chromium (the 5th sample, S_5) was prepared at the laboratory scale. Appropriate care was taken during sample collection, transportation, storage, and preparation, to ensure that the species distribution present in the original sample was maintained up to the point of analysis. Polyethylene plastic bottle containers of 500 mL capacity were used for sampling. After collecting, the samples were stored at 4°C to minimize chemical reactivity. The analysis of major species was completed within 24 hours especially for Cr^{+6} and Cr^{+3} .

Sample Preparation for Analysis

Chromium, in its most stable state (Cr^{+3}) can be analyzed by Flame Atomic Absorption Spectrophotometer (FAAS), by gravimetric analysis with a number of reagents such as hydrolysis of potassium cyanate to form an insoluble hydroxide (Perkin-Elmer, 2000). Cr^{+6} can also be analyzed by FAAS and by titration, with standard $Na_2S_2O_3$ with I_2. If the aliquot (to be tested were concentrated) enough (above 0.01M); then analysis by titration or gravimetric techniques were considered. FAAS for chromium speciation was considered only to determine total Cr (all oxidation states). In this study, the sample preparation follows two procedures one for titration the other for FAAS analysis:

For the determination of trivalent and hexavalent chromium; 4 mL of the wastewater was diluted to 100 mL volumetric flask with redistilled water. From the diluted sample, aliquot of 5 mL were taken for the quantification of Cr^{+6} and Cr^{+3}, all the analysis were done in five replicates.

For Flame Atomic Absorption Spectrophotometer (FAAS) analysis, 50 mL of wastewater sample in a glass beaker were taken and 5 mL of concentrated HNO_3 was added on it. The contents of the beaker were covered with watch glass and digested on a hot plate at 180^0C; refluxed until the acid volume was reduced to about 5 mL; then additional 5 mL of concentrated HNO_3 was added to complete the digestion. All samples were digested in similar manner and stored in dark refrigerator at 4^0C till the analysis. While FAAS analysis was run, dilutions were accounted in all subsequent calculation (Perkin-Elmer, 2000).

Determination of Hexavalent Chromium

For the determination of Cr^{+6}, 4 mL of the wastewater sample solution was transferred into 100 mL volumetric flask and diluted with redistilled water till the mark. A portion of this sample was transferred into titration flasks, followed by addition of H_2SO_4 (1:5) and a known excess quantity of 0.1 N Mohr's salt was added in order to reduce Cr^{+6} to Cr^{+3} (reaction 1).

$$2H_2CrO_4 + 6FeSO_4 + 6H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O \text{------------------------(1)}$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O \text{------------(2)}$$

The remaining iron salt was titrated with 0.1 N $KMnO_4$ (reaction 2). Then, the amount of the hexavalent chromium was then calculated as:

$$Cr^{+6}\ (mg/L) = \frac{(V*L-V_1)*3.33)}{G} * 1000 \text{ -------------------------------- (3)}$$

Where: V-volume of Mohr's salt solution added, mL; L-correction ratio between solution of Mohr's salt and $KMnO_4$; V_1- volume of 0.1 N $KMnO_4$ solution spent for the titration of the rest Mohr's salt, mL; 3.33- titer of 0.1 N $KMnO_4$ against Cr^{+6}, mg/L; G-volume of sample taken for the analysis, mL; 1000-coefficient for reduction to the content of Cr^{+6} in a liter of the electrolyte (Douglas A. Skookg *et al*.,2004).

Determination of Content of Trivalent Chromium

The amount of trivalent chromium in was determined by titration using standard solution of $KMnO_4$ by oxidizing Cr^{+3} to Cr^{+6} with $(NH_4)_2S_2O_8$ and calculated as (equation 4 and 5) :

$$Cr_2(SO_4)_3 + 3(NH_4)_2S_2O_8 + 8H_2O \longrightarrow 2H_2CrO_4 + 6H_2SO_4 + 3(NH_4)_2SO_4 \text{ ------------(4)}$$

$$Cr^{+3}\ (mg/L) = \frac{[(V*L-V_1)-(V*L-V_2)]*2.53}{G} * 1000 \text{ ---------------------------- (5)}$$

Where: V_1- volume of 0.1 N $KMnO_4$ solution spent for the titration of Cr^{+6}, mL; G-volume of sample taken for analysis, mL; L- correction ratio between solution of Mohr's salt and $KMnO_4$; V-volume of Mohr's salt added, mL; V_2-volume of 0.1 N $KMnO_4$ solution spent for the titration of Cr^{+3}, mL; 2.53-titer of 0.1 N $KMnO_4$ solution to Cr_2O_3 mg/L (Douglas A. Skookg *et al*.,2004).

Reduction of Hexavalent Chromium to Trivalent Chromium and Precipitation

The wastewater containing Cr^{+3} and Cr^{+6} was quantified stoichiometrically, then the Cr^{+6} reduced by reacting with ferrous sulfate in acidic media pH 2 to 3.5 using acid (H_2SO_4) as catalyst. A retention time of 45 minutes was usually given to ensure adequate mixing and reaction time; this process reduces Cr^{+6} to Cr^{+3}. The total chromium concentrations in wastewater samples were calculated according to Equation 4 and 5 respectively. The maximum dose required was 50 mg/L of ferrous sulfate for 10 mg/L of Cr^{+6}. The removal efficiency of the metal from its solution was calculated as:

$$\frac{(C_i - C_f)}{C_i} * 100\% \text{ ---------------- } (6)$$

Where: C_i-initial concentration; C_f-final concentration

Instrument Calibration (IC)

For calibration of the instrument, a series of standard solution of the interest metal were prepared and determined directly using FAAS. Four points including the blank calibration curves were tabulated for each metal. For all metal species triplicate measurements at each concentration were made and the acceptance criterion for calibration linearity was pre-specified by correlation coefficient (R^2) value of 0.99 (Konieczka and Namiesnisk, 2009). Instrument detection limit (IDL) concentration versus response of the instrument was calculated as (Miller J.N. and Miller J.C., 2010):

$$IDL = Y_b + 3S_{y/x} \text{ ---------------- } (7)$$

Where: IDL- Instrument detection limit; $S_{y/x}$-residual standard deviation and Y_b-Y intercept from the calibration regression equation

The results of the calibration for the different metals are tabulated here in Table 1.

Table 1: Instrument calibration parameters

Metal	Concentration of working standards (mg/L)	Correlation coefficient of calibration curves (R^2)	Linear range (mg/L)	Calibration Equation
Cr	0, 2,4, 8	0.9991	0-8	y=0.01x + 0.0006
Fe	0, 2, 4, 6	0.9991	0-6	y=0.0562 + 0.0072
Cu	0,1,2, 4	0.9986	0-4	y=0.0255x + 0.0012
Pb	0, 2.5, 5, 7.5	0.9998	0-7.5	y=0.0293x + 0.0028

Method Detection Limit (MDL)

MDL is the lowest concentration of analyze that can be detected and reliably distinguished from zero, but not necessarily quantified, the concentration at which a measured value is larger than the uncertainty associated with it. MDL can be expressed in response units and is taken typically as three times the noise level for techniques or three times the standard deviation of the sample (Gonzalez *et al.,* 2007). Seven blank samples were digested following the same procedure as the samples and each of the samples were determined for elements of interest (Cr, Fe, Cu, and Pb). The MDL for each element was calculated as:

MDL = 3SD of the blank; n = 7------------------ (8)

Where: SD-pooled standard deviation of the absorbance; n-number of samples of the blank

The calculated values (Table 2) were lied in the range of 0.008 to 0.018 mg/L, where the lowest is for Fe and the highest for Cr. All the values were found to be in the required control limit, less than 0.1 mg/L. So, it is possible to determine the heavy metals even at trace levels.

Table 2: Method detection limit from blank solution and Instrument detection limit (mg/L)

Metal	MDL*	IDL
Cr	0.018	0.00917
Fe	0.008	0.00574
Pb	0.016	0.00812
Cu	0.017	0.00902

MDL*-Method detection limit; IDL-Instrument detection limit

Recovery Test

In order to see the validation of the method, spiked sample analysis was performed. A known amount of the standard solution was taken and added to the wastewater sample. Samples were taken and measured in triplicate by following the stated sample pretreatment method. The test was performed on one of the sample type of the two wastewater samples, before and after treatment. From the standard Cr, Pb, Cu and Fe metal solutions, known amount the metal was added to the wastewater. The spiked samples underwent the same entire sample preparation and analysis steps and their mean recovery result was calculated as (Harvey D., 2000):

$$\% \text{ R} = \frac{(C_M \text{ in the spiked sample} - C_M \text{ in the unspiked Sample})}{C_A} \text{ ---------------- } (6)$$

Where: % R-percentage of recovered amount; C_M-concentration of the metal; C_A-concentration of metal added for spiking

For this study a known amount of the metals concentration is spiked and recovered quantity was tabulated in Table 3.

Table 3: Percent recoveries of metals from matrix spike of chrome plating wastewater before treatment and after treatment (mean ± SD, n=5)

Metals	Before treatment		After treatment		Amount of standard sample added (mg/L)
	%R**	RSD*	%R**	RSD*	
Cr	96.75 ± 2.38	2.45	90.91 ± 3.9	4.2	4
Cu	93.16 ± 2.75	2.95	96.16 ± 4.64	4.82	2
Fe	90.91 ± 1.87	2.05	91.16 ± 1.84	2.01	4
Pb	95.73 ± 8.81	9.20	95.46 ± 12.93	13.54	1.25

Where: %R**-percentage recovery; RSD*-Relative standard deviation

Data Analysis

Data were processed using descriptive statistical techniques and SPSS version 16. The significance of variation between wastewater concentrations were determined by pair comparison between the mean and one way ANOVA at $p<0.05$.

Results and Discussion

Physical and Chemical Characterization of Chrome Plating Wastewater

The data recorded on the physicochemical characterization of the main polluting heavy metal ions and other parameters viz., pH, and heavy metal levels found in the electroplating effluents at HAACEI before removal of Cr are presented in Table 3 and 4 respectively. The hexavalent and trivalent chromium content of the wastewater were ranged from 121960 ± 0.5 mg/L to 259990 ± 0.96 mg/) and 710 ± 0.26 to 26650 ± 0.89 mg/L. Chromium was taken as a target metal for treatment process. The interest in chromium is governed by the fact that its toxicity depends critically on its oxidation state (Cielak-Golonka M., 1995). The wastewater was acidic in nature and the pH ranged from 2.3 ± 0.01 to 2.8 ± 0.03 with mean value of 2.64 ± 0.012.

Table 1: Mean concentration (mean ± SD mg/L, n=5) of metals in chrome plating wastewater before treatment

Parameters	Collection points				
	S_1	S_2	S_3	S_4	S_5
Cr^{+6}	121960 ± 0.5	276840 ± .96	259990 ± .96	177830 ± .38	148190 ± .07
Cr^{+3}	10960±1.46	26650± 0.89	17590± .006	2700 ± .15	710 ± 0.26
pH	2.8 ± 0.03	2.5 ± 0.00	2.3 ± 0.01	2.8± 0.01	2.8 ± .02
SO_4^{2-}	3270 ± 0.01	5690 ± 0.32	8270 ± 0.25	5110 ± 0.56	2100 ± 0.02
TSS	430.22±0.81	1259.33± 0.04	1037.33±0.54	1000.16±0.21	720.74±0.56
TDS	1204.2±0.46	30826.66±0.03	29259.33±0.63	28166.61±0.38	14784.21±0.25
EC**	111.83±0.29	323.03±0.06	172.23±0.06	141.53±0.06	162.7±0.10

EC**-The unit is in mS/cm

Total Suspended Solids (TSS)

The TSS in the wastewater is ranged from 430.220 ± 0.81 gm/L to 1259.33 ± 0.04 mg/L as cited in Table 4. It is evident from the results that the wastewater contains high TSS which above the permissible limits when compared with the standard set by National Environmental Quality Standards (NEQS, 2000) and (EEPA, 2003). The highest value was recorded in sample (S_2) ; this is because there may be a maximum dissolution of iron metals in addition to the other heavy metal components. This study confirms that these effluents may cause problem if discharged into river or stream (EEPA, 2003).

The high value of total dissolved solids is a good indication that there an existence of maximum dissolved salts of heavy metals and the corresponding maximum Electrical Conductivity is also related the maximum availability of ions in the wastewater which can harm if discharge to the environment (NEQS, 2000).

Heavy Metal Concentrations

Concentrations of the heavy metals were analyzed using FAAS. During the measurement of the content of metals, further dilution was made in all the digested wastewater samples, to bring the concentration of the interest metal within the instrument calibration. Heavy metal concentrations found in the present study from the raw the four wastewater samples and one synthetic wastewater is presented in Table 5.

Table 5: Mean concentration (mean ± SD mg/L, n=5) of heavy metals in chrome plating wastewater before treatment by FAAS test

Para Meters	Collection points				
	S_1	S_2	S_3	S_4	S_5
Cr	122400 ± 100	327133.3±1858.32	287800± 100	189783.3 ± 28.87	150033.3± 57.74
Pb	120.33 ± 0.58	2079.66 ± 1.53	1676.67 ± 5.77	406.33 ± 5.51	ND
Fe	2973.33 ± 23.09	8986.66 ± 23.09	2040 ± 40	58 ± 0.01	ND
Cu	400 ± 0.01	1986.66 ± 23.0	1676.66 ± 5.77	893.33 ± 46.19	ND

ND-below detection limit

Chromium concentrations in all samples were found significantly higher than the other metals; the values ranged from 327,133.3 mg/L (highest in S_2) and 122,400 mg/L (lowest in S_1). Significant differences ($p<0.05$) were found among the wastewater analyzed. The main source of chromium was from the composition of the bath; since the major composition of chrome plating were CrO_3 and H_2SO_4.

The extents of Fe concentrations (Table 5) were in the range of 58 mg/L to 8,986.66 mg/L, having highest value in S_2 and lowest in S_4. Similar to chromium the result for Fe shows significant differences ($p<0.05$) among the wastewater samples. It is most likely introduced through the dissolution of ferrous base metals and the materials to be plated.

Pb might have been released from the anode (electrode) of the plating bath. The concentration of Pb detected in the wastewater samples were ranged from 2079.66 ± 1.53 mg/L to 120.33 ± 0.58 mg/L; highest in S_2 and lowest in S_1 (Table 5). From the statistical analysis, significant differences ($p<0.05$) were observed among the wastewater samples.

Sources for Cu in this wastewater is mainly from the wearing away of Cu sheet which connects the lead electrode with the power supply. The concentration of Cu in the wastewater samples found in the range of 1986.66 ± 23.0 to 400 ± 0.01 mg/L; highest in S_2 and lowest in S_1. One-way ANOVA showed significant differences ($p<0.05$) between the wastewater samples.

pH

The pH of the wastewater was ranged from 2.3 to 2.8 and the pH of the synthetic wastewater was adjusted to 2.8 with H_2SO_4. This pH values may adversely affect the aquatic life and the environmental natural resources due to its high acidic nature (Postel *et al*., 1997). The high acidity of the wastewater was from the bath composition that is, the added H_2SO_4 and the acidic nature of chromic anhydride (CrO_3).

Wastewater Treatment

To treat concentrated wastewater from the plating process as well as diluted wastes already being treated at the facility was cost driven. The decision also reflected sludge disposal costs, equipment requirements and safety considerations. The concentration ranges of the wastewaters are: Cr from 122,400 ± 100 mg/L to 327,133.3 ± 1,858.32 mg/L; Pb from 120.33 ± 0.58 mg/L to 2,079.66 mg/L and Fe from 2,040 ± 40 mg/L to 8,986.66 ± 23.09 mg/L cited in Table 5.The distribution of this heavy metals found are beyond the assimilative capacity of nature as the standards set by World bank (World Bank, 1998) and National Environmental Quality Standards (NEQS, 2000).

The Cr^{+6} are first reduced to Cr^{+3} using ferrous sulfate; the pH is limited to 2 to 3.5 through the addition of sulfuric acid. The removal of chromium values from the electroplating wastewater comprised contacting the acidic solution containing sulfate ion and trivalent chromium ion with at least about 4 milimoles of calcium oxide (CaO) against 3 milimoles of trivalent chromium. The above conditions enable neutralization reaction to form adequate amorphous, dense solid, grainy solid, that can easily precipitate (Sorg *et al*., 1979). The water remaining after separation of the precipitate contains less than 50 mg/L chromium which is close to some reported results (Hemming *et al*. 1978).

The treatments were carried out at varying pH values: 7.5, 8.0, and 8.5. The results of the set of experiments are given in Table 6. The lime was added according to the stoichiometric ratio in the first set of the experiments and stirred at 120 rpm. A retention time of 45 minutes was maintained to ensure adequate mixing and complete reaction with the chromium or other heavy metals: Cu, Fe and Pb. After sedimentation, the initial concentration which ranges from 124 to 3271.33 mg/L was reduced to concentration range of 30.69 to 758.94 mg/L (65% to 75.3%) removal efficiency which is much greater than the permissible limit. Reasonably, an efficient removal of iron is observed at the pH 7.5. The second set of experiment was done at pH 8.0; the lime concentration was increased slowly, understanding that the added lime does not only react with the total chromium it can also react with the other heavy metals like Pb, Cu, and Fe found in the wastewater sample. When the pH and the amount of lime balanced with continuous string; the formation of yellow precipitate is resulted. Then, for complete precipitation the stirring was stopped and allowed to settle for 30 minutes. Finally, the concentrations of the chromium, after treatment, were found in the range of 22.69 mg/L to 415.46 mg/L, and the removal efficiency range is 74.2 to 87.3%. The maximum dose of lime at pH 8.5, which gives the maximum chromium removal efficiency of 99.81% to 99.99%, is obtained.

The Removal Efficiency of Copper and Lead

The results as cited in Table 6, shows that the percent removal of copper with increasing pH and different lime dosage. As the pH increases, the efficiency to remove copper from the wastewater increases. The maximum practical removal is defined as the removal beyond which a minor improvement was made with increasing lime dosage and pH. This indicates the effect of the lime is more significant at higher initial copper concentration. This observation is further demonstrated at pH 8.5, where the removal efficiencies increased to the maximum with 89.71% mean value. The trend, increase in removal of metal with increase in dose of lime, is apparent at pH 8.5, which is found true for all metals studied in this work.

The result as cited in Table 6 shows that the initial concentrations of Pb samples were: 1.2, 20.79, 10.8 and 4.06 mg/L are significantly reduced to 0.02, 0.04, 0.04 and 0.02 mg/L respectively, in the first set of experiments. At first, the pH of the wastewater was adjusted to 7.5 and the removal efficiencies obtained were 20.83, 20.79, 10.8 and 4.06%. Further addition of lime increases the removal efficiency of lead at pH 8.0. Unlike the other three metals (Cu, Fe and Cr) the percent removal of lead was lower with small increment from the first set of the experiment. The removal efficiencies recorded was 33, 43, 36.4 and 31.8%. Addition of more lime at pH 8.5 enhances the percent removal to 97.5, 99.8, 96.29 and 99.5%. This is the pH at which the maximum removal was attained. Further addition of lime cannot increase removal Pb, on contrary it destabilizes the precipitate.

The removal of all the four heavy metals were found to be efficient at alkaline solution (pH= 7.5 to 8.5) which can be applied for the removal of the wastewater collected in the Industry (HAEI).

Table 6: Effective lime dosage for the removal of heavy metals under different metal concentrations and pH

Sample	Lime dose (mg/L)	Total Cr (mg/L)		Fe (mg/L)		Pb (mg/L)		Cu (mg/L)		% R of Fe	%R of Cu	% R of Cr	% R of Pb
		Initial	Final	Initial	Final	Initial	Final	Initial	Final				
pH 7.5													
S_1	150	124	30.69	29.73	1.87	1.2	0.95	4	0.91	93.73	77.25	75.29	20.83
S_2	4655	3271.33	758.94	89.86	2.52	20.79	13.58	19.86	3.77	97.2	81	76.8	20.79
S_3	4093	2876.33	724.84	58	2.09	10.8	8.01	16.76	3.49	96.4	79.2	74.8	10.8
S_4	2699	1896.66	460.88	20.4	1.47	4.06	3.15	8.93	2.16	92.79	75.8	75.7	4.06
S_5	213	150.03	84.3	ND	ND	ND	ND	ND	ND	-	-	65.8	-
pH 8.0													
S_1	200	124	22.69	29.73	1.64	1.2	0.80	4	1.19	94.48	70.25	81.7	33
S_2	4735	3271.33	415.46	89.86	1.52	20.79	11.85	19.86	1.56	98.3	61	87.3	43
S_3	4143	2876.33	425.69	58	1.61	10.8	6.87	16.76	1.43	97.22	64.25	85.2	36.4
S_4	2779	1896.66	292.08	20.4	1.39	4.06	2.76	8.93	1.5	93.2	62.5	84.6	31.8
S_5	263	150.03	38.71	ND	ND	ND	ND	ND	ND	-	-	74.2	-
pH 8.5													
S_1	260	124	0.23	29.73	1.03	1.2	0.03	4	0.41	96.53	89.8	99.81	97.5
S_2	4795	3271.33	0.21	89.86	2.67	20.79	0.04	19.86	1.35	97.03	93.2	99.99	99.8
S_3	4213	2876.33	0.02	58	1.97	10.8	0.04	16.76	1.31	96.6	92.2	99.99	96.29
S_4	2699	1896.66	0.29	20.4	2.22	4.06	0.02	8.93	1.46	89.12	83.65	99.98	99.5
S_5	2123	150.03	0.04	ND	ND	ND	ND	ND	ND	-	-	99.97	-

Conclusion and Recommendations

Electroplating wastewater is characterized for metal concentrations to be discharged into the water bodies. The results have indicated that metal concentration loading were very high. On the basis of laboratory scale studies, the extent of removal of chromium by limewater suspension is effective. Experimentally, 99.97% to 99.99% chromium removal efficiency achieved. Chemical precipitation by limewater is inexpensive which removes/precipitates the Cr and the other heavy metals (Cu, Pb and Fe) at optimum pH level. Competing reactions, at varying levels of pH and other factors typically make calculation for proper chemical dosages made impossible. Therefore, frequent tests are necessary for confirmation of optimal treatment conditions. On the other hand, overdosing of the lime can diminish the effectiveness of the treatment.The results show that there were significant differences ($p<0.05$) in all heavy metal concentrations among the examined wastewater samples. The treated water should be stabilized before discharging into the river; if needed to be discharged further dilution with tap water should be done and the precipitate recovered can be land filled in well designed grave. The removal method is cost effective and environmental friendly.

Therefore, it is suggested that although conventional precipitation of chrome plating wastewater treatment approach would allow the industry to remove the heavy metals effectively, it should be recognized that reduction of the waste at the source can minimize the ongoing cost, by implementing proper bath operating parameters and modification of equipments to scale up the results at the Industrial level.

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