Proceedings of Civil and Water Resources Engineering Conference
3-4 November 2017, BIAM Foundation, 63 Eskaton, Dhaka, Bangladesh
ISBN: 978-1-925488-52-4

Efficiency of Different Alkalis in Removing Chromium from Chrome Tanning Liquor Waste In Tannery Industries of Bangladesh

Md. Billal Hossain[1], Arnob Barua[2] and Md. Delwar Hossain[3]

This research presents the process of removing chromium as well as color and COD from chrome liquor through chemical precipitation. Initially chromium concentration of sample was 5607ppm. After conducting series of jar tests, residual chromium for 5000mg/l of MgO, NaOH and $Ca(OH)_2$ was 0.21ppm, 0.76ppm, 5.61ppm respectively and sludge volume ratios were 1:1.26:2.22. For cost efficiency, different combinations of $Ca(OH)_2$ and others were used. 5:1 ratio of $Ca(OH)_2$:NaOH showed better removal & higher cost efficiency.

Keywords: chemical precipitation, chromium, color, COD, lime, MgO, NaOH, sludge volume, cost efficiency.

Name of the Broad Field of Research: Civil and Environmental Engineering,

Introduction:

Chromium pollution by tannery operations are ranked within the top ten pollution problem[1]. Basic Chromium Sulphate ($Cr(OH)SO_4$) is usually used for chrome tanning step for hide stabilization against microbial degradation. Cr ion concentration in the tannery wastewater were found to be 2500-8000 ppm[2] . Chromium causes the water and soil contamination and indirectly causes the serious health problem and environmental problems[3].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(0.5mg/l for surface waters by ECR,1997[4]) . Chromium exists in environment both as trivalent and hexavalent forms, and the hexavalent is much more toxic than the trivalent[5]. Hexavalent chromium is considered a potential lung carcinogen[6]. High concentration of toxic chemicals from chrome tanning liquor has already taken considerable dimension to threaten public Health and environment. Chemical precipitation is the most widely used method because of its maturity in technique, simplicity in equipment, flexibility in operation[7]. The main objective of this study was to find out an effective precipitating agent for chemical treatment of the tannery Chrome liquor . In precipitation method soluble Chromium ions are converted to insoluble Chromium hydroxide by adding an alkali-precipitating agent. This method has benefit of recovering chrome liquor for further tanning process.

[1]Undergraduate student, Dept. of Civil Engineering, Bangladesh University of Engineering & Technology
[2]Undergraduate student, Dept. of Civil Engineering, Bangladesh University of Engineering & Technology
[3]Professor, Dept. of Civil Engineering, Bangladesh University of Engineering & Technology
[1]billal1204172@gmail.com, [2]arnobtuku@gmail.com [3]delwar@ce.buet.ac.bd

ISBN: 978-1-925488-52-4

Literature Review:

S. S. Tahir and R. Naseem (1996)[8] performed their analysis on tannery wastewater to investigate an alternative for Cr removal from an electroplating wastewater using the electro-chemical precipitation (ECP) process. Dinesh Mohan, Kunwar P Singh, Vinod P Singh(2006)[9] developed an efficient process for the decontamination of trivalent chromium from tannery effluents. A low cost activated carbon (ATFAC) was prepared from coconut shell fibers (an agricultural waste), characterized and utilized for Cr(III) removal from water/wastewater. Fenta Minas (2011)[10] investigated the applications of chemical precipitation method for chromium removal and its recovery in one of the leather industries in Ethioipia. Abass Esmaeili , Alireza Mesdaghi nia and Reza Vazirinejad[11] investigated Chromium (III) Removal and Recovery from Tannery Wastewater by Precipitation Process. Sowmya T.P, Prof. G.K. Mahadevraju[12] experimented Remmoval Of Hexavalent Chromium From Industrial Waste Water By Chemical Treatment

Methodology:

Jar test:

The chrome liquors were collected from chrome tanks of two different tanneries Apex and Reliance Tannery before liming. A series of jar tests were conducted to determine the effect of pH, sludge volume, settling rate. For performing jar tests six beakers were used and 250 ml of Chrome liquor was added to each beaker. Different amounts of alkalis were added in the sample for making different concentrations of alkali mixtures. For example, 1.25g alkali was added in the 250ml for alkali concentration of 5000mg/l in the chrome water. pH was taken into optimum level 8-8.5. Solutions of alkalis were added to the beaker as per the requirement of a particular test. The samples were stirred by the flocculator for 40 minutes at rpm 90. As pH of waste sample was increased, $Cr(OH)_3$ was formed which is insoluble in water. So after flocculation, flocs were allowed to be settled down. The effects of each factor on the three precipitating agents were measured by fixing the effect of the other variables. The supernatant was collected cautiously with pipette and pH, color, COD and chromium content in the treated water was determined. After flocculation by jar test, when the flocs begin to settle down. The settling rate of sludge is being measured for 1 hour within 20 minutes interval.

Determination of Cr:

From the collected supernatant sample, some were taken for the determination of Chromium. For the determination of Cr, first the supernatant were filtered by using filtered paper then 9 ml was taken and 1 ml HNO_3 was added to the sample for the proper digestion of the Chromium. Then it was heated for two hours in COD reactor. After heating, it was being cooled for 30 minutes and then the sample was diluted to 10 times by taking 1 ml digested sample and adding 9 ml distilled water in a test tube. The diluted sample was again diluted to 10 times, further dilution was done until we got sample that was 10000 times diluted than supernatant sample. The samples that were diluted to 10, 100, 1000, 10000 times were taken to the AAS machine for the determination of Chromium. The dilution was done for making the AAS machine easier

ISBN: 978-1-925488-52-4

for determination of Chromium. If there is possibility of higher chromium content, the sample which is 10000 times diluted is used for determination of Chromium.

COD Determination:

Prior to COD determination, first we took 2 ml sample and added it to COD vile in a test tube. There were high range vile and low range vile, if the sample seemed to contain high range of COD we took high range and otherwise low range vile was used. After that we heated the mixture with COD reactor for two hours and cooled it for 30 minutes. After cooling, without any disturbance, it was taken to the spectrophotometer for the determination of COD.

Color Determination:

For determination of color, the sample was filtered with filter paper. Then it was taken to the spectrophotometer which measures the amount of photons (the intensity of light) absorbed after it passes through sample solution. It gives the measurement by comparing the color of distilled water with the sample. So, we put distilled water then made it zero in the spectrophotometer after zeroing it we put the sample and took the reading.

Result & Discussion:

The characteristics of the chrome liquor are shown in Table 1.

Table1: Characteristics of chrome tanning wastewater

Pollutants parameter	Unit	Apex Tannery Sample
pH		3.4
BOD5	mg/l	2835
Color	Pt-Co	7500
COD	mg/l	12100
Cr	ppm	5607
Turbidity	NTU	74
DO	mg/l	2.76
EC	mS/cm	80

The results show that the tanning chrome water is highly acidic and it has massive level of Cr, BOD and COD which is much higher than ECR limit. So it is highly toxic and will do catastrophic effects on environment if it is exposed without proper treatment.

Effect of concentration of precipitating agents:

The removal efficiency of Cr(III) varies with the concentrations of precipitating agents. Cr removal efficiency was observed by adding varying doses of precipitating agents to 250 mL Chrome liquor. The curve shows that greater concentration brings greater Cr removal efficiency.

ISBN: 978-1-925488-52-4

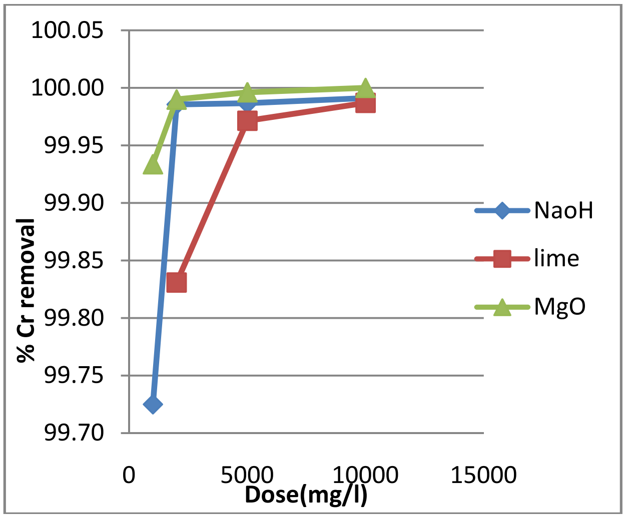


Figure 1**:** Chromium concentration in the supernatant solution after treated by three precipitating agents

Performance of chromium removal by MgO was better than NaOH and $Ca(OH)_2$. The concentrations of alkalis were 1000 mg/l, 2000 mg/l, 5000 mg/l and 10000 mg/l.

Effects of Sludge Volume and Settling Rate:

After the jar test, the sludge begins to settle down in graduated cylinder. The ratio of sludge volume after 1 hour at optimum pH values V_{MgO} : V $Ca(OH)_2$: V_{NaOH} was 1 : 1.26:2.216. Here from the data we can see that, the sludge volume produced by MgO is much less than sludge volume produced by $Ca(OH)_2$ and NaOH. The reason for the smaller volume of sludge by MgO is the sludge formed by MgO is grainy, dense and easily settle able. Whereas the sludge formed by NaOH and Ca(OH)2 are gelatinous and dewatering is also difficult.

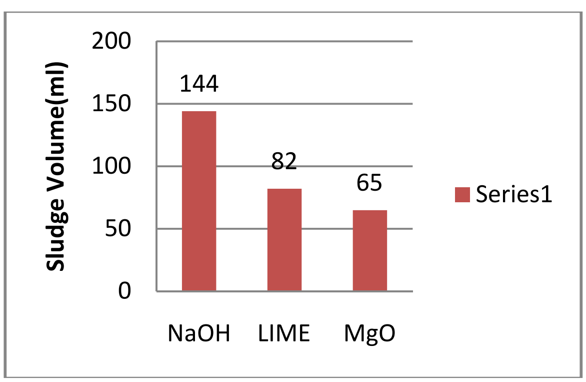


Figure 2**:** sludge volume produced by the three precipitating agents

Here from the data we can see that, the sludge volume produced by MgO is much less than sludge volume produced by $Ca(OH)_2$ and NaOH. The reason for the smaller volume of sludge by MgO is the sludge formed by MgO is grainy, dense and easily settle able. Whereas the sludge formed by NaOH and $Ca(OH)_2$ are gelatinous and dewatering is also difficult. This is important, because less sludge not only helps to reduce the volume of treatment plants but also recovering chromium from such sludge

ISBN: 978-1-925488-52-4

is much easier than sludge with huge volume. As the reaction proceeds, the amount of precipitate increases as small size precipitate gets adhered together and lead to maximum precipitation, sometimes other chemical entities (ions and molecules) also get adhered with precipitate and mass of precipitate increases. When the reaction mixture is kept for settling, the removal of chromium ion increases with increase of settling time. Settling rate can be measured in terms of sludge volume per unit time or the volume of supernatant per unit time.

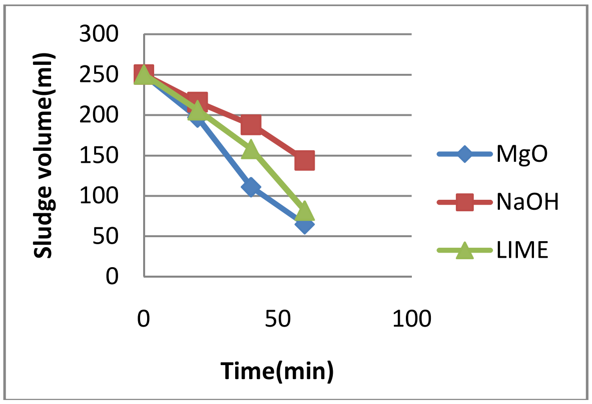


Figure 3: Precipitation settling rate for the three precipitating agents

Removal of COD:

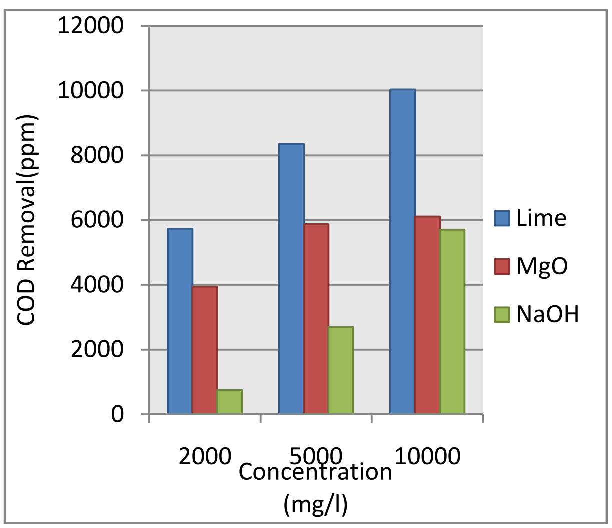


Figure4: Comparison between the precipitating agents on COD removal

Here, we can see that, COD removal efficiency increased with the increment of concentration of doses of these alkalis. If we compare these alkalis in case of removal efficiencies of COD, it can be said that, lime is the most effective in COD removal than NaOH , MgO.

Removal of Color:

Color removal efficiency is found satisfactory in the precipitation method. The effluent appeared very clear in the naked eye. Overall 98% to 99.9% of removal efficiency is achieved through treatment with NaOH, MgO and $Ca(OH)_2$.

ISBN: 978-1-925488-52-4

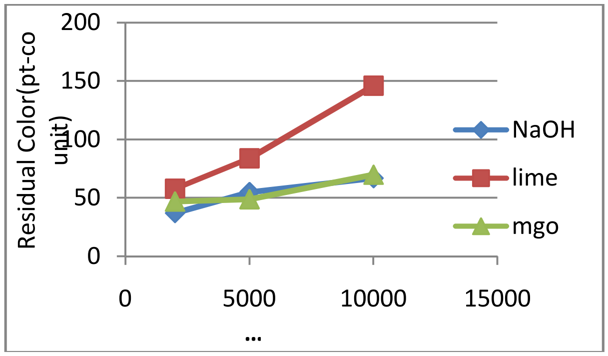
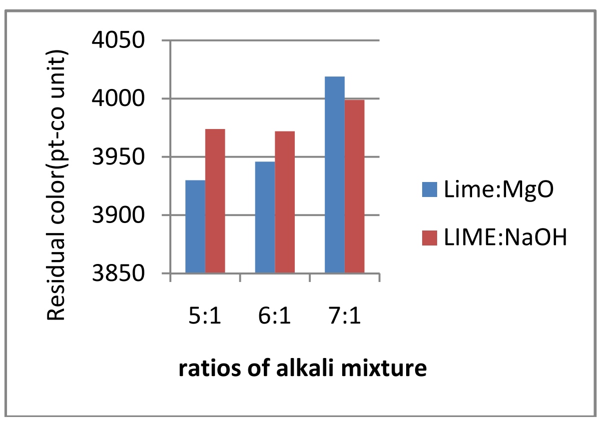


Figure5: Comparison between the precipitating agents on color removal

The graphical presentation showing the effects of concentration of alkalis on the color shows that, color removal efficiency is decreased with the increased concentration of alkalis. Color increased after 24 hr settling time because at equilibrium stage substance that is responsible for color might come to the supernatant layer.

Removal of Cr, Color and COD using combination of alkalis:

In case of Lime:MgO mixtures of ratio (5:1, 6:1, 7:1) the color removals were 3930 , 3946 , 4019 respectively . Therefore, we can see that, if we increase the percentage of lime the color removal efficiency will decrease.



- Figure 6: Comparison of color between different ratios of Lime and MgO and Lime and NaOH

- Best COD removal was achieved from 7:1 ratios of both MgO and NaOH. There was also some irregularity in the result.

ISBN: 978-1-925488-52-4

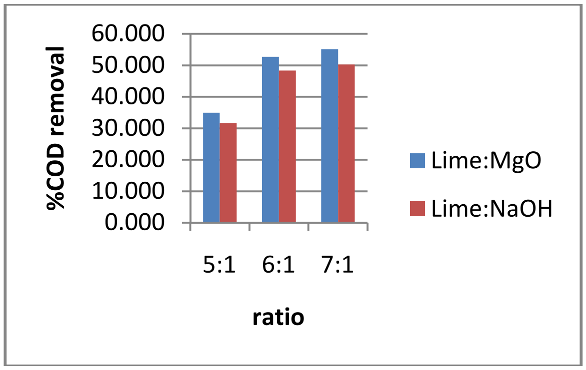


Figure 7: Comparison of COD removal efficiencies between different ratios of Lime and MgO and Lime and NaOH

If we observe the figure below we can see that, chromium removal efficiency of lime: MgO mixture is better than lime:NaOH mixture. When the ratio is 5:1, residual Cr after the treatment of lime:MgO was 0.337ppm and with lime:NaOH residual Cr was found 0.517ppm.

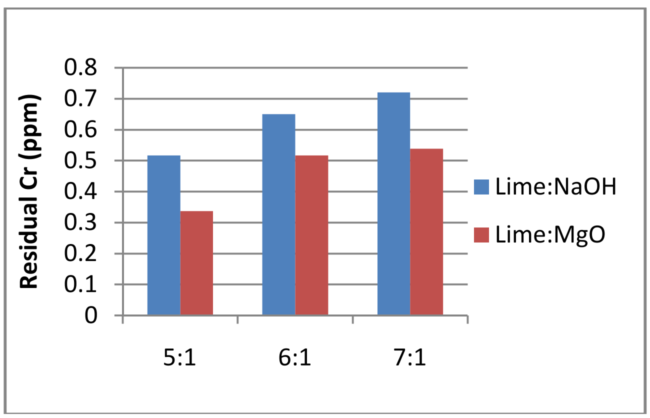


Figure 8: Comparison of final concentration of Cr between different ratios of Lime & MgO and Lime & NaOH

Cost Effectiveness:

Though with all considerations, MgO is the most effective precipitating agent in chromium removal among these three alkalis. But if we do cost analysis, we see that, using only MgO is not cost effective. Per Kg cost of MgO,NaOH and Lime are 2500, 1800 and 18.5Tk respectively. Therefore, mixing of alkalis with limes can be done to make the treatment cost effective. In this study, we tried mixing NaOH and MgO with lime at different ratios and observed its removal efficiency of different parameter.

ISBN: 978-1-925488-52-4

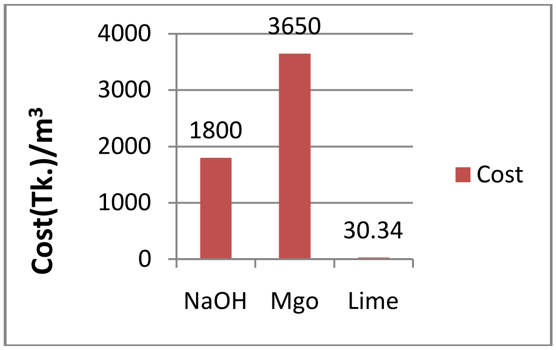


Figure 9: Cost analysis of precipitating agents used to treat Chrome liquor

If we use 7:1 ratios of lime:MgO instead of only MgO or only NaOH. The cost would be reduced 4.97 times in case of NaOH and 6.38 times in case of MgO. For 7:1 cost reduction was found more.

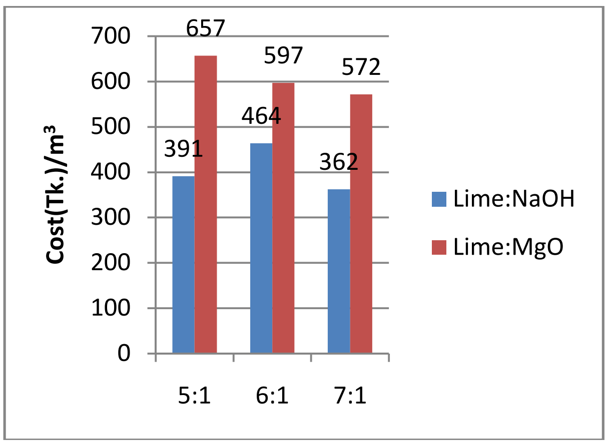


Figure 10: Cost analysis of different ratios of Lime and MgO and Lime and NaOH

Conclusion:

1. COD removal was insignificant by the chemical treatment process. There was still a significant amount of biodegradable waste was present. Therefore effluent should be taken to CETP for further treatment.
2. pH is the dominant factor in treating the chrome liquor by chemical precipitation method because at higher pH Cr(III) was in insoluble form.
3. Color removal efficiency decreases with the greater concentration of doses. Concentration of residual color was higher in Lime treatment than other alkalis.
4. MgO is the best precipitating agent as its sludge accumulation rate was found much less than NaOH and $Ca(OH)_2$. So recovery is easier than other precipitating agent. Settling rate of NaOH is too slow that, greater retention time will be needed for the treatment of waste
5. In this study, cost analysis was done and it was found that using MgO and NaOH was not cost effective. Therefore, they can't be used in large scale in developing countries. Combination was done for increasing cost efficiency

Reference:

1. http://www.thedigproject.dk/planets/leather-and-its-toxic-effects-on-humans-and-the environment.
2. Hafez A. I., El-Manharawy M. S. and Khedr M. A. (2002), "Ro Membrane Removal of Untreated Chromium from Spending Tanning Effluent", A pilot scale study, part 2, Desalination, 14: 237-242.
3. FAO (2013). World Statistical Compendium for raw hides and skins, leather and leather footwear 1993-2012. Trade and Markets Division
4. *Environment Conservation Rules,* 1997 *(ECR,* 97), Gazette Notification, 27 August, Ministry of Environment and Forest, Government of the Peoples Republic of Bangladesh
5. Kowalski Z. (1994), "Treatment of Chromic Tannery Wastes", J. Hazard. Mater. 37, page:137-141.
6. Wang W. (1986), "The Effect of River Water on Phytotoxicity of Ba, Cd and Cr", Journal on Environment Pollution, Vol. 11, page: 193.
7. Mottalib M. A., Islam M. S., Alam M. N. and Abser M. N. (2015), "Removal of Chromium from Tannery Wastewater by Tannery Lime Liquor; A Very Cost Effective Method", International Journal of Current Research, Vol. 7, Issue 06, pages: 16795 -16798.8.
8. S.S.Tahir, R.Nasee (2007),"Removal of Cr(III) from tannery wastewater by adsorption onto bentonite clay", Journal on Separation and Purification Technology, Volume 53, Issue 3,Pages 312-321
9. DineshMohan, Kunwar P.Singh, Vinod K.Singh(2006), "Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth", Journal of Journal of Hazardous Materials, Volume 135, Issues 1–3, Pages 280-295
10. Minas, F.(2011)," Application and investigation of chemical precipitation method for Chromium removal and its recovery in one of the leather industries in Ethiopia", A Thesis submitted to the School of Graduate Studies Addis Ababa University
11. Abass Esmaeili, Alireza Mesdaghi nia and Reza Vazirinejad,(2005)." Chromium (III) Removal and Recovery from Tannery Wastewater by Precipitation Process", American Journal of Applied Sciences 2 (10): 1471-1473,
12. Sowmya T.P, Prof. G.K. Mahadevraju, (2013)," Removal Of Hexavalent Chromium From Industrial Waste Water By Chemical Treatment", International Journal of Innovation Research and Development, Vol.2 ,Issue 5