IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 12, Issue 10 Ver. I (October. 2018), PP 01-06
www.iosrjournals.org

aRemoval Of Chromium From Tannery Waste Liquor By Using Lime Liquor In Regarding The Reduction Of Environmental Pollution And Reuse It In Leather Production

[a]Syed Badrul Hasan, Md. Abdul Mottalib[*], Arnob Hore, Noor Mohammed And Fatema-Tuj-Zohra
Institute of Leather Engineering and Technology, University of Dhaka, Dhaka-1209, Bangladesh
corresponding author: Md. Abdul Mottalib

Abstract: *Basic chromium sulfate is the most widely used chemical for tanning processes, but 60-70% of total chromium salt reacts with the hides. Rest of the amount about 30-40% of the chromium remains in the liquid wastes. Therefore, the recovery and reuse of the chromium content of these wastewaters are necessary for environmental protection and economic reasons. Removal of chromium was carried out by using precipitation process. Maximum precipitation of chromium was obtained from a mixture of chrome and lime liquors in the ration of 1:1(v/v) and the pH of the solution became 7.5-8.5. Precipitation of chromic hydroxide converted into basic chromium sulfate by treating sulfuric acid.*

This recovered basic chromium sulfate was used in the manufacture of goat skin. Three goat skins were tanned conventionally only differ in tanning step as one skin was tanned by commercially available basic chromium sulfate, one was tanned by recovered basic chromium sulfate and third one was tanned by a mixture of chrome powder (20%) and recovered basic chromium sulfate (80%). Physical tests results like tensile strength, stitch tear strength, tear strength, ball bursting test, water vapor permeability, flexing endurance, color rub fastness of all three finished leather revealed that the leather tanned by 100% and 80% recovered basic chromium sulfate were almost similar to the leather which was tanned by pure basic chromium sulfate.

Key words: *Chrome liquor, Lime liquor, Precipitation, Environmental pollution, Tensile strength.*

Date of Submission: 04-10-2018 Date of acceptance: 16-10-2018

I. Introduction

Tanning is a process of converting putrescible outer coverings of animals to non-putrescible leathers with definite physical, chemical and biological properties so that they can be used in our daily life and industries. Soaking, unhairing & liming, deliming, bating, pickling, tanning and retanning processes are the major stages of tanning process. In general, a maximum of 240 kg hide substance can be used as leather out of 1100 kg fresh weight or 1000 kg salted weight (as bought by the tanneries). The remaining parts are waste or by-products. Therefore, in any case, hair, fat, non-collagenous proteins, mucopolysacharides etc. have to be eliminated from the hide. Alkali (mainly hydrated lime), sodium sulfide etc. are used for this purpose. Chrome tannin the commonly used tanning agent was first introduced about 100 years ago but still now it is the main mineral tanning material. Chromium salts (basic chromium sulfate) are the most widely used tanning substances today. Unfortunately skins react with only 60-70% of the chromium salts used in the tanning process and the remainder being left in the water phase.

Sulfide and chromium are the two major chemical constituents of the wastewater ejected from the tanning industry. These chemicals mixed with water are discharged from the tanneries and pollute the ground water permanently and make it unfit for drinking, irrigation and general consumption [1]. Chromium has also a very bad effect on human health. A little amount of trivalent chromium (50 to 200 micrograms) has been recommended for good health but hexavalent chromium is one of the common factors for causing cancer in human body [2].

According to G. Maliotis, maximum permissible levels of chromium, which can be contained in the effluent when released is 0.5 m/L [3]. Therefore, it's the order of the day how to manage this big amount of tannery effluents. Some methods had been used for removing of chromium are chemical or electrochemical precipitation [4], cation exchange membranes [5], solvent extraction and filtration [6], oxidation/reduction, filtration, ion exchange, membrane separation and adsorption [7]. But in most cases prior experiments introduce extra cost for removing or recovering of chromium. The main objective was to eliminate this extra cost and to reduce environmental pollution caused by discharged lime liquor. Maximum chromium can be recovered from the spent liquor when it was mixed with lime liquor in the 1:1(v/v) ratio [8]. Lime effluent is used as

precipitating agent; hence, there is no need of additional chemicals and no more cost involved in this process as well as one can reduce pollutants from lime liquor.

Three leathers (goat) were assessed for physical properties such as tensile strength, stitch tear strength, tear strength, ball bursting test, water vapor permeability, flexing endurance, color rub fastness. One of them was tanned by conventional tanning process using basic chromium sulfate powder, another was tanned by recovered basic chromium sulfate solution and a mixture of basic chromium sulfate powder (20%) and recovered basic chromium sulfate solution (80%) are used as tanning agent for another skin. All three leathers showed excellent physical and chemical test results.

II. Experimental:

Collection of samples:

Wastewater-fresh lime liquor and chrome liquor were collected from tannery industrial area at Savar, Dhaka, Bangladesh and transferred to the laboratory for the determination of pH and chromium contents as soon as possible.

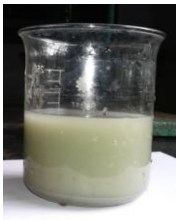

Fig: lime liquor (waste water)

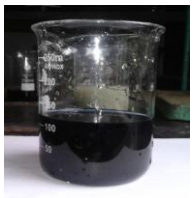

Fig: chrome liquor (waste water)

Formation of precipitation:

In order to form precipitation, chrome liquor was treated with lime liquor. According to the simple acid-base reaction, precipitation of $Cr(OH)_3$ was formed. 40 mL of chrome liquor were taken in four different conical flasks, then 10, 20, 30 and 40 mL of lime liquor was added so that the ratios of chrome liquor and lime liquor were 40:10; 40:20; 40:30 and 40:40 v/v respectively. The mixtures were stirred for overnight at room temperature and left for a few hours for sedimentation. The chromium precipitates were in the form of compact sludge and was filtered through whatman no. 42 filter paper. The filtrates were analyzed for the determination of pH and chromium content. The maximum precipitation can be gained when the waste liquors are mixed at 1:1 (v/v) ratio [8].

Weigh of precipitate: The filtrate sludge was dried at room temperature and then at 110^{o}C for 2 hour to remove all amount of water. After cooling it was weighed again. $Cr(OH)_3$, $Ca(OH)_2$ and other compounds contribute to the sludge.

Calculation:

The pH of the reaction mixture have a vital role to reduce chrome content from the waste liquor and maximum amount of chromium reduced, over 99% at pH 8.4 when chrome and lime waste liquor were mixed at a ratio of 1:1 (v/v) [8].

Volume of chrome waste liquor	= 40 mL
Volume of lime waste liquor	= 40 mL
Weight of the blank filter paper, w_1	= 0.778 g
Weight of the dried filter paper after filtration, w_2	= 3.723 g
Weight of precipitate, (w_2-w_1)	= (3.723-0.778) g = 2.945 g

Recovery of basic chromium sulfate:

In conventional tanning process 80-100% water is used in pickling step. Half of the pickled bathe is drained out before tanning. Then 8% basic chromium sulfate is mixed with the rest of the pickled bath along with other ingredients. As 60-70% of chrome salt can penetrate into the leather and rest of the salt is disposed with the effluent.

Total 2.945 g of dried sludge was added into 100 mL distilled water in a 500 mL beaker and then sulphuric acid was added to it until pH raise to 2.8-3.0. The mixture was stirred for 1-2 hours to obtain maximum solubility at 40-60^{o}C.

$Cr(OH)SO_4$	+	$Ca(OH)_2$	=	$Cr(OH)_3$ +	$CaSO_4$	
$Cr(OH)_3$ +	H_2SO_4		=	$Cr(OH)SO_4$	+	$2H_2O$
$Ca(OH)_2$ +	H_2SO_4		=	$CaSO_4$	+	$2H_2O$

Recovered basic chromium sulfate liquor was separated by filtration. Weight of the sludge remain in the filter paper was 1.659 g which might be contained calcium salt and others unknown materials. The amount (1.286 g) of $Cr(OH)_3$ in the first sludge was determined by subtracting these two sludge's/solids. This amount of $Cr(OH)_3$ produces 2.06 g of $Cr(OH)SO_4$ by acid treatment.
2.06 g of $Cr(OH)SO_4$ produced from 40 mL chrome waste liquor.
Therefore, 1g $Cr(OH)SO_4$ can be produced from 19.42 mL chrome waste liquor.

According to experimental data we found, the weight of the sludge gained from the tanning and lime effluent was 1.286 g. After recovering of basic chromium sulfate, the weight of the residue was 1.659 g which contains $CaSO_4$, $Ca(OH)_2$ and other constituents.

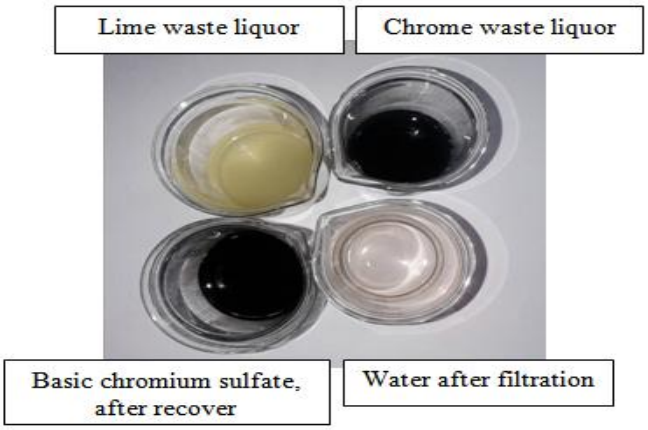

Fig: different stages of laboratory test

Tanning in drum:
Three pieces of pelt (goat skin weighted 1.8 kg, 1.4 kg and 1.4 kg) were tanned with fresh basic chromium sulfate, mixed (80% recovered basic chromium sulfate) and recovered basic chromium sulfate.
Calculation for waste water needed to tan a piece of pelt (1.4 kg):
According to conventional process 8% basic chromium sulfate was used for tanning and 4% for rechroming. Therefore, a total of 12% basic chromium sulfate was needed.
So, amount of basic chromium sulfate was needed for tanning 1.4 kg pelt = (1400×12%) g = 168 g
According to above calculation, 1g basic chromium sulfate can be produced from 20 mL chrome waste liquor.
So, (20×168) mL or 3.26 liters chrome waste liquor was used for recovering the required basic chrome sulfate.

Module for chrome recovery:

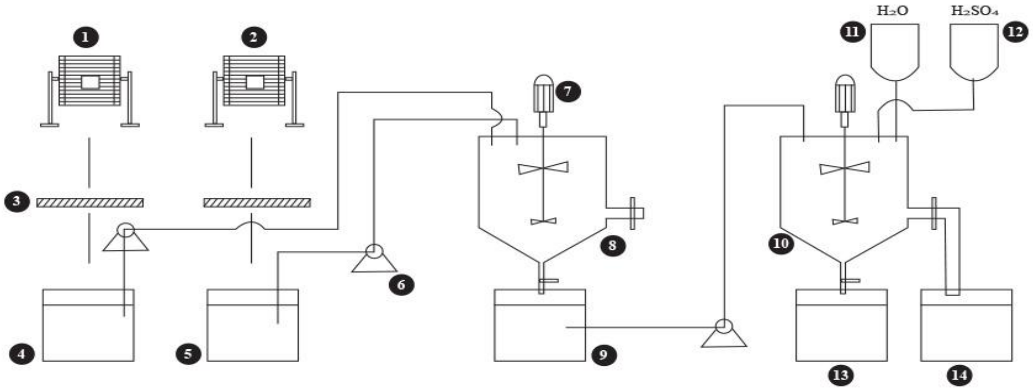

Fig: flow diagram of chrome recovery unit

1. Chrome liquor containing drum
2. Lime liquor containing drum
3. Screen
4. Catch pit for chrome liquor
5. Catch pit for lime liquor
6. Pump
7. Stirrer
8. Main reactor
9. Sludge storage tank
10. Chrome liquor regenerator tank
11. Water containing tank
12. Sulphuric acid containing tank
13. Sludge storage tank
14. Recovered basic chromium sulfate liquor storage tank.

III. Results and discussion

Three goat skins were tanned conventionally only differ in tanning step as one skin was tanned by basic chrome powder (Fig. 1), one was by recovered basic chrome sulfate liquor and a mixed solution of chrome powder (20%) (Fig. 2) and produced chrome sulfate solution was used for tanning the third one (Fig. 3).

Fig. 1 **Fig. 2** **Fig. 3**

The main physical properties namely tensile strength, stitch tear strength, tear strength, ball bursting (lasto meter), water vapor permeability, flexing endurance and color rub fastness were tested and their results are shown in Table 1. The tests were carried out in accordance with IULTCS (International Union of Leather Technologists and Chemists societies) and SATRA (Shoe and Allied Trade Research Association). Relevant chemical property namely Cr_2O_3 content of three types of leathers were tested. From the results of chemical and physical properties of analyzed samples it was revealed that the quality of three types of leathers were mostly similar.

Table 1: Data from various physical and chemical tests of the three leathers:

Sl. No.	Test Name (unit)	Leather Type			Standard Value for upper leather (according to UNIDO) [14]
		Processed with fresh chromium	Processed with fresh and recovered chromium	Processed with recovered chromium	
1.	Chromic oxide content (%)	3.264	2.960	2.707	Min 2.5
2.	Tensile strength (N/mm^2)	26.989	24.254	20.807	Min 20
	Elongation (%)	54.54	55.56	54.00	Min 40
3.	Stitch tear strength (N/mm)	91.138	79.850	71.997	Min 60
4.	Flexing endurance test (Break pipiness scale rating after 50000 cycle)	3/4	4	4/5	Max 3/4
5.	Tear strength (N/mm)	27.655	31.646	29.528	Min 40
6.	Grain crack load/ lastometer test (N)	441.299	402.072	333.426	Min 200
	Distension (mm)	8.12	7.40	8.44	Min 7
7.	Water vapor permeability ($mg/cm^2/hr$)	7.191	7.512	5.424	Min 1
8.	Dry color rub fastness (Grey scale rating after 1024 cycle) a. Color change of leather b. Staining on felt	a. 5 b. 4/5	a. 5 b. 4/5	a. 5 b. 4	a. Min 3 b. Min 3

IV. Discussion

Chrome tanning compounds in leather or in tanning baths and materials were determined and calculated as chromic oxide (Cr_2O_3) by the perchloric acid method. According to IUC 8, upper leather should have minimum 2.5% Cr_2O_3. The results showed in Table 1 explained that all three leathers have higher values than the minimum requirement. The leather processed by fresh basic chromium sulfate, mixed basic chromium sulfate and recovered basic chromium sulfate have 3.264%, 2.960%, 2.707% chromic oxide (Cr_2O_3) content respectively.

The tensile strength is maximum tensile stress recorded in extending a test piece to breaking point. Tensile strength is good realm to check whether the leather upper has sufficient structural resistance [9, 10]. The percentage elongation is the tensile strain of the upper leather of the shoe in the test length at breaking stage. The elongation at break shall provide a medium value, so that the leather has enough elasticity to adapt user's feet and to the movements derived from the use of footwear [11]. The elongation should not be too excessive to avoid the ease of footwear deformation [9, 11]. The IUP 6 test method demonstrated that the minimum requirement for the tensile strength is greater than 20 N/mm^2 and percentage of elongation is greater than 40%. Comparing this minimum requirement with the test result showed in Table 1 that all the three leathers have shown good performance in tensile strength but almost same in percentage of elongation.

The tear strength is the median force required to propagate a cut in a specified test specimen. The leather upper should possess high flexibility to prevent the appearance of cracks and tears in the ball area of the footwear upper [9, 11]. The samples used for stitch tear strength and tearing resistance, using the DIN 53331 and IUP 8 testing method respectably. The test results have been presented in table 1. The DIN 53331 test method ascertained that the minimum average tear load of leather upper should be greater than 60 N/mm. While IUP 8 demonstrated that minimum 40 N/mm load is needed for tearing the upper leather. Comparing these standard requirements with the test results illustrated that all three uppers achieved the minimum requirement for stitch tear strength but not for tearing resistance. The samples designated as leathers processed by fresh basic chromium sulfate, mixed basic chromium sulfate and recovered basic chromium sulfate have shown very less performance, 31.646 N/mm, 29.528 N/mm, 27.665 N/mm respectively for tearing resistance.

The vamp and linear flexes are used to determine the flexing endurance of leather uppers and their surface finish after repetitive use in the same and opposite flexing cycle. The tendency for cracks to form in the crease caused by walking can be determined [9]. The leather and its finish shall have high flexibility to prevent the appearance of cracks and tears in the ball area of the footwear upper [9, 11]. The samples were used for flexing endurance using the IUP 20 testing method by using flexometer. The test result of this method has been presented in Table 1. The IUP 20 test method embarked that the performance requirement for the ball flexes to be no significant damage at 50,000 cycle at dry stage. The laboratory test result defined that the crease starts to happen after 25,000 cycle as the break pipiness rating is 2/3, 3/4, 4 and after 50,000 cycle the rating was measured as 3/4, 4, 4/5 for leather processed by fresh basic chromium sulfate, mixed basic chromium sulfate and recovered basic chromium sulfate respectably. Hence according to the minimum requirement, only the leather processed by fresh basic chromium sulfate achieved good performance.

The ball burst is used to define the capability of the finished upper leather to withstand for the ball shaped steel material to crack as instantaneously increasing enforcement. The grain layer shall have a high elasticity, which allows it to withstand the elongation stresses to which it is subjected during footwear lasting, especially on the toe area [11, 12]. The leather upper of both goat and sheep is by far used for the distension and grain strength tests using the ball burst technique with the IUP 9 test method. The test result of this mechanical test is presented in table 1. The IUP 9 standard revealed that the minimum performance requirement for leather uppers of footwear for distention at the crack is greater than 7 mm and require min 200 N load. Comparing with the test result expressed that all the samples of the grain strength were above the minimum performance of the leather upper.

The water vapor permeability is to assess the upper leather's breathability, mainly in leather coated with very thick films. Persuading this breathability prevents the heat generated and accumulation, and consequently avoids the sweating of the foot. The samples were used for water vapor permeability test using the SATRA PM 172 testing method. The test result of this method has been presented in Table 1. The SATRA PM 172 test method embarked that minimum requirement for WVP is 1 $mg/cm^2/hr$. The test results indicated that leather processed by fresh basic chromium sulfate, mixed basic chromium sulfate and recovered basic chromium sulfate having very good water vapor permeability and their values were 7.191 $mg/cm^2/hr$, 7.512 $mg/cm^2/hr$ and 5.424 $mg/cm^2/hr$ respectably.

The color fastness to rubbing is resistance of a material to damage and transfer or bleeding of the materials surface color during mild dry or wet abrasion after repetitive rubbing. Leather upper has to possess adequate fastness to rubbing, so that rubbing does not substantially change the leather appearance [11, 13]. For unlined footwear, it is important to provide a good fastness on the grain side to avoid staining on stockings or feet. The mechanical test for the color fastness has been taken for the finished goat leather that are made ready

to be used as upper for leather footwear manufacturing. The test method of SATRA PM 8 has been carried out. The test result of color fastness is presented in Table 1. The performance requirement for the color fastness at dry condition according to SATRA PM 8 is 3 (according to grey scale rating) after 1024 cycles. Comparing the test results with the standard requirement illustrated that inferring the felt pad grade the all three leathers has achieved the standard.

V. Conclusion

Chrome tanning is the chemical process by which putrescible animal hides and skins are converted into leather. Trivalent chromium in the form of basic chromium sulfate, is commonly used for this process. During chrome tanning leather takes around 60-70% of the applied chromium and the remaining is discharged as spent chrome liquor directly into effluents. Chromium occurs in the environment primarily in two valence states, trivalent chromium (Cr III) and hexavalent chromium (Cr VI). Chromium (III) is much less toxic than chromium (VI). Human studies have clearly established that inhaled chromium (VI) is a human carcinogen, resulting in an increased risk of lung cancer.

On the other hand if lime liquor discharges directly from the tanning industry it will pollute soil and water and aquatic life would not be survive at high alkaline water. Calcium hydroxide would inevitably come in contact with carbon dioxide during this process and leave behind an insoluble form of calcium carbonate.

However, the recovery process of chromium from chrome waste liquor using waste lime liquor is efficient, relatively simple and cheap. Almost complete precipitation of chromium occurred at a volume ratio of 1:1(v/v) of lime waste liquor from chrome waste liquor. The use of lime waste liquor as precipitating chemical reduces the cost of chromium recovery as well as reduces the pollution load. All three finished leathers revealed that the leather tanned by full and mixed recovered basic chromium sulfate liquor were almost similar to the leather which was tanned by fresh basic chromium sulfate. On the other hand it aids in increasing profit of the industry and very importantly it saves the environment.

Acknowledgements:

The authors would like to acknowledge the financial assistance of the Ministry of Science and Technology, The Governments of The People's Republic of Bangladesh for carrying out this research work.

References:

[1]. S. Srivastava, A. H. Ahmed and I. S. Thakur; Removal of chromium and pentachlorophenol from tannery effluents. Bioresoure Technol, 2007, **98**, 1128-1132.
[2]. John, F. Papp; Annual report- Chromium.US Department of interior BUREAU of Mines, 1994.
[3]. G. Maliotis; Chromium uses and markets, Published by industrial minerals information ltd- Park house, park Terrace worceter Park, Surrey KT4 7HY- England, 1996.
[4]. M. Bosnic, J. Buljan and R. P. Daniels; Pollutants in Tannery Wastewater, United Nations Industrial Development Organization (UNIDO), Regional Programme for Pollution Control in the Tanning Industry in South-East Asia, 2000, report US/RAS/92/120, 1-26.
[5]. E. A. Mehmet, D. Sukru; A New Approach To Modification of Natural Adsorbent For Heavy Metal Adsorption, Bioresource Technology, 2007, **99**, 2516–2527.
[6]. M. Rafatullah, S. Othman, H. Rokiah, A. Anees; Adsorption of methylene blue on low-cost adsorbents: A review, Journal of Hazardous Materials, 2009, **177**, 70–80.
[7]. E. Pehliva, H. Kahraman, E. Pehlivan; Sorption equilibrium of Cr (VI) ions on oak wood charcoal (Carbo Ligni) and charcoal ash as low-cost adsorbents, Fuel Processing Technology, 2011, **92**, 65–70.
[8]. M. A. Mottalib, S. H. Somoal, M. S. Islam, M. N. Alam and M. N. Abser; Removal of chromium from tannery wastewater by tannery lime liquor; a very cost effective method, international journal of current research, 2015, **7(06)**, 16795-16798.
[9]. SATRA, Testing Equipment Catalogue, 2011.
[10]. ESA (Ethiopian Standards Agency), The quality standards for leather and leather products, Addis Ababa, Ethiopia, 2012.
[11]. INESCOP (Center for Technology And Innovation), Manual For Oxazolidine Tanned Leather: Environmentally Friendly Oxazolidine-Tanned Leather (LIFE08 EN/E/000140), 2013, available at
[12]. http://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=home.showFile&rep=file&fil=OXATAN_Manual_Curticion.pdf Internacionale, Product Performance Standards & Re-stricted Substances", Third body laboratory, 2013.
[13]. Woolworths Quality Assurance, Footwear Quality Standard and Testing Requirements, 2013.
[14]. Acceptable quality standards in the leather and footwear industry, United Nations Industrial Development Organization (UNIDO), 1996, Sales no. UNIDO.95.4.E, **95-60209**, 95.

asyed Badrul Hasan "Removal Of Chromium From Tannery Waste Liquor By Using Lime Liquor In Regarding The Reduction Of Environmental Pollution And Reuse It In Leather Production. ""IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT) 12.10 (2018): 01-06