

Low Cost Recovery and Reuse of Chromium from Spent Chrome Liquor of Hazaribagh Tannery

Adnan Hossain Khan¹, Minera Pervin², A.M. Sarwaruddin Chowdhury² and Manoranjan Saha^{2*}

¹Bangladesh College of Leather Technology, Dhaka University, Dhaka-1000, Bangladesh

²Department of Applied Chemistry and Chemical Engineering, Dhaka University, Dhaka-1000, Bangladesh

Received on 16.02.2010, Accepted for Publication on 30.06.2010

Abstract

Chrome and lime tannery waste liquors that produced from cow shoe upper leather manufacturing were collected from East Asia Tannery in Hazaribagh area near Dhaka city. The chrome effluent was treated with different volumes of lime effluent with continuous stirring. At the volume ratio of lime effluent to chrome effluent, 1:5 the total precipitation of chromium occurred. The pH value was observed 7.5 ± 0.1 at the stage of complete precipitation. The chromium precipitate was then collected through filtering, washed three times with distilled water, air-dried and grinded. The grinded chrome powder was converted to basic chromium sulfate solution using concentrated sulfuric acid and sodium hydroxide solution. Goatskins were retanned as shoe upper leather in conventional method using converted basic chromium sulfate solution. Physical and chemical parameters of this manufactured leather were done and found to be similar to shoe upper leather using commercial basic chromium sulfate. The filtrate obtained after chromium recovery was safely disposed after aeration.

I. Introduction

Heavy metals released by a number of industrial processes are major pollutants in marine, ground, industrial and even treated wastewaters¹. According to the world health organization^{2, 3} the metals of most immediate concern are arsenic, chromium, cadmium, cobalt, copper, lead, nickel, mercury and zinc. The treatment of the effluents and removal of heavy metals have received considerable attention because of their association with various health problems to the majority of living organisms⁴.

Chrome tanning is the chemical process by which putrescible animal hides and skins are converted into leather. Trivalent chromium (Cr^{3+}), in the form of basic chromium sulfate, is commonly used for this process. During chrome tanning leather takes around 50-60% of the applied chromium and the remaining is discharged as spent chrome liquor directly into effluents.

After 2nd world war, numerous attempts have been made to find technically and economically viable means for recovering the chromium. All these attempts can be divided into two broad categories; process change during leather manufacturing and chromium recovery from effluents. In 1959 Petruschke⁵ concluded that ion exchange would be impractical for chromium recovery because dilute acid solution had to be used in the regeneration step to prevent a breakdown of the resin. Weber⁷ calculated that recovery of chromium by ion exchange would be very expensive because of blockage of the exchange columns and high regeneration costs. Aravindhan et al.⁶ studied on bioaccumulation of chromium from tannery wastewater using chemically modified seaweed *Sargassum wightii* and 83% of chromium recovery was possible by 6 hours of time through adsorption process. However, the most suitable result on chromium recovery was observed through chemical precipitation method and a number of individuals have reported experimental results^{5,8,9}. Fields⁹ conducted experiments using sodium bicarbonate, sodium carbonate,

calcium hydroxide, magnesium oxide and sodium hydroxide in combination with a polymer. He observed that sodium hydroxide gave the clearest supernatant while magnesium oxide gave the most compact precipitate. Constantin and Stockman⁵ observed effectiveness in the chromium removal using different alkali. In their opinion, the order of the used alkali was: calcium hydroxide > sodium hydroxide > ammonium hydroxide > sodium carbonate. The order filterability of the chromium sludge was found to be: calcium hydroxide > sodium carbonate > ammonium hydroxide > sodium hydroxide. Apart from alkaline precipitation process, incineration in alkaline pH of 8 to 9 at a temperature range 760 to 980 °C was observed^{10,11,12} but found to be less cost effective. So far our knowledge is concern, no investigation has been done to recover chromium from tannery chrome spent liquor using lime spent liquor as precipitating agent and then reuse of that recovered chromium in leather processing. This recovery process is relatively simple and cheap. Therefore the objective of this process is to find an economically viable way to recover and reuse of chromium from tannery spent chrome liquor and compare the tanning quality of that recovered chromium with commercial chrome tanning agents.

II. Materials and Methods

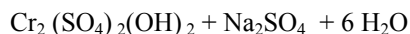
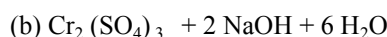
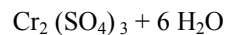
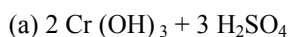
Spent lime liquor (SLL) and spent chrome liquor (SCL) were collected from East Asia Tannery, Hazaribagh, Dhaka, during the manufacturing of a conventional chrome tanned cow softy shoe upper leather. These liquors were then allowed to settle down overnight, decanted and screened using clean cotton cloth without folding. At room temperature (25°C), different volumes of SLL (0.5 ml, 1.0 ml, 1.5 ml, 2.0 ml, 2.5 ml, 3.0 ml, 3.5 ml, 4.0 ml) were mixed with a fixed volume (20 ml) of SCL in a magnetic stirrer with continuous stirring. After mixing of SLL to SCL precipitation occurred and the mixer was filtered. Filtrate was collected to measure the presence of chromium by the

*To whom all correspondence should be made, E-mail: manoranjansaha2005@yahoo.com, Phone : +88-017132151647

official method of measuring chromium – III by Society of Leather Technologist and Chemist (SLC-208). After the addition of 4.0 ml of SLL into 20 ml of SCL complete precipitation occurred and the pH was found 7.5 ± 0.1 . After complete precipitation the mixer was left over night and precipitate was filtered to separate from solution, washed three times with distilled water to make the chromium precipitate free from any impurities, dried in a glass oven at 90°C for 12 hours.

Dried chrome precipitate powder was grinded for uniformity and the powder was converted into basic chromium sulfate solution using calculated amount of sulfuric acid (98%) and sodium hydroxide.

Preparation of tanning liquor was carried out according to the following reactions:



Reaction (a) shows that for one molecule of chromium hydroxide (52g of Cr), 3/2 molecules of sulfuric acid are necessary to transform all of hydroxide to chromium sulfate. And reaction (b) shows that for one molecule of chromic sulfate, two molecules of sodium hydroxide are necessary to prepare basic chromium sulfate¹³.

Commercial basic chromium sulfate (4%) and equivalent amount of prepared basic chromium sulfate solution were applied for the production of shoe upper leather from wet blue goatskins based on their shaved weight. The manufacturing process has been listed in Table – 1.

Table. 1. The manufacturing process of shoe upper leather using recovered chromium and commercial chromium tanning agents from wet-blue goatskin.

Operational steps and used chemicals

Sample: Wet-blue goat skin

Quantity: 4 pieces.

Thickness- 0.9 - 1.0 mm

Shaved weight was taken (2500 grams)

Wet-Blue pH: 4.0/ 4.1

Acid Wash: 200% water, 35°C
0.5% Wetting Agent
0.5% Oxalic Acid

Rechroming: 100% Water, 35°C
0.5% Formic Acid

2.0% Glutaraldehyde (INTAN GR)
4.0% of commercial basic chromium sulfate (CHROMOSAL B)
or equivalent amount of prepared basic chromium sulfate solution
(Based on shaved weight)

Basification: 4.0% Anionic resin (INTAN CRD)
1.0% Anionic fat liquor (INGRASSANTE 99E)
1.0% Sodium Formate

Neutralisation: Leave Overnight
Next Day-Drain, Wash
100% Water, 35°C
1.0% Nutralizing syntan (INTAN NGN)
0.3% Sodium Bi Carbonate
0.8% Sodium Formate

Retanning: 3.0% Acrylic polymer (INTAN TP 340)
Drain, Wash
100% Water
4.0% Mimosa
4.0% QUEBRACHO
4.0% Amphoteric compounds (BASYNTAN AN)
4.0% Anionic polymer (INTAN UP 225/N)
4.0% Anionic tanning powder (INTAN TM)
1.0% Anionic fat liquor (INGRASSANTE 99E)
2.5% Dye
1.0% Buffering sodium salt (SINTERAL SB)

Dye Fixing: Dye in Second Feed
100% Water, 55°C
1.5% Formic Acid
Drain, Wash

Fat Liquoring: 100% Water, 55°C

Application Time and pH

Run for 30'
Check pH - 3.8/ 3.9
Drain, Wash

Run for 20'
Check pH - 3.5
Run for 30'

Run for 20'+20'+20'

Run for 30'
Run for 30'
Check pH - 4/ 4.1

Run for 60'
Check pH - 4.6/ 4.7
Run for 30'

Run for 30'+60'

Run for 10'+20'

	3.0% Anionic Filler (SINTERAL 312)	Run for 20'
	4.0% Anionic Oils (INGRASSANTE S/D3)	
	3.0% Anionic fat liquor (INGRASSANTE M65)	
	3.0% Anionic Oils (INGRASSANTE A792)	
	1.0% Anionic fat liquor (INGRASSANTE 99E)	Run for 60'
	+ 3.0% Anionic polymer (INTAN EMS)	Run for 30'
	0.5% Formic Acid	Run for 10'+20'
	Drain, Wash	
Top Dyeing:	200% Water, 50°C	
	1.0% Dye	Run for 20'
	1.0% Formic Acid	Run for 10'+20'
Top Fat: 1.0%	Cationic nitrogenous derivative (INGRASSANTE CT3100)	Run for 15'
	Drain, Wash	

(All the INGRASSANTE and INTAN group chemicals are from ALPA Chemicals, Italy, Dhaka office and SINTERAL groups are from BASF Chemicals, Germany, Dhaka office.)

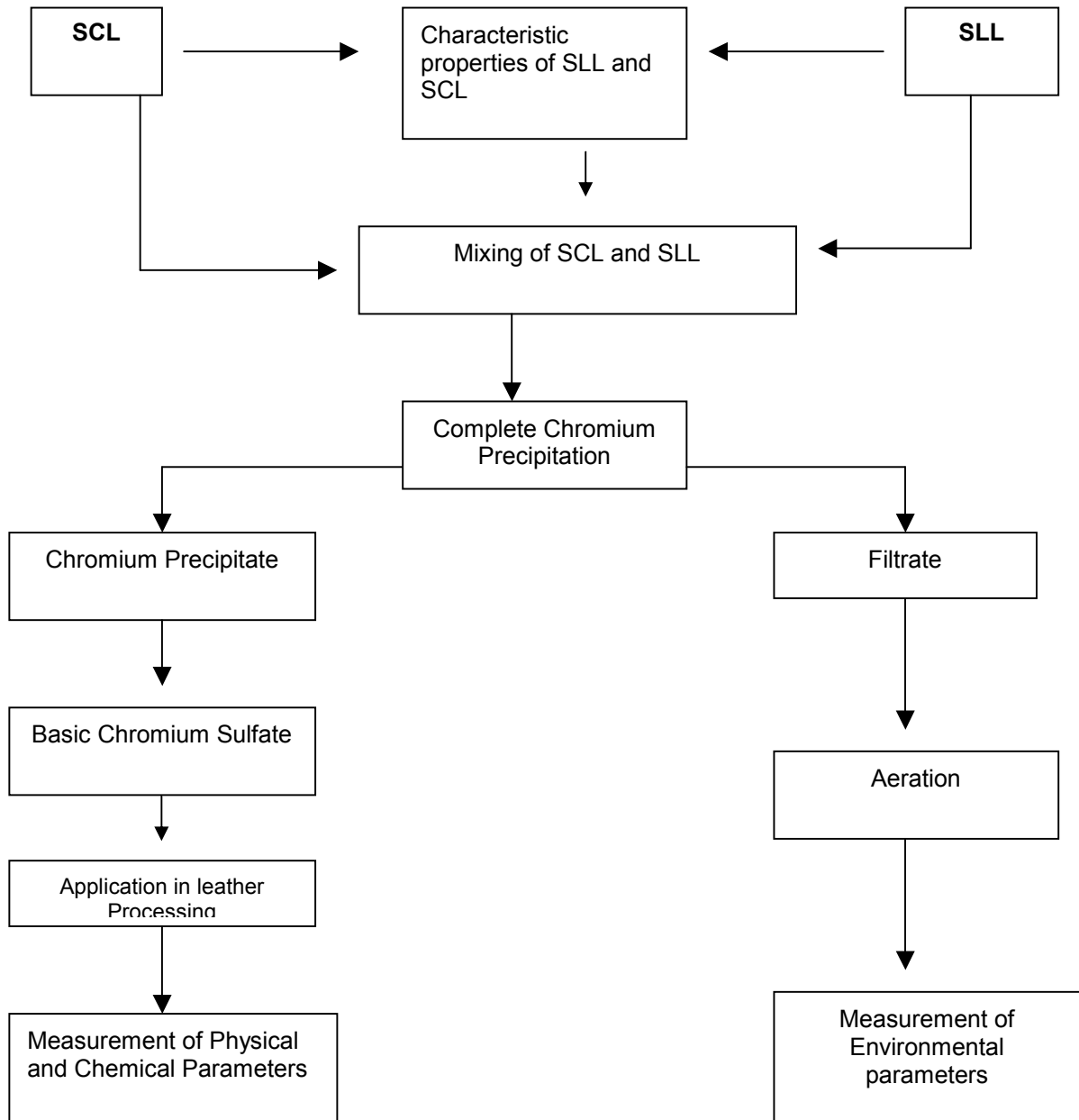


Fig. 1. Different steps of the procedure.

Table 2. Chromium – III concentration in solution after each step of mixing of SLL with SCL.

Sample ID	SLL (mL)	SCL (mL)	Amount of Cr ⁺³ in solution (mg/L)	% Removal of Cr ⁺³
LC-00	0.0	20	3200	00.00
LC-01	0.5	20	2850	10.90
LC-02	1	20	2460	23.12
LC-03	1.5	20	2144	33.00
LC-04	2	20	1500	53.12
LC-05	2.5	20	1470	54.06
LC-06	3	20	750	76.56
LC-07	3.5	20	140	95.62
LC-08	4	20	Nil	100.00

Table 3. Physical parameters of manufactured shoe upper leather using recovered basic chromium sulfate and commercial basic chromium sulfate.

Name of the Physical Test	Tensile Strength (Kg/cm ²)	Tongue Tear Strength (Normal) (Kg/cm)	Tear Strength (Baumann) (Kg/cm)	Stitch Tear Strength (Kg/cm)	Vamp Flexing	Ball Bursting Load (Load/kg)	Softness (mm)
Test results with commercial basic chromium sulfate	200	30	30	80	100,000 times (no grain crack)	25.22	3.3
Test results with Recovered basic chromium sulfate	266	30.5	31.7	64.77	100,000 times (no grain crack)	27.38	3.4

Table 4. Chemical parameters of manufactured shoe upper leather using recovered basic chromium sulfate and commercial basic chromium sulfate.

Chemical Parameters	Commercial basic chromium sulfate	Recovered basic chromium sulfate
Cr ₂ O ₃ , %	3.8	3.9
Ash Content, %	1.9	2.1
Fat, %	3.2	2.6
Shrinkage temperature, °C	98	97

Table. 5. Environmental parameters of SCL after complete chromium precipitation and aeration.

Parameters	SCL after complete chromium precipitation	After 24 hours of aeration	After 48 hours of aeration	Discharge Standards ¹⁵
COD (mg/L)	520	350	264	200-400
BOD ₅ (mg/L)	250	140	140	100-150
TDS (mg/L)	3000	1700	1500	2100
Cr ⁺³ (mg/L)	Nil	Nil	Nil	2
pH	7.53	6.75	6.07	6-9

The manufactured shoe upper leather was then examined for their physical and chemical parameters by standard methods (Table – 3 and Table- 4).

After complete precipitation the filtrate was collected and taken for aeration. After aeration important effluent parameters were measured. Different steps of the procedure are shown in Figure –1.

III. Result and Discussion

The chromium – III concentration was observed to be 2850, 2460, 2144, 1500, 1470, 750, 140 mg/lit after each step of mixing of the SLL to SCL. After final addition of 4.0ml of SLL to 20.0ml SCL, chromium – III was found to be absent in solution. The results are recorded in Table-2.

Manufactured shoe upper from wet blue goatskins with recovered chromium was then examined for its physical and chemical standards (Table – 3 and Table- 4). All the results were found to be similar with the leather produced using the commercial basic chromium sulfate powder. Similar results were also observed in chromium recovery and reuse process done by Tahiri et al. and Cabeza et al.^{13,14} from shaving waste by alkaline method.

Filtrate of SCL after complete chromium precipitation was taken for aeration for 24 hours and 48 hours at room temperature (25 °C) and the environmental parameters were measured. The results are shown in Table-5. It is obvious that the stripping of natural air into wastewater through aeration process reduces COD, BOD₅ (Biochemical Oxygen Demand after 5 days) and TDS values. After 48 hours of aeration the values of COD, BOD₅, TDS and pH are 264, 140 and 1500 mg/lit and 6.071 belong to the standard discharge limit of Bangladesh¹⁵. Aeration process provides available oxygen into wastewater, which combines with metals producing metal oxides, converts nitrogen into non – toxic nitrogenous compounds and also decomposes organic compounds^{16,17}.

IV. Conclusion

The recovery process of chromium using SLL from SCL is efficient, relatively simple and cheap. The complete precipitation of chromium occurred at a volume ratio of 1:5 of SLL to SCL. The use of SLL as precipitating chemical reduces the cost of chromium recovery. The result obtained

from recovered chromium in leather processing was similar to that from commercial chromium. Filtrate obtained after the complete precipitation of chromium can be drained directly into the river after 48 hours of aeration.

Acknowledgement

We are very thankful to BASF Bangladesh Ltd. and ALPA Chemicals Bangladesh Ltd. for their support in this investigation.

- Allen, S. J. and P.A. Brown, 1995. Isotherm analyses for single component and multicomponent metal sorption onto lignite. *J. Chem. Technol. Biotechnol.* **62(1)**, 17-24.
- Ulmanu, M., E. Maranon, Y. Fernandez, L. Castrillon, I. Anger, D. Dumitriu, 2003. Removal of copper and cadmium ions from dilute aqueous solution by low cost and waste material adsorbent. *Water Air and Soil Pollut.* **142**, 357 – 373.
- Ajmal, M., A. M. Sulaiman, A. H. Khan, 1993. Surface entrapment of toxic metals from electroplating waste and their possible recovery. *Water Air and Soil Pollut.* **68**, 485 - 492.
- Kostal, J., G. Prabhukumar, U. L. Lao, A. Chen, M. Matsumoto, A. Mulchandani, W. Chen, 2005. Customizable biopolymers for heavy metal remediation. *J.Nanoparticle Research.* **7**, 517 – 523.
- Thomas, C.V., L.D. Mackenzie, B.J. Gregory and L.S. Linda, 1988. Evaluation of Chromium Recovery Opportunities in a Leather Tannery. *Hazardous Waste & Hazardous Materials.* **5**, 343-352.
- Aravindhan, R. , B. Madhan, J. R. Rao, B. U. Nair, T. Ramasami, 2004. Bioaccumulation of chromium from tannery wastewater: An approach for chrome recovery and reuse. *Environ. Sci. Technol.* **38(1)**, 300-306.
- Weber, W., 1973. Report of IULCS Effluents Commission. *J. Soc. Leather Technol. Chem.* **57**, 63.
- Hauck, R.A., 1972. Report on methods of chromium recovery and reuse from spent chrome tan liquor. *J. Amer. Leather Chem. Assn.* **67**, 422.
- Fields S., 1978. Some practical aspects of chrome recycling. *The Leather Manufacturer.* **2**, 15.
- Jones, B. H., 1979. Chromium recovery through incineration of liquid and solid tannery wastes – the ultimate solution. *J. Amer. Leather Chem. Assn.* **74(II)**, 395.
- Cartier, J. E., 1980. An ash stabilization process for the recovery and reuse of chromium from chrome – laden tannery waste and a treatment process for pollution control of tannery wastewater. *J. Amer. Leather Chem. Assn.* **75(9)**, 322.

12. Tancous, J. J., R. Bellingham, W. Kallenberger, A. McDonell, 1981. Conservation of chromium in the tanning industry. *J. Amer. Leather Chem. Assn.* **76(5)**, 164.
13. Tahiri, S., M. Bouhria, A. Albizane, A. Messaoudi, M. Azzi, S. Alami.Younssi, and J. Mabrou, 2004. Extraction of proteins from shavings with sodium hydroxide and reuse of chromium in the tanning process. *JALCA*. **99**, 16 – 25.
14. Cabeza, L.F. M.M. Taylor, G.L. DiMaio, E.M. Brown, W.N. Marmer, R. Carrio, P.J. Celma, and J. Cot, 1998. Processing of leather waste: Pilote scale studies on chrome shavings. Part II. Purification of chrome cake and tanning trials. *JALCA*. **93**, 83 – 98.
15. Bangladesh Centre for Advanced Studies (BCAS), 1999. Guide to The Environmental Conservation Act 1995 and Rules 1997. p 80-81.
16. Eto, M., 1974. Organophosphorous pesticides – Organic and Biological Chemistry. CRC Press, Cleaveland, p. 161.
17. DE, A. K., 2007. Environmental Chemistry. New age international publishers ltd., New Delhi, p – 184.

