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An Efficient Recovery of Chromium From Tanning Liquor waste and its Reutilization for the Production of Quality Leather

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Abstract

The conventional methods for the treatment of tannery effluents are highly expensive due to the presence of large amount of chemicals used in the processing and their environmental toxicity. In this study, chromium has been recovered from tanning waste liquor which is discarded usually in the open streams. This tanning liquor has been treated with different concentrations of alkalies such as sodium hydroxide (NaOH), ferric chloride ($FeCl_3$) and magnesium oxide (MgO) to recover chromium using the precipitation method. The precipitation of chromium at controlled range of pH by MgO yielded the well concentrated sludge resulting the total dissolved solids in low quantity in the supernatant when compared with the other two treatments (NaOH and $FeCl_3$). The prepared chromium sulphate liquors from recovered chrome cake has been employed at similar conditions parallel to fresh basic chromium sulphate to determine the effects on quality of leather. The resulted leathers showed almost very good properties e.g. shrinkage, tear strength, tensile strength, bursting strength, fullness, grain smoothness, etc.

Key Words: Leather Industry; Tanning liquor; Chromium Recovery; Precipitation Methods.

1. Introduction

Chrome tanning is commonly used about in 90% of tanneries all over the world due to the superior properties of resulted leather. Tanning liquor after processing needs special attention in terms of environmental restrictions [1]. The chromium toxicity of this liquor depends on its oxidation state. Chromium in Cr VI form is much more toxic as compared to chromium Cr III.

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The research studies have shown that Cr VI has high ability to penetrate into human cells and causes the pathogenic effects such as skin ulcers, allergic reactions, perforations of the respiratory surface area. Therefore, the treatment of such toxic substance is required for safe prevention [2]. However, due to the distinctiveness of the chromium tanning and its leathers better properties, chromium is applied widely even in the future practices it might be changed [3]. Tanneries wastes include; tanned & non tanned solids tannery sludge with effluent (liquors) and waste gases [4]. However, chromium is found in different concentration in the tanning waste water as per applied dosage [5-8]. Hence, the components in liquor like sulfide, chromium and sulfates may slow the anaerobic process [5]. The treatment of tanneries liquor has been increasing environmental concern due to the presence of pollutants having low biodegradability [9-10]. Currently, the chromium is separated from tanneries waste water by using different techniques such as adsorption, solvent extraction, electrolytic extraction, & ion exchange method [11]. However, due to the specific chemical properties of chromium the selection of technique is complicated for implementation. Therefore, we have emphasized to recover chromium from waste liquor by simple method and its reutilization in leather processing without effecting leather quality.

2. Material and Methods

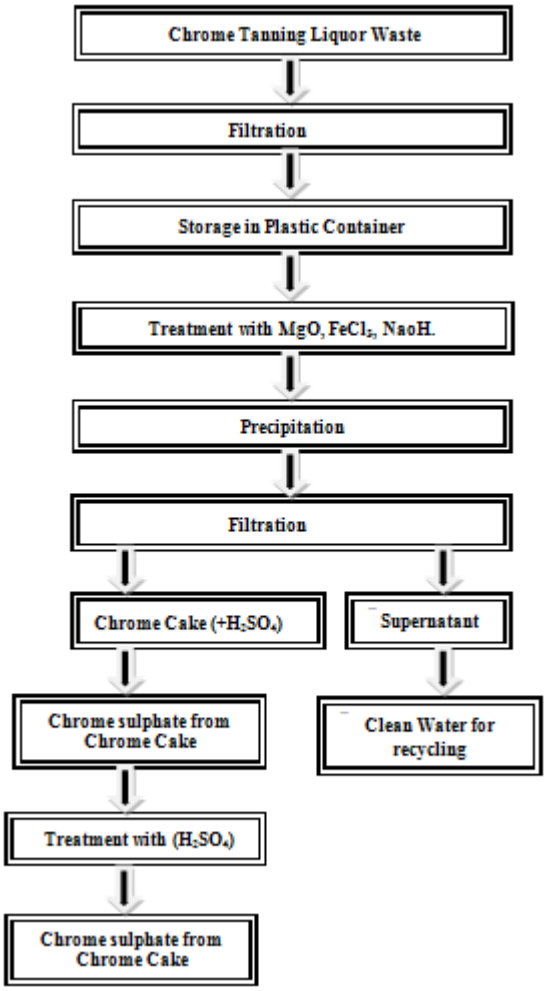

Figure 1: Preparation of Tanning Liquor

Table 1: Leather Process

Process	% of Chemical	Duration	Note
Soaking	300% Water 20 °C 1% NI Detergent	30 minutes	Drain
Washing	300% Water 30 °C	10 minutes	Drain
Liming	200% Water 04% Sodium Sulphide 04% Calcium Hydroxide	20 minutes	Left for 2hrs in stationary Conditions. drumming for every 15minute, then skin left 24hours in same bath.
Re-liming	300% Water 2% Calcium Hydroxide	20 minutes	Drumming was carried out for 20 minutes. Then occasional handling for the next 24 hours run 5 minutes in every hour.
Washing	300% Water	5 minutes.	Three time wash to remove extra Lime.
Deliming	200% Water 2% Ammonium Sulphate	60 minutes	Drumming for 60 minutes. Check cross section of Skin by phenolphthalein for Completion of deliming. pH was 8.0 .
Washing	300% Water 25-30 °C	05minutes	Drain
Bating	100% Water 35 °C 1.5% Bating (Bacterial bate)	60 minutes	Wash the skin and scudding, washing & drain float
Degreasing	150% Water 30 °C 1% Enzyme	60 minutes	
Washing	300% Water	05 minutes	Drain
Pickling	60% Water 10% Salt 1% Formic Acid 0.2% Sulphuric Acid in same float	10 minutes 20 minutes	pH 2.8
Tanning	4% Basic Chromium Sulphate 2% Basic Chromium Sulphate 2% Sodium Bicarbonate	30 minutes 60 minutes 20 minutes	pH3.4 Pile Wet blue for Four days
Neutralization	200% Water 35°C 1.5% Sodium Formate	30 minutes	pH 5.8
Retanning	200% Water 65°C 4% Prepared chromium Sulphate tanning agent*	30 minutes 60minutes	
Fatliquoring	2% UPN 4% SR 4% Blended Oil (64/S) 1% Formic Acid	30 minutes	pH 3.8 Drain & Pile skin, air dried at room temperature.

*Three products A, B&C were applied in three experiments without changing other process

Chrome tanning liquor waste was collected from processing at tannery area of Leather Research Centre and subjected to check various parameters as per their standard methods such as pH (ASTM D1239), color, chlorides (APHA, 4500), sulphates (APHA, 4500, 20th Edition), total chromium (ISO,3500). The pH of tanning liquors waste were adjusted at 8.5-9.0 after adding three different chemicals (MgO, $FeCl_3$,NaOH). The samples were subjected for sedimentation in plastic containers for 6hrs as shown in **Figure 1**. Then, the precipitated samples were observed for sludge quantity and analyzed for total dissolved solids (TDS) according to standard test methods [12-14]. The recovered chrome cake was re-dissolved in commercial 5% solution of conc.H_2SO_4 in 200ml distilled water and digest on water bath with agitation until pH was adjusted at 2.5-2.8 to convert into chromium sulphate. After adjusting pH it was applied with the combination of commercial chrome presented in Table 1 in tannery area. Four goat skins were selected to apply each prepared product followed tannery process according to **Table .**

2.1 Physical characterization of Crust leather

Sample for physical testing were cut and then conditioned at standard atmospheric conditions i.e. temperature 23 $\pm$ 2 ^{o}C and 50 $\pm$ 5 relative humidity for 24 to 48 h [15-17]. Physical properties such as tear strength, grain crack, percentage elongation and tensile strength were measured on Universal Testing Machine UTM Tinius Olsen LTD H5KS UK .

3. Results and Discussions

In the tanneries, the chrome is used which distribution has widely known as shown in table 2.

Table 2: Chrome Distribution

Chrome Dosage applied*	Crust Leather	Chrome tanning Waste Liquor
5%	3.8-4.0%	1.9-2.0%

Calculated on shaved weight of leather

Therefore, in this study, fresh tanning liquor was collected, filtered and analyzed for various parameters such as pH value,total chrome (%), etc. These results are shown in Table 3. The results revealed that the due to the presence of high quantity of chlorides, chromium and sulphates respectively the value of COD & BOD were out of limits.

Table 3: Analysis of Tanning liquor Waste

Parameter	Result
Color	Blackish green
Total Cr(%)	2.0
Total Cr(mg/l)	4100
Sulphates (mg/l)	3550
COD mg/L	680
BOD mg/L	2300
Total Kjehdahl Nitrogen mg/L	1200

The precipitation by NaOH resulted a very gelatinous form of sludge. While, the precipitation using MgO yielded the low quantity of sludge but higher recovery of chromium. The reaction can be expressed via this chemical equation

$$Cr_2(SO_4)_3 + 3\,MgO + 3H_2O \rightarrow 2Cr(OH)_3 + 3\,MgSO_4 \quad \text{……Equation 1}$$

$$2\,Cr(OH)_3 + 3\,H_2SO_4 \rightarrow Cr_2(SO4)_3 + 6\,H_2O \quad \text{……Equation 2}$$

These results revealed that the chromium was totally precipitated easily from waste tanning liquors from tanneries.

When the tanning liquor was treated with $FeCl_3$ the brownish flocculates were formed at the bottom of cylinder and the liquor was blackish. The similar flocculation of tannery waste water process was investigated where the ferric chloride ($FeCl_3$) was used to reduce the organic load by elimination of chromium before biological treatment [18-19]. After separation of sludge from each container it was analyzed for total dissolved solids (TDS). These results are presented in **Table 4**. These results confirmed the suitability of MgO treatment for the treatment of tanning liquor due to the low amount of TDS as compare to other treatments. Therefore, this method was adopted to prepare the basic chromium sulphate from recovered chrome.

Table 4: Results of total dissolved solids (TDS) after different treatments

Treatment with Alkalies	pH	TDS (ppm)
Sodium hydroxide	8.4	408
Ferric chlorides	7.0	445
Magnesium oxide	7.2	248

The recovered chrome was re-dissolved in Conc.H_2SO_4 & pH was adjusted to apply in re-tanning process. These products were prepared as shown in the **Table 5.**

Table 5: Characteristics of Prepared chrome

Product	Formulation	%Moisture	Basicity (%)	Cr_2O_3(%)
A	75parts Recovered Chrome+25parts Commercial Chrome	33.76%	32%	25.0%
B	50parts Recovered Chrome+50parts Commercial Chrome	24.76%	34%	18.88%
C	25parts Recovered Chrome+75parts Commercial Chrome	21.15%	33%	25.01%

The Wet blues leathers after the tanning process were tested to determine the chrome contents, shrinkage temperature, grain smoothness and color as presented in **Table 6**. The leather made in this study were also assessed for fullness, softness and grain smoothness. The procedure for rating of leather was adopted to award the points for each functional property by leather experts (1-10). The higher amount of Cr_2O_3 was found higher in sample C. The shrinkage temperature was found higher in Fresh Commercial chrome as well as in Sample C.

The results revealed that the suitable bonding ability was observed in both samples. The smoothness and color of wet blues leathers were comparable with the commercial chrome. The resulted wet blues were checked for various parameters as shown in table 6.

Table 6: Characteristics of Processed Wet blue with Commercial Chrome and Recovered Chrome

Parameters	Commercial Chrome	Product A	Product B	Product C
% Cr_2O_3 in wet blue	3.80±1.0	3.78±1.3	3.86±1.4	3.98±1.4
Shrinkage Temperature (^oC)	118±2	116±2	115±2	118±2
Grain Smoothness	8±1.0	8±1.0	7±1.0	8±1.0
Color	7±1.0	7±1.0	8±1.0	9±1.0

The resulted Crust leathers were subjected for various physical parameters as presented in **Table 7**. The physical properties of Crust leathers tanning from product C was found superior and comparable with the commercial chrome. These results revealed that the recovered chromium may be used in the fresh chromium tanning's bath, with 1 part of recovered chrome and 3 parts of basic chroumium sulphate for the complete tanning actions.

Table 7: Physical properties of Resulted Crust Leather after application of Recovered Chrome

Physical Characteristics	Fresh Commercial Chrome	Product A	Product B	Product C
Shrinkage (^oC)	122±1	120±2	119±1	120±2
Tear Strength (N/mm)	52.73±1.2	51.20±1.6	50.67±3.4	51.42±3.0
Tensile Strength (kg/cm^2)	21.58±3.0	20.00±2.5	22.01±0.5	24.15±0.4
Bursting Strength (kg/mm)	49.30±2.00	42.20±3.0	38.50±2.6	37.55±1.6
Elongation (%)	63.44±4.5	58.13±2.0	60.16±2.3	61.0±4.2
Fullness	8±1.0	7±1.0	8±1.0	9±1.0
Grain Smoothness	8±1.0	8±1.0	7±1.0	8±1.0
Softness	8±1.0	8±1.0	7±1.0	8±1.0
Color	8±0.5	8±0.5	8±0.5	9±0.5

4. Conclusion

In a conventional tannery process, the 50%-60% chrome is exhausted in leather while the remaining goes into the effluent.

The chromium present in the tanning liquor has been recovered by precipitation method. Three different ratios

of recovered chrome samples were prepared in combination with fresh chrome and compared through application in leather processing.

The good quality leathers were made and results were found better and comparable with the commercial tanning materials. Therefore, it is concluded that chrome in tannery effluent can be efficiently recovered through precipitation by MgO and recycled in leather processing without effecting quality of final product.

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5. Recommendations

On the basis of results, it can be recommended that this methodology may be adopted for the recovery of chromium from chrome tanning waste liquor. After re-dissolving and pH adjustment the recovered chrome can be reused along with fresh chromium sulphate for tanning of leather. Percentage of reused of recovered chrome may depend upon the required type and quality of leather.