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Recovery of chromium from spent chrome liquor for reuse

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ABSTRACT

In leather processing, chrome tanning is the most popular due to its high thermal stability and flexibility. In chrome tanning, 8% basic chromium sulfate (BCS) is used based on pelt weight. The pelt absorbs only 60% of chromium and 40% of chromium remains in the spent liquor. In Bangladesh, generally this trivalent chromium, Cr(III) is directly discharged into the environment without any treatment, which affects the corresponding ecological system causing serious health hazards like cancer when converted into hexavalent Cr. The Cr is deposited in ionic form into the crops and fatty tissue of animals and fish. This deposited Cr enters the human body through Cr-contaminated vegetables, fish, and meat consumption. The utilization of this remaining Cr from waste liquor could break the cycle at the same time provide a waste-to-wealth approach. In this work, recovered chrome from spent Cr liquor was used for the tanning process instead of BCS for wet-blue production and compared with conventionally tanned leather. The basicity of the recovered Cr was 33% and the amount of Cr was 3380 mg/L, respectively. The pollution load in the wastewater was characterized after reused by Biochemical Oxygen Demand (BOD) (1156 mg/L), Chemical Oxygen Demand (COD) (2345 mg/L), chloride (42 mg/L), sulfide (35 mg/L), etc. Mechanical properties were analyzed by examining the tensile strength of a maximum of 289 kg/cm^2 in the parallel direction and 364 kg/cm^2 in the perpendicular direction and the percentage of elongation of a maximum of 62% in parallel and 54% in the perpendicular direction. This study could be applicable for reducing the pollution load as well as reusing the spent Cr from discharged waste liquor.

Keywords: Environment, pollution, chromium, recovery, tanning.

1. Introduction

In recent years, environmental pollution has become a challenge all over the world. Different chemical industries dispose of a lot of hazardous waste to the environment, which affects the environmental ecology. Leather industries are one of the most hazardous industries where raw animal skin is converted into tanned leather by various chemical and mechanical processes. The prime objective of tanning is to transform the putrescible hide into stable, non-putrescible leather. Chrome tanning is the most popular method in leather industries to obtain the best physical properties such as hydrothermal stability, quality dyeing, and softness to the leather [1]. In chrome tanning, 60-70% of Cr is uptake by the leather and the rest is discharged as an effluent resulting in the accumulation of metal salts with soil [2]. In basic chromium sulfate (BCS), trivalent chromium is used which is generally nontoxic in nature but when it is converted into hexavalent chromium it has a serious impact on soil and water [3]. Additionally, it has an impact on pigment and enzyme content, seed germination, and seedling development [4]. Chronic chromium exposure for the duration of five months to fourteen years is a significant risk factor for the emergence of genetically based illnesses. Giddiness, eye irritation, skin allergies, and gastrointestinal ulcers in the nasal septum are among the short-term negative effects of tannery effluent streams [5, 6]. Occupational asthma, peptic ulcer, pneumonia, and dermatitis are the long-term sequelae [7]. Due to the enormous amount of chromium released by the leather industry, the environmental effect of the chromium found in wastewater has become more serious. About 1 m^3 of Cr-containing effluent is released for every ton of rawhide or skin processing with a chromium concentration of 27500 mg/L [8]. The negative impacts of chromium and chrome tanning forced the researchers to develop a suitable technology to reuse and recover chromium from effluent. This aids to reduce the amount of chromium in the waste stream with multiple recycling [9].

Various methods are available through which chromium can be treated from tanning liquor such as chemical precipitation, coagulation, solvent extraction, membrane filtration, ion exchange, and adsorption [10-12]. Chrome recovery by magnesium oxide is the most popular but slow process. Several studies are also available by precipitating Cr with lime, sodium hydroxide, and sodium carbonate by changing pH and basicity [13].

Recovered chromium was collected in the chromic oxide form and for basic chromium sulfate preparation additional chemicals processes are need to convert it from chromic oxide to basic chromium sulfate. Several researches were found where recovered chromium was used as tanning agent chromium recovery through electro oxidation technique using titanium anode and its recovery & reuse was costly [14], recovered chrome mixed with fresh basic chromium sulfate and reused in tanning process increases mechanical properties where recovered chromium ratio was lower than fresh chrome sulfate [15], recovery and reuse of chromium using neutralization process involved higher pH where chromium particle sizes were bigger which hindered

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chromium penetration into leather fiber resulting lower mechanical properties [16].

In this study, the mixture of recovered chromium powder and recovered chromium liquor was used as a hybrid tanning agent as an alternative to conventional chrome tanning agent. A comparison between the obtained properties and pollution load of conventional tanning and hybrid tanning was conducted to assess the application possibility of the hybrid tanning agent in the tanning process.

2. Materials and Methods

2.1 Sample collection

Recovered chrome liquor and chrome powder (Fig.1) were collected from SAF Leather Ltd., Noapara, Jashore. Goatskin was collected from the nearby local market in Khulna.

Fig.1 Recovered chrome liquor and chrome powder

2.2 Chemicals and reagents

The chemicals potassium thiocyanate (Loba, India), manganous sulfate solution (Loba, India), potassium iodide (Loba, India), sulphuric acid (Merck, India), sodium azide (Loba, India), potassium hydroxide pallets (Merck, India), sodium thiosulfate (Merck, India), ferrous ammonium sulfate (Merck, India), aluminum sulfate (Merck, India), starch (UNI-CHEM, China), ferroin indicator (Loba, India) were collected from the local scientific store, Khulna.

2.3 Basic chromium sulfate preparation

Collected spent liquor and chrome powder were first mixed and then analyzed for pH and chromic oxide content [17]. The basicity of the hybrid liquor was raised to 33% according to the standard method [18]. Finally, prepared liquor was ready for use as an alternative to conventional basic chromium sulfate (Fig.2).

Fig.2 Experimental chrome tannin

2.4 Tanning process

Two pieces of goatskin were cut into half making four pieces and then two pieces were used for experimental purposes with prepared hybrid chrome liquor and the rest

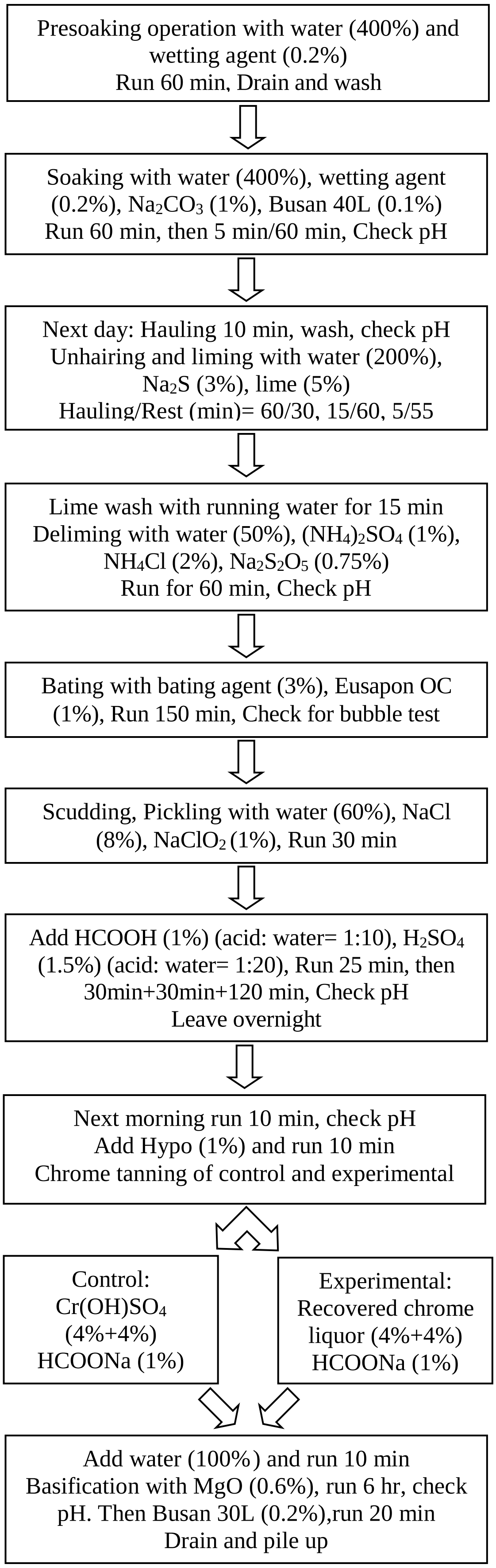

Fig.3 A schematic diagram of the tanning process

two pieces were used for conventional tanning with basic chromium sulfate [19, 22-27]. The flow chart of the tanning process in shown in Fig.3.

2.5 Mechanical operations

Sammying and shaving were carried out after the ageing of crust leather to maintain uniform thickness and stretchiness.

2.6 Retanning

The target of this process was a further modification of the initial tanned leather by filling the void space, levelling up, or controlling loose grain [29].

2.7 Dyeing

Natural or synthetic dyes were applied as a background coloring material to the substrate [28].

2.8 Fat liquoring

This process was conducted to lubricate each fibrils of the collagen fiber to slide over when stretched. It accelerates the tensile property of a substrate [30]. The finished leather is shown in Fig.4.

Fig.4 Finished leather (A-control, B-experimental)

2.9 Pollution load determination

Chrome tanning effluent was analyzed for biochemical oxygen demand (BOD), chemical oxygen demand (COD) through the titrimetric method [20].

2.9.1 Biochemical oxygen demand (BOD)

Following standard method APHA 5210 B [19], distilled water of 300 mL was poured into a BOD bottle where 1 mL of sample was inserted. Later on, 2 mL manganese sulfate along with 2 mL of alkaline azide solution was added. After brown precipitation, 2 mL sulfuric acid was introduced and shaken firmly to avoid precipitation. From BOD bottle, 203 mL sample was taken and titrated against sodium thiosulfate solution, where starch was the indicator. BOD_5 (mg/L) was calculated by equation (1):

$$BOD_5 = (DO_1 - DO_2) \times \text{Dilution factor}........(1)$$

2.9.2 Chemical oxygen demand (COD)

Following APHA standard method 5220 C [19], 2.5 mL of sample was placed in a test tube and added with 1.5 mL of potassium dichromate, 2.5 mL of mixed sulfuric acid reagent. The test tube was kept in an oven for 2 hours at 150°C. After cooling to room temperature, it was titrated against ferrous ammonium sulfate solution by adding 2 drops of ferroin indicator. COD (mg/L) was calculated by equation (2):

$$COD = \frac{(\text{Blank} - \text{Sample}) \times 0.1 \times 8 \times 1000}{\text{Sample volume}} \times \text{Dilution factor}........(2)$$

2.10 Mechanical properties

For determination of the physical strength of produced crust leather, samples of 110 mm × 25 mm were taken according to standard sampling location from skins and the tests were carried out under a temperature of 20 ± 2°C and relative humidity of 65 ± 2% for 48 h. Mechanical properties like tensile strength (TS), and elongation at break (EB) were assessed under ISO 3376 through a tensile tester machine (SATRA Technology Center, SER no. 172-1-1514, England) with the help of Eq. (3) and Eq. (4) [21] (Fig.5).

$$\text{Tensile strength} = \frac{\text{Breaking load (kg)}}{\text{Thickness (cm)} \times \text{width (cm)}} \qquad (3)$$

$$\text{Elongation (\%)} = \frac{(L_B - L_o) \times 100}{L_o} \qquad (4)$$

Where, L_B and L_o are the breaking distance and initial distance, respectively.

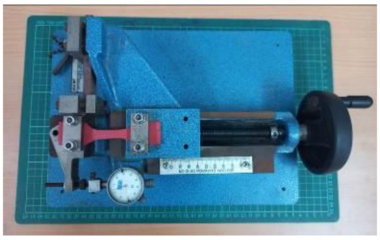

Fig.5 Tensile strength and elongation test of produced leather

3. Results and Discussion

Chromium recovery and reuse have become important issues nowadays. In this study, spent tanning liquor was used for tanning purposes and the mechanical properties of produced crust leather were compared with conventionally tanned leather.

Table 1 Characterization of spent chrome liquor before reuse and after reuse

Parameter	Before (mg/L)	After (mg/L)	[9]
BOD	1765±1.21	1156±1.53	1800-2540
COD	3897±3.72	2345±2.38	4320-5830

Spent chrome liquor was collected from the conventional chrome tanning process where 8% of basic chromium sulfate was used. The pH, basicity, and total Cr of the spent liquor were 2.7±0.22, 33±1.18%, and

3380±2.85 mg/L, respectively. The spent chrome liquor before and after reuse was characterized for biochemical oxygen demand (BOD), and chemical oxygen demand (COD), and the data are tabulated in Table 1.

From Table 1, it can be seen that the value of BOD and COD is reduced after reutilization and lower than the standard value. The pollution load values after the tanning process for BOD, and COD were 1156 mg/L, and 2345 mg/L, respectively. These were significantly reduced from the previous study [9]. The penetration of Cr particles is better at pH 2.7 and as penetration was increasing, the amount of Cr particles in the remaining spent bath reduced which ultimately lowered the pollution load for BOD and COD. Shrinkage temperatures of produced leather in both conventional and experimental studies were shown in Fig.6.

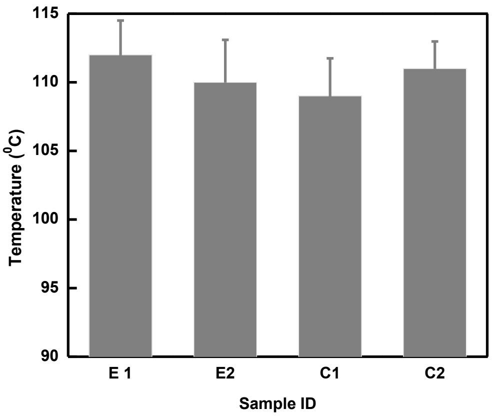

Fig.6 Shrinkage temperatures produced leather in both conventional and experimental

Fig.6 depicts the shrinkage temperature of the control sample (C1 & C2) through the conventional tanning process lies within the standard range set by Covington [6]. The experimental samples E1 & E2 are also seen to match within a similar range as the control is as well as satisfy other previous studies mentioned in Table 2. Therefore, it reflects an almost similar quality of tanning through used chromium.

Table 2 Comparison of shrinkage temperature with previous studies

Shrinkage temperature (°C)	Reference
115±1.3	Kanagaraj et al. [9]
116	Sundar et al. [31]
104.5	Khan et al. [32]
111±1.4	This study

Mechanical properties of produced crust leather are shown in Table 3 and Table 4.

Table 3 Percentage of elongation for conventional and experimental samples

Sample ID	% of elongation		[32]
	Parallel	Perpendicular	
Conventional	60±2.82	52±1.41	Max.
Experimental	61.5±0.71	53.5±0.71	70%

Tensile strength and % of elongation values were calculated in both parallel and perpendicular directions. In the case of conventional tanning, higher elongation was found in the parallel direction, which was 60% and lower elongation in the perpendicular direction, which was 52%.

In the experimental sample, the same results were observed. Furthermore, in comparison between the conventional and experimental samples, the experimental sample showed better elongation in both parallel and perpendicular directions. As leather has elasticity and plasticity properties, leather fibers showed more stretchiness along the parallel direction of the skin, which might be why test samples showed higher elongation in the parallel direction.

Table 4 Tensile strength for conventional and experimental sample

Sample ID	Tensile strength (kg/cm^2)		[32]
	Parallel	Perpendicular	
Conventional	281.5±4.91	353.5±7.71	Min.
Experimental	285.5±4.95	359.5±6.36	250

In the case of conventional tanning, the tensile strength value was 281.5 kg/cm^2 in the parallel direction but in the perpendicular direction, it was 353 kg/cm^2. In the experimental sample, the values were 285 kg/cm^2 in the parallel direction and in the perpendicular direction 359 kg/cm^2. In leather, fibers are oriented normally in both perpendicular and parallel directions. During the tensile test, samples were tested alongside the perpendicular direction and showed higher strength values than in the parallel direction. The experimental sample showed higher tensile strength than the conventional sample. This might be because the experimental sample could uptake more Cr and get fixed with collagen fiber.

6. Conclusion

The present tanning method showed that tanning with recovered chrome tannin containing 33% basicity showed almost similar mechanical properties and lowered pollution load in the tanning process. During tanning process, a significant amount of chromium remains in the spent liquor without any chemical deformation. Therefore, as long as this free chromium particles remain in the spent liquor, it could be recovered and reused in the tanning process for several cycles. This proposed method could reduce the pollution load from the discharged spent chrome liquor reducing the hazardous Cr intake load as well as ensure the use of chrome from the spent chrome liquor.

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