Textile & Leather Review

ISSN 2623-6281 | www.tlr-journal.com | 10.31881/TLR

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How to cite: Mottalib MA, Chandra M, Naher UHB, Goni MA. Recovery and Reuse of Chromium from Tan Yard Solid Waste in Leather Manufacturing. Textile & Leather Review. 2023; 6:622-651. https://doi.org/10.31881/TLR.2023.116

How to link: https://doi.org/10.31881/TLR.2023.116

Published: 29 October 2023

Recovery and Reuse of Chromium from Tan Yard Solid Waste in Leather Manufacturing

Md. Abdul MOTTALIB[1*], Mohan CHANDRA[1], Umme Habiba Bodrun NAHER[1], Md. Abdul GONI[2]
[1]Institute of Leather Engineering and Technology, University of Dhaka, Dhaka, Bangladesh
[2]Department of Biological and Physical Sciences, South Carolina State University, Orangeburg, SC 29117, USA
*abdul.mottalib@du.ac.bd

Article
https://doi.org/10.31881/TLR.2023.116
Received 16 August 2023; Accepted 19 October 2023; Published 29 October 2023

ABSTRACT

Chrome tanning is the most popular and widely used method utilizing basic chromium salts in leather processing. Only 60-70% of these salts react with collagen to form leather. The rest remains unreacted being released as toxic waste and causing severe environmental pollution in many developing countries. In the current study, a significant approach was made to utilize solid waste with a clean environment perspective. The chromium was extracted as basic chromium sulfate using H_2SO_4 from tannery waste and reused in the leather manufacturing procedure. Extracted solid sludge was examined by Atomic Absorption Spectrometry and elemental analysis before and after the separation of chromium (III). It revealed that 97% of chromium was extracted from tan yard sludge. Recovered chromium sulfate was reused in goat skin processing. Batch experiments were carried out by applying recovered basic chromium sulfate, and a combination of fresh and recovered basic chromium sulfate solutions separately. Fresh basic chromium sulfate was used as the control method. The structure and morphology of the final processed leather were characterized by Field Emission Scanning Electron Microscope (FESEM) and Thermogravimetric analysis (TGA). The identical structural morphologies of all processed leather were confirmed in the FESEM study. The physical and chemical characteristics of all finished leather were found very similar. The TGA analysis data proved that raw leather processed by recovered chromium is thermally more stable than others. These research findings signify a new potential effort of separating important chemicals from solid sludge and reusing them. This technique is simple, cost-effective, eco-friendly, and sustainable as it reduces environmental pollution from tannery chromium waste.

KEYWORDS

chromium recovery, morphology, pollution, sludge

INTRODUCTION

Environmental pollution caused by the emission of toxic liquid and solid waste from different tanning industries has drawn significant attention in recent years. The leather manufacturing sector is one of the top chemical and water-consuming (35-56 m^3/ton of raw hides) industrial enterprises generating significantly large quantities of different toxic pollutants [1]. Various tanning industries discharge their mixed effluents which are enriched with suspended solids, unpleasant odour, dissolved solids, fats, high

COD and BOD as well as high amounts of chromium and calcium content [2]. Although the leather industry significantly contributes to Bangladesh's national economy through income and employment opportunities, it also creates an enormous amount of solid and liquid waste from its manufacturing system [3]. About 90% of raw leather is tanned worldwide by using basic chromium sulfate in leather manufacturing processes [4,5]. Applications of chromium salts in raw leather tanning which is known as chrome tanning offer many advantages in tannery industries such as being cheaper, relatively available and versatile providing excellent cross-linking properties as leather tanned with chromium compounds exhibit very good physical and chemical properties. In traditional leather manufacturing, 8-12% (w/w respect to wet hide) basic chromium sulfate (BCS) is used and 60-70% of BCS reacts with the collagen fibres of hides and skins to form leather, and about 30-40% of BCS remains unreacted in tanning processes which end up as waste are released as mixed toxic effluents from leather industries without any prior treatments [6,7].

On the other hand, only 20-25% of raw hides/skins are turned into finished leather during the manufacturing processes in tannery industries. 75-80% of the initial raw materials remain unreacted which end up as solid waste and are continually discharged into the surrounding environment [6-9]. A major quantity of solid waste is generated from fleshing, trimmings, splitting, and shaving steps along with sludge produced in treatment plants [7]. Among all solid waste discharged from different steps in leather manufacturing processes, 12.5% of solid sludge generated in effluent treatment plant (ETP) contain a significant amount of chromium that is toxic and harmful to the environment [10]. About 3.5–4.5% of chromium found in wet blue trims, splits, and shaving dust exist as Cr_2O_3 whereas the sludge from Common Effluent Treatment Plant (CETP) contains about 2.5% chromium (III) [11,12]. Chromium-contaminated sludge produced by wastewater treatment plants is one of the primary environmental pollution concerns from leather tanning industries in many developing countries [13]. Both solid and liquid waste are responsible for pollution and subsequent degradation of the quality of the natural environment like soil, water, air etc. Thus, waste generated from various leather industries severely affects human, animal, plant, and aquatic lives. Due to the environmental pollution caused by chromium, less chrome or chrome-free tanning has attracted considerable attention [14,15]. Most of the leather industries in Bangladesh were set up adjacent to the residential areas within Dhaka, the capital city of the country. Due to the environmental pollution concern in and around Dhaka city, all leather industries were moved recently and relocated from the Hazaribagh urban area to a new site known as Tannery Industrial Estate Dhaka (TIED) which is located at Hemayetpur area in Savar upazila. A common effluent treatment plant was supposed to be established in the vicinity of leather industries in Savar which can be used to treat all kinds of tannery liquid waste before discharge. Unfortunately, till now there has not been any central effluent treatment plant set up properly in the respective area. In addition, there was poor planning, deficiencies and incomplete installation of waste treatment facilities in the new Tannery Industrial Estate at Hemayetpur area. Therefore, solid waste generated from different leather industries at Hemayetpur in Savar, Bangladesh are being discharged into the surrounding environment thus contaminating water bodies, soil, air etc. in the corresponding areas**.** The unplanned dumping of tannery solid waste and CETP sludge from Savar Tannery Industrial Estate is posing a serious threat to the surrounding ecosystem which is drastically affecting water quality, soil textures, and agricultural activities in the respective areas. Fig. 1 shows the dumping of solid waste from various tannery industries in Bangladesh.

Figure 1. Solid waste dumping site at TIED in Savar, Bangladesh

This tannery solid waste dumping site is located close to the bank of the Dhaleswari River. As a result, chromium-containing solid waste can easily be washed away or leached into the river by heavy rainwater, flooding, landfills, and other ways which can severely pollute surface water bodies, and sediment beds in the river, as well as soil, crops, and vegetables in the adjacent areas. Fishes and other aquatic living species may be accumulating toxic chromium species from contaminated water bodies and sediments. Chromium intake can result in an increased fish mortality rate from contamination. Chromium-containing solid waste may also be polluting groundwater by leaching. It can be also overtaken by plants which may affect their growths as well as crop yields. Therefore, it is speculated that toxic chromium (III) may be translocated into the human body from industrial waste through the food chain.

Chromium toxicity in different environmental segments depends upon its oxidation states. The trace amount of trivalent chromium is essential for biochemical metabolism processes in the human body especially for diabetic patients whereas the trace quantity of hexavalent chromium is extremely harmful, mutagenic, and cancer-causing [16,17]. Excessive intake of chromium (III) through the food chain and other means of exposure, can cause many harms to the human body like headache, dizziness, eye, skin, and lung irritation, allergic response, liver poisoning, renal and nervous system breakdown, gastrointestinal ulcer, nasal septum, long-term illnesses including occupational asthma, ulceration, bronchitis, genetic abnormalities, and dermatitis [18-21]. Kolomaznik et al*.* also reported the toxicity of chromium (III) which was found to be linked to high blood pressure, lung cancer, and kidney failure [22]. Trivalent chromium in soil or water bodies can be converted into hexavalent form in different ways [23]. Exposure to Cr(VI) can cause occupational asthma, eye irritation and damage, eardrum perforation, respiratory irritation, kidney diseases, liver failure, pulmonary congestion and oedema, nasal irritation and damage, respiratory cancer, skin irritation, and tooth erosion [24]. Considering the adverse effects of toxic chromium in the environment, proper treatment of tannery effluents and chromium-containing solid waste is crucial before they are discharged into the environment. Many methods including electrocoagulation [25], chemical precipitation [26], ion exchange [27], membrane processes [28], solvent extraction [29], and electro-dialysis [30], have been used previously to remove harmful chromium (III) from tannery effluents. The removal of heavy metals like Cr from wastewater using biosorption technology has gained popularity in recent years as it is both cost-effective and environmentally friendly [31-33]. The present study aimed to utilize chromium-containing solid tannery waste in a clean environment perspective where a new potential approach was made to separate chromium compounds from tannery sludge and reapply them in raw leather manufacturing processes and thus reduce environmental pollution. The study also focused on the investigation of different physicochemical and chemical characteristics of leather treated with recovered chromium compounds and then compared them with the standard characteristics of leather tanned by fresh basic chromium sulfate solutions.

EXPERIMENTAL

Materials and Methods

Sample collection

Central Effluent Treatment Plant (CETP) solid sludge waste sample was collected from the Tannery Industrial Estate Dhaka (TIED) located at Hamayetpur in Savar, Dhaka, Bangladesh. The sample was brought into the laboratory. Moisture content was determined as quickly as possible. The sample was then dried, powdered, and homogenized.

Sample preparation for acid digestion

The chromium content in the sludge sample was determined by Atomic Absorption Spectroscopy (AAS) and the solid sample was digested according to the literature [34]. The powdered sludge sample was dried in an oven for three hours at 105 °C. 0.5 g of dried sample was transferred into a round flask. The flask was filled with 10 mL of concentrated HNO_3 acid and 5 mL of concentrated HCl acid. The combination was agitated at 90-95 °C for 4-5 hours on a hotplate with a magnetic stirrer. After cooling the mixture to ambient temperature, it was filtered through Whatman no. 40 filter paper. Finally, the filtrate was diluted to 100 mL by adding distilled and deionized water [34]. The resulting solution was sealed in small sample bottles and kept in a refrigerator for further analysis.

Extraction procedure of basic chromium sulfate

10 g of dried powdered sludge sample was taken in a 500 mL beaker. The powdered sludge sample was turned into paste form after the addition of an appropriate amount of distilled and deionized water. 4 mL of 5% (v/v) sulfuric acid was then transferred into the beaker and more distilled-deionized water (about 10 mL) was added to the mixture. The beaker with sludge and acid mixture was placed on a hot plate with a magnetic stirrer. The mixture was stirred at about 60 °C for 2 hours to obtain maximum extraction. Chromium was extracted from the mixture as a basic chromium sulfate solution, which was collected by decantation. The extraction procedure was repeated 4 to 5 times in a similar way to separate all chromium efficiently. Finally, the liquid mixture was filtered, and the pH of the recovered liquor was adjusted at 2.3-2.8 by an appropriate quantity of dilute sodium hydroxide solution. The recovered basic chromium sulfate liquor was preserved in the refrigerator before further use. The residue sludge was preserved and the chromium content in the remaining residue was determined. The different steps which were performed to extract basic chromium sulfate from the tannery sludge sample are displayed in Figure 2.

Figure 2. Small-scale extraction of chromium from tannery sludges

Analysis of residual sludge after chromium extraction

After extraction, the chromium solution was separated by decantation followed by filtration, and the remaining residue was referred to as residue sludge. The residual sludge may be suitable as fertilizer in agricultural activities depending on the presence of macronutrients. The chromium contents in the sludge before and after chromium recovery were determined by an atomic adsorption spectrophotometer (AAS), which were found as 5.5% and 0.19%, respectively. Since the residual sludge contains 0.19% chromium, before use as fertilizer, the residual sludge needs to be treated with alkali like magnesium oxide (MgO) to reduce the chromium level. Elemental analysis (C, H, N, S) of sludge before and after the chromium extraction were performed by an elemental analyzer (Vario Micro V1.6.1 GmbH, Germany) which showed the relative quantities of carbon, hydrogen, nitrogen, and sulfur. The results of elemental analysis of solid sludge before and after the separation of chromium are shown in Table 1.

Table 1. Elemental analysis data of CETP sludge and residue before and after extraction of chromium

Sludge	Cr (%)	C (%)	H (%)	N (%)	S (%)
before Cr recovery	5.5	37.27	6.093	5.31	1.069
after Cr recovery	0.19	35.59	5.928	4.26	1.242

After chromium recovery, the remaining residue contains 0.19% of chromium. However, very significant quantities of essential elements such as nitrogen, carbon, hydrogen, and sulfur were found in the residue, and the differences among their quantities remained almost the same in the solid sludge before and after the separation of chromium (III) (Table 1).

pH optimization

The CETP sludge was chemically treated with sulfuric acid to extract chromium as basic chromium sulfate. Different concentrations of sulfuric acid solutions, including 5%, 6%, 8%, and 10%, were added separately to CETP sludge to maximize the extraction efficiency and the respective procedures were repeated to optimize the chromium extraction. The pH of each of the corresponding mixtures was thus obtained with different percentages of acid solutions which have been shown below in Table 2.

Table 2. The magnitudes of pH in the sludge mixtures with different concentrations of H_2SO_4

Sulfuric acid, %	5	6	8	10
pH obtained	2.0	0.87	0.24	0.09

The application of 5% sulfuric acid solution turned the pH of the mixture to 2.0 which was acceptable. However, higher sulfuric acid concentrations caused the lowering of the pH of the recovered liquors below 1.0 and thus made the resulting liquors unsuitable for use in chrome tanning. The optimal pH of chrome tanning is 2.0.

Proposed plant for basic chromium sulfate recovery from CETP sludge

The present study focused on small-scale laboratory experiments to extract and separate chromium (III) from solid tannery sludge as basic chromium sulfate. However, considering chromium extraction efficiency and significant results of this interesting approach, we are highly convinced to see the large-scale industrial applications of this method of chromium recovery from solid sludge and reuse in tannery industries. A mechanism has been proposed to apply this chromium separation and reuse technology in a real large-scale industrial environment (Fig. 3). The solid sludge from CETP will be stored in a tank. A pump will be used to transport chromium-containing solid sludge from the storage tank to the main reactor tank. Later on, hot water (60-70 °C) will be added to the reactor tank and a homogeneous sludge mixture will be prepared by using the stirrer blades. The sulfuric acid will be added to the sulfuric acid storage tank. The flow of acid and hot water will be controlled by a stopper valve. Following the extraction, a pump will be used to transport the recovered chromium in an aqueous solution to a filtering and screening tank. The appropriate amount of sodium hydroxide solution will be supplied via a separate tank for pH adjustment. Finally, the recovered liquor was kept and saved in a tank before use. After chromium recovery, the remaining sludge was collected in a separate tank, and it could be utilized as fertilizer after further purification by the treatment with magnesium oxide, MgO. In the laboratory scale experiment, recovered chrome liquor was used in the leather manufacturing processes without any further purification. The proposed mechanism of chromium extraction from CETP sludge is shown in Figure 3.

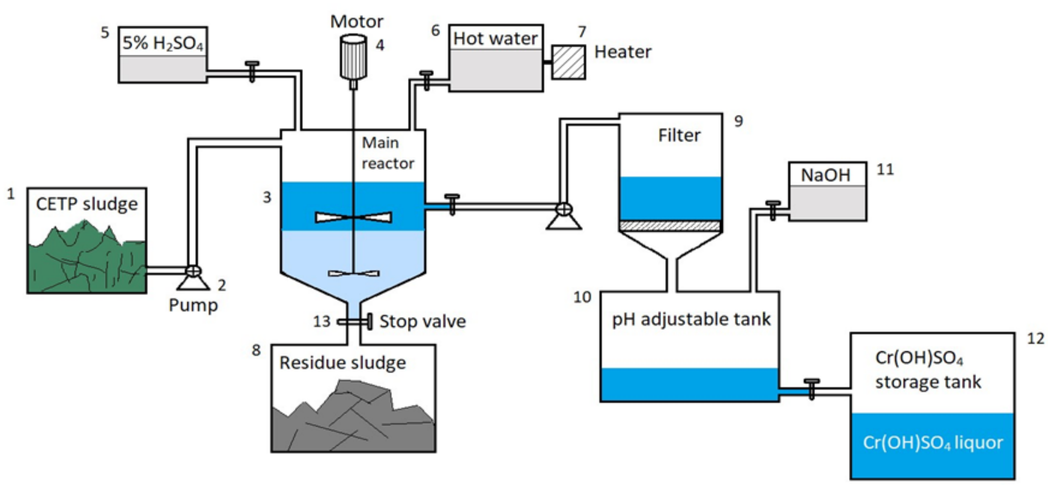


Figure 3. Flow diagram of chromium recovery from solid tannery sludge from a large-scale industrial applications perspective

1. CETP solid sludge storage tank
2. Pump
3. Main reactor
4. Stirrer with blade
5. Sulfuric acid storage tank
6. Water storage tank
7. Heater
8. Residue sludge storage tank
9. Filtering/ screening tank
10. Filtrated liquor storage tank
11. Sodium hydroxide storage tank
12. Basic chromium sulfate storage tank
13. Stop valve

Tanning process

Tanning is the process that converts putrescible and non-usable hides/skins into imputrescible and usable leather [35]. Basic chromium sulfate that had been recovered was employed in the production of raw leather according to the traditional tanning process guidelines. Fig. 4 shows the various steps in raw leather manufacturing which were applied gradually to process raw leather with recovered basic chromium sulfate solution [10].

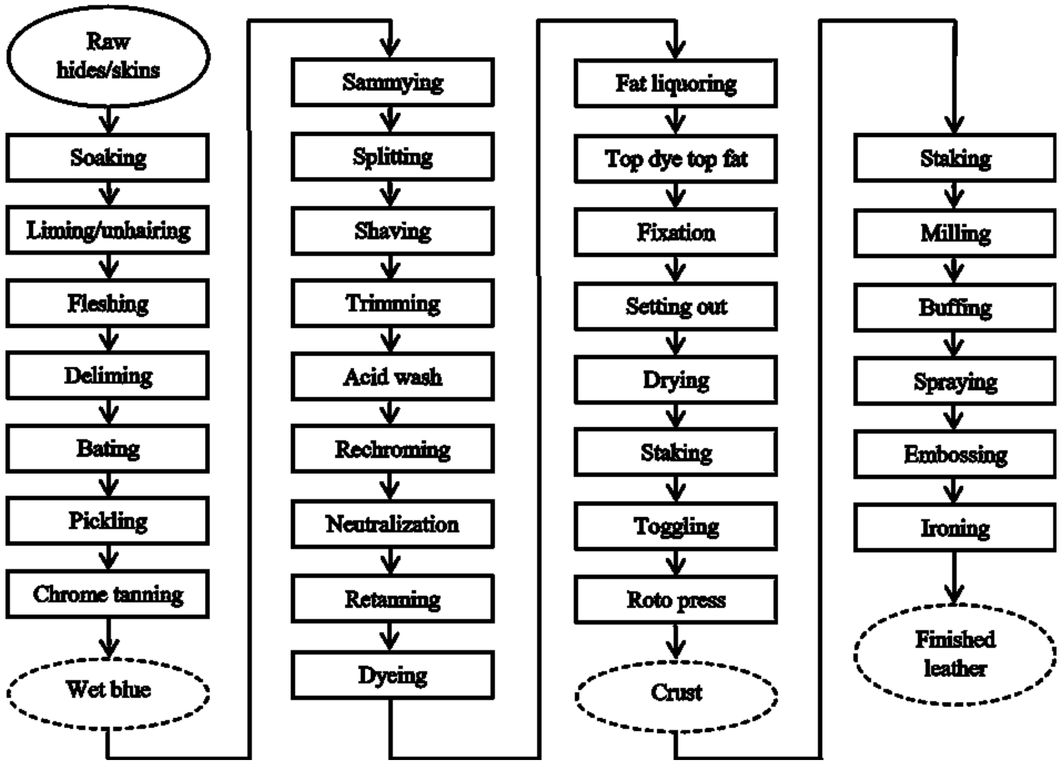


Figure 4. Different steps in raw leather processing

Analysis of physicomechanical properties of processed leather

The treated, re-tanned leather was divided into smaller pieces (two portions for each sample, parallel and perpendicular to the spine for each test as required). For a particular test, each of the cut leather samples was conditioned for 48 hours in accordance with the accepted practices, and smaller leather pieces were kept at a relative humidity of 65±2% and a temperature of 23±2 °C [36]. To assess the typical quality of processed leather, physical and chemical tests were carried out on the leather samples. The percentage of elongation, stitch and Baumann tear strength, tensile strength, grain crack resistance, flexing endurance, vamp flexing, and distension at break tests were performed following the standard procedures of SLC [37]. Hydrothermal stability and chromic oxide content in the finished leather were also examined. Each of the processed leather samples was performed in three duplicates of each of the characteristics tested. The standard qualities of the processed leather attained from several studies were thought to be illustrated by the average result on each test.

RESULTS AND DISCUSSION

Solid sludge collected from the Common Effluent Treatment Plant (CETP) at Tannery Industrial Estate Dhaka was analysed for the determination of total chromium and calcium content using the Atomic Absorption Spectrophotometry technique (AAS). The amount of chromium and calcium found in the tannery sludge before and after the chemical treatment with sulfuric acid solutions is shown in Table 3.

Table 3. Metals analysis data of solid tannery sludge before and after the chromium separation

Metal	Before recovery of chromium (g/kg)	After recovery of chromium (g/kg)
Cr	55	1.9
Ca	32.3	24.1

Before any chemical treatment, the chromium content in the original tannery sludge was 55 g/kg. However, after the addition of sulfuric acid solution and subsequent reactions, the resulting tannery sludge showed a significant amount of chromium which was reduced by the acid treatment and a smaller quantity of chromium remained in the residual sludge which was 1.9 g/kg (Table 3). The results revealed that 97% chromium was successfully extracted from raw tannery sludge after treatment with dilute sulfuric acid. A significant amount of calcium was found in the sludge samples before (32 g/kg) and after chromium recovery (24.1 g/kg) which indicated the presence of unreacted calcium hydroxide or insoluble calcium sulfate in the tannery sludges. In CETP, unconsumed or unreacted basic chromium sulfate was usually treated with lime to form insoluble $Cr(OH)_3$. The chemical reaction that occurs in the CETP is shown below:

$$Cr(OH)SO_4 + Ca(OH)_2 = Cr(OH)_3 \downarrow + CaSO_4 \quad (1)$$

This trivalent chromium hydroxide formed in the treatment plant is usually contaminated with other insoluble proteinous substances. The discharge of tannery sludges with excessive trivalent chromic hydroxide from different leather industries without proper purification or treatment process and subsequent dumping of them in open places has been causing severe environmental pollution in many developing countries like Bangladesh.

In the present study, chromium was extracted from tannery sludge by treating it with sulfuric acid at 60 °C which after the reaction formed basic chromium sulfate, $Cr(OH)SO_4$. Unconsumed or unreacted calcium hydroxide present in the original solid sludge sample may also react with sulfuric acid to form calcium sulfate which was less soluble than $Cr(OH)SO_4$ in an aqueous system at 25 °C (RT). After chromium recovery, a major portion of calcium remains in the residual sludge. However, relatively minor quantities of calcium might have been transferred into the solution with chromium. The chemical reactions which occur in the recovery process are shown below:

$$Cr(OH)_3 + H_2SO_4 = Cr(OH)SO_4 + 2H_2O \quad (2)$$

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O \quad (3)$$

Estimation of chrome recovery

Each waste sample contained 2.20 kg of solid tannery sludge. A total of 4 L of water and 2 L of 5% sulfuric acid were used to extract chromium from 2.20 kg sludge. Finally, the volume of the reaction mixture was reduced to 4.8 L by heating slowly evaporation. The procedures were repeated three times. The results of chromium recovery from tannery sludge have been shown in Table 3.

According to the results shown in Table 3, 55 g/kg and 1.9 g/kg of chromium were found in the sludge sample before and after chromium extraction respectively.

$$\text{Efficacy of removal extraction} = \frac{55-1.9}{55} \times 100 = 96.55\ \% \quad (4)$$

According to the above results, 116.82 g Cr as $Cr(OH)_3$ can be recovered from 2.20 kg sludge. 52 g Cr can produce 165 g $Cr(OH)SO_4$ (atomic mass of Cr = 52 and FW of $Cr(OH)SO_4$ = 165). $Cr(OH)_3$ in the sludge sample will react with H_2SO_4 to form soluble basic chromium sulphate, $Cr(OH)SO_4$. Therefore, 116.82 g Cr can produce 370.67 g $Cr(OH)SO_4$. 370.67 g $Cr(OH)SO_4$ is present in 4.8 L recovered liquor, therefore, 77 g $Cr(OH)SO_4$ is present in 1 L recovered liquor.

The amount of calcium remaining in $Cr(OH)SO_4$ solution was (32.3-24.1) g/kg **=** 8.2 g/kg which was not separated from the recovered liquor and was present in the resulting liquor as an impurity. According to the above calculation, 18.04 g of calcium ions remain in the 4.8 L of recovered basic chromium sulfate liquor. This recovered basic chromium sulfate was reused in the processing of raw skins without any further purification.

Tanning in drum

Three pieces of raw goat skins were collected and cut to make six sides. They were processed conventionally in the following three batches (2 pieces of side per batch A, B & C): (A) raw skin was treated with 100% recovered basic chromium sulfate, (B) a combination of recovered chromium and fresh basic

https://doi.org/10.31881/TLR.2023.116

chromium sulfate was added to the raw goat skins, (C) 100% fresh basic chromium sulfate was used to process the raw goat skin samples as a control experiment. Chrome tanning of sample (A) and sample (B) was carried out by recovered chromium while re-chroming of corresponding leather samples (A) and (B) was performed by recovered and fresh basic chromium sulfate solutions respectively. Tanning and retaining of sample (C) were performed only with the fresh basic chromium sulfate. The wet blue cross-section demonstrated chromium penetration in the pelt matrix. Excellent chromium penetration was found in all three categories of samples.

Physical and chemical properties of processed and analyzed leather

Comprehensive physical and chemical tests were conducted on the leather which was tanned using recovered chromium, fresh chromium, and a combination of recovered and fresh chromium respectively which evaluated the physical and chemical attributes of the processed leather and these characteristic properties were compared with the leather standard parameters reported in literature [35,37]. Various characteristics of physicochemical parameters such as hydrothermal stability, tensile strength, chromic oxide content, tear strengths (Stitch and Baumann), and percentage of elongation at break, grain crack resistance, and distension tests were investigated in the processed leather and the results of these analyses were tabulated as shown in Table 5. All the tests were replicated in three and the average results reported were here.

Table 5. Chemical as well as physical features of the processed leather

The test's name	Sample A	Sample B	Sample C	Standard value
Shrinkage temperature (°C)	115±1	115±1	115±1	107
Chromic oxide content (%)	4.17±0.2	4.42±0.2	4.46±0.3	2.5-5
Tensile strength (kg/cm^2)	225±8	253±2	256±5	200
Elongation (%) at break	62±2	66±1	59±2	40
Stitch tear strength (kg/cm)	95±3	105±2	99±4	80
Baumann tear strength (kg/cm)	32.1±0.1	32.3±0.8	33.4±0.8	30
Grain crack load (kg)	21.8±0.2	20.5±0.3	23±0.6	20
Distension (mm) Min.	7.45±0.3	7.5±0.2	8.1±0.1	7

*Sample A: Tanned with 100% recovered basic chromium sulfate; Sample B: Tanned with a combination of recovered and fresh basic chromium sulfate; Sample C: Tanned with 100% fresh basic chromium sulphate

Hydrothermal stability (shrinkage temperature)

Shrinkage temperature (Ts) refers to the resistance of a material to heat [35]. It measures the specific temperature at which a particular material shrinks. Shrinkage temperatures of the leather samples were determined following the procedures of the IUP-16 method [38]. The processed Leather strip with 8 cm × 1 cm dimension was heated slowly in water and a glycerol mixer. The stability of each leather sample was confirmed up to 115 °C temperature with no visible shrink which was greater than the standard leather shrinkage temperature observed for upper leather (107 °C) [38]. According to earlier research, vegetable re-tanned leather shrank at 86.34 °C, which is much lower than the information from processed goat leather [39]. Other similar studies conducted by Yorgancioglu et al. and Ferdous et al. also reported the shrinkage temperature of chrome-tanned leather which was 103.5 °C [40] and 105 to 110 °C [41]. Interestingly, the shrinkage temperatures of all manufactured goat leather from the present study were considerably higher than the data reported previously in the literature [40-42] following the conventional method which demonstrated that the leather processed with recovered basic chromium salts was hydrothermally more stable.

Chromic oxide content

Chromic oxide contents in the leather samples were determined following the standard method of IUC 8 [43]. The amounts of chromic oxide in leather tanned using fresh basic chromium sulfate, fresh and recovered basic chromium sulfate, and recovered basic chromium sulfate were determined to be 4.460.3%, 4.420.2%, and 4.170.2%, respectively which were within the UNIDO standard of 2.5-5% [35]. These results showed that excellent chromium penetration was achieved in all tanned leather.

Tensile strength

Tensile strength is the maximum load required to break the unit cross-section area of a leather sample [35]. The Society of Leather Technologists and Chemists (SLTC) established the IUP 6 method to measure the tensile strengths and percentages of elongations of leather samples and both tests were performed according to this method [20,44]. The magnitudes of tensile strengths for samples A, B and C were found to be 225±8, 253±2, and 256±5 kg/cm^2 respectively which were much greater than the worldwide standard value of 200 kg/cm^2 for leather used in shoe uppers [35]. Ferdous et al. reported the tensile strength of goat-skin leather in the range from 247.62 to 292.59 kg/cm^2 [41] whereas Saravanabhavan et al. cited the magnitudes of tensile strengths at 238 kg/cm^2 [45]. Tensile strength data from the current study and data from earlier, related studies were compared, and the results revealed that all leather processed with recovered basic chromium salts possess all standard qualities and are in line with the values established by international standards.

Percentages of elongation at break

The tensile strain in the shoe upper leather at the breaking stage is measured as the percentage of elongation at break [46]. For the leather to be elastic enough to adjust to the user's feet and movements brought on by wearing shoes, the elongation at break must have a medium value. The percentage of elongation tests on the processed goat leather was performed following the standard procedures of IUP 6 [44]. The results of percentages of elongation of the experimental leather samples showed a range between 59±2 and 66±2 which were significantly higher than the standard value of elongation at 40%. The proportion of leather elongation demonstrated in a previous study by Unango et al. was reported at 45% [47]. The processed leather likewise showed comparable amounts of elongation (43–45%), as reported in earlier studies [48]. All processed goat leather had elongation at break percentages that were much higher than both the UNIDO standard and the data previously published in the literature.

Stitch tear strength

The standard procedure DIN 53333 described in the literature was used to determine the stitch-tearing strengths of all manufactured leather [49]. Stitch tear strength represents the load required to break the leather sample in between two holes with a distance of 6 mm between the centres of the holes, the diameter of each hole is 2 mm, and the thickness is 1 cm. The stitch tearing strengths of leather tanned by recovered basic chromium sulfate, a combination of fresh and recovered and fresh basic chromium sulfate were found to be 95±3, 105±2, and 99±4 kg/cm which were significantly higher than the standard value of 80 kg/cm for shoe upper leather indicating that all tanned leather possess better quality regarding stitch tear strength [35].

Baumann tear strength

The Baumann tear strength is the amount of load required to tear a 1 cm thick leather sample [35]. The testing method SATRA PM 162 was used to assess the Baumann tear strength in the treated goat leather. Baumann tear strengths of all processed goat leather were significantly higher than the benchmark value of 30 kg/cm, indicating that they can be used as shoe upper leather [35].

Grain crack strength or lastometer test

Grain crack strength demonstrates the load required to crack (hair-like) the leather sample [35]. The procedure obtained from the method IUP 12 was used to determine the grain crack strengths of the finished goat leather [50]. The grain layer must have higher elasticity to endure the stresses which are needed to use leather in footwear during lasting, particularly in the toe area. The Grain crack strengths of the processed leather samples A, B, and C were found to be 21.8±0.2, 20.5±0.3, and 23±0.6 respectively which were greater than the conventional cut-off value of 20 kg for shoe upper leather [35].

Thermogravimetric analysis (TGA) of leather samples

All leather samples undergo thermal analysis utilizing a TGA 8000TM device from Perkin Elmer in the United States. Each leather sample used in this study weighed around 4-5 g, and it was heated in a platinum pan at a steady rate of 10 °C per minute under a spontaneous flow of N_2 to a temperature of 700 °C. The outcomes of the TGA study of all processed leather are displayed as thermogravimetric curves and differential thermal analysis (DTA) curves which are shown in Figures 5, 6, and 7.

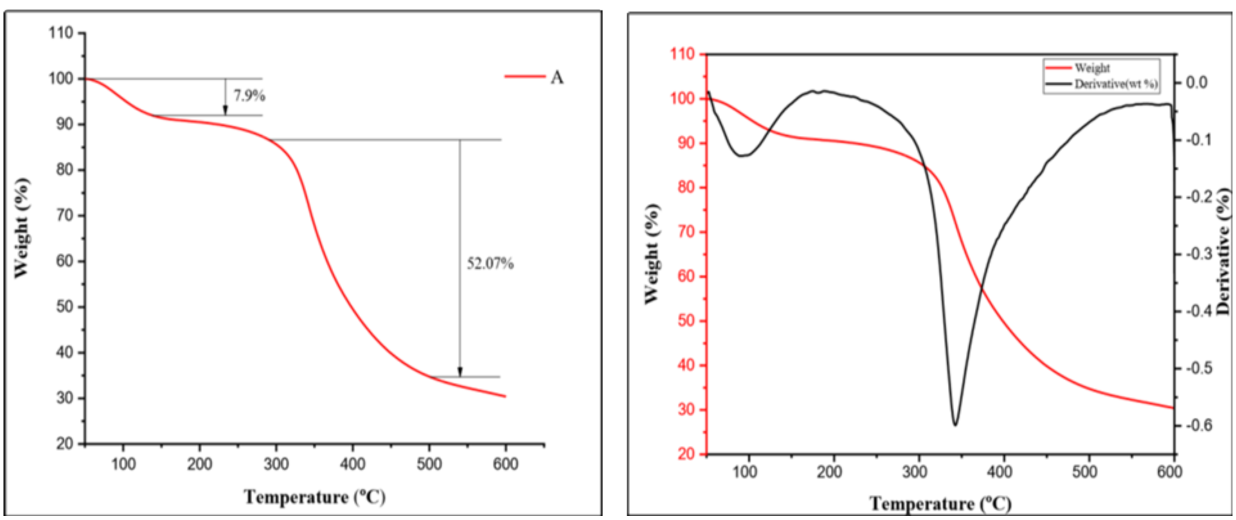


Figure 5. TGA and DTA curves of recovered basic chromium sulfate-tanned leather

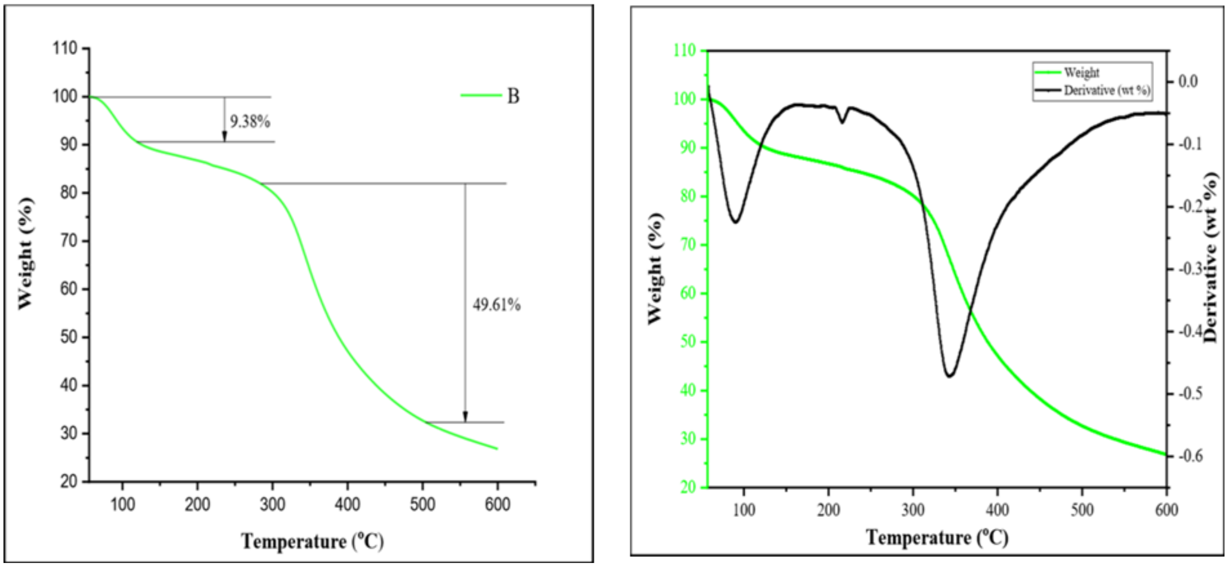


Figure 6. TGA and DTA diagrams of leather tanned by a combination of recovered and fresh basic chromium sulfate

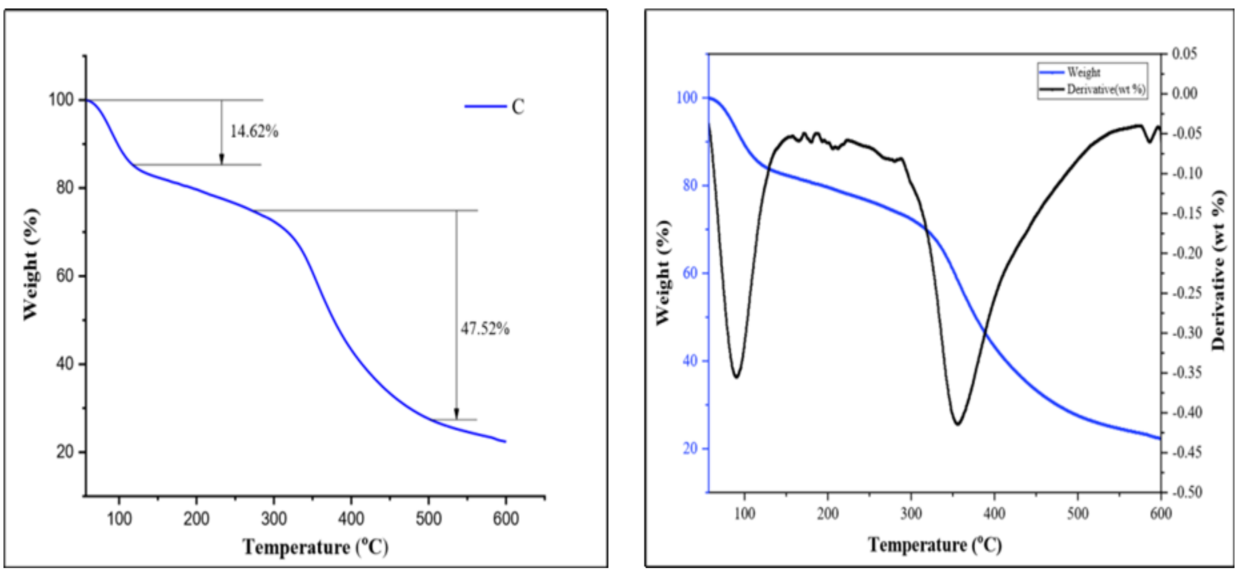


Figure 7. TGA and DTA diagrams of leather tanned by fresh basic chromium sulfate

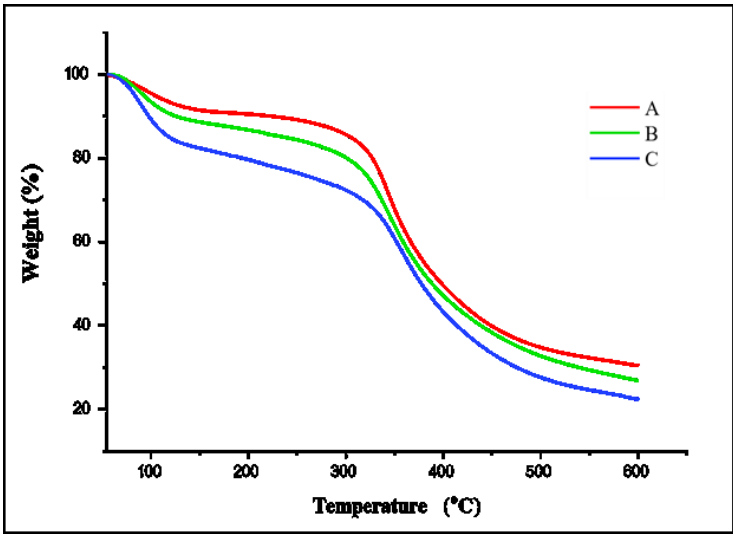


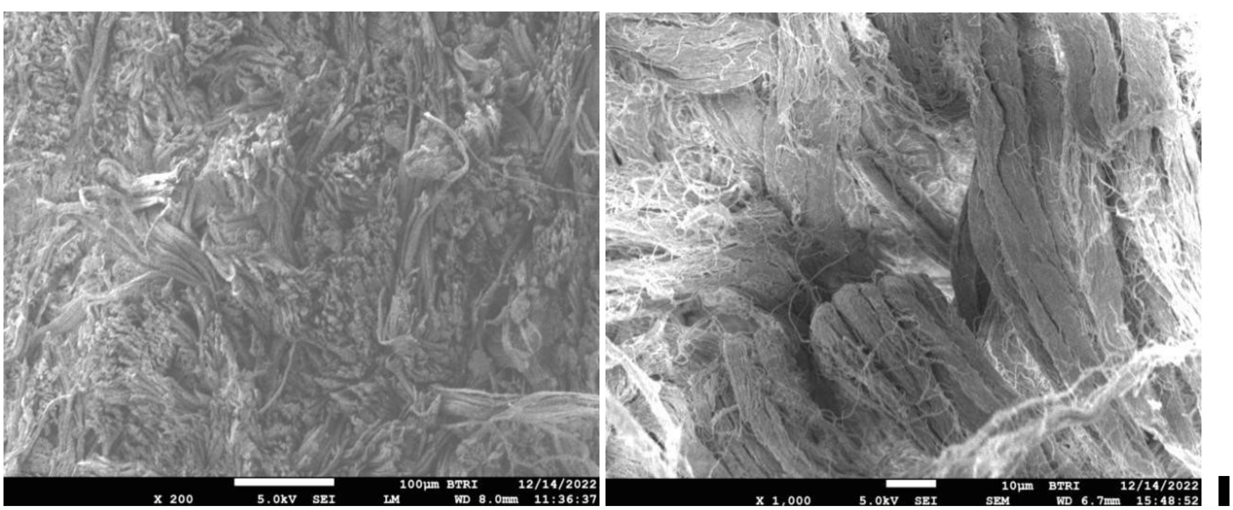
Figure 8. Combined TGA diagrams of leather tanned by (A) recovered chromium (B) a combination of fresh and recovered chromium, and (C) fresh chromium

It has been apparent from Figure 8 that inherent moisture contents have been retained in the leather at 100 °C. Weight losses occurred two times and a similar pattern of changes was observed in all the leather samples upon heating. Due to the removal of moisture and other volatile species from the leather samples at the initial stage of heating (80 to 140 °C), weight losses of roughly 10-15% were observed. Maximum weight loss occurred in sample C (Figure 8). When the samples were heated at 300 °C, the second step of degradation in the corresponding leather samples began and weight losses were gradually increased up to 500 °C. The maximum weight loss (50-60%) was observed at 300 to 400 °C in all manufactured leather species. The appearance of extremely sharp breakpoints (shoulder peak) in the TGA diagrams indicated that the leather species had disintegrated at that temperature (Figure 8). The TGA study of all processed goat leather produced results that were remarkably similar to findings previously reported in the literature from studies that looked at leather that had been chrome-tanned and found that they disintegrated at temperatures between 300 and 400 °C [40,51]. All the finished goat leather samples were found to be stable up to 300 °C which indicated their excellent thermal stability. Among all goat leather treated with three different basic chromium solutions, the thermal stability of the leather tanned by recovered chromium was higher than those observed with leather tanned by a combination of recovered and fresh chromium as well as 100% fresh chromium solutions. Since a small amount of calcium remained in the recovered basic chromium sulfate and the same chrome mixture was employed in leather manufacturing without purification, the presence of calcium in the system might have played an important role in chromium penetration into the leather or it might have partially participated in the tanning process which might have caused the increase in thermal stabilities of the tanned goat leather. Similar results of thermal stabilities of the processed leather were also observed in other studies conducted previously by Gao et al. [52]. Calcium ions might have a positive contribution in stabilizing the collagen structure in the hide which ultimately facilitated the crosslinking between chromium ions and collagen fibres leading to the formation of more durable and stable finished leather [52].

Fibre structure analysis by FESEM (Field Emission Scanning Electron Microscopy)

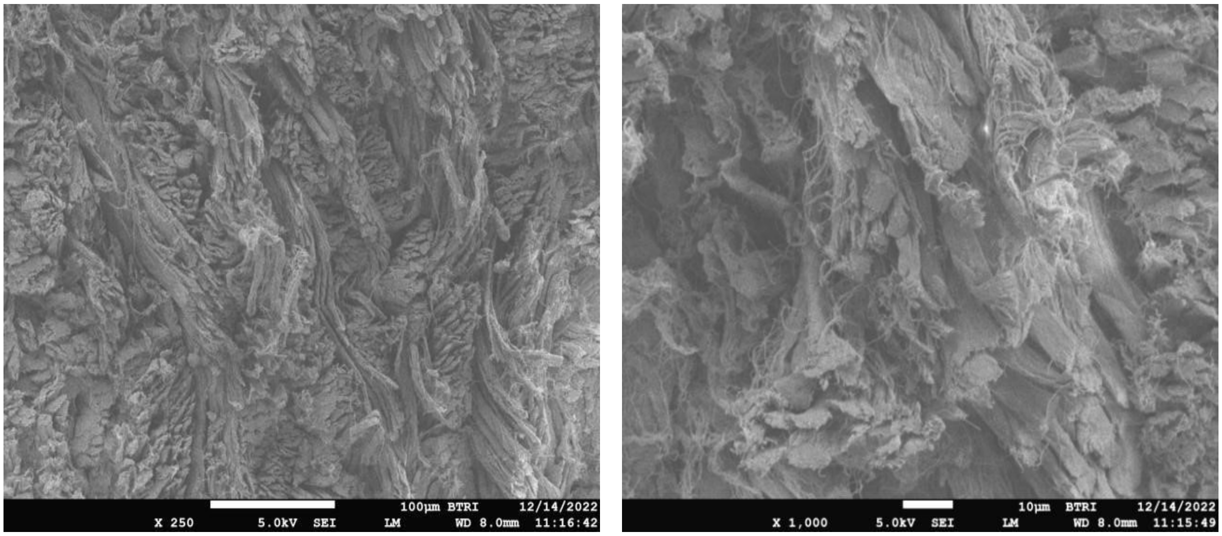
Field Emission Scanning Electron Microscopy (FESEM, model no: JSM-7610F) technique was employed to evaluate the morphology such as grain size, shape, fibre bundle, and fibre structure of the flesh surfaces and the cross-sectional area of the processed leather samples [53]. FESEM is usually conducted in a high vacuum environment because gas molecules tend to affect the electron beam and the emitted secondary and backscattered electrons are being used for imaging. An electron beam focused by an electromagnetic lens scans the sample surface and the reflected or interacting electrons create a picture of the sample's surface and topography. FESEM photographs of the leather tanned by fresh chromium and recovered chromium solutions were obtained at different magnifications and the results are shown in Figures 9-12.

Cross-sectional area analysis of the processed leather by FESEM



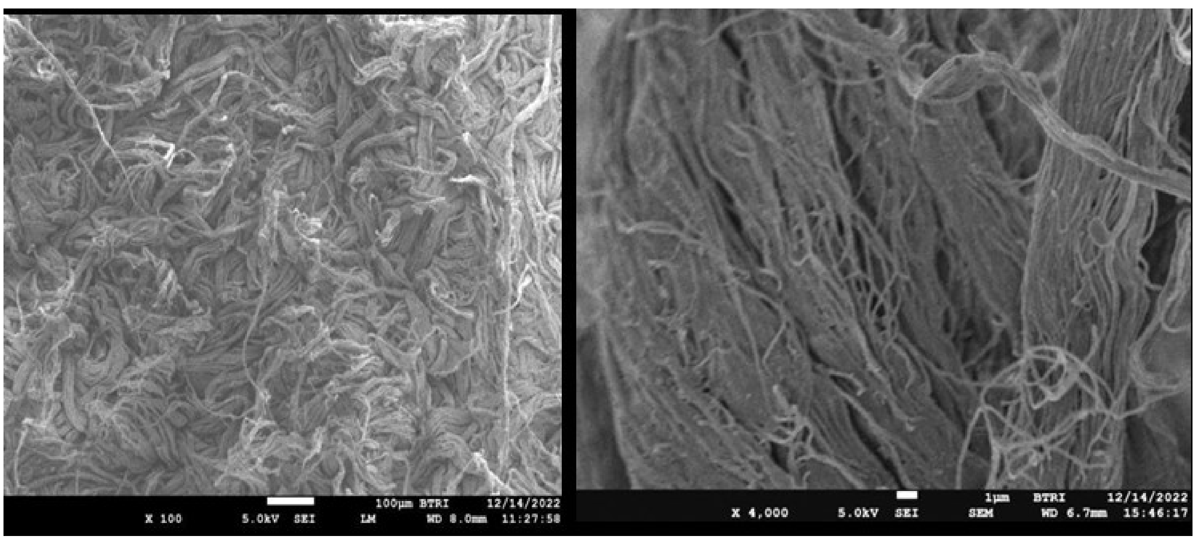
a) b)

Figure 9. SEM images of the cross-sectional area of leather processed by 100% fresh basic chromium sulfate; a) 200 x magnification; b) 1000 x magnification



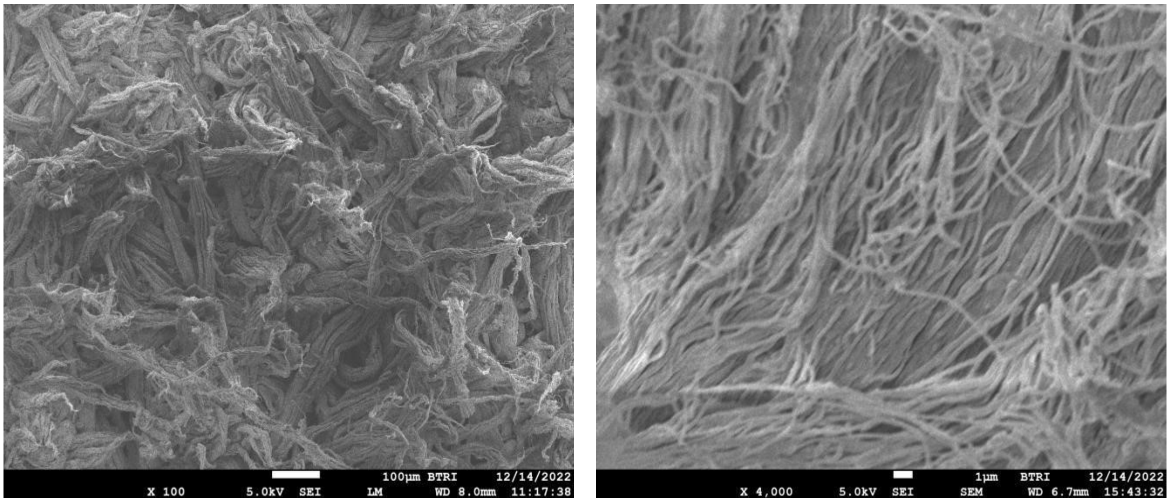
a) b)

Figure 10. SEM micrographs of the cross-sectional area of leather processed by 100% recovered basic chromium sulfate a) 250 x magnification; b) 1000 x magnification



a) b)

Figure 11. SEM micrographs of the flesh side of leather processed by 100% fresh basic chromium sulfate a) 100 x magnification; b) 4000 x magnification



a) b)

Figure 12. SEM micrographs of the flesh side of leather processed by 100% recovered basic chromium sulfate a) 100 x magnification; b) 4000 x magnification

A FESEM study was carried out to investigate the influence of tanning on the fabric structures of processed leather. The cross-sectional areas of leather tanned by 100% fresh basic chromium sulfate (Figure 9) and 100% recovered basic chromium sulfate were examined by FESEM at different magnifications of 200× and 1000× (Figure 10). In both Figures 10 and 11, the SEM micrographs showed similar fibre bundle structures and uniform distribution fibres. The SEM analysis results displayed in Figures 11 and 12 indicated that the leather tanned with recovered chromium possesses higher fibre bundle compactness than the corresponding leather processed with fresh chromium solutions. However, SEM micrographs at 1000× magnification showed that the raw goat leather tanned by fresh chromium salt endowed with more spaces between the fibres than the respective leather manufactured by recovered chromium solution. Figures 11 and 12 show the results of FESEM analysis of the flesh sides of the processed leather samples at magnifications of 100× and 4000×. The goat leather that was tanned using both fresh chromium and recovered chromium solutions possesses similar rope-like structures as revealed from SEM micrographs obtained at 100× magnification (Figures 11, 12). However, SEM micrographs attained at 4000× magnification demonstrated that the leather tanned by fresh chromium solution contained more spaces among the fibre bundles. However, the same SEM magnification images showed that the leather tanned by recovered chromium shows more even distributions of fibre bundles with minimum or no gaps among them (Figures 11, 12). The results of the FESEM analysis showed that the recovered chrome solution had a favourable impact on the structural makeup of the resultant fibres when used as a tanning agent. It has been observed that the raw goat leather tanned with recovered chromium solutions was endowed with more compactness and well-defined rope-like structures. Calcium ions present in the recovered chromium solution have acted as a buffering agent which might have maintained the pH within the optimum range for the tanning process. It has been realized that the tanning process was being proceeded efficiently and the penetration of chromium ions occurred uniformly throughout the hide. Calcium ions might have also played a significant role in stabilizing the collagen structures in the hide. This process of stabilization might have facilitated the formation of the crosslinking between chromium ions and collagen fibres which eventually led to the manufacturing of more durable and stable leather products [52]. The findings of the TGA analysis of the goat leather samples that had been tanned using recovered basic chromium sulfate solutions were in good agreement with the significant outcomes of the SEM analysis of the corresponding leather sample A.

EDS analysis and electronic photographs, elemental mapping of the three categories of leather

All three categories of processed leather samples have been analysed by Energy Dispersive Spectroscopy (EDS) using SEM (Zeiss, model EV0 18, Germany). Electronic photographs of three categories of the finished leather provided significant information on elemental distribution. EDS test results and electronic photographs of the leather manufactured by the 100% recovered chromium leather, a combination of recovered and fresh chromium (2:1, w/w) and 100% fresh chromium salt are shown in Figures 13, 14 and 15 respectively. Electronic photographs and EDS results of the leather samples showed the presence of different elements such as Cr, Ca, N, S and C with their respective percentages. Analyses of EDS and electronic photographs of all three leather samples processed by recovered, a combined and fresh chromium salt showed the percentages of chromium as 15%, 13% and 11%, respectively. Electronic photographs also showed higher concentrations of carbon in all three categories of leather samples in comparison to other elements. The characteristic resonance of carbon in the EDS spectra was more intense and dominated over the peaks of other elements. Elements overlay mapping data of the estimated elements indicated the presence of a higher concentration of chromium (15%) in the leather processed by recovered chromium than those observed with other processed leather. However, the chromium concentration in the leather manufactured by the combination of recovered and fresh chromium was also found relatively higher than the leather processed with 100% fresh chromium. Element mapping data of the processed leather showed the concentrations of calcium in the leather manufactured by recovered, combination and fresh chromium which were 4%, 3% and 2% respectively. Chromium penetration to leather during the tanning process might have been influenced by the calcium contents present in all processed leather. The standard physical quality and thermal stability of the leather have improved over time due to the presence of higher chromium and calcium contents in the leather processed with recovered chromium salt.

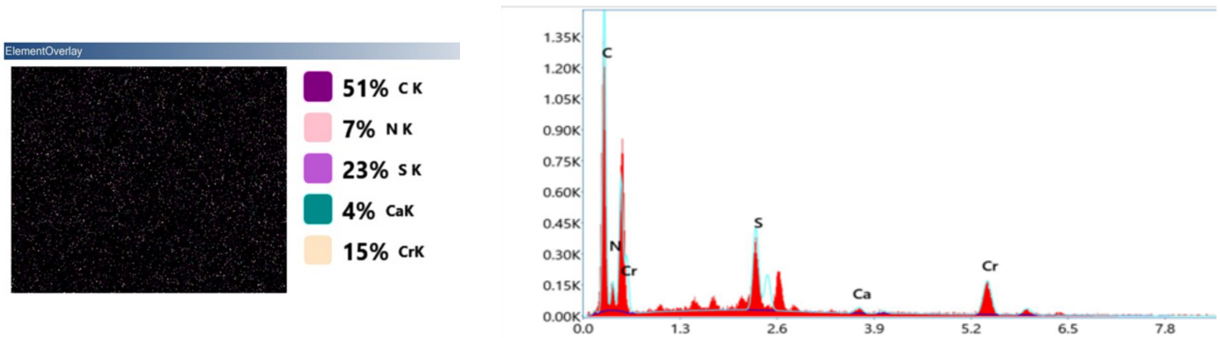


Figure 13. Element Overlay and EDS of leather processed by 100% recovered chromium, sample A

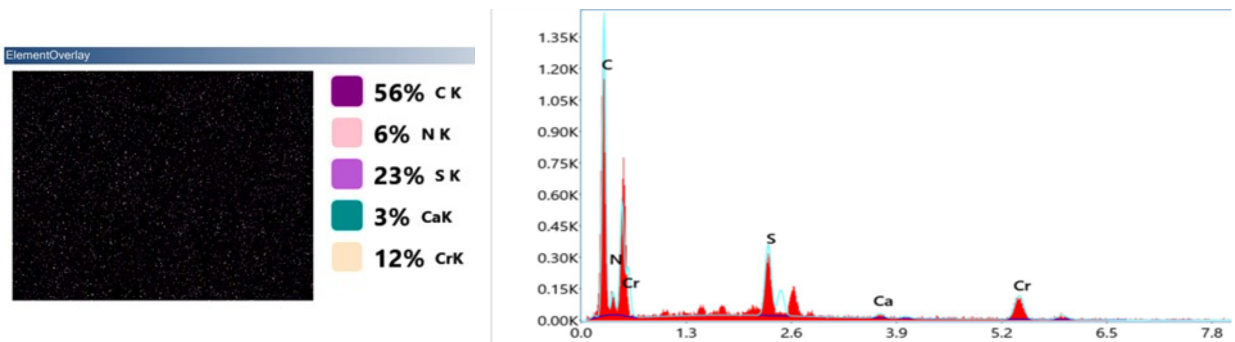


Figure 14. Element Overlay and EDS of leather processed by a combination of recovered and fresh chromium (2:1;w/w), sample B

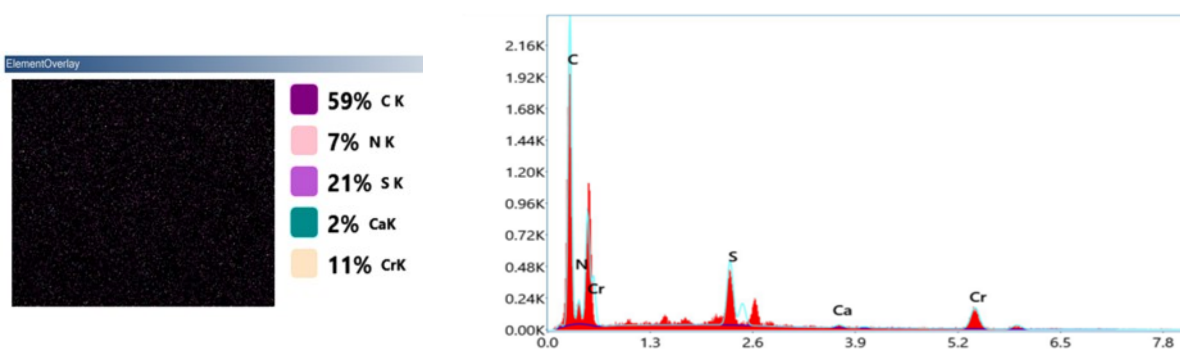


Figure 15. Element Overlay and EDS of leather processed by 100% fresh chromium, sample C

Chemical Costing [in BD Currency (Taka)]

Commercial price of basic chromium sulfate:

Price of 1 kg fresh basic chromium sulfate salt = 150 Taka [25 kg pack= 3750 Taka]

Chemical cost for recovery:

Cost of tannery sludge = 0 Taka

5% sulfuric acid was used in the extraction process and it was prepared by the dilution of concentrated sulfuric acid (98% sulfuric acid). Therefore, a volume of 5% sulfuric acid = 2000 mL which was prepared by the dilution of 102 mL of 98% sulfuric acid.

Weight of 102 mL, 98% sulfuric acid = 187.68 g

Weight = volume x density = 153 x 1.84 = 187.68 g [Density of 98% sulfuric acid = 1.84 g/mL]

Price of 1000 g commercial grade H_2SO_4 = 80 Taka

Therefore, the cost of 187.68 g sulfuric acid = 15.01 Taka

Price of 4 litre water = 0.168 Taka [1000 litre water = 42 Taka, Dhaka WASA]

Electricity use = 1.44 units (kWh)

Electricity cost = 1.44 x 7.66 = 11.03 Taka [1 unit = 7.66 Taka, DPDC]

Manpower and others =10 Tk.

Basic chromium sulfate recovery cost:

Cost of 370 g recovered basic chromium sulfate = (15.01+ 0.168+ 11.03 + 10.00) = 36.21 Taka

Overhead cost 20% = 13.03 Taka,

Therefore, the cost of 370 g of recovered basic chromium sulfate = (36.21 + 13.03) = 49.24 Taka.

Therefore, the cost of 1000 g or 1 kg recovered basic chromium sulfate = (49.24 x 1000)/370 = 133.08 Taka

Cost-effectiveness:

The price of 1 kg fresh basic chromium sulfate salt = 150 Taka (Market price).

Cost savings for 1 kg of basic chromium sulfate = (150.00− 133.09) = 16.91 Taka or 0.152 USD. Finally, (16.91 x 100) = 1691 Taka or 15.2 USD per 100 Kg of chromium salt can be saved from this approach. Therefore, the present approach is economically viable and can be very profitable for tanning industries. In addition, from the environmental pollution perspective, the current method offers significant benefits to save the environment and ecosystem from tannery chromium pollutants.

CONCLUSION

Proper management of solid and liquid waste released from different tannery yards has become a serious issue in many developing countries including Bangladesh. An innovative method was developed to utilize solid tannery waste with a potential view of minimizing environmental pollution in which important chromium compounds were separated from industrial solid waste and reused further in raw leather processing technology. About 97% of chromium was extracted from solid tannery sludge as basic chromium sulfate and reused in leather tanning processes. Physico-chemical, structural, and thermal studies were performed on the processed leather. The findings demonstrated that the raw leather manufactured by recovered chromium salts possesses chemical and physical characteristics qualities which were highly similar to those observed in the finished leather processed with fresh basic chromium sulfate solutions. The raw goat leather tanned by recovered chromium exhibited higher thermal stability than the leather processed with fresh basic chromium sulfate solutions. The results of the FESEM study indicated that the leather tanned with recovered chromium possesses higher fibre bundle compactness with well-defined rope-like structures than the corresponding leather processed with fresh chromium solutions. The magnitudes of shrinkage temperature (hydrothermal stability), tensile strength, percentages of elongation at break, Baumann tear strength, stitch tear strength, and grain crack strength found in the goat leather tanned with recovered basic chromium salts were significantly higher than the corresponding standard threshold values. This was the confirmation that processed leather was endowed with all desired characterises physical and chemical properties to be used in different fields. The presence of calcium in the recovered basic chromium sulfate solution might have assisted the uniform distribution of chromium ions within the leather fibres which could facilitate the crosslinking with collagen fibres resulting in the formation of better compact fibre structures in leather processed by recovered chromium solutions. On the other hand, the cost-benefit data showed that the tanning of raw leather by treating it with the recovered basic chromium sulfate was much cheaper than the application of fresh basic chromium sulfate in the respective system. These interesting research findings offer significant environmental benefits as the new method developed and demonstrated in this study showed a very higher percentage of the extraction of chromium from tannery waste sludge. This relatively new approach to managing tannery solid waste minimizes costs, promotes reuse, is environmentally friendly and can effectively reduce environmental pollution. Thus it can be sustainable for the leather industries in developing countries for the application of green manufacturing of various leather products soon.

Author Contributions

Conceptualization – Mottalib MA; methodology – Chandra M; formal analysis – Chandra M; investigation – Chandra M; resources – Mottalib MA; writing-original draft preparation – Mottalib MA, Chandra M; writing-review and editing – Naher UHB and Goni MA; visualization – Mottalib MA; supervision – Mottalib MA. All authors have read the manuscript and agreed to publish it.

Conflicts of Interest

The authors declare they have no conflicts of interest.

Funding

This research is funded by the Centennial Research Grant, University of Dhaka, Bangladesh (grant no. 47966)

Acknowledgement

The authors are grateful to the University of Dhaka, Bangladesh for providing financial support for conducting this research.

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