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Recovery and reuse of spent chrome tanning effluent from tannery using electro-oxidation technique

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ABSTRACT

Leather manufacturing is one of the industrial activities, contribute significantly to economy and employment. Chromium being a carcinogen, the discharge of chrome tanning wastewater is associated with serious health hazards and significant negative environmental impacts. The present research deals with the recovery and reuse of chrome tanning effluent by mineralizing the organic contaminants present in the chrome tanning wastewater through electro-oxidation technique. The EO process was carried out by using titanium as anode for 120 min with variation in current density (3.0 V; 12 A and 4.0 V; 15 A). COD and TOC were found to decrease gradually with respect to time. The treated chrome liquor was then subjected to the reduction reaction using sodium metabisulfite so as to reduce the hexavalent chromium, to trivalent state. The leather produced using the recovered chrome liquor along with fresh chrome tanning agent was found to have good hydrothermal stability and adequate chromium content. This method of treating tanning effluent is an economically viable and environment-friendly alternative method for avoiding the disposal of chrome effluent.

Keywords: Spent chrome tanning effluent; Basic chromium sulfate (BCS); Electro-oxidation; Titanium electrode; Chemical oxygen demand (COD); Total organic carbon (TOC) Hydrothermal stability

1. Introduction

The need to strike a fine balance between economy, society and environment gain importance for the industries to attain sustainability. Industrial activities such as electroplating, metal cleaning dye processing, cement manufacturing, and tanning are the major sources of discharge of chromium into the environment. The leather manufacturing results in the discharge of a substantial volume of wastewater containing high concentrations of chlorides, aliphatic sulfonates, sulfates, aromatic and aliphatic ethoxylates, sulfonated polyphenols, acrylic acid condensates, fatty acids, dyes, proteins, soluble carbohydrates and Na_2S [1].

The primary objective of tanning is to convert the putrescible hide into leather, which is stable and non-putrescible. Chrome tanning is a popular tanning method which involves treatment of pelts with basic chromium sulfate (BCS). BCS, by crosslinking the collagen fibers engenders hydrothermal and mechanical stability to leather [2] only about 65% of the BCS used for tanning is taken up by the pelt and the remaining chromium salt is discharged along with the wastewater [3,4]. Though the chromium used for tanning is discharged in trivalent state, it may undergo oxidation under the natural conditions to form hexavalent

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chromium [5]. The environmental impact of the chromium present in the wastewater become more significant as the amount of chromium released by the leather industry is huge. For every ton of rawhide or skin processed, about 1 m^3 of chromium containing wastewater with chromium concentration of 27500 mg/L is discharged [6].

Hexavalent chrome is more toxic than trivalent chrome and is a serious environmental pollutant. It also affects the seed germination, seedling growth, pigments and enzymes content [7]. Chronic exposure to chromium for a period of five months to fourteen years represents a relevant risk factor for the development of diseases associated with genetic damage. The temporary ill effect of tannery wastewater streams includes giddiness, eye-irritation, skin allergy [3], gastrointestinal ulcer in the nasal septum [5]. The longterm effects are occupational asthuma, peptic ulcer, bronchitis, and dermatitis [8]. Disposing of this effluent without treatment causes harmful effects. Several types of research have been carried out to treat the chromium wastewater generated by chrome tanning industries. One of the widely recommended methods of managing chrome effluent is by treating the effluent with magnesium oxide, and reuse of the regenerated chromium. However, due to quality issue and the need for safely disposing of the supernatant with high TDS deter the tanners to effectively practice this method.

There are various methods used for the removal and reusing of chromium such as coagulation, biosorption, membrane filtration process, ion exchange etc. [9,10]. Tahiri et al. [11] had studied integrated treatment for better management of both spent chrome tanning effluent and vegetable tanning effluent. The electrochemical method is highly efficient in treating wastewater from tanneries to reduce BOD, TOC, and COD levels to permissible limits [12]. The electrochemical oxidation process is a promising alternative to obtain a reusable effluent. Titanium electrodes have been widely used for the removal of organic pollutants because of the cost-effectivity [13], large surface area, wide electrochemical potential windows, high mechanical strength and good stability. During the electrooxidation process, hydroxyl radical ($OH^\bullet$) are generated in the anode and it disintegrates the organic matter and eventual mineralization can be achieved [14]. Yilmaz NayirandKara [15] studied the treatment of wastewater from container washings through combined electrocoagulation–electrooxidation. The final products of electrooxidation treatment are CO_2 and H_2O, making it a sludge free technology and providing a lead to an environment-friendly option [13].

In the present research, it is aimed to study the possibility of treating and reusing the chromium containing wastewater. BCS used for tanning is in the trivalent state with basicity around 33%. After the completion of tanning, the basicity of the chromium is around 45% and the size of the Cr species also increases. The wastewater also contains organic matter released from the pelt. The increased basicity and size of the Cr species and the presence of organic matter render the chrome containing wastewater not amenable for reuse [16,17]. The reduction of Cr (VI) to Cr (III) will decrease the mobility of chromium in the environment [18]. In the present research, it is proposed to subject the wastewater to electro-oxidation to disintegrate the organic matter. As a result of oxidation, trivalent chromium will be oxidized to the hexavalent state. As reported by (Lin and Vesilind, 1995) hexavalent chromium can be reduced under acidic conditions (usually pH 2–3). The most commonly used reducing agents are gaseous sulphur dioxide, sodium sulphite, sodium metabisulphite and ferrous sulphate [19]. Wójcik and Hubicki [20] investigated the reduction of hexavalent chromium by the strongly basic anion exchange method. In this research work, the hexavalent chromium has been reduced using sodium meta bisulfite and the chromium free from organic contaminants is reused for the tanning.

2. Materials and method

2.1. Raw material

Wet salted Indian Goat skin was taken for the experiment. It was soaked, limed, delimed and pickled. The pickled pelt was cut along the backbone into two halves. The right half was tanned using fresh BCS (control) [21]. The spent liquor from this conventional chrome tanning process was taken for electro-oxidation (refer 2.2) and the treated liquor was then reduced and reused for tanning the remaining left half of the skin (Experiment).

2.2. Electrooxidation reactor set-up

The EO treatment was carried out using laboratory scale reactor consisting of titanium as both cathode and anode material positioned vertically with dimensions of length 10 cm width 7.5 cm and 13.5 cm height. And the electrodes were spaced 2.0 cm apart. The rector tank volume of about 3 L was used for the EO treatment, A rectifier was set up to amplify the direct current supply of range 0–30 V. During the EO process the electrochemical cell was maintained at 25°C by recirculation of water, using temperature-controlled water pumping jacketed medium [22–24].

2.3. Experimental details

Spent chrome is being recovered from the spent chrome tanning bath by various methods, such as precipitation of chromium by using MgO, electrocoagulation techniques, ion exchange and adsorption method [25,26]. El-Khateeb et al. [27] carried the elimination of chrome tanning effluent using electrocoagulation process assisted by chemical oxidation. The present study aims at the recovery and reuse of chromium by electrooxidation method mainly to attenuate the organic pollution load in the spent chrome effluent so that the chromium can be recovered and reused. The right (control) portion of the skin samples was tanned using fresh chrome, 6% of BCS to the weight of skin [28]. Chrome liquor was offered in two stages, 3% in each stage, for an interval of 1 h. After ensuring the complete penetration of chrome in the skin, the spent chrome tanning waste water was collected and subjected to electrooxidation process. The electrooxidation technique was carried out using titanium as an electrode material for 120 min of retention time with varying current density (Trial I: 3.0 V; 12 A and Trial II: 4.0 V; 15 A respectively) in order to optimize the reaction condition. About 20 mL of the samples were withdrawn from the reaction tank for every 30 min, to assess the pollution load characteristics [22]. The pollution load was assessed in the collected samples by analysing the chemical oxygen demand (COD), total organic carbon (TOC). The EO treated chrome liquor contain hexavalent chromium (Cr (VI)), which was then reduced by using 20% w/v sodium metabisulfite to bring to trivalent chromium (Cr (III)) [29]. The reduction reaction was performed for 4 h with continuous stirring and the temperature was maintained at 60°C. To the recovered chrome liquor, sulfuric acid was added to maintain the original pH of 2.7–3.0 for carrying out the tanning process. Finally, based on the result of chrome content estimation in the reduced chrome liquor 60% w/v of BCS was added to the recovered chrome tanning liquor in order to satisfy the amount of lost chromium during the previous trial. Tanning process was carried out for left portion of the skin (experimental) sample. Using recovered chrome liquor, tanning process was followed as per the same method followed for the control sample. The flow diagram 1 given below shows the scheme of recovery and reuse of chrome effluent from the spent tanning bath [30].

2.4. Analysis of pollution load

The COD analysis was performed according to the methodology described by Vyrides and Stuckey (2009). In this method of analysis, the digestion mixture was prepared by adding 3 g of dried $K_2Cr_2O_7$ to 167 mL of concentrated H_2SO_4, and 33 g of $HgSO_4$, and made up to 500 mL with deionized water. The mixture was then left to cool at room temperature before being diluted to 1000 mL. The sulphuric acid reagent (2.5%, w/v) was prepared by dissolving Ag_2SO_4 in H_2SO_4, and the sampling and digestion of the sample were carried out in accordance with the methodology described under the analysis of water and wastewater [24]. Total organic carbon (TOC) analysis was performed using element arvario TOC select instrument for the samples collected for every 30 min during the electrooxidation process [31].

2.5. Chrome content estimation in the effluent and in tanned leather

The chromium content was estimated for the fresh chrome liquor, spent chrome liquor, EO treated liquor, reduced liquor and recovered chrome liquor samples, and in 60% w/v BCS added liquor. The amount of trivalent and hexavalent chrome was estimated using ICP-OES instrument (Prodigy XP-High Dispersion ICP). For the estimation of chromium content in the control and experimental leathers, samples from the butt portion of the control and

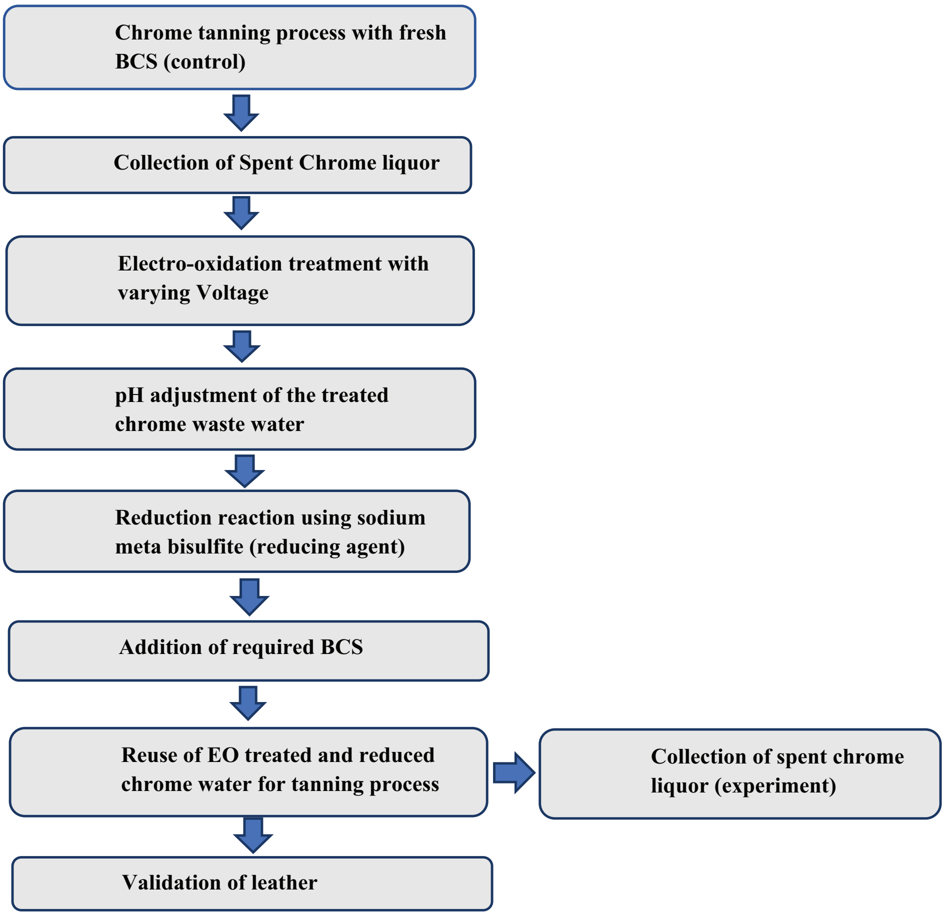

Fig. 1. Flow diagram representing the recovery and reuse of spent chrome effluent by using electro-oxidation method and reduction reaction.

experimental wet blue samples were taken. About 1 g of wet blue samples from each batch was taken and made into pieces. The cut pieces were taken in a crucible and dried in hot air oven at 102°C, ± 3 for 3 h. After drying the samples were placed in the desiccator for 30 min to attain room temperature, then the cut samples pieces were weighed. The dried leather pieces were digested using the triacid mixture, such as $HClO_4$ (11.5 mL), HNO_3 (5.0 mL) H_2SO_4 (3.5 mL). After the completion of oxidation, the contents of the flask were diluted and heated to remove any free chlorine. The oxidized reaction mixture was then cooled, to the known volume of the oxidized mixture sufficient volume of 3 M H_2SO_4 was added and then diluted to 50 mL. Two drops of diphenyl carbazide (1 mL of 0.25% solution in 50% acetone) were added to the sample and the concentration of chromium in the above solution was estimated by measuring the absorbance at 540 nm against the reagent blank. The chrome content in the oxidized mixture is estimated by using a standard titration procedure. The percentage of chromium is expressed on a moisture-free basis [30,32].

2.6. Testing of leather

The control and experimental samples for physical testing were analysed as per IULTCS methods. The shrinkage temperature, a measure of the hydrothermal stability of control and experimental leather, was determined using SATRA TM17 testing method. The samples were conditioned at 26°C and 65% Relative Humidity for 48 h. Physical properties such as tensile strength, percentage elongation at break, tear strength and grain crack strength were investigated as per standard procedures [30,33]. The organoleptic properties such as colour, softness, grain tightness and general appearance were assessed visually and evaluated for both control and experimental wet blue and crust leathers samples by leather experts and are rated on a 0–10 point scale. Higher points indicate better property [30].

FTIR analysis was carried out by JASCO FT/IR-4200 for comparing the functional group changes between the leather tanned with fresh chrome liquor (control) and recovered chrome liquor(experiment). The morphology of fresh chrome tanned and recovered chrome tanned sample was evaluated by SEM analysis. The crust leathers were mounted on to aluminium stub and coated with thin layer of gold to make the leather conducting. The SEM analysis was performed using a scanning device attached to a PhenomPro at 5 kV (Phenom, Netherland) accelerating voltage.

3. Result and discussion

3.1. Optimization of current density in the EO process

The electro-oxidation treatment in spent chrome tanning effluent was carried out by using titanium as an electrode material for 120 min retention time with varying current density (3.0 V; 12 A and 4.0 V; 15 A respectively). Pollution load analysis was done in the samples collected periodically every 30 min. during EO process, the COD and TOC values were higher in the initial spent chrome effluent because of the presence of biological materials such as discharged proteins and also due to the presence of chromium and neutral salts. The COD and TOC results for the electro-oxidation (EO) treated chrome liquor showed a decrease in the organic pollution load. COD reduction was found to be 63%, at 3 V; 12 A; and 90%, at 4 V; 15. And also, TOC reduction was found to be 78%, at 3 V and 12 A; and 94%, at 4 V and 15 A. COD and TOC mg/L reduction at 30 min with respective current density are showed in Table 1, and Fig. 2. Therefore, from the COD and TOC results, it was optimized that EO process at 4.0 V; 15 A showed a better reduction of organic pollutants, than EO process carried out with 3.0 V; 12 A. Since the amount of organic pollution load is quantitatively less in the effluent treated at 4 V; 15 A for 120 min retention time, this effluent was then taken for further processing.

3.1.1. Anodic oxidation reaction model happening during Electrooxidation process

Water discharge to hydroxyl radical.

$$M + H_2O \rightarrow M\left[OH^{\bullet}\right] + H^+ + e^- \tag{1}$$

Oxidation of organics R with electrogenerated OH radicals (main reaction)

$$M\left[OH^{\bullet}\right] + RM \rightarrow RO\left[\ \right] + H^+ + e^- \tag{2}$$

Oxygen evolution (side reaction)

$$M\left[OH^{\bullet}\right] + M \rightarrow \frac{1}{2}O_2 \uparrow + H^+ + e^- \tag{3}$$

3.1.2. The reaction involved during reduction of hexavalent chromium to trivalent chromium

Reduction of hexavalent chromium is carried out by using sodium metabisulfite as the reducing agent [29]. Sodium metabisulfite, when added to water, forms sodium bisulfite [Eq. (4)]. In the presence of acid and hexavalent chromium Cr (VI), the sodium bisulfite has the following reaction as shown in Eq. (5). (Pollution Prevention and Control Technology for Plating Operations, Cushnie 1994).

$$Na_2S_2O_5 + H_2O \rightarrow 2NaHSO_3 \tag{4}$$

$$3NaHSO_3 + 2H_2CrO_4 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 5H_2O + 3NaHSO_4 \tag{5}$$

Table 1
COD reduction for EO processes at Trial 1 (3V; 12 A) and Trial 2 (4 V; 15 A)

Sample name	Trial 1		Trial 2	
	COD	TOC	COD	TOC
Initial	12500	3000	12500	3000
30 min	9850	2850	8660	2640
60 min	7550	2050	5840	1880
90 min	5760	960	3600	840
120 min	4600	640	1200	180

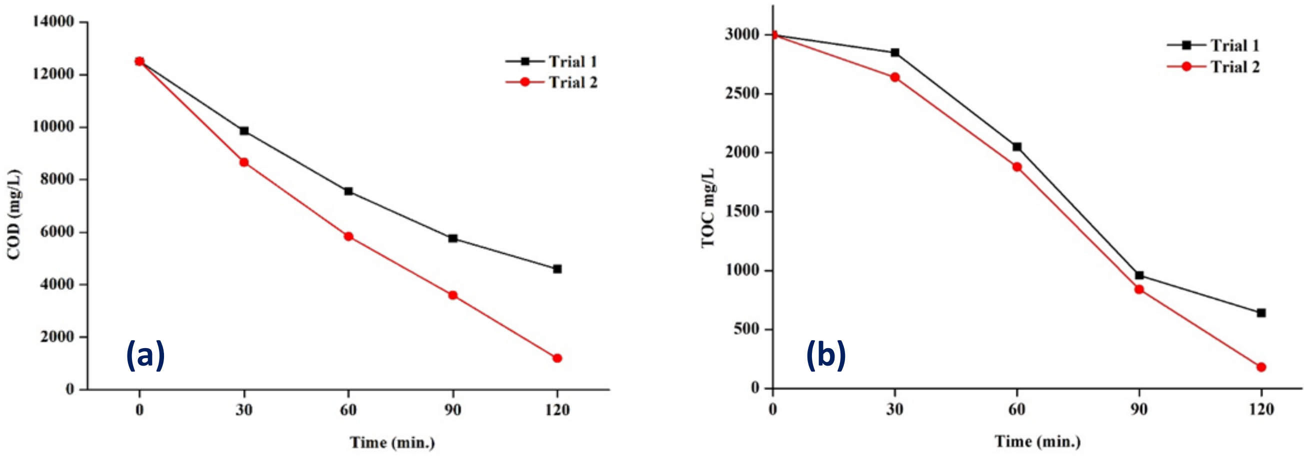

Fig. 2. (a) COD and (b) TOC reduction for EO processes at 3 V; 12 A (trial 1) and 4V; 15 A (trial 2).

3.2. Apparent current efficiency and energy consumption

The apparent current efficiency with respect to TOC reduction was calculated using the following formula [34,35].

$$\eta F = \frac{\left(\Delta\ \text{TOC} \times V \times F\right)}{8 \times A \times t \times 1000} \tag{6}$$

where ΔTOC is the net Total Organic Carbon (TOC) removed (mg/L) after a treatment time t, V is the voltage at which the treatment was carried out, F is Faradays constant (96,487 C/equiv.), 8 is the equivalent weight of oxygen, A refers to ampere maintained during the process, t is the treatment duration in (s). Energy consumption (Esp), the amount of electrical energy (in kilowatt hour) essential to reduce one gram of total organic carbon (TOC) in the untreated waste effluent, was calculated using the formula [34,36].

$$E_{sp} = \frac{\left(10^3 \times V \times A \times t\right)}{TOC_{(i-f)}} \tag{7}$$

where P is the rated power (kW) of the reactor, V and A is the voltage and ampere respectively at which the treatment was carried. t is the duration of the treatment in (h), $TOC_{(1-f)}$ is the TOC mg/L at time t, and factor 10^3 converts mg to kg. The current efficiency (ηF) and Energy consumption (Esp), for the TOC reduction, was found to be respectively as shown in Table 2.

3.3. Chrome content analysis

Chrome content estimation was carried out in fresh chrome liquor, spent chrome liquor, EO treated liquor, reduced chrome liquor and recovered chrome liquor samples. The results (Table 3) showed high trivalent chrome (Cr III) content in fresh chrome (5368 mg/L) and recovered chrome liquor (5294 mg/L) which are appropriate for tanning process. Spent chrome liquor collected after the tanning process had about 38% unreacted trivalent chrome, after EO process due to oxidation hexavalent chrome content was found to be high. In order, to convert this hexavalent chrome to trivalent chrome 20% w/v of sodium metabisulfite was added. About 60% w/v of BCS was added to the reduced chrome liquor, so as to satisfy the chrome content for the tanning process. Chrome (Cr_2O_3) content analysis in a moisture-free wet blue sample tanned using fresh chrome liquor (control) and recovered chrome liquor (experiment), showed comparable chrome content (Table 4).

Table 2
Current efficiency and energy consumption of EO processes

EO trial	TOC reduction (%)	Current efficiency	Energy consumption (Wh/g)
Trial 1 (3 V; 12 A for 120 min)	78	0.98	112.5
Trial 2: (4 V; 15 A for 120 min)	94	1.2	666.6

Table 3
Chromium estimation for fresh chrome liquor, spent chrome liquor, EO treated liquor, reduced liquor, recovered chrome liquor samples

Sample	Cr III mg/L	Cr VI mg/L
Fresh chrome liquor	5368	BDL
Spent chrome liquor	2063	342
EO treated liquor	371	1463
Reduced liquor	1827	BDL
Recovered chrome liquor	5294	BDL

*BDL – Below Detection Level (Detection limit: 0.5 mg/L)

3.4. Physical testing report

Leathers tanned by using fresh chrome liquor and recovered chrome liquor were assessed for physical testing parameters such as shrinkage temperature, tensile strength, tear strength, grain crack strength and moisture content. The

Table 4
Chrome estimation for control and experiment wet blue samples

Sample name	Chrome content, %
Wet blue tanned using fresh chrome liquor (control)	4.25
Wet blue tanned using recovered chrome liquor (Experiment)	4.14

Table 5
Physical testing of crust leather samples tanned with fresh BCS

Physical testing parameters	Control	Experiment
Shrinkage temperature, °C	110 ±2	106 ±3
Tensile strength, kg/cm^2	263 ±3	256±5
Tear strength, kg/mm	34±2	30±1
Grain crack strength, kg	35±2	32±4
Moisture Content, %	53±4	56±3

results are presented in Table 5. It is observed from the table that the leathers obtained from both the control and experimental process were of similar characteristics. Therefore, from the physical testing data, it can be understood that leather tanned with recovered chrome liquor shows the same physical properties comparable to control leather tanned with fresh chrome liquor as specified by general norms. The organoleptic assessment for both control and experimental leather samples were visually evaluated by experts and is rated in a 0–10 point scale. The assessment was carried out for colour, softness, grain tightness and general appearance. The organoleptic properties of the experimental leather were also found to be on par with that the conventionally produced leathers. The results are presented in Fig. 3.

3.5. Instrumental characterization of leather

3.5.1. FTIR characterization

The FTIR spectrum is shown in Fig. 4, of the control and experimental wet blue (tanned using fresh chrome liquor and recovered chrome liquor respectively) samples, showed absorbance bands at around 3320, 2937, 2850 cm^{-1} indicating the presence of –NH stretching coupled with hydrogen bonding of –OH, –CH$_2$ asymmetrical stretch, and –CH stretching respectively [37,38]. The characteristic band at around 1645, 1540 and 1330 cm^{-1} represent the amide–I, amide–II and amide–III respectively as reported by Jackson et al. (1995). The peak at 798 cm^{-1} and in the range of 411–645 cm^{-1} may be due to protein-specific bands. It has been reported that Cr III displays characteristic absorptions of chromic oxide at less than 800 cm^{-1} [39,40]. Therefore, from FTIR spectrum, it is understood that the collagen of the skin matrix of both control and experiment samples is in complexation with chromium through the tanning process, carried out by using Cr III compound, which shows an absorption band at less than 800 cm^{-1} in the IR spectrum. Thus, the FTIR spectrum of both control and experimental samples showed similar peaks around the same region, which attributes to the similar functional groups of both samples [41].

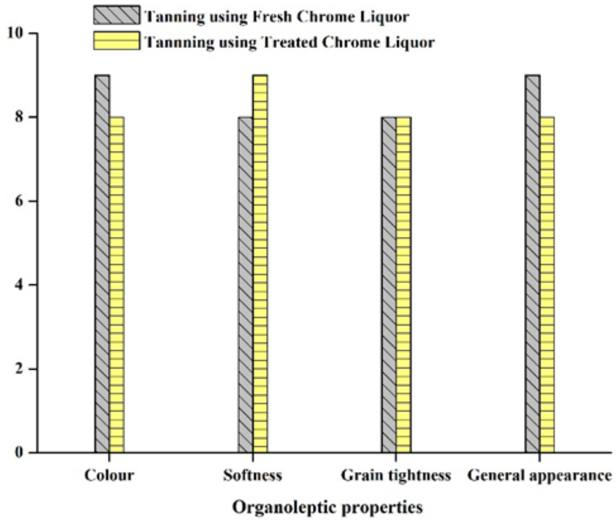

Fig. 3. Organoleptic properties of crust leather samples tanned with fresh chrome liquor (control) and recovered chrome liquor (experiment).

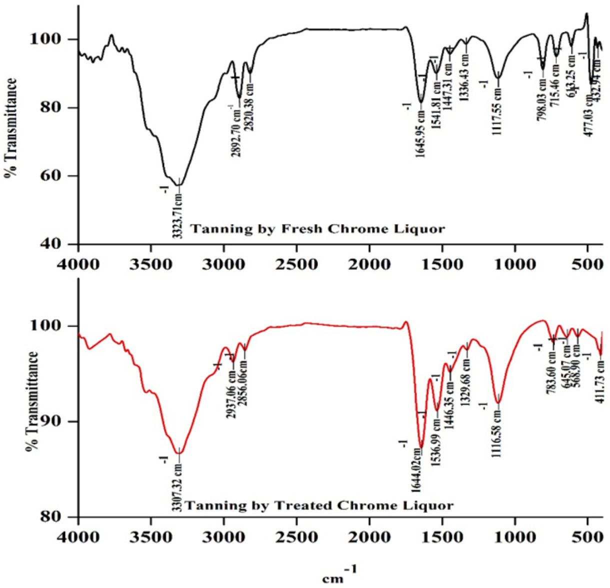

Fig. 4. FTIR spectrum of crust leather samples tanned with fresh chrome liquor (control) and recovered chrome liquor (experiment).

3.5.2. Scanning electron microscopic (SEM) analysis

The crust leathers assessed by viewing the grain surface of leather samples using SEM to study the grain surface morphology. Fig. 5 shows the SEM images of the grain surface for the crust leather samples tanned using fresh chrome (control) and recovered chrome (experiment) liquor. Both control and experiment samples exhibit a clear grain surface, which specifies that there is no physical deposition. Analysis carried out in the magnification ranges (250×, 500× and 1000×) confirms the above observation, where the hair follicles look clean without any foreign materials in all cases. The grain surface

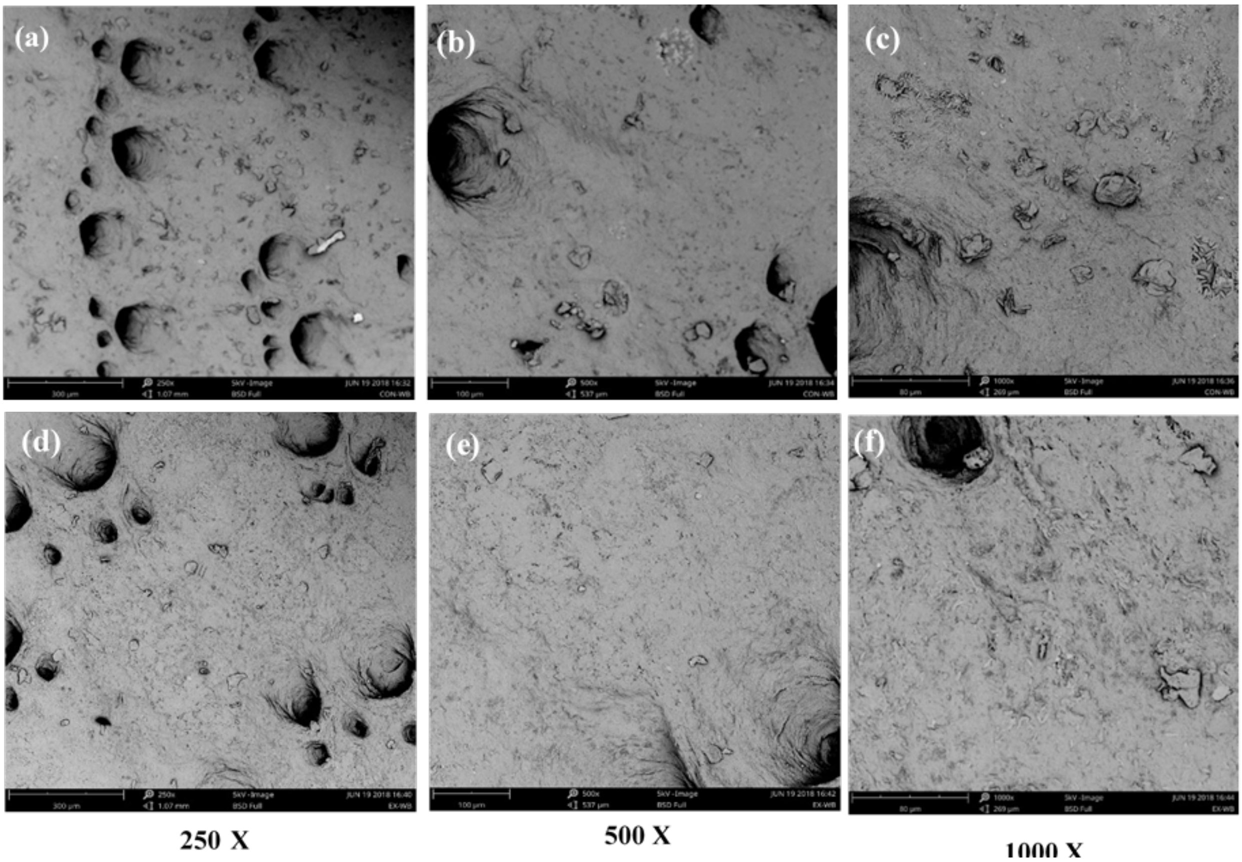

Fig. 5. SEM images (a), (b) and (c) control and (d), (e), (f) experimental crust leather tanned with fresh chrome and recovered chrome liquor respectively.

of the leather tanned using recovered chrome liquor seems to be flat without any wrinkles compared to the leather tanned with the fresh chrome liquor.

3.6. Cost-benefit

It was optimized that EO process at 4.0 V; 15 A showed a better reduction of organic pollutants in chrome tanning wastewater. Therefore, the electrical energy required for the treatment of 1.0 m^3 of chrome tanning wastewater is 12.0 kWh. Assuming the cost per unit of electrical energy is USD 1.74 per 1.0 m^3 of wastewater. It is clearly indicated that the cost of treatment is significantly lower than similar methods such as reverse osmosis (RO), advanced oxidation process (AOP) etc.

4. Conclusion

The EO treated spent chrome liquor was tested for organic pollution load analysis, the best removal efficiency of (90%) COD and (94%) TOC was absorbed during 4 V; 15 A at 120 min. whereas, only (63%) COD and (78%) TOC was found to at 3 V; 12 A at 120 min. Chrome estimation for recovered chrome liquor showed the presence of (Cr III) percentage as in fresh chrome liquor. The leather tanned using fresh chrome liquor and recovered chrome liquor showed a comparable result for Physical testing, chrome content estimation. FTIR analysis made carried out for the functional group comparison in the control and experimental wet blue samples and SEM analysis to study the surface morphological similarities between control and experimental wet blue samples showed on par results. Hence, it was concluded that through electro-oxidation technique organic pollution load in the spent chrome tanning liquor can be brought down and the treated effluent can be reused after the reduction of hexavalent chromium. Therefore, this method ensures the reuse of chrome effluent in a vital way.

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