# Total Elimination of Polluting Chrome Shavings, Chrome, and Dye Exhaust Liquors of Tannery by a Method Using Keratin Hydrolysate

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Ⓢ Supporting Information

**ABSTRACT:** The solid and liquid waste management of tanneries has become a serious problem in the leather industry. In this study, we have attempted and succeeded in eliminating these pollutants by a novel method that has not been done anywhere so far. Keratin hydrolysate (KH) from poultry feathers has been utilized along with chrome shavings (CS) for total elimination of the polluting solid and liquid wastes in a tannery. In this process, 100% fixation of the Cr from the chrome exhaust liquor and the dye from the dye exhaust liquor is achieved by the reactions of CS with KH. The infrared spectra of the different stages of CS confirm the fixation of Cr in the chrome shavings–keratin hydrolysate (CSKH) complex. In this work, apart from elimination of tannery pollutants, a leather-like flexible sheet is obtained that can be used in the footwear and leather goods industry. In the scanning electrom microscopy evaluation, the surface morphology of the product exhibits smoothness because of the incorporation of poly(vinyl alcohol) and ethylene glycol. The above findings will open new avenues for further research in solid and liquid waste management of tannery effluents.

**KEYWORDS:** Tannery effluents, Value addition, Cost effective, Green environment
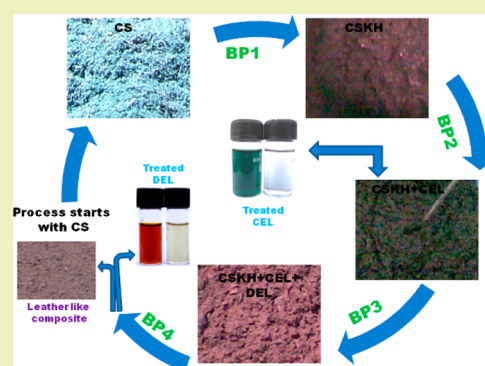
## INTRODUCTION

The leather industry has posed an environmental problem to terrestrial and aqua medium with the advent of usage of chromium (Cr) salts in the tanning process. Although researchers are trying their best to combat the chromium pollution in the leather industry, they have not succeeded in completely removing it from the effluent until now. Similarly, skin, hide, hair, including chromium containing materials such as chrome shavings (CS), buffing dust, chrome splits, and trimmings of light and heavy leathers are giving rise to significant amounts of solid wastes, which are usually dumped in landfills. The management of these solid residues is highly important, as most of this waste contains toxic chemicals including Cr(III), which is frequently converted into carcinogenic Cr(VI).[1,2] As per data from 2006, about 6.5 million tons of wet salted hides and skins are processed annually and 3.5 million tons of various chemicals are used in the leather process worldwide annually. A considerable part of this amount is discharged as effluent. On average, 45–50 m$^3$ of waste liquor and 800 kg of solid waste per ton of raw hides are discharged by the leather industry.[3–5] Because the treatments of both liquid and solid wastes are quite expensive, few tanners opt to do away with treatment of the above pollutants, either letting them into watersheds or disposed into landfill sites.[6–9]

To reduce the environmental burden of these toxic pollutants, researchers are trying to develop suitable methodologies to get rid of these toxicants. Rao et al.[10] demonstrated for the first time that the high protein content of CS can be utilized for reduction of Cr(VI) during the preparation of the chrome tanning agent. However, currently, only a small quantity of CS is used for the preparation of leather boards, parchment-like membrane, lamp shades, chandeliers, and related materials like chappal uppers, hand bags, purses, wallets, and so on.[11] For the management of solid waste like hair and feathers, Sehgal et al.[12] demonstrated the solubilization of keratins from poultry feathers and its characterization. In another study,[13] they investigated the retanning of nappa garment leathers by keratin filler (KF). Later, Sastry et al.[14] showed that solubilized keratins can be used as a novel filler in the retanning of upper leathers. In this study, cow uppers were retanned with KF prepared from poultry feathers and physical

**Scheme 1**
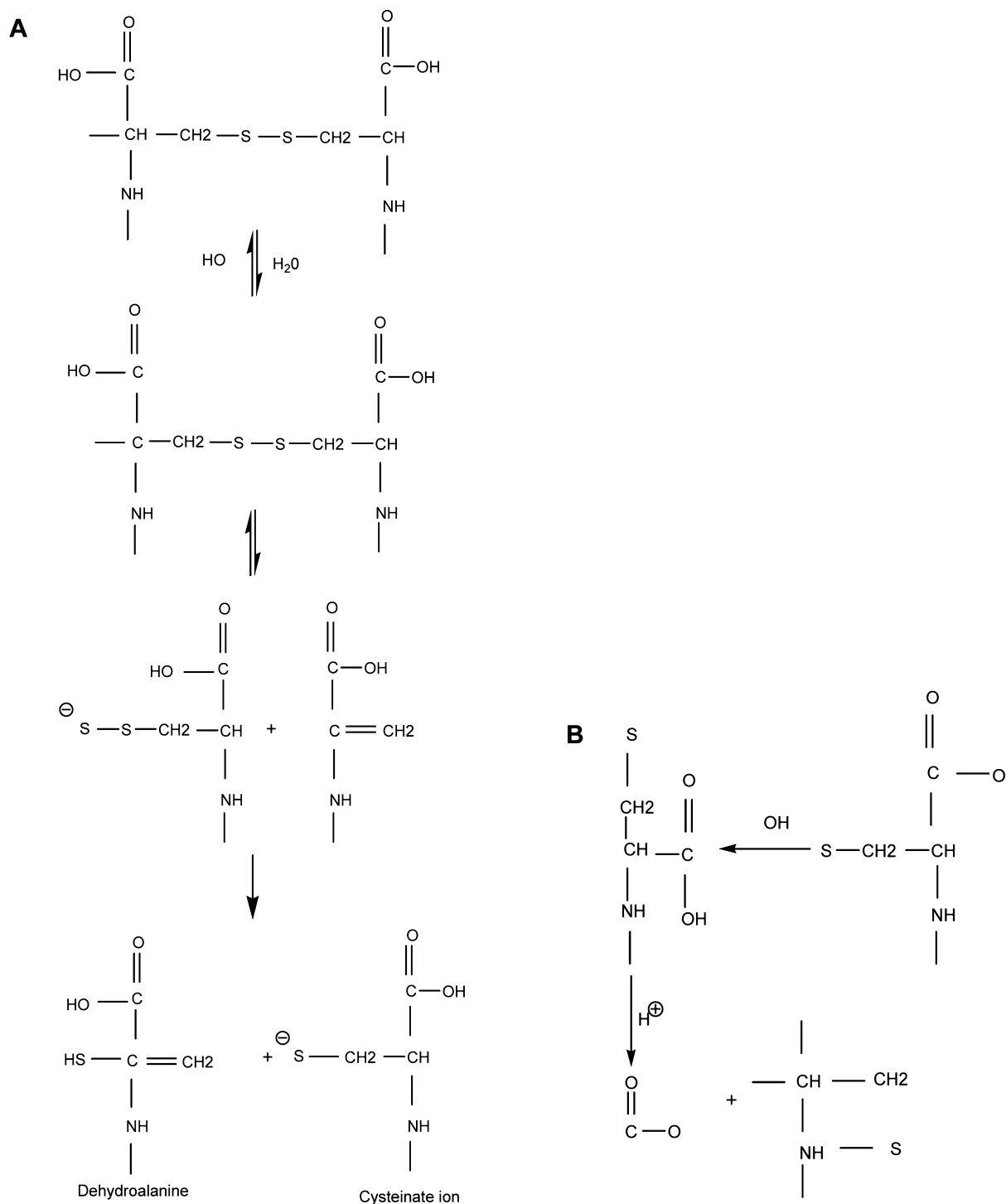


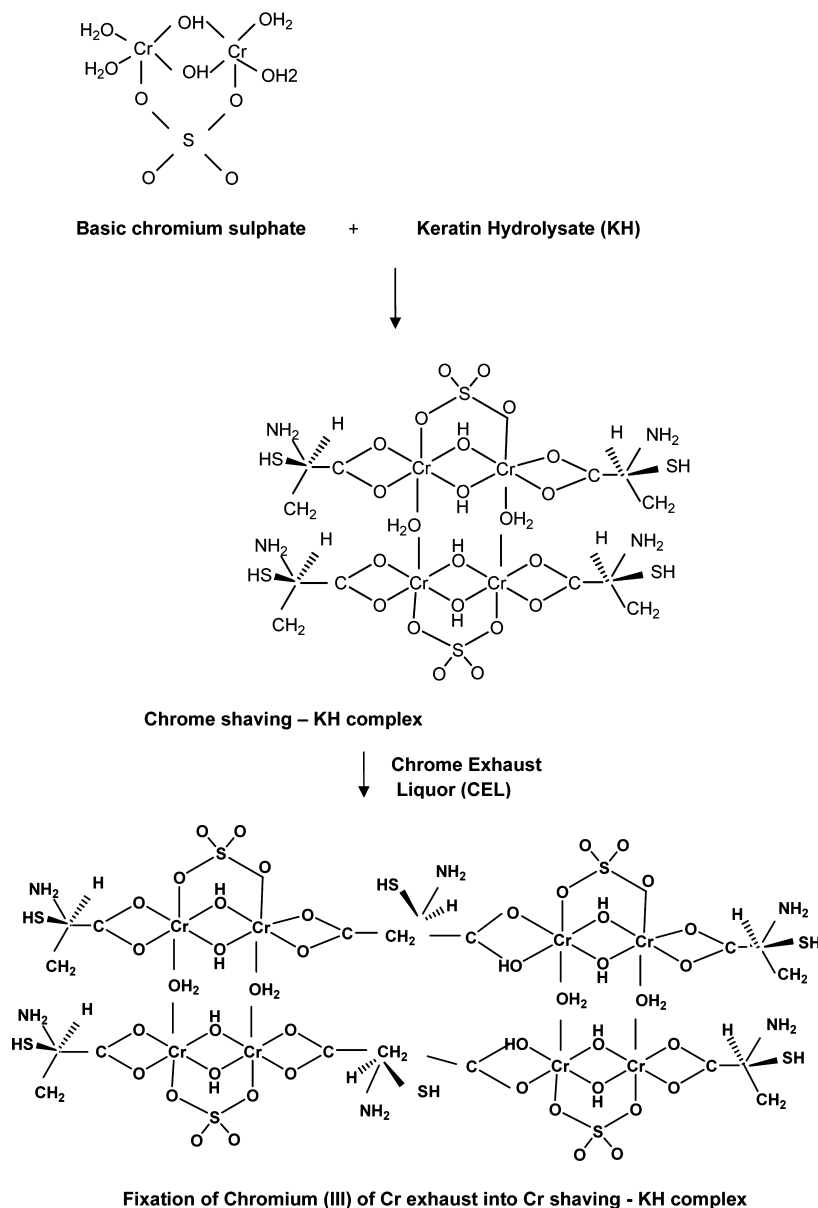**Mechanism of Disulphide Bond Rapture by Alkali in Keratin**          **Further hydrolysis of Keratin**

properties of the crust leathers were evaluated. Ramamurthy et al.[15] described the application of KH, derived from poultry feathers, on chrome tanned leathers for Cr exhaustion and fixation. It was observed that among different concentrations, usage of 2% of KH on goat skin at the end of a rechroming operation provided better results. The authors[16] further described the application of KH in light and heavy leathers during chrome tanning and retanning stages and observed that >94% of Cr(III) was exhausted in the bath, when 2% of KH

was introduced at the rechroming stage. Ramamurthy et al.[17] also investigated the role of KH for improvement of the properties of chrome tanned heavy leathers. The cytological and biochemical tests revealed that application of KH improved the strength and other desirable properties of the leather, particularly first transverse layers.

Although KH has been tested in leather processing, elimination of liquid and solid wastes of tanneries using KH has yet to be reported. Moreover, other major limitations are

**Scheme 2**



**Basic chromium sulphate    +    Keratin Hydrolysate (KH)**

**Chrome shaving – KH complex**

**Chrome Exhaust Liquor (CEL)**

**Fixation of Chromium (III) of Cr exhaust into Cr shaving - KH complex**

the preparation of KH requires high temperature, pressure, and concentrated acids or alkalis,[18−20] and also require prolong time,[21] for hydrolysis of keratin proteins. In these processes, the disulfide linkages of keratin break down and water-soluble polypeptides, oligopeptides, or amino acids are obtained.[22−24] To address these limitations, this paper aims to explore the extraction of KH from poultry feathers in mild reaction conditions, utilizing the obtained KH in cost-effective elimination of liquid and solid wastes of tannery industries. The results showed that Cr(III) and dye exhaust liquors of a tannery can be totally eliminated by the incorporation of KH into dry CS. The resultant products can also be used in making value-added products such as leather-like composite sheets, which may find potential application in the leather goods and footwear industry as insole materials for shoes and chappals. We therefore strongly believe that the proposed methodology for the total elimination of solid and liquid waste from tanneries will reduce the environmental burden of toxic chemicals and

the costs to tanneries from the final byproducts by realizing the popular slogan "wealth from waste".

## ■ EXPERIMENTAL SECTION

**Materials.** Poultry feathers were collected from a local poultry outlet and washed thoroughly with water. The water was drained and feathers were dried under sunlight and taken for further studies. The CS was obtained from Tannery Division of our Institute. Chrome exhaust and dye exhausts liquors were collected from a commercial tannery in Pallavaram, Chennai, India.

**Preparation of Keratin Hydrolysate (KH).** 1 kg of dried feather was pulverized to render the feather into a soft mass using a pulverizing machine (Premium Pulman Pvt. Ltd., India). 200 g of the powdered feather was hydrolyzed by the method of autoclave using 6% NaOH. The quantity of water used was 2.3 L. The autoclave was run for 60 min at 120 °C with the pressure of 276 kPa. The pH of this alkaline hydrolyzed keratin was above 12.0, which was then adjusted to pH 2.8 using 50% $H_2SO_4$ (V/V) because in the processing of leather tanning using basic chromium sulfate (BCS), the pH of the pickled pelt will be brought to 2.8, the condition optimal for tanning with

BCS. The total quantity of the KH prepared was 6.5 L, including the addition of a required quantity of water. The stepwise mechanism of the hydrolysis of keratin is illustrated in Scheme 1A,B.

**Treatment of KH Treated CS with Chrome and Dye Exhaust Liquors.** 1 kg of dry CS was placed in a 10 L plastic tub and 6.5 L of KH (pH 2.8) was added slowly, and the solution was mixed well. Because the CS was in a dry state, the KH was absorbed by the CS and the resultant mass, referred as CSKH, was obtained. (The fixation of KH into the chrome shavings through the carboxyl terminal group of the keratin protein is depicted in panel A of Scheme 2.) The product CSKH was dried under sunlight in a stainless steel tray measuring 70 × 70 cm. After the product was partially dried (moisture content 60%), the material (CSKH) was placed in a 20 L tub and 10 L of chrome exhaust liquor, obtained from a commercial tannery (pH 3.5), was added, and the mixture was stirred mechanically for 1 h. The Cr(III) ions present in the chrome exhaust liquor interacted with the excess carboxyl groups of the CSKH and bound to the CSKH. The pH of the content was further increased by addition of 2% sodium bicarbonate on the wet weight of CSKH, leading to the fixation of Cr(III) (Scheme 2). The process is similar to basification in a chrome tanning operation in leather processing, where the Cr(III) is fixed into the collagen matrix at pH 4.0. The product was allowed to dry under sunlight in the stainless steel tray until 59% moisture was intact. The product was neutralized to pH 5.0 with 2% sodium bicarbonate on the wet weight of CSKH. To this partially dried CSKH, containing bound Cr(III), was added 10 L of dye exhaust liquor slowly, stirring mechanically for 1 h. The dye along with fat liquor present in the dye exhaust liquor was absorbed into the Cr(III) bound CSKH. The dye was then fixed with 1% formic acid on wet weight of CSKH and the product was dried to a semisolid consistency. During the stage of addition of dye exhaust, it was observed that the color of the product did not change remarkably, indicating that more quantity of dye exhaust solution could be absorbed in the CSKH. The whole process is schematically presented in Scheme 2. The samples were collected at four stages and analyzed for moisture, protein, and total Cr(III) content. The stages were Stage 1, CS before the treatment with KH (BP1); Stage 2, after the treatment with KH (BP2); Stage 3, after the treatment of chrome exhaust liquor (BP3); Stage 4, after treatment of dye exhaust liquor (BP4). BOD and COD determinations were also carried out before and after the treatment of chrome exhaust liquor into the CSKH complex (Table 1).

**Table 1. BOD and COD before and after Treatment of Chrome Exhaust Liquor**

| COD before treatment of chrome exhaust liquor (ppm) | COD after treatment of chrome exhaust liquor (ppm) | BOD before treatment of chrome exhaust liquor (ppm) | BOD after treatment of chrome exhaust liquor (ppm) |
|---|---|---|---|
| 1200−3000 | 800−2000 | 500−1200 | 350−900 |

**Preparation of Leather-like Composite Sheets.** 1 kg of the semidried product (solid content 49%) prepared as described above (CSKH material incorporated with Cr(III) of chrome exhaust liquor and dye of dye exhaust liquor) was pelletized in the meat mincer into fine particles, which was then made into a paste in an industrial mixer. 400 mL of 2.5% PVA (poly(vinyl alcohol)) and 20 mL of ethylene glycol were then added into 1 kg of the paste. The product was then cast into sheets of 60 × 60 cm and dried. The leather-like composite sheets were trimmed at the edges and pressed with a hydraulic heat pressing machine under the pressure range of 34 474 KPa (344.74 bar)−41 368 KPa (413.68 bar) at a temperature range of 80−90 °C. To increase the strength of the composite sheets, a bandage-like porous cloth was pasted between two sheets with the help of an adhesive commonly used in the footwear and leather goods industry. The mechanical properties such as tensile strength, extension at break (%) and tearing strength of the leather-like composite sheet before and after pasting the bandage cloth were determined by ISO methods ISO 3376:2011 and ISO 3377-1:2011.[25−27] The tests were performed at

standard temperature of 20 ± 2 °C and relative humidity of 65 ± 5%. The results are presented in Table 2.

**Table 2. Mechanical Properties of Leather-like Composite Sheets**

| sample no. | sample | tensile strength (MPa) | extension at break (%) | tearing strength (N) |
|---|---|---|---|---|
| 1 | standard parchment leather | 27.15 ± 0.94 | 28.24 ± 0.81 | 25.62 ± 0.65 |
| 2 | leather-like composite sheet | 36.75 ± 0.68 | 27.64 ± 0.71 | 28.78 ± 0.42 |
| 3 | leather-like composite sheets pasted with porous cloth | 87.92 ± 0.23 | 79.86 ± 0.85 | 67.41 ± 0.59 |

**Analysis of Moisture, Protein, and Total Cr Content of the Samples.** The moisture of all four samples (BP1, BP2, BP3, and BP4) was determined using standard procedures.[28] Estimation of total protein content of the samples was carried out by the Micro Kjeldahl method,[29] using ammonium sulfate as a standard. Estimation of total chromium of the samples was performed by the standard perchloric acid digestion method.[30] All results are presented in Table 3.

**Physicochemical Characterization of the Samples.** Fourier transform infrared (FTIR) spectroscopy analyses of the dried samples (BP1, BP2, BP3, and BP4) were performed using a Nicolet 360 FTIR spectrometer at 400−4000 cm⁻¹, adopting a standard protocol to evaluate the various functional groups of the sample and confirmation of the fixation of Cr(III) into the CSKH.[31] The thermogravimetric analysis (TGA) of the four samples was carried out using a TAQ50 instrument at 20−800 °C to evaluate the thermal stability of the samples.[32,33] Differential scanning colorimetry (DSC) of the samples was carried out using a TA-DSC Q200 to determine the thermal transitions and structural stability of the samples.[34,35] The surface morphology and the cross section of the composite sheet produced out of chrome exhaust and dye exhaust treated CSKH were studied through scanning electron microscopy (SEM) analysis.[36] The composite sheets were cut into 5 × 2 mm dimensions and mounted on an aluminum stub using double sided adhesive tape. The samples were then sputter coated with gold using an Edwarols E306 sputter coater. The surface morphology and cross section of the sample was then recorded on the SEM instrument (Helica Cambridge stereo scan R440) operated at an accelerated voltage of 10 kV.

## ■ RESULTS AND DISCUSSION

**Interaction between Keratin Hydrolysate and Chrome Shavings.** Wet blue leathers are shaved to get required thickness to the leather. These shavings will have different surface area. The length of shavings varies from 0.5 to 10 cm and width may vary from 0.1 to 1 cm. The porosity of the chrome shavings vary from 0.05 to 1 μm.[37] The incorporation of hydrolysate into dry chrome shavings was carried out because the absorption of KH will be effective, as the increased surface area obtained by the mechanical action of the shaving machine by which the chrome shavings were produced and because by this action, the fiber bundle of the collagen is opened up to the microfibrils level, the interior domain is a available for interaction with liquid keratin hydrolysate. This is not a mere physical absorption by KH but a chemical link with CS. This is protein−protein interaction and protein−Cr(III) ion interaction, where the nitrogen atom of the amino terminal group present in the terminal amino acid of the microfibril of the chrome shavings is linked with the carbon atom of the carboxylic acid of the terminal amino acid of the hydrolyzed keratin through a peptide bond and forms dipeptide, tripeptide,

**Table 3. Chemical Analysis of Samples**

| sample no. | sample | percentage of moisture | percentage of total protein on moisture free basis | percentage of chrome(III) on moisture free basis |
|---|---|---|---|---|
| 1 | poultry feather powder | 8.1 ± 0.3 | 91.04 ± 0.79 | |
| 2 | keratin hydrolysate | 90.8 ± 0.65 | 6.92 ± 0.32 | |
| 3 | chrome shavings (BP1) | 19.1 ± 0.43 | 75.89 ± 0.47 | 4.37 ± 0.05 |
| 4 | chrome exhaust liquor | 88.56 ± 1.13 | | 1.77 ± 0.08 |
| 5 | dye exhaust liquor | 83.33 ± 1.07 | | |
| 6 | chrome shavings + keratin hydrolysate (BP2) | 12.56 ± 0.51 | 82.18 ± 0.71 | 3.65 ± 0.40 |
| 7 | chrome shavings + KH + chrome exhaust liquor (BP3) | 52.5 ± 0.79 | 34.26 ± 0.84 | 10.74 ± 0.26 |
| 8 | chrome shavings + KH + chrome exhaust liquor + dye exhaust liquor (BP4) | 51 ± 0.47 | 33.49 ± 0.50 | 9.68 ± 0.08 |

and oligopeptide clusters. In the same manner, the nitrogen atom of the terminal amino acid of the hydrolyzed keratin joins with the carbon atom of the carboxylic acid present in the terminal amino acid of the microfibril of the chrome shavings and forms a dipeptide. Large quantities of dipeptide, tripeptide, and oligopeptide clusters are produced in the above interaction. The large quantities of available clusters of these peptides absorb the Cr(III) ions of chrome exhaust liquor and are fixed in the CSKH complex. That is, the free carboxylate ions present in the dipeptide, tripeptide, and oligopeptide clusters of the CSKH complex react with Cr(III) ions of chrome exhaust liquor and are fixed into the complex, as indicated in Scheme 2.

The estimation of total protein and Cr(III) content of the samples BP1, BP2, BP3, and BP4 on a moisture free basis (Table 3) clearly reveals the stepwise incorporation of KH in BP2. The protein content in BP2 is by increased to 82.18% ± 0.47 from 75.89% ± 0.47 of BP1. Similarly, the total chromium content in BP3 is increased to 10.74% ± 0.26 from 3.65% ± 0.4 of BP2. The increased value of chrome content in the sample BP3 is due to the fixation of Cr(III) into the KH treated CS (CSKH).

The chrome exhaustion studies were also carried out, and the samples of the treated and untreated chrome exhaust liquors are presented in the Supporting Information (Figure S1) for comparison. Here the color of the treated chrome exhaust liquor is almost colorless, indicating the full absorption of chromium(III) into the CSKH complex. From the results, it can be concluded that whatever quantity of chromium offered from chrome exhaust liquor to the CSKH complex is fixed into the complex irreversibly, leading to 100% fixation chromium and total elimination of liquid chromium pollutants of tannery. In the same manner, the dye from the dye exhaust liquor is also fixed into the CSKH complex, resulting in total elimination of two main liquid pollutants of the tanning industry.

**Fixation of Dye into Chromium Fixed CSKH Complex.** The illustrated dyes shown below are generally used in the leather industry. The C.I. Direct Red is fixed by the amino group of the dye to the terminal carboxyl group of the chromium fixed CSKH complex in the process of fixation of dye exhaust liquor.

The coloration of this dye is due to the presence of the hydroxide group in conjunction with the azo group. This is fixed to the amino group of the proteinaceous part of the chromium fixed CSKH complex through a sulfonic acid group. In the premetallized dyes, also, the amino group of the proteinaceous part of the chromium fixed CSKH complex is fixed through a sulfonic acid group. The acid dye, polar Brilliant Red 3B, is fixed to the chromium fixed CSKH complex through the OH group of the dye and linked to the chromium moiety of the CSKH−Cr complex.
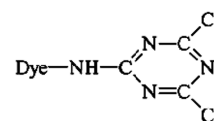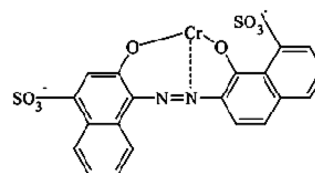
Direct Dyes (Basic Dyes): C.I. Direct Red 118
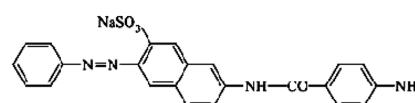


Basic Orange 2 Dyes
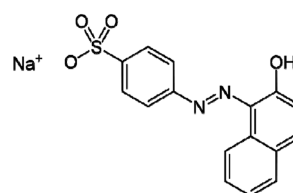


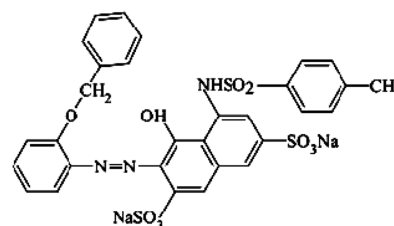Reactive dyes: I.C.I Procions



Pre-metalized Dyes: C.I. Acid Blue 158



Acid Dyes: Polar Brilliant Red 3B



Some of the other dyes that are commonly used in dyeing of leathers are Reactive Yellow 85, Reactive Yellow 95, Reactive Orange 35, Reactive Red 24, Reactive Red 45, Reactive Brown 11, Reactive Blue 49, Reactive Black 39, and Reactive Black Mix. These are reactive dyes constituting dichloro triazine, monochloro triazine, and vinyl sulfone dyestuffs.

In the category of acid dyes, the following are some of the acid dyes: Acid Yellow 42, Acid Yellow 99, Acid Yellow 194, Acid Orange 56, Acid Red 97, Acid Blue 7, Acid Brown 75, and Acid Black 194. Acid dyes are complex in nature and they are large aromatic molecules composed of many linked rings. Acid dyes usually have a sulfo or carboxy group on the molecule that facilitates the solubility of the dye. Some of the basic dyes are Direct Methylene Blue, Crystal Violet, Basic Fuchsin, Violet 51, Direct Violet 9, Direct Orange 142, Direct Orange 26, Direct Red 31, Direct Red 23, and Direct Brown 44. The basic dyes are typically cationic or positively charged. Basic dyes consist of amino groups or alkyl amino groups as their auxochromes. Some of the other dyes used in the leather industry are mordant dyes, vat dyes, solvent dyes, and metal complex dyes.

The dye used in the submitted work is Green BG, which is a prominent acid dye. The dye exhaustion studies carried out in the course of the experiment are reported. The degree of dye exhaustion was analyzed using a UV−vis spectrophotometer V650 instrument (Figure 1). In the UV−vis spectra (B), the
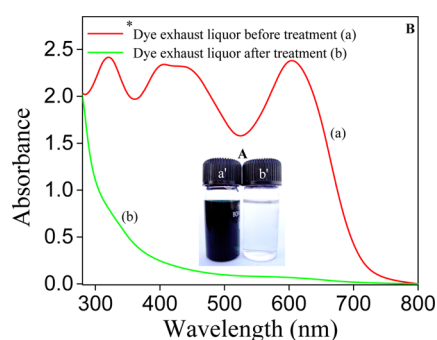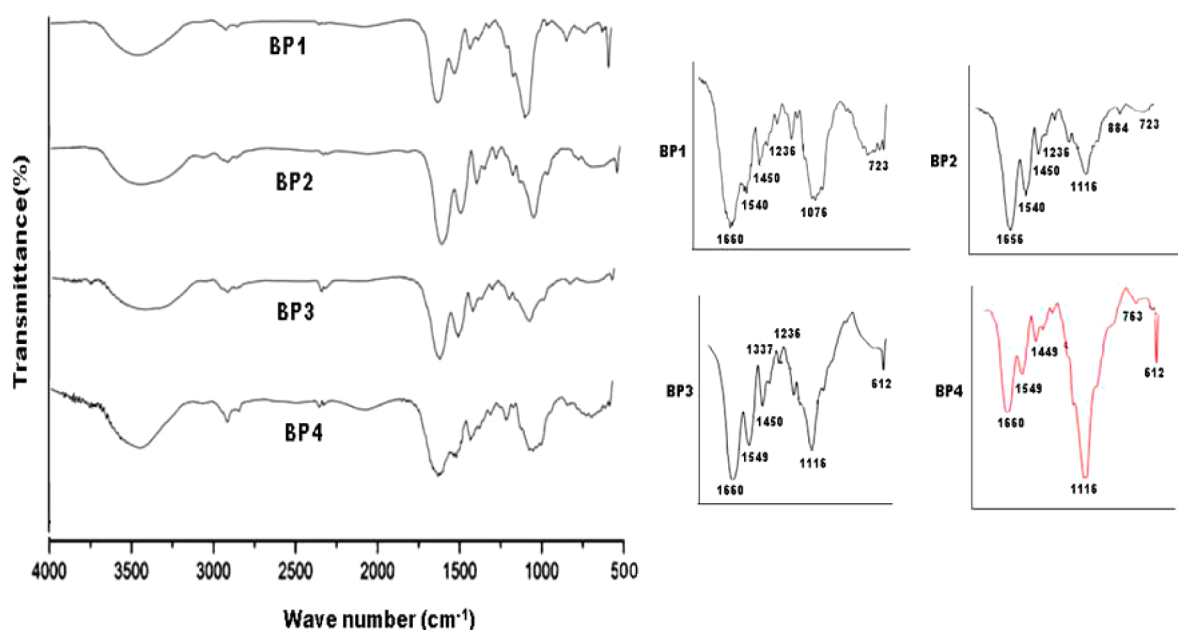
colored line (a) shows absorbances of 2.42, 2.34, and 2.38 in the wavelength range of 280−800 nm at 5 times dilution and gives three peaks around 320, 405, and 605 nm; however, the treated dye exhaust liquor without dilution (b) does not show any peaks around these regions, which shows the complete absorption of dye into the chromium treated CSKH complex. The concentration of dye Green BG, of the exhaust liquor was estimated with the help of standard curve of known concentrations of dye and it was calculated that 99.63% of the dye was absorbed immediately after the treatment and the remaining 0.37% of the dye is also absorbed during the process of sun drying of the materials (CS + KH + chrome exhaust liquor + dye exhaust liquor), leading to 100% absorption of dye.

Samples of the dye exhaust solutions before (a′) and after (b′) the treatment are photographed (A) and presented for comparison. In this photograph, it can be observed that the color of the dye exhaust liquor is almost colorless, indicating the total absorption of dye in the chromium treated CSKH complex.

To confirm the process of dye exhaustion, two more dye exhaust liquors were obtained from the tannery and dye exhaustion studies were carried out. One dye exhaust liquor contained an acid dye, Navy Blue, and the other dye exhaust liquor contained a metal complex dye, Yellow GR. The methodologies were followed as mentioned in the previous dye exhaustion studies and the results were as good as those of the previous dye exhaustion work. Both the dye exhaust samples were analyzed before and after treating with chromium treated CSKH, using the UV−vis spectrophotometer V650 instrument, and the results are furnished in the Supporting Information (Figures S2 and S3). The concentration of the acid dye, Navy Blue, of the exhaust liquor was estimated with the help of a standard curve of known concentrations of dye and it was calculated that 99.45% of the dye was absorbed immediately after the treatment and the remaining 0.55% of the dye was absorbed during the process of sun drying of the materials (CSKH + chrome exhaust liquor + dye exhaust liquor), leading to 100% absorption of dye. In the same manner, the



**Figure 1.** (A) Color photograph of samples of dye exhaust liquor before (a′) and after (b′) treatment. (B) UV−visible spectra of dye exhaust liquor before (a) and after (b) treatment with chromium treated CSKH complex, respectively. An asterisk indicates 5 time dilution of dye solution before treatment.



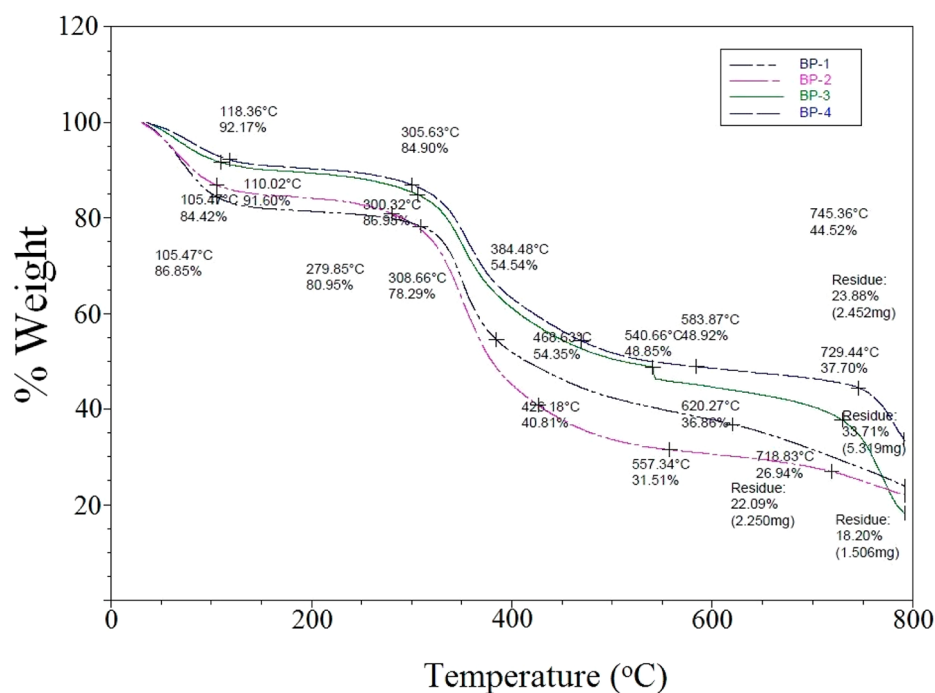**Figure 2.** IR spectra of samples BP1, BP2, BP3, and BP4.

**Figure 3.** TGA of samples BP1, BP2, BP3, and BP4 depicted by different sources, and their degradations are shown stepwise.
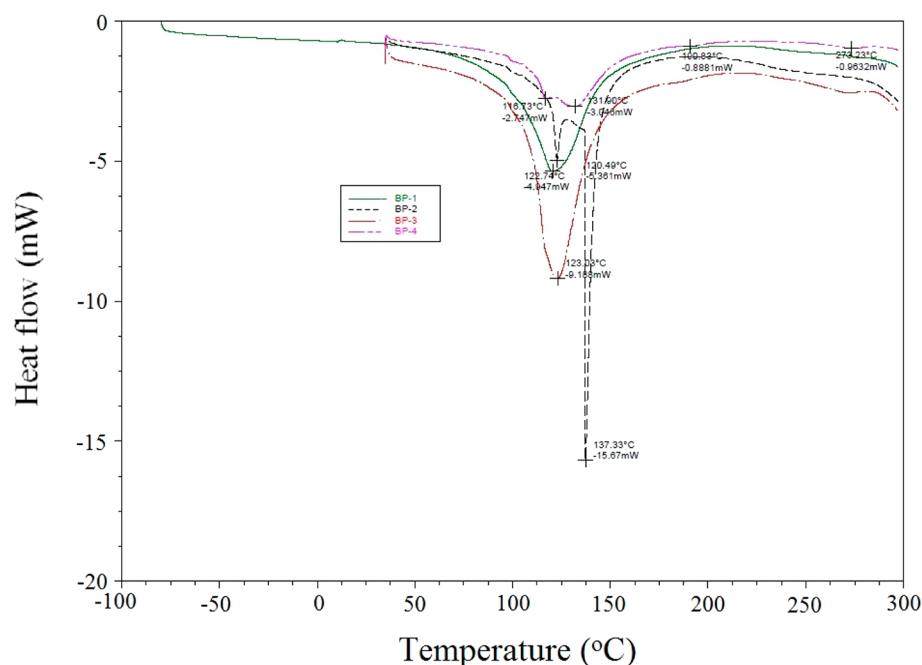


**Figure 4.** DSC analysis of samples BP1, BP2, BP3, and BP4 depicted by different sources, and their endothermic peaks are noticed at different temperatures. Thermal stabilities were increased due to cross-linking of molecules.

concentration of the dye exhaust containing a metal complex dye, Yellow GR, was also estimated with the help of a standard curve of known concentrations of dye. It was calculated that 99.1% of the dye was absorbed immediately after the treatment and the remaining 0.9% of the dye was absorbed during the process of sun drying of the materials (CSKH + chrome exhaust liquor + dye exhaust liquor), leading to 100% absorption of dye. (More details in the Supporting Information.) These experiments clearly confirm the efficacy of the dye exhaustion studies.

**Instrumental Interpretations.** *FTIR Studies.* The FTIR spectra of the samples were recorded to understand the incorporation of KH in CS and absorption of chrome and dye exhaust liquor by the obtained CSKH. The spectra (Figure 2) demonstrated the appearance of absorption band at 1116 cm$^{-1}$ in all the four samples, indicating the presence of sulfonate group, which might have formed during the interaction of basic Cr sulfate and amine groups of collagen present in CS. Apart from this, the characteristic peaks of the amine groups present in collagen are noted at 3443, 3458, 3454, and 3453 cm$^{-1}$ in BP1, BP2, BP3, and BP4, respectively. Further, in all the
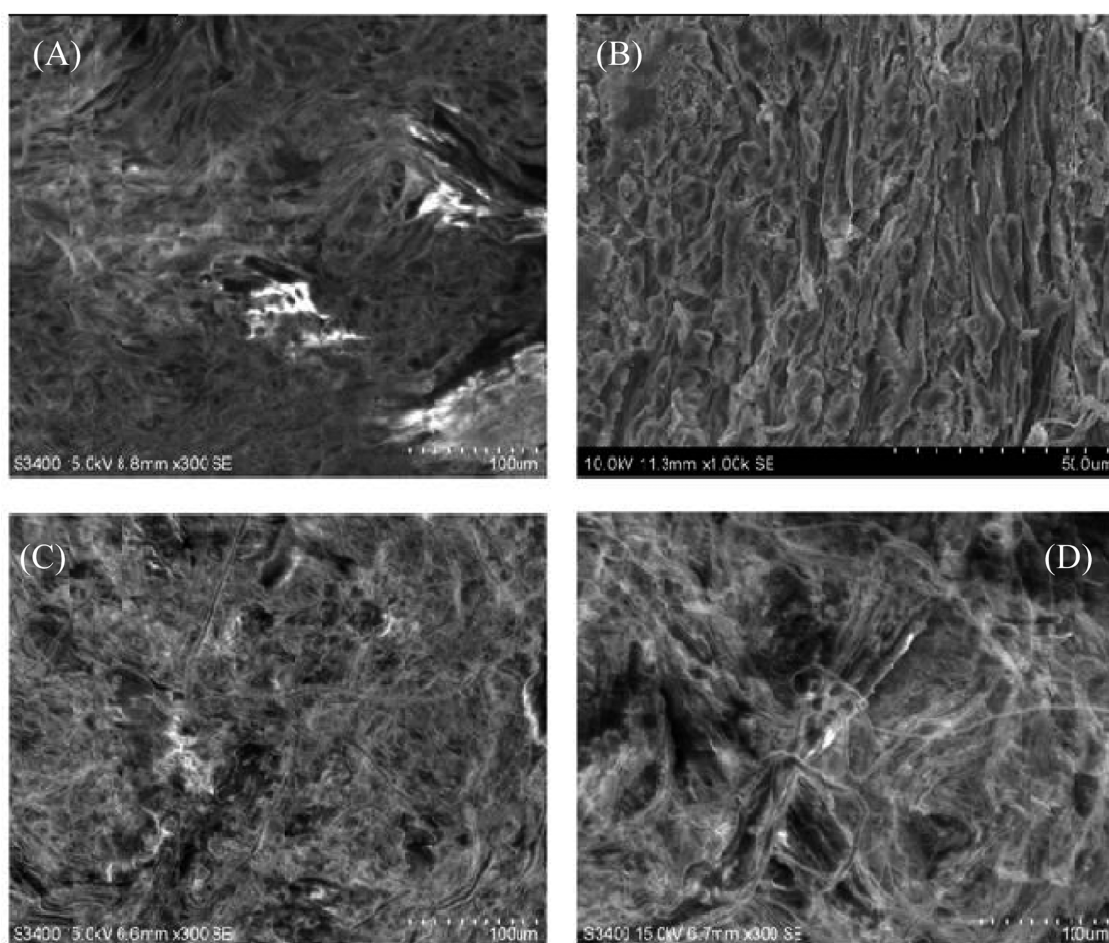
**Figure 5.** SEM images of composite sheet made out of CSKH complex treated with chrome exhaust liquor and dye exhaust liquor. Panels A and B show cross sections and panels C and D show surface morphology.

samples, the C=O stretching vibration band of amide 1 is noticed at 1660 cm$^{-1}$ in BP1, at 1656 cm$^{-1}$ in BP2, at 1660 cm$^{-1}$ in BP3, and at 1660 cm$^{-1}$ in BP4, indicating the presence of the peptide group of CS in BP1 and the peptide group of CSKH of BP2, BP3, and BP4. An additional peak at 1549 cm$^{-1}$ that corresponded to the carboxylate group was observed in BP3 and BP4. The carboxyl group formed during the alkaline hydrolysis of keratin interacted with basic chromium sulfate of chrome exhaust liquor, forming a salt of carboxylic acid. However, the intensity of carboxylate group was reduced in BP4 compared to in BP3, which might be due to interaction with dye exhaust liquor. Thus, following incorporation of KH into CS, large numbers of carboxyl and amino functional groups available in CSKH for binding with Cr(III) and dye from tannery liquid wastes and successfully removed Cr(III) and dye from chromium and dye exhaust liquor of tannery liquid pollutants. The increased protein and Cr(III) content in BP2 and BP3 (Table 3), respectively supports the above observation.

*TGA Studies.* The TGA analyses of prepared samples are given in Figure 3. Thermograms of all the samples have shown more or less similar trends of weight loss with increase in the temperature. Considering thermograms of all the samples, BP1 loses 60% weight at 557.0 °C, whereas sample BP2 loses 68.5% weight at the same temperature (Figure 4). In the case of sample BP3, 54.3% of weight loss is recorded at 557.0 °C, whereas in the case of sample BP4, the percentage of weight

loss is 49%. At 620 °C, BP1 (10.26 mg) lost 63.14% (6.47 mg) of its weight. At the same temperature, BP2 (10.18 mg) lost 70.85% (7.21 mg) of its weight. Approximately 7% more weight loss was observed in BP2. BP3 (8.27 mg) lost 58.75% (4.85 mg) of its weight at 620 °C. Comparatively, a smaller percent of weight loss was observed in BP3 at 620 °C. BP4 (15.77 mg) lost 53.48% (8.43 mg) of its weight at 620 °C. In a comparison of the thermograms of all samples, BP4 recorded a smaller loss of weight at 620 °C. The weight loss in the cases of CS (BP1) and CSKH (BP2) are more because they are heat labile, a condition that leads to the disorganization of the molecular structure of keratin protein or polypeptide. However, in BP3, the collagen is well cross-linked through interaction with the carboxyl group of KH through binding with Cr(III). The cross-linking process stabilizes the structure and, therefore, retards the disorganization of BP3. The percentage of weight loss that is further reduced in sample BP4 might be due to the strong structural stability that occurred during dye fixation in chrome exhaust liquor treated CSKH.

*DSC Analysis.* The DSC curves of different treated samples demonstrated chromium and dye fixation following treatment of CSKH with chrome and dye exhaust liquor, respectively (Figure 4). In the DSC curve of sample BP1, the endothermic peak is noticed at 121 °C, which can be attributed to the denaturation state of the collagen fiber and disorientation of hydrogen bond as a result of the denaturation and evaporation of water molecules. In the case of sample BP2, two distinct

endothermic peaks are noticed; one at 123 °C and a sharp peak at 137 °C with −16 mW heat flow. This is because the thermostability of keratin protein is more, in comparison to the other proteinaceous materials. In sample BP3, the DSC endothermic curve has a peak at 123 °C with −10 mW heat flow, indicating a more stabilized structural configuration through the interaction of the carboxyl group of KH with the basic Cr(III) of chrome exhaust liquor. In the case of sample BP4, four different DSC peaks are observed at 117, 132, 191, and 273 °C. This is due to the formation of CSKH and chrome exhaust liquor complex and the denaturation temperature, which is prolonged because of the structural stability caused by the chrome tanning and dye fixation. Consistent with these results, the FTIR, TGA, and DSC studies clearly indicate the incorporation of KH in CS (forming CSKH) and subsequent fixation of chromium and dye in CSKH, leading to elimination of chromium and dye from tannery wastewater.

*Scanning Electron Microscopy Studies of Composite Sheet.* A leather-like composite sheet has been prepared following absorption of Cr(III) and dye exhaust liquor in CSKH (see the Experimental Section) to make a value-added product from the waste material and ultimately reduce the cost of liquid and solid waste management process. To increase further the strength of this composite sheet, a bandage-like porous cloth was pasted between two sheets with an adhesive normally used in the footwear and leather goods industry. The results showed that following incorporation of the porous cloth between two composite sheets, the strength of composite sheet increased more than double in comparison to the original composite sheet (Table 2). The surface morphology and the cross section of the as-prepared leather-like composite sheet have been studied through SEM analysis. In the cross section of the composite sheet (Figure 5A), the fibrous structure of the CS is seen embedded in the mass of keratin protein with PVA and ethylene glycol. The thick dark lines show the air gap between the filaments formed when the sheets were dried. Figure 5B shows the cross section of the composite sheet. The coarse filamentous arrangement of the chrome shavings is clearly noticed with air gap in between. In this photomicrograph, the amorphous KH along with PVA and ethylene glycol can be seen. The image demonstrated the fibrillar structure of the CS. In the cross section of the micrograph, the arrangement of filaments and their close association with KH and poly(vinyl alcohol) is clearly seen. The KH together with PVA and ethylene glycol binds the fine chrome shavings filaments during the formation of composite sheet. Figure 5C indicates the surface morphology of the composite sheet. In this photomicrograph, the smooth surface of the sheet can be seen as the sheets were pressed with a hydraulic heat pressing machine after the sheets were dried. In Figure 5D, which is also the surface morphology of the composite sheet, the haphazard interwoven chrome shaving structure of the filaments is clearly noticed. This is also a smooth surface and the smoothness of the surface is due to KH, poly(vinyl alcohol) and ethylene glycol.

*Present Scenario of Leather Industry Compared to Present Investigation.* To asuade the problem of solid and liquid pollution of the tanning industry, scientists are putting their best efforts in the field of waste management. Kolomaznik et al.[38] have used the filter cake isolated after alkaline hydrolysis of chrome shavings for the precipitation of Cr(III) ions from the spent liquor. This process increased the content of Cr(III) in filtrate cake, thereby facilitating its subsequent use, while the

wastewater was purified from the soluble salts of Cr. The protein of the filtered cake after hydrolysis of chrome shavings has been used to trap the Cr(III) ions from the spent liquor and eliminating the Cr from the outgoing spent exhaust liquor, thus purifying the liquid pollutants. Subsequently, Kolomaznik et al.[39] described the automatic control of recycling technology for Cr from liquid and solid tannery waste. The research work specified the technology with regard to the economy of the process and design of the control algorithm in the economic optimum. Because the process is conducted with minimum operating costs and the process is done under a computer controlled system, the efficacy of the result is assured. However, it involves a computer controlled system and other infrastructures like a hydrolysis reactor, precipitating tank, Cr sludge dissolving tank, etc. that have some limitations with regard to application in rural tanneries and tanneries of underdeveloped countries. Moreover, the generation of CS from the leather industry is accounts for about 10% of the total raw skins/hides processed, amounting to 0.8 million tons/per year globally (as per data of 2002).[40] As per data of 2011,[41] the skins/hides processed, amount to 15 million tons per year (50 000 tons per day). The wastewater discharged was 1500 million liters per day and the solid waste generated was 6 million tons per year. R. O. Oruko (as per data of 2014)[42] et al. described the solid wastes generated in Nairobi that are posing serious environmental pollution problems from the leather industries. They have analyzed the samples collected in the tanning stages of leather processing, soil, and waters for pollutants such as sodium chloride, sulfide, chromium and total phenols in raw dried skins, lime fleshings, shavings, and buffing, and the results were found to be above NEMA/NCSWC standards.

To address these issues, we have developed a very simple methodology to incorporate the KH into CS, which increases the carboxyl and amine functional groups in the CS. The obtained CSKH material binds Cr(III) from chrome exhaust and dye from dye exhaust liquors of tannery liquid pollutants. The bound Cr(III) and dye were then irreversibly fixed in CSKH through treatment with sodium bicarbonate and formic acid, respectively. Finally, a leather-like composite sheet was made from the Cr(III) and dye absorbed CSKH material. This composite sheet can also be used in the footwear industry as an insole material in shoes and chappals and also in leather goods for the manufacture of hand bags, parchment papers, folders, file covers, etc. We therefore strongly believe that by adopting our proposed methodology, both the liquid and solid waste of the tanning industry, namely chrome exhaust, dye exhaust liquors, and CS could be treated in a cost-effective way without using any expensive chemical and sophisticated instruments and/or equipment, which are often required in reverse osmosis,[43] and clarifiers,[44] for wastewater treatment. Further, this simple and straightforward methodology can be adopted by any small, medium, and large scale tanneries for cost-effective liquid and solid waste management. Therefore, the proposed methodology will certainly reduce the environmental burden of toxic chemicals and reduce the cost of tanneries from the final byproduct.

## ■ CONCLUSION

A simple methodology has been developed for environmental benign and cost-effective treatment of both liquid and solid waste of the tannery industry. The KH has been incorporated initially in the CS and the obtained CSKH material has been used for the elimination of chrome and dye exhaust liquor of a

tannery. The results showed the absorption and the fixation of Cr(III) and dye chrome and dye exhaust liquor, respectively leading to 100% fixation into CSKH material. Finally, a value-added product such as a leather-like composite sheet has been obtained from the solid waste of Cr(III) and dye absorbed CSKH material favoring complete utilization of both liquid and solid waste of tannery industry. This is an important factor to be reckoned with and an essential benchmark in the field of solid and liquid waste management of the tanning industry. Another important factor in this study is that we are treating the end of the pipe pollutants generated by the leather industry, the treatment which generally involves a huge amount of expenditure. Three major pollutants of the leather industry, viz. CS, chrome exhaust liquor (left after the chrome tanning and rechroming), and dye exhaust liquor (left after the dyeing and fat liquoring operation) are completely used in the proposed methodology. The poultry feather, the nonutilization of which is again a potent pollutant, is also used in this process. Therefore, liquid and solid waste of the tannery industry can be treated in an economically viable procedure and contribute substantially toward a clean and green environment.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

Color photographs of chrome exhaust liquor before and after the treatment with CSKH complex, standard curve of Green BG dye, UV−visible spectra of Navy Blue dye exhaust liquor before and after treatment with chromium treated CSKH complex, respectively, color photograph of Navy Blue dye exhaust liquor before and after treatment, standard curve of Navy Blue dye, UV−visible spectra of Yellow GR dye exhaust liquor before and after treatment with chromium treated CSKH complex, respectively. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00071.

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### Notes

The authors declare no competing financial interest.

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