Preparation of High Exhaust Chrome from Leather Shavings and Hydrocarbons with its Application in Leather Processing for Green Tanning Technology

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Summary: The use of chrome in tanning has made the remarkable advances to achieve the best quality and quantity of leather. But the chrome tanning process is associated with the generation of heavy metal containing solid wastes and toxic effluents. To solve the environmental issues we emphasized on the development of high exhaust chrome complex from chrome containing leather wastes that could minimize the toxic effluents up to negligible limit. Therefore in the synthetic process of chrome tanning material, the chrome shavings and the hydrocarbons have been utilized as a reductant as well as the potential masking intermediates. These chrome tanning materials have been prepared using leather shavings alone in product A, partial replacement of shavings by hydrocarbons for product B and then replacement of hydrocarbons by molasses for product C. The materials have been employed for the tanning of goat skins parallel to the commercial basic chromium sulfate (BCS).

The comparative tanning studies revealed that, the quality of leather made from product B is either better or comparable with those of product A, C and the conventional tanning material. Shrinkage temperature of this leather was more than 120 °C after an offer of 1.65 % Cr_2O_3. The amount of Cr_2O_3 in the leather resulted from product B has been found more than others with the simultaneous elevation in spent chrome liquor. Hence the exhaustion rate of product B has been noted up to 95 %. While the physical characterstics of resulted leather from product A, B, and C have been found comparable to that of conventional tanned leather. Therefore, this methodology would not only reduce toxic effluents and chrome containing solid wastes but also provide quality leather and higher economic return.

Introduction

The leather industry is a major consumer of by-product from the meat industry. Due to the intrinsic nature of leather, processing and chemicals employed, which is a significant generator of liquid and solid wastes [1]. For instance during chrome tanning process, only 75-80% commercial chromium sulfate exhausts in leather and remaining goes in liquid waste [2]. This waste contaminates sea as well as the inland water supply and effects the food resources. World Health Organization (WHO) standard of toxicity level in drinking water is up to 0.05 ppm. whereas around the tannery areas in Pakistan this level has been reported over 3 ppm, indicating a serious health problem for local community [3].

In addition to liquid waste, a significant amount of Cr_2O_3 moves in leather shavings along with other organic compounds [4]. During the processing of one metric ton of raw hides only 200 kg of leather final product is obtained along with 250 kg non tanned, 200 kg tanned leather wastes and 50,000 kg waste water. Thus only 20% of the raw material is converted to leather [4-7]. It has been estimated that the annual cost of treating tannery waste is more than 5% of the turn over [4]. The traditional way of handling of these chrome tanned solid wastes in most of the countries is land filling, tannery closures or incineration [8]. Such disposition of chrome tanned solid wastes would be very risky. Since, under these conditions the oxidation reaction of Cr^{+3} to Cr^{+6} is possible, because in basic solution this reaction occurs with ease by peroxides or hypohalides. Acidic rain can leach chromium Cr^{+3} from waste dump after which soluble chrome salts may reach the sources of potable water [4].

As we know the chrome containing leather waste is not ordinary because it has a treasure of valuable material [9]. This mainly consists of collagen and chromium III complexes which could be treated to give the potential resources of protein and chromium [10]. In past, the leather researchers have made their efforts on the reutilization of leather

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wastes. Before 1970, the reports were focused on the uses without pre-treatment *e.g.* on the manufacturing of insulators, building material, fibrous sheets and shoe soles etc. Later on a lot of publications appeared on hydrolyzation of chrome containing leather wastes to re-cycle the protein in different products *e.g.* food, agriculture, pharmaceutical etc [11-15], using different extraction methods [16-20]. During the last 15 years a systematic research work has been performed on extraction of protein, its characterization and utilizations in many products first at laboratory and then on pilot scale [21-26]. But the chrome cake remained as a waste in these processes [23], because of the complicated operations *i.e.* acidic dissolving, alkaline precipitation, filtering and washing for the recovery and purification of chrome [8, 24]. However, the de-chroming process not only decreases the utilization ratio of chrome-shavings but also increases the treatment cost [27].

Therefore, the investigations of reasonable and effective way to beneficial utilization of chrome containing leather wastes becomes very urgent. Recently Rao *et. al.*, [2], and Fengxia. C *et. al.*, [2, 28] have used chrome shavings as a reductant in the preparation of chrome tanning salt. But such utilization may only solve the disposition problem of chrome tanned leather solid wastes. To solve both the liquid and solid wastes problems "two in one base strategy" we emphasized to develop a process for the synthesis of high exhaust chrome complex where chrome shavings have been used as a raw material without de-chroming followed by modification to masked complex. This material would not only solve the disposition problem of chrome containing solid wastes but also minimize the chromium in spent chrome liquor upto negligible limit, as well as would improve the quality of leather and economic benefits.

Results and Discussion

Traditionally, commercial basic chromium sulfate is prepared by the direct reduction of dichromates with sugar (molasses) or sulferdioxide in the presence of sulfuric acid [38, 39]. Besides sugar other reducing agent such as coconut pith, bagasse, oils, glycerol, and vegetable tanning materials have also been used to reduce dichromate into chromium sulphate [40-44]. It has been reported earlier that the chrome liquors prepared by different reducing agents differ in their properties due to the formation of different types of intermediate chemicals [41]. For instance sugar/glucose produces intermediates like oxalic acid, formic acid, aldehydes, carbon dioxide and other precursors of humic acid [42, 43]. Such organic intermediates are capable of forming complexes with metal ions by the substitution of aqua or sulfato groups [43, 44].

Employing this strategy, three different products A, B and C have been prepared and characterized. Product A has been synthesized using chrome shavings alone as a reductant because it contains variable amount of Cr_2O_3 and 70-80% protein material suitable for the reduction of Cr^{+6} to Cr^{+3}. In case of product B the 50% amount of the chrome shavings have been replaced by those hydrocarbons that may produce very potential intermediates (Masking Agent) for more stable chrome complexes. While for product C, the hydrocarbons were removed by molasses.

These laboratory prepared tanning materials were subjected to analysis for chromium oxide contents [45], basicity and the pH value of the liquor [46, 47] as shown in (Table-1). It could be noted that the lower amount of Cr_2O_3 in the developed products A, B and C as compared to the commercial basic chromium sulfate (BCS) is perhaps due to the formation of intermediate products of protein and other hydrocarbons during the reduction of Cr^{+6} to Cr^{+3}.

Table-1: Characteristics of Tanning Material.

Name of Product	pH of liquor	% Moisture	% Basicity	% Cr_2O_3
Commercial BCS	2.9	08 (powder)	33	24
Product A	3.8	49	36	19.5
Product B	3.7	47	37	19.0
Product C	3.6	48	34	19.2

The commercial basic chromium sulfate, product A, B and C were employed at same conditions for comparative tanning studies. Wet blue leathers made in this tanning study were tested to determine the chrome contents, shrinkage temperature, grain smoothness and the color as given in (Table-2).

The higher percentage of Cr_2O_3 was found in wet blue leathers made by product B. Better thermal stability of the wet blue leather resulted from product B revealed the better bonding ability of tanning material with fiber as compared to product A, C and commercial BCS.

Table-2: Characteristics of Wet Blue Tanned with Commercial BCS, Product A, B and C.

Parameters	Commercial BCS	Product A	Product B	Product C
% Cr_2O_3 in wet blue	3.70 ± 0.10	3.68 ± 0.12	3.98 ± 0.10	3.71 ± 0.11
Shrinkage temperature (°C)	118 ± 2	116 ± 3	122 ± 2	116 ± 3
Grain Smoothness	8 ± 1	8 ± 1	8 ± 1	8 ± 1
Color	8 ± 1	8 ± 1	7 ± 1	8 ± 1

The smoothness of grain of wet blue leathers tanned with products A, B and C were found comparable to that of the conventional chrome tanned leather. However, the color of the wet blue made from product B was slightly dark then those of product A, C and commercial basic chromium sulfate. This may be due to the formation of very stable co-ordination complexes of chromium with intermediates generated in synthetic process of product B.

Since all the tannings were made using similar percentages of float, chemicals and the environmental conditions. Therefore, total spent chrome liquor was collected and then analyzed for chrome contents, sulfates, chlorides, COD, (Chemical Oxygen Demand) total solid and the rate of exhaustion.

It has been found that the percentage amount of Cr_2O_3 in spent liquor gradually decreased from 0.53, 0.51, 0.50, and 0.40% for commercial BCS, product A, C, and B, respectively (Table-3). The exhaustion rate of product B was found very high as compare to product A, C and the commercial BCS. The increase of chrome contents in wet blue as well as the lowest amount of Cr_2O_3 in spent chrome liquor confirmed the highest exhaustion rate of product B.

Table-3: Analysis of Spent Liquor.

Parameters	Commercial BCS	Product A	Product B	Product C
% Cr_2O_3	0.53 ± 0.01	0.51 ± 0.02	0.40 ± 0.02	0.50 ± 0.02
COD (ppm)	9810 ± 26	9867 ± 33	8001 ± 31	9840 ± 37
TS (ppm)	63400 ± 52	61800 ± 73	42400 ± 61	61839 ± 81
Chlorides (ppm)	18420 ± 29	18500 ± 38	11100 ± 32	18370 ± 37
Sulfates (ppm)	2080 ± 20	2124 ± 28	2065 ± 23	2085 ± 31
Exhaustion rate	80 ± 2	80 ± 3	95 ± 2	81 ± 3

Although, the amount of sulfates and the COD of spent liquor of product A, B and C was found comparable to the commercial BCS, but the chlorides and TS (Total Solid) values of product B were found lower than those of product A, C and commercial BCS indicating the significant decrease in pollution load.

The physical properties of crust leather made from product B indicated good improvement, to that of the product A, C as well as the commercial BCS (Table-4). This could be due to the generation of the intermediates from protein and the hydrocarbons used in the synthesis of complex B. This was also supported by the fullness property of the leather resulted from product B. It has also been noted that the softness of the leather from product B was slightly superior to that of the product A, C as well as commercial BCS.

Experimental

Material

As this work has been performed to determine the rate of penetration and even distribution of laboratory prepared and commercial chrome tanning materials, hence similar compact goat skins with above average area (approximate 5.5-6.0 sq.ft) were selected. Twelve goat skins (three for each experiment) were processed up to pickling (pH 2.8-3.0) at similar conditions for comparative tanning studies.

Three different tanning materials were prepared by the reduction of sodium dichromate in acidic medium using chrome-shavings alone (Product-A), 1:1 ratio of chrome-shavings and hydrocarbons (Product-B) and 1:1 chrome shavings and molasses (Product-C) as a reducing agents.

Table-4: Physical Properties of Crust Leather Resulted from BCS, Product A, B and C.

Physical Characteristics	Commercial BCS	Product A	Product B	Product C
Shrinkage (°C)	121 ± 1	117 ± 2	123 ± 1	118 ± 3
Tensile Strength (kg/cm^2)	19.55 ± 1.50	18.90 ± 1.00	20.02 ± 2.00	19.15 ± 1.5
Tear Strength (N/mm)	46.76 ± 2.5	47.30 ± 2.00	60.42 ± 3.00	47.45 ± 2.50
Elongation (%)	60.33 ± 2.0	65.81 ± 2.0	88.30 ± 2.5	67.40 ± 3.0
Bursting Strength :	46.30 ± 2.00	37.2 ± 2.50	40.0 ± 2.50	45.2 ± 3.00
Load (kg)	10.85 ± 0.03	10.10 ± 0.04	10.98 ± 0.03	9.85 ± 0.04
Distension (mm)	8 ± 1.0	8 ± 1.0	8 ± 1.0	8 ± 1.0
Grain Smoothness				
Fullness	7 ± 1.0	8 ± 0.5	8 ± 0.5	7 ± 1.0
Softness	8 ± 1.0	8 ± 1.0	9 ± 0.5	7 ± 1.0
Color	8 ± 0.5	8 ± 1.0	8 ± 1.0	8 ± 1.0

Method for the Preparation of Product B

The reaction was carried out in three neck flask equipped with reflux condenser, stirrer, dropping funnel and a temperature controlled heat source. The quantity of the material was based on the weight of sodium dichromate. The order of chemical addition was as follows;

Sodium dichromate (100 g) was dissolved in 200 ml of water and 50 g of hydrocarbons (source of aromatic dibasic acid after oxidation) in reaction flask. It was heated up to 40 °C. Then sulfuric acid (90 mL) was added drop wise over a period of one hour with stirring. The mixture was refluxed for 30 min. Chrome shavings (50 g) was added with continuous stirring over a period of 20 min. Then the mixture was stirred at 90 °C for 1 h. The resulted complex was checked for chromium (VI) and completely reduced by adding sodium hydrosulfite. The non reacted hydrocarbons were removed by distillation at 80 °C.

All chemicals used for the synthesis of tanning materials as well as for leather processing were of commercial grade. Basic Chromium sulfate (BCS) and sodium dichromate were purchased from Industrial Chemical (Pvt) Ltd Pakistan. While the tannery chemicals like, retanning agents, fatliquors and dyes were of Shafi Reso Chem Pakistan, Munzing Chemie GmbH Germany and Clariant, respectively. The chemicals used for the analysis of tanning materials, leathers, and the spent liquors were of analytical grade from Merck Germany.

Tanning Process

The pickled goat skins were tanned with the commercial basic chromium sulfate (BCS), product A, B and C as follows:

A floatless tanning method was applied using all the tanning materials equal to 1.65% Cr_2O_3 in one installment (all percentages are based on pelt weight). The pelts were drummed for 3 h in 30% float. The pH of the float was found from 2.9-3.0.

Then the skins were basified at a pH from 3.8-4.0 using 1% sodium bicarbonate solution in 20% water given in three installments at 10 minutes interval followed by 2 h running. The wet blue leathers made in this study were subjected to aging for three days and then analyzed for different characteristics. The remaining wet blue leathers were subjected to re-chroming and post tanning processes such as applying of syntans, fatliquors, dyes, and then converted in to crust for garment leather.

Characterization of Wet Blue and Analysis of Spent Liquor

The shrinkage temperature and the amount of chromium oxide from wet blue leathers were measured using standard methods [29, 30] (one sample from each skin with a replicated for each experiment). The wet blue leathers made in this study were also assessed for appearance and grain smoothness. These leathers were rated by awarding scale 0-10 points for each characteristic by three leather experts where the higher points indicate better property.

The spent liquor was collected and analyzed for chromium contents, COD, TS, sulfates and chlorides by conventional analytical methods and exhaustion rate was also calculated by the method reported earlier [31-33].

Physical Characteristics of Crust Leather

Samples for physical testing were cut and then conditioned at international atmospheric conditions *i.e.* temperature 23 ± 2 °C and 50 ± 5 relative humidity for 24 to 48 h [34]. Physical properties such as tear strength, grain crack, percentage elongation and tensile strength were measured using their standard methods [35-37] (Universal Testing Machine UTM Tinius Olsen LTD H5KS UK). The crust leathers made in this study were also assessed for fullness, softness and grain smoothness. The procedure for rating of leather was adopted to award the points for each functional property by leather experts.

Conclusions

It is concluded that the utilization of leather solid wastes (chrome shavings) as a reductant in the conversion process of Cr^{+6} to Cr^{+3} would be a best way of "wealth from wastes". On the other side, the hydrocarbons would not only act as a reductant but also generate very potential intermediates for the masking of chrome. The highest amount chrome contents in the leather as well as the lowest percentage of Cr_2O_3 in spent chrome liquor from product B confirmed its highest exhaustion rate. Therefore product B would not only be helpful to control the pollution load up to negligible limits but also save a huge amount being spent on effluent treatment as well as on extra use of chemicals in processing. Although environmental impact analysis indicated that the amount of sulfates are comparable to those of conventional tannings but chlorides and the TS value of product B are very low indicating the significant control on pollution load.

As for quality of leather, the comparative tanning studies revealed that the wet blues as well as the crusts made from product B are either better or comparable to those of product A, C and the conventional tanning material.

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