TANNING STUDIES WITH BASIC CHROMIUM SULFATE PREPARED USING CHROME SHAVINGS AS A REDUCTANT: A CALL FOR 'WEALTH FROM WASTE' APPROACH TO THE TANNING INDUSTRY

by

J. RAGHAVA RAO, P. THANIKAIVELAN#, K. J. SREERAM AND B. UNNI NAIR*

Chemical Laboratory

#Centre for Leather Apparels & Accessories Development

Central Leather Research Institute

Adyar, Chennai 600 020, India

ABSTRACT

Leather processing is associated with the generation of both solid and liquid wastes. Various in plant as well as end-of-pipe treatment methodologies are available for the management of liquid wastes. Although several options do exist for handling solid wastes, the presence of chromium causes concern for many of the applications. Chrome shavings contribute to almost 10% of the solid wastes generated from processing raw hides/skins. In this study, chrome shavings have been advantageously used as a reductant for the manufacture of basic chromium sulfate thereby providing a comprehensive closed cycle. Two BCS products developed with chrome shavings alone for reduction (complete replacement of molasses, product A) or partial replacement of molasses (product B) have been employed for tanning of goatskins. Studies reveal that the quality of the wet blue leathers is on par with the leathers tanned with commercial BCS. Shrinkage temperature of the leathers is comparable and is above 100°C at an offer of 1.25% Cr_2O_3. Chromium exhaustion is in the range of 75 - 80% with 1318 - 1490 ppm of chromium in the spent tan liquor. Wet blue leathers tanned with product A possess more fullness among all the leathers, which may be due to the presence of intermediate protein products formed during BCS preparation. This is further confirmed with the scanning electron microscopic analysis. Performance of the crust leathers is comparable to that of conventional tanned leathers in spite of reduction in syntans by 20%. This methodology provides a means for recovering wealth from waste.

INTRODUCTION

Greener and cleaner environment is the key issue among the public and industrial bodies.[1] Green chemistry as a concept represents the chemical processes, where environmental pollutants can be replaced by eco-friendly alternatives. It involves designing newer routes for chemical synthesis and products, which protects our environment. The safe disposal of process wastes is also important while designing a new synthesis route. The impact of such disposal on environment is often neglected. Hence, it is of prime concern that any green solution concept must protect the environment through the entire life cycle of the process as well as product.

Leather processing industry is known to be associated with the generation of liquid, solid and gaseous wastes.[2] There are numerous options available to contain liquid and gaseous wastes. They include in-process as well as end-of-pipe treatment solutions. Attempts have also been made to combat the liquid discharge from the tanning processes to zero level.[3] Solid wastes from the tanning industry are unavoidable.[4] This is because leather processing primarily associated with purification of a multi-component, skin, to obtain a single protein, collagen. The intrinsic nature of the leather processing steps and the nature of chemicals employed are also responsible for the generation of certain quantum of solid wastes.[5] The formation of solid wastes starts at the very first operation namely, desalting the raw material, and prolongs through almost all unit processes and operations till the end of the process sequence, namely buffing operation. The nature and quantum of solid wastes produced while processing 1 t of raw material are given in Table I. As stated earlier, based on the nature of solid wastes generated from the leather processing, they can be categorized in to chemical and protein based solid wastes. It is recognized from Table I that the quantum of chemical and protein wastes is almost similar and the total quantum of waste is more or less equal to the weight of the raw material.[6] The chemical wastes are generally dumped at the land sites or incinerated.[7] In few cases, they find some commercial use such as brick making, reuse in leather processing (e.g. salt), land filling. Protein based solid wastes acquire much attention due to its high value. Protein based wastes can further be classified in to untanned and tanned wastes. The ratio of the quantum of tanned and untanned wastes is almost equal as evidenced from Table I. The untanned wastes such as fleshings and trimmings find use in glue/gelatin manufacture, recovery of proteins and fats, biogas generation, biofertilizer (vermiculture), poultry or animal feeds and cosmetics manufacture.[8]

*Author for correspondence. Tel: + 91 44 24411630; Fax: + 91 44 2491 1589; email: clrichem@mailcity.com

TABLE I

Nature and Quantum of Solid Wastes Produced from Processing 1 Metric Ton of Raw Material

Solid waste	Quantity (kg)	% on total chemical sludge (480 kg)	% on total protein bearing waste (565 kg)
Salt from desalting	80	16.6	-
Salt from solar evaporation pans	210	43.8	-
Raw trimmings	55	-	9.7
Hair (pasting ovine)	110	-	19.5
Lime sludge (mostly ovine)	65	13.5	-
Fleshing	110	-	19.5
Wet blue trimmings	30	-	5.3
Chrome tanned unusable splits (bovine)	65	-	11.5
Chrome shavings (mostly bovine)	90	-	15.9
Buffing dust (inclusive of shaving of bovine after crust)	60	-	10.6
Crust trimmings	45	-	8.0
Dry sludge from ETP	125	26.1	-

The tanned wastes primarily consist of chromium and protein. Historically, the tanned wastes were disposed of in landfills. However, due to the local pollution control agency restrictions as well as the presence of valuable protein source, the tanning industry seeks alternatives to dumping.[9] The direct application of tanned wastes is many fold such as the manufacture of bonded leather,[10] leather boards,[11] fibrous sheets grafted with acrylates,[12] insulators and building materials after reacting with polyisocyanates,[13] composites for footwear,[14] sound-proof roofing material,[15] etc. The indirect utilization of tanned wastes is generally based on separating the protein-bound chromium and using the protein and chromium fractions for several applications. The combination of alkali and enzymes is able to recover the chromium from the protein fractions and is widely employed in many parts of the world.[16,17] Further improvements in the above process have been made such that two protein fractions namely, hydrolysable and gelable protein products were obtained apart from a recyclable chromium cake.[18,19] Many researchers have recovered chromium by wet air oxidation[20] and peroxide[21] treatment. Investigations based on detanning of the chrome wastes for gelatin preparation[22] and isolation of collagen fibres[23] have been made. Attempts have also been made to acid hydrolyze the tanned wastes in to a chromium containing protein hydrolysate usable in the retanning of wet blue leathers.[24] In this work, an attempt has been made to find a non-invasive, closed circuit, less-intensive, green route for the disposal of chrome based solid wastes taking chrome shavings as a model disposable material.

Chrome shavings are small, thin pieces of leather formed during shaving operation, which is being done to achieve the desired thickness for various end uses of the leather. Of the protein bearing solid waste generated when processing hides, chrome shavings account for 15 - 30%. When comparing with the weight of raw material processed, it accounts for almost 10%. Kaiwar and Rao have shown that the "reductive coefficient" of L-cysteine is $168 \times 10^3\ M^{-1}s^{-1}$, glutathione (a tripeptide formed from L-glutamic acid, L-cysteine and L-glycine) is $450 \times 10^3\ M^{-1}s^{-1}$ when compared to $0.65 \times 10^3\ M^{-1}s^{-1}$ for D-glucose for reducing chromate to Cr(III), indicating higher reductive efficiency for the polypeptides.[25] Hence, in this approach, chrome shavings have been used as a reductant for the preparation of basic chromium sulfate (BCS).

Commercially, basic chromium sulfate salt is prepared by the direct reduction of dichromate with sugar-sulfuric acid mixture or sulfur dioxide.[26,27] It has been shown that the chrome liquors prepared by different reducing agents differ in their properties largely due to the formation of different types of intermediates.[28] A variety of reducing agents such as coconut pith, bagasse, glycerol, oils, vegetable tanning materials, etc for the preparation of basic chromium liquor has been reported.[29-32] In the case of sugar/glucose, formation of organic intermediates such as oxalic acid, formic acid, aldehydes, glyoxalic acids, carbon dioxide and other precursors of humic acids has been reported.[33-35] The organic intermediates are capable of forming complexes with the metal ion by substitution of the aqua or sulfato group.[36]

Recently, two BCS products were made where in one case reduction is completely achieved by chrome shavings whereas in the other case only 50% of the amount of molasses is replaced by chrome shavings.[37] Both the BCS preparations have been standardized and characterized for their constituents.[37] In this work, the prepared BCS products have been employed for tanning pickled skins. The characteristics of the leathers at wet-tanned as well as post-tanned (crust) stage have also been evaluated. Scanning electron microscopic analysis has been carried out to explore the effect of prepared products on the fullness of the leathers. Spent liquors have been analyzed for environmental impact.

EXPERIMENTAL

Materials

Pickled goatskins (pH 2.8-3.0) were chosen as raw material for tanning studies. Since this work involves the study of the extent of diffusion and distribution of tanning agent, more compact goatskins of larger area (4 - 6 sq.ft) were selected. Two BCS products prepared by the reduction of sodium dichromate in acid medium using chrome shavings as a reductant (product A) and 1:1 ratio of chrome shaving and molasses as reductants (product B).[37] All chemicals used for leather processing were of commercial grade; while the chemicals used for the analysis of leather and spent liquors were of analytical grade.

Tanning Studies

Nine pickled goatskins (pH 2.8-3.0; three skins for each experiment) were tanned with the prepared products (A & B) as well as commercial BCS salt as follows: (all percentages are based on fleshed weight of the limed goat skins) A float less tanning method was employed using the product equivalent to 1.25% Cr_2O_3 (given in 1 installment). The pelts were drummed for 45 min, flooded with 100% water and further run for 45 min. The pH of the solution was found to be 3.0. The skins were basified to a pH 3.8-4.0 using sodium bicarbonate (1.2% in 10% water, given in 3 installments at 10 min interval followed by 2 hrs running). The wet blue leathers made in this study were subjected to post tanning operations employing fatliquors, syntans and dyes and converted into upper leathers. However, in the case of wet blue leathers obtained using product A and B, the offer of synthetic tanning agents was reduced by 20%.

Wet Blue Characteristics

The shrinkage temperature of the chrome-tanned leathers (one sample from one skin with a replicate for each experiment) was measured using a Theis shrinkage tester.[38] The amount of chromium present in the tanned leathers (one sample from one skin with a replicate for each experiment) was measured using standard procedure.[39] The wet blue leathers made in this study were assessed for color, grain smoothness, fullness, fluffiness and general appearance by hand and visual examination. The leathers were rated on a scale of 0-10 points for each functional property by experienced tanners, where higher points indicate better property.

Analysis of Spent Tan Liquors

The spent tan liquor was collected and analyzed (with a replicate) for chromium content, COD and TS contents by conventional analytical methods.[40,41] The exhaustion of chromium was also calculated.

Scanning Electron Microscopic Analysis of Leather Samples

Samples from the wet blue leathers tanned using products A and B and BCS salt were cut from the official sampling position.[42] Samples were first washed in water. Samples were then dehydrated gradually using acetone and methanol as per standard procedures.[43] Excess solvent from the samples was removed by placing them between filter papers. Samples were then cut into specimens of uniform thickness. All specimens were then coated with gold using a JEOL JFC-1100E ion-sputtering device. A JEOL JSM-5300 scanning electron microscope was used for the analysis.

Strength and Bulk Properties of Crust Leathers

Samples for various physical tests from the crust leathers were obtained as per IULTCS method.[42] Specimens were conditioned at $80 \pm 4°F$ and $65 \pm 2\%$ R.H. over a period of 48 h. Physical properties such as tensile strength, % elongation at break, tear strength and grain crack strength were examined as per the standard procedures.[44-46] Tensile and tear strength tests were carried out both along and across the backbone line. The mean of the values corresponding to along and across backbone was calculated and averaged. The grain crack strength values for all the leathers was measured and averaged. The crust leathers were assessed for softness, fullness, grain flatness, grain smoothness, grain tightness (break) and general appearance by hand and visual examination. The leathers were rated on a scale of 0-10 points for each functional property by experienced tanners, where higher points indicate better property. The average of the rating for the three leathers corresponding to each experiment was calculated for each functional property.

TABLE II
Analysis of Wet Blue Leathers Tanned with Products A, B and Commercial BCS

Parameters	BCS	Product A	Product B
[a]Shrinkage temperature (°C)	112 ± 2	111 ± 2	112 ± 3
[a]% Cr_2O_3	3.14 ± 0.09	3.17 ± 0.12	3.23 ± 0.10
Grain smoothness	7 ± 1	8 ± 0.5	7 ± 1
Fullness	6 ± 1	8 ± 1	7 ± 1
Fluffiness	7 ± 0.5	8 ± 1	8 ± 0.5
Color	8 ± 0.5	8 ± 1	8 ± 1
General appearance	7 ± 0.5	8 ± 0.5	8 ± 1

[a]one sample from one skin with a replicate for each experiment

RESULTS AND DISCUSSION

Chrome Shavings and Their Use as Reductant: Since chrome shavings contain 3-3.5% Cr_2O_3 and 70-80% protein matter, they form a suitable material for the reduction of Cr(VI) to Cr(III). Employing this strategy, two different BCS products were prepared and characterised.[37] A brief summary of the reduction of dichromate using chrome shavings and characteristics of the products is given as end note. The % Cr_2O_3 content of products A and B are 15 and 19%, respectively.[37] The lower chrome content in the developed products compared to that of conventional BCS can be attributed to the formation of intermediate protein products during the reduction of Cr(VI) to Cr(III) and neutral salts.

Characteristics of Wet Blue Leathers: Wet blue leathers developed in this study were subjected to chromium content, shrinkage temperature and visual assessment analysis. The values are given in Table II. Shrinkage temperatures of the wet blue leathers tanned using products A and B are more than 109°C and comparable to that of control leathers. The chromic oxide content in the wet blue leathers are in the range of 3.0 - 3.3%. Visual assessment data indicates that grain characteristics are improved in the leathers tanned using products A and B. Fullness of the leathers tanned using both the products is better than the conventional chrome tanned leathers. This may be due to the presence of intermediate protein products, which improves filling especially in product A tanned leathers. Color of the wet blue leathers tanned using products A, B and commercial BCS is comparable.

Scanning Electron Microscope Analysis: Scanning electron micrographs showing the grain surface of the leathers tanned with commercial BCS, products A and B at a magnification of x250 are given in Figs. 1a-c, respectively. It may be expected that the leathers tanned with product A could have some micro-deposition of proteinous materials, since product A was prepared by using chrome shavings alone as reductant. However, all the samples display a clear grain surface without any foreign particles. Scanning electron micrographs showing the cross section of the leathers tanned with commercial BCS, products A and B at a magnification of x250 are given in Figs. 2a-c, respectively. It is clearly seen that the sample that had been tanned with the product A (Fig. 2b) seems to be devoid of macro pores between the fibre bundles. There seems to be a cementing of fibre bundles with some spongy kind of foreign material in an irregular fashion. In other words, the fibre bundles seem to be coated with an unusual substance, which is evidenced from a higher magnification (x750) scanning electron micrograph of the same sample (Fig. 2e) where the edges of the fibre bundles are not clearly visible. This is because the product A has been prepared by using chrome

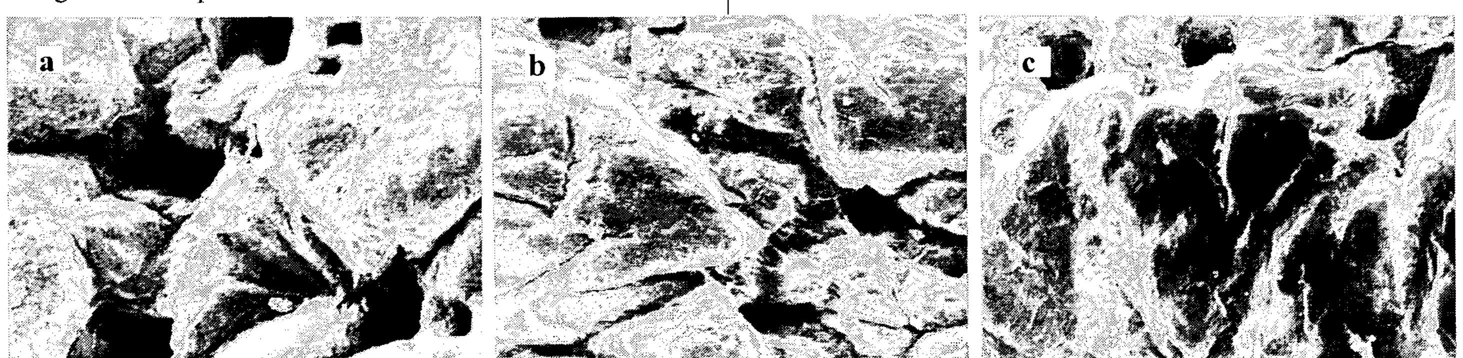

Figure 1. - Scanning electron micrographs of the leathers after chrome tanning showing the grain surface (x250)
(a) tanned with BCS, (b) tanned with product A, (c) tanned with product B

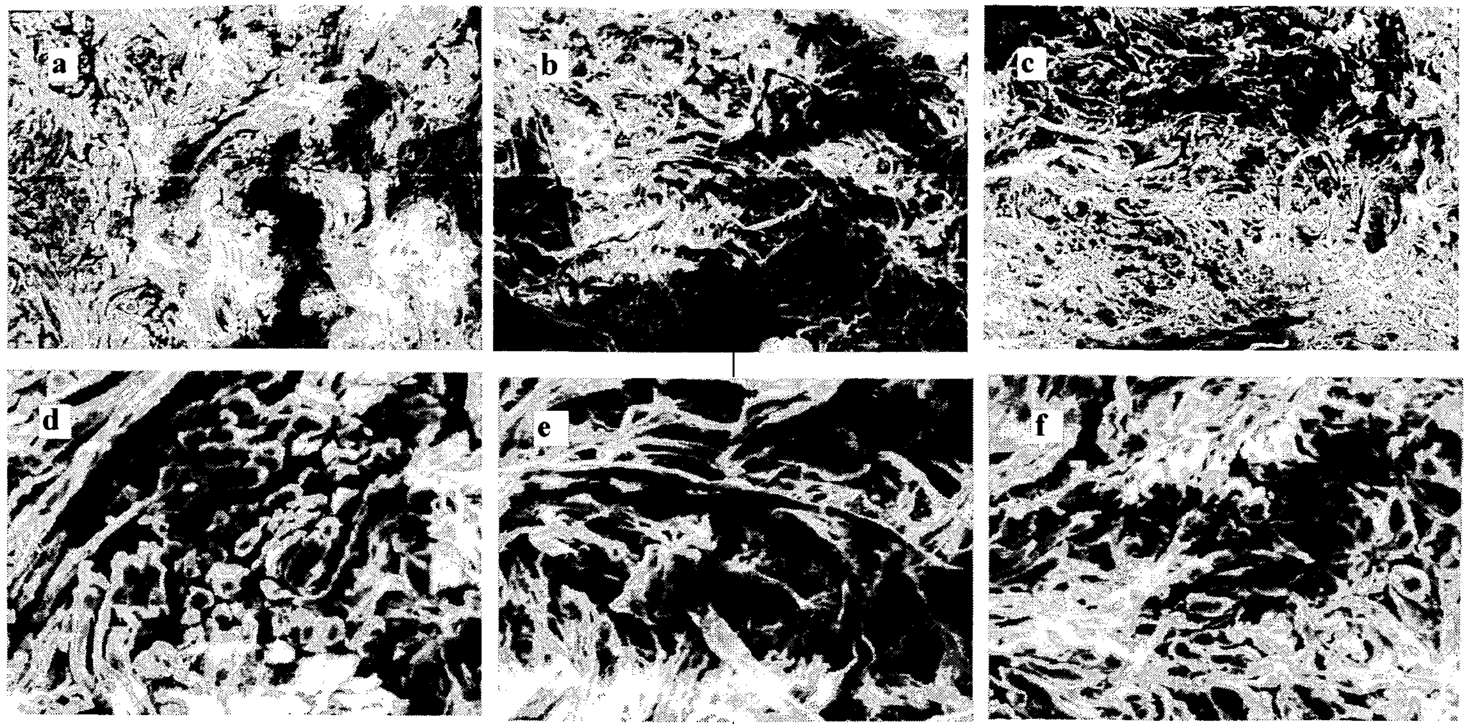

Figure 2. - Scanning electron micrographs of the leathers after chrome tanning showing the cross section. (a) tanned with BCS (x250), (b) tanned with product A (x250), (c) tanned with product B (x250), (d) tanned with BCS (x750), (e) tanned with product A (x750), (f) tanned with product B (x750)

shavings alone as a reductant. Although chrome shavings undergo hydrolysis due to high acidic condition, they may not be subjected to complete oxidation due to insufficient acidity. Hence, the partially disintegrated shavings could coat the fibrils as shown in Fig. 2e. However, the sample tanned with product B (Fig. 2c) does not show such a visible coating even though the preparation of product B employs chrome shavings for reduction. This is due to the fact that only 50% of the amount originally required for complete reduction of Cr(VI) is used during the initial phase of the reduction of product B preparation and the complete reduction is fulfilled with molasses. Further, the morphological features of the fibre bundles of product B tanned sample are more or less similar to that of BCS tanned sample as evidenced from Figs. 2a, 2c, 2d and 2f.

Spent Chrome Liquor Analysis: The spent chrome liquor collected from all the tanning trials were analyzed for chromium, COD, TS, chlorides, sulfates and chrome exhaustion. The data is presented in Table III. It is seen that the amount of chromium (as Cr_2O_3) is in the range of 1926 - 2178 ppm indicating that the uptake of chromium in the leathers are of similar order. The chromium exhaustion of all the tanning trials is in the range of 75 - 80%. Although chlorides, sulfates and total solids are comparable for all the tanning systems, the COD of spent chrome liquors from product A and B is more than that of commercial BCS based tanning system. This indicates the presence of intermediate organic products in the products A and to some extent in B. However, pickleless chrome tanning using products A and B would help in reduction of pollution loads.

Performance of the Leathers: Physical testing data of the crust leathers made in this study are given in Table IV. It is evident that the strength characteristics have improved when product A was used for tanning. This could be due to the presence of intermediate protein products, which help in sliding the fibers. The strength properties of all the crust

TABLE III
Spent Tanning Liquor Analysis

Parameter	BCS	Product A	Product B
Chromium as Cr_2O_3 (ppm)	2020 ± 36	1950 ± 24	2160 ± 18
COD (ppm)	2326 ± 28	4566 ± 38	3652 ± 32
TS (ppm)	49280 ± 78	48203 ± 65	49321 ± 65
Chlorides (ppm)	12450 ± 36	11412 ± 42	11758 ± 38
Sulfates (ppm)	1984 ± 18	1950 ± 22	2060 ± 16
% chromium exhaustion	76 ± 3	79 ± 2	78 ± 3

TABLE IV
Physical Testing Data of Crust Leathers Tanned with Products A, B and BCS

Parameters	BCS	Product A	Product B
[a]Tensile strength (kg/cm^2)	250 ± 8	288 ± 6	260 ± 8
[a]% Elongation at break	65 ± 4	82 ± 3	68 ± 5
[a]Tear strength (kg/cm)	55 ± 4	62 ± 4	57 ± 5
[b]Grain crack strength			
Load (kg)	21 ± 2	36 ± 3	24 ± 4
Distension (mm)	8.4 ± 0.3	11.9 ± 0.2	9.2 ± 0.1

[a]Average of mean of along and across backbone values for three leathers
[b]Average of load and distention values for three leathers

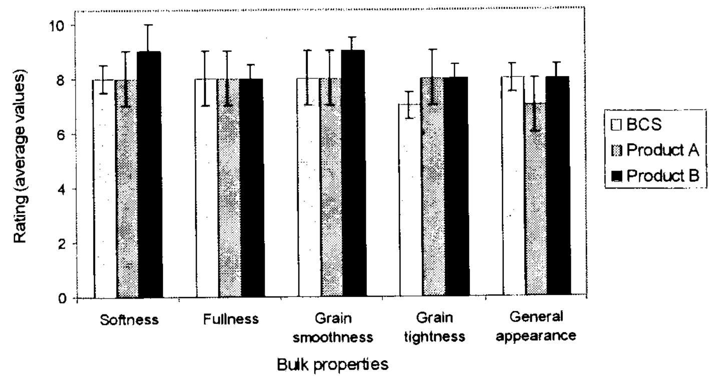

Figure 3. - Comparison of bulk properties of the crust leathers tanned with products A, B and BCS

leathers that have been tanned using products A and B are comparable or improved to that of commercial BCS tanned leathers. The organoleptic properties of the crust leathers are shown in Fig. 3. It is seen that the grain characteristics and softness of the leathers made using products A and B are slightly better compared to commercial BCS tanned leathers. Fullness of the leathers tanned using products A and B is comparable to that of control leathers in spite of reduced offer of synthetic tanning agents, which is due to the presence of intermediate organic products. This is in agreement with the scanning electron microscopic analysis and strength property evaluation. In general, leathers tanned with product A, B and commercial BCS are comparable.

CONCLUSIONS

The concern for ecological imbalances due to industrial activity is increasing among developing countries. Leather industry is one among them in generating waste in the form of liquid and solid. Chrome bearing solid wastes poses serious environmental threat due to the presence of chromium. A novel way of utilizing both chromium and protein matter has been identified by way of employing shavings as a reductant in the place of molasses for the reduction of Cr(VI) to Cr(III) in the manufacture of BCS.

The developed products have been employed for tanning pickled goatskins and the characteristics of the leathers have been compared with commercial BCS tanned leathers. The shrinkage temperature and chromium content of the leathers are comparable to the commercial BCS tanned leathers. The chrome exhaustion of all the tanning trials including control is in the range of 75 - 80%. The environmental impact analysis indicates that the amount of chlorides, sulfates, chromium and TS is comparable to that of conventional chrome tanning stream except COD. However, the pickle-free chrome tanning can reduce the pollution loads. The quality of the leathers made using the developed products exhibits improved fullness and strength properties. The performance of the leathers made using the developed products is comparable to conventional chrome tanned leathers in spite of the reduced offer of syntans. Hence, this approach provides a means for proper utilization of chrome shavings without any complicated methods for separating chromium and protein. The presence of protein is taken advantage of using it as potential reductant for the preparation of BCS and chromium for tanning source. Therefore, this approach demonstrates recovery of wealth from chrome shaving solid wastes.

Note: It is known that Cr(VI) in acid medium has an absorption maximum at a wavelength of 350 nm.[47] The reduction of chromium(VI) during the product preparation was monitored in a Perkin Elmer Lambda 35 UV-visible spectrophotometer in the wavelength range of 300-500 nm. The maximum absorbance was 1.4 at 350 nm during the initial stage of reduction (after proper dilution). There was a progressive decrease in the absorption at 350 nm during the course of the reaction, and it reached a minimum at the end of the reaction (after proper dilution). This indicates the complete reduction of chromium(VI) in the final product.[37] Products A and B contain 15 and 19% Cr_2O_3, 6.5 and 7.0% moisture and 45 and 39% total sulfates.[37] pH of 10% solution of products A and B is 2.8 and 2.9, respectively. Both the products exhibit masking due to the formation of intermediate protein products, which was substantiated through spectral, hydrolysis and species-wise distribution analysis.[37]

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