Non-polar Medium Enables Efficient Chrome Tanning

by

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Abstract

Converting raw hides and skins into leather through chrome tanning in water medium creates huge environmental burden by contaminating the precious water resource on the one hand and discharging more chromium on the other. Here, a non-polar green solvent, heptane, alternate to water has been evaluated for chrome tanning employing both pickle-based and pickle-less method. The preceding (pre-tanning) and succeeding (post-tanning) processes were water mediated for comparison. The results show that the color and other organoleptic properties of both wet blue and crust leathers are comparable to conventional leathers. The strength and structural properties of experimental crust leathers are comparable to that of control leathers. The main benefits in switching over to heptane medium are improved exhaustion of chromium during both pickle-based and pickle-less chrome tanning, better chromium distribution and recycling ability. The process also helps in reducing the chemical oxygen demand, biological oxygen demand and total solids levels in the composite liquor significantly.

Introduction

The conventional way of leather making activities are highly water intensive process.[1] Approximately 30-50 liters of water is used for the processing of one kilogram of raw hides/skins. Leather manufacturing processes are broadly classified into four steps such as pre-tanning, tanning, post-tanning and finishing. Of which, tanning is a mandatory process to convert the putrescible raw hides/skins into non-putrescible leather. Trivalent chromium is one of the versatile tanning agents and today 90% of the world's leather production is based on chrome tanning process.[2] However, the conventional chrome tanning process discharges huge volume of wastewater with high quantity of chromium. The uptake of chromium by hides/skins in the conventional tanning process is between 60 to 70% and the remaining is discharged as waste. Such large discharge leads to serious chemicals loss and environmental problems.[3] Conventional treatment systems adopted for the removal of chromium from waste streams produce large quantities of chrome-containing sludge, which has been listed among the hazardous wastes. This along with shortage of water availability poses significant pressure amongst tanners in the world to continue chrome tanning. Sundar *et al*. have reported closed loop aluminum–chrome combination tanning and two-stage tanning as cleaner chrome tanning processes.[4] Reverse tanning process has been proposed for reducing water consumption and wastewater discharge.[5,6] Suresh *et al*. has reported a high-exhaust chrome tanning process without conventional pickling process, which leads to significant reduction in Cr and TDS emission compared to conventional tanning process.[3] Zhang *et al*. has demonstrated a salt-free high exhaust chrome tanning using non-swelling aromatic acids, which resulted in reducing pollution effectively.[7]

Although many techniques have been developed to increase the exhaustion of chromium and reduce the salt emission from tanning industries, the usage of water and discharge of wastewater could not be completely eliminated. Recently, use of green solvents alternate to water with recycling option is gaining importance for chrome tanning.[8-11] In the present work, the consumption of water is completely eliminated by adopting an alternate green solvent namely heptane for chrome tanning. Heptane was chosen following the GlaxoSmithKline solvent selection guide based on the environmental health hazards and LD_{50}.[12] Both pickle-less as well as pickle based chrome tanning processes were investigated using heptane in comparison to aqueous medium. The tanned leathers were characterized for chemical, physical, organoleptic and structural properties. The ability to recycle the used solvent was also examined.

Materials and Methods

Materials

Wet salted goat skins were sourced from local suppliers at Chennai and conventionally processed into pickled/delimed pelts at the Pilot Tannery, CSIR-Central Leather Research Institute. All the chemicals used for leather processing were of commercial grade. Analytical grade heptane was sourced from S. D. Fine-Chem. Ltd., Mumbai, India. Chrome tanning trials were carried out in a stainless steel drum.

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Chrome tanning in Heptane Medium

Two pickled/delimed goat pelts measuring 4.5±1 sq. ft. were used for each experiment employing pickle-based and pickle-less chrome tanning in heptane and water medium. In the case of pickle-based chrome tanning, pickled pelts (with 73±2% moisture content)[10] were individually treated with 7% basic chromium sulphate (BCS) salt (percentage based on pelt weight) in stainless steel drum for 1 h. Then 100% w/v heptane was added as a medium and run for 30 min. After checking the penetration of chromium, the pH was found to be 2.7. In the subsequent basification step, pH of the chrome tanning bath was increased to 4.0 using 1% sodium formate for 10 min drumming followed by the addition of 1.5% sodium bicarbonate in 3 installments at 10 min interval and finally drummed for 1 h. In the case of pickle-less chrome tanning process, the pH of the delimed pelt (with 77±3% moisture content)[10] was adjusted to 5.5±0.5 using 0.3% formic acid (diluted with 10% water) on the weight of the pelt. Then the float was drained. The pH adjusted delimed pelt was drummed with 7% BCS for 1 h. Then 100% w/v heptane was added as a medium and drummed for 2 h. After checking the penetration of chromium, the pH was found to be 3.7. The total duration of both pickle-based and pickle-less chrome tanning processes was around 3 h. The chrome tanned leathers were subjected to hand and visual examination by an experienced tanner. Samples were drawn to analyze various chemical and structural analyses. Then both control and experimental wet blue leathers were converted into crust upper leathers using a conventional post tanning process in aqueous medium.

Determination of Shrinkage Temperature (T_s)

The shrinkage tester apparatus (SATRA STD 114, SATRA Technology Centre) was used for determining the shrinkage temperature of chrome tanned leathers. The chrome tanned leathers with the sample size of 1 × 3 cm^2 was attached in the hook provided in the shrinkage tester. The boiler tube filled with water was heated using Bunsen burner and it was gradually increased. Temperature at which the sample shrinks to one-third of its length was noted as shrinkage temperature. Triplicates were carried out for each sample and the average values were calculated.

Analysis of Chrome Tanned Leathers

The chrome tanned leathers were analysed for chromium content employing the standard procedure.[13] A known weight of tanned leather sample was digested and oxidised using acid mixture (nitric acid + sulfuric acid + perchloric acid). The resultant dichromate solution was complexed with diphenyl carbazide and the absorbance of the formed complex was measured using a UV-Visible spectrophotometer (UV 1800, Shimadzu). Then the chromium content was calculated on moisture-free basis. Triplicate measurements were carried out for each experiment and the average values were calculated. Bulk properties of control and experimental chrome tanned leathers such as fullness, grain smoothness, color, wrinkles and general appearance were assessed by experienced leather technologist through hand and visual assessment.

Analysis of Leachable Chromium

A known weight of the sample from experimental chrome tanned leathers was placed in a beaker with 50 ml of distilled water and heptane separately. In the case of control chrome tanned leathers (water mediated), a known weight of leather sample was placed in a beaker with 50 ml of distilled water. The samples immersed in the solvent were agitated in a shaker at low rpm for 3 h. The chromium content in the solution was analyzed using alkaline peroxide procedure employing a UV-Visible spectrophotometer (UV 1800, Shimadzu) by measuring the absorbance at 372 nm.[14] The amount of chromium was then calculated using molar absorption coefficient (ε) value of $4.8 \times 10^3\ M^{-1}cm^{-1}$. Triplicates were carried out and the average values were calculated. Chromium leached from chrome tanned leather sample (%) was calculated by dividing the amount of chromium in the leachate by the amount of chromium in the chrome tanned leather sample and multiplying by 100.

Analysis of Spent Chrome Liquor

Spent chrome liquor was collected from both control and experimental chrome tanning processes. Chrome content in the collected liquors was analyzed using alkaline peroxide procedure and the concentration of chromium was determined at 372 nm using a UV-Visible spectrophotometer (UV 1800, Shimadzu).[14] The amount of chromium was then calculated using molar absorption coefficient (ε) value of $4.8 \times 10^3\ M^{-1}cm^{-1}$. The percentage exhaustion of chromium was calculated from the amount of chrome tanned liquor collected. Triplicates were carried out and the average values were calculated.

Composite Liquor Analysis

Composite liquors were collected from chrome tanning up to post-tanning processes from both control and experimental processes. The composite liquors were analyzed for chemical oxygen demand (COD), biological oxygen demand (BOD) and total solids (TS) as per the standard procedures.[15] Effluent loads were calculated by multiplying the COD/BOD/TS concentration values (mg/L) with the volume of effluent (L) per ton of raw skins processed.

Scanning Electron Microscopic Analysis

The chrome tanned leather samples from control and experimental chrome tanning processes were dehydrated gradually using acetone and methanol as per standard procedure.[16] Excess solvent was removed from the samples by placing them between filter papers. Post tanned leathers were directly analyzed without dehydration. Leather samples were then cut into specimens of uniform thickness and coated with gold using an ion-sputtering device. The leather samples were mounted on aluminum stubs and analyzed using scanning electron microscope (SEM, Hitachi S-3400N) at an accelerating voltage of 5 kV in different magnifications.

Analysis of Crust Leathers

Samples for various physical tests were obtained from control and experimental crust leathers as per IUP method.[17] Crust leathers were conditioned at 80±4°F and 65±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 then examined employing standard procedures.[18-20] Crust leathers from control ad experimental processes were assessed for softness, fullness, grain smoothness and general appearance by hand and visual examination. The crust leathers were rated on a scale of 0–10 points for each functional property by an experienced leather technologist, where higher points indicate better properties.

Studies on the Recycling of the Spent Heptane Liquor

The feasibility of recycling of spent chrome-heptane liquor for the subsequent batches was examined for pickle-based chrome tanning in heptane medium employing the similar tanning recipe followed in previous section. After completing the chrome tanning process for the first batch, the spent tan liquor was quantitatively collected and analyzed for the amount of chromium. For the 1st recycle process (second batch), the required amount of fresh BCS was calculated and added to the pelt and drummed for 1 h. Then the spent chrome-heptane liquor containing balance amount of BCS was added. The total volume was adjusted to 100% (v/w) by the addition of fresh heptane and drummed for 30 min. After that the pelt was checked for the penetration of chromium and the pH was found to be 3.3. Basification was done using 0.5% of sodium formate and drumming for 10 min followed by adding 1% sodium bicarbonate in 3 installments at 10 min interval. The drum was run for 1 h and the pH of the leather was found to be 3.8. Then the chrome tanned leather was piled. Finally, the spent liquor was collected and reused in 2nd recycling process (third batch) as described above.

Results and Discussion

Assessment of the Wet Blue Leathers

The visual assessment data of both control and experimental wet blue leathers prepared through pickle-based and pickle-less chrome tanning processes using heptane and water medium are given in Table I. It is observed that leathers tanned in heptane medium show either comparable or even better color, grain smoothness and fullness properties in comparison to leathers tanned in water medium. However, leathers tanned in heptane medium show slightly more wrinkles in comparison to their counterparts processed in water medium. This needs to be improved further to match the appearance of conventional wet blue leather. Digital photographs of the control and experimental chrome tanned leathers as shown in Figure 1 reflect the above observations. It is obvious that the color of the wet blue leathers from pickle-less chrome tanning is slightly darker than those from pickle-based chrome tanning both in heptane and water mediated processes. Scanning electron micrographs showing the grain surface of control and experimental wet blue leathers processed through pickle-based and pickle-less chrome tanning are presented in Figure 2a-d. The grain surface of both control and experimental leathers reveal clear hair pores without any foreign particles. This indicates that there is no deposition of chromium in spite of the use of a non-polar medium for both pickle-based and pickle-less chrome tanning. The cross-sectional images (Figure 3a-d) show comparable fiber structure for both control and experimental wet blue leathers.

Chromium Exhaustion/Distribution and Shrinkage Temperature Analysis

Chromium exhaustion, distribution and shrinkage temperature data of pickle-based and pickle-less chrome tanning in heptane and water medium are shown in Table II. Exhaustion levels of chromium for both pickle-based and pickle-less chrome tanning in heptane medium are higher compared to the process carried out in water medium (control), as also visually revealed from the respective exhausted process liquors (insets in Figure 1). This may be due to the insolubility of BCS in heptane medium and

Table I

Visual assessment data of the control (C) and experimental (E) wet blue leathers.

Parameters	P_C	P_E	PL_C	PL_E
Color	Good	Good	Good	Good
Grain Smoothness	Good	Excellent	Good	Good
Fullness	Good	Fuller	Good	Fuller
Wrinkles	Less	More	Less	More

P_C – Pickle-based control; P_E – Pickle-based experimental; PL_C – Pickle-less control; PL_E –Pickle-less experimental.

On a scale of 0 to 10, the qualitative descriptors such as excellent, good, average and poor are weighed as ≥9; ≥7 and ≤8; ≥4 and ≤6; and ≤3, respectively. While the terms such as fuller, more and less are weighed as ≥9; ≥7 and ≤8; and ≥4 and ≤6, respectively. Higher numbers indicate better properties except wrinkles.

Table II
Chromium exhaustion, distribution and shrinkage temperature data of pickle-based and pickle-less chrome tanning in heptane and water medium.

Sample	Exhaustion of chromium (%)	Cr_2O_3 (%, dry weight basis)			Shrinkage temperature (Ts)°C
		Butt	Neck	Belly	
P_C	73±2	5.18	5.14	5.15	106±2
P_E	84±2	5.60	5.54	5.56	109±1
PL_C	86±3	6.08	5.99	6.01	108±2
PL_E	93±2	6.31	6.27	6.29	110±1

P_C – Pickle-based control; P_E – Pickle-based experimental; PL_C – Pickle-less control; PL_E –Pickle-less experimental.

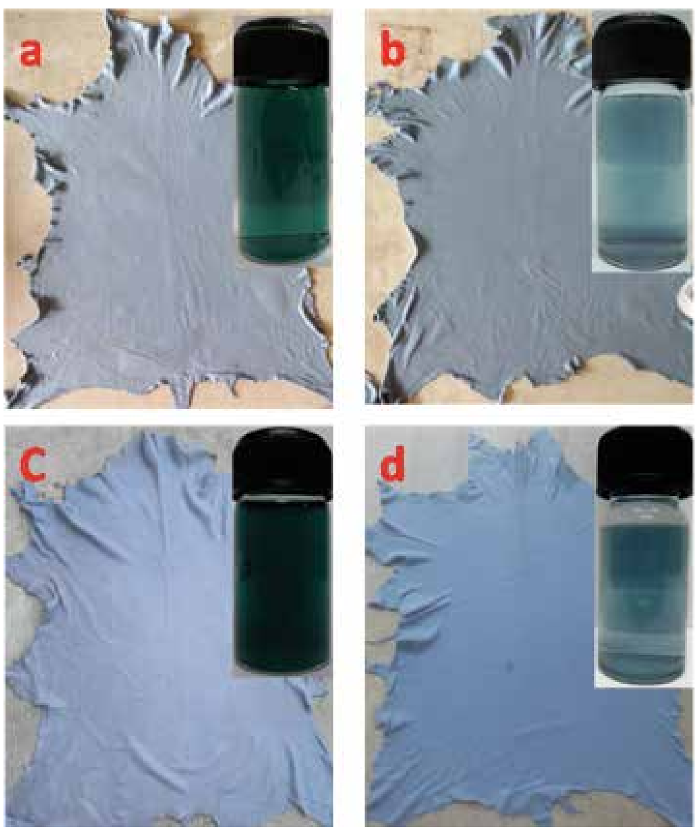

Figure 1. Digital photographs of control and experimental chrome tanned leathers and their respective exhausted process liquors from (a) pickle-less chrome tanning in water medium (b) pickle-less chrome tanning in heptane medium (c) pickle-based chrome tanning in water medium and (d) pickle-based chrome tanning in heptane medium.

the selective solubility of BCS in the inherent water present of the skin matrix. This unusual situation produces high concentration gradient, which drives more chromium into the skin matrix. The improved uptake of chromium in reflected in the distribution of chromium in the various areas of the skin matrix. It is seen that the leathers processed in heptane medium possess higher amount of chromium in all the regions of leather compared to those processed in water medium. Both pickle-based and pickle-less chrome tanned leathers show reasonably uniform chromium distribution along the entire surface area (butt, neck and belly). The thermal stability of pickle-based and pickle-less chrome

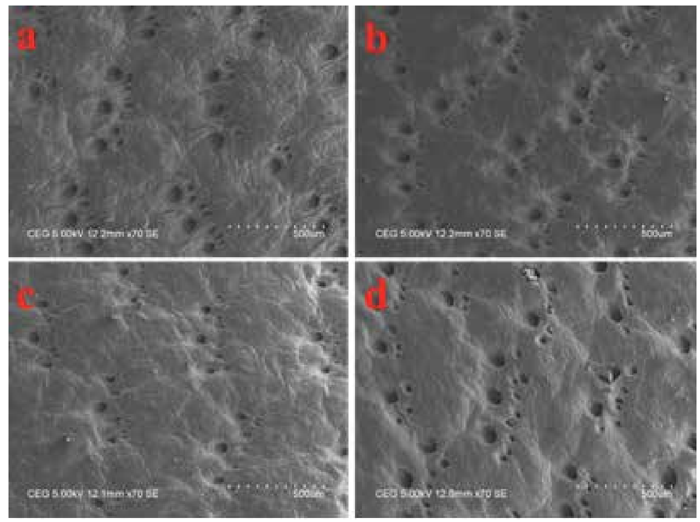

Figure 2. Scanning electron microscopic images of showing the grain surface of control and experimental wet blue leathers from (a) pickle-based chrome tanning in heptane medium (b) pickle-based chrome tanning in water medium (c) pickle-less chrome tanning in heptane medium and (d) pickle-less chrome tanning in water medium.

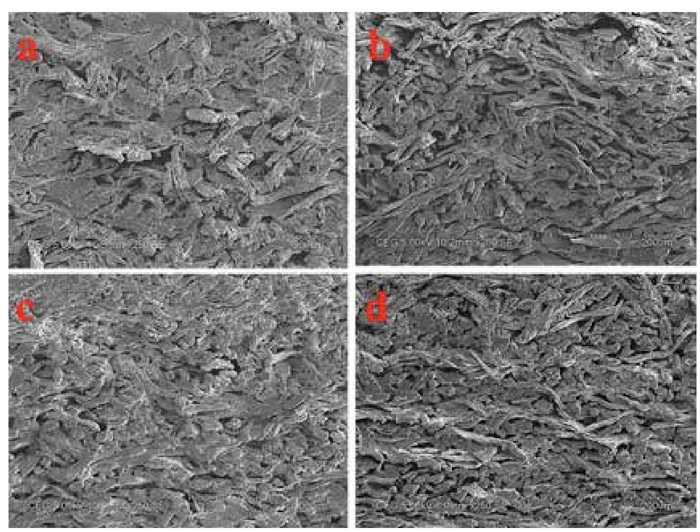

Figure 3. Scanning electron microscopic images showing the cross section of control and experimental wet blue leathers from (a) pickle-based chrome tanning in heptane medium (b) pickle-based chrome tanning in water medium (c) pickle-less chrome tanning in heptane medium and (d) pickle-less chrome tanning in water medium.

tanned leathers processed in heptane and water medium was evaluated through shrinkage temperature analysis. It is seen that the shrinkage temperature of leathers processed in heptane medium is slightly higher than that of control leathers (water mediated). These results suggest that replacing water with heptane for chrome tanning improves not only the uptake of chromium but also the thermal stability of leathers.

Leaching Analysis

The extent of leaching of chromium from chrome tanned leathers is of paramount importance for any new tanning systems as this will provide clues on the extent of presence of free or unreacted chromium as well as the extent of fixation or crosslinking of chromium with collagen functional groups. The chromium leaching and the amount of chromium present before and after leaching in the tanned leathers from pickle-based and pickle-less chrome tanning processes carried out in heptane and water medium are shown in Table III. It is seen that the amount of leaching of chromium is about 2% from both control and experimental wet blue leathers when water and heptane were used as leaching solvents. The experimental leather shows fairly reduced leaching of chromium when compared to control leather. The leaching is much lower when heptane was used as leaching solvent, which may be due to the poor solubility of chromium in heptane medium. These values are lower than those reported in the literature.[11] This indicates that the remaining amount of chromium (about 98%) is fixed strongly with the leather matrix. Further, the amount of chromium present in leathers after leaching is comparable to that of before leaching.

Composite Liquor Analysis

The chrome tanned leathers processed by pickle-based and pickle-less chrome tanning using heptane medium was post tanned conventionally (in water medium). Spent liquors of

Table III

Analytical data on leaching studies in control (C) and experimental (E) wet blue leathers

Sample	**PL_C**	**PL_E**		**P_C**	**P_E**	
Cr_2O_3 (%, dry weight basis) in wet blue leather before leaching	6.03	6.30		5.16	5.60	
Leaching solvent	Water	Heptane	Water	Water	Heptane	Water
Leaching of Cr from wet blue (%)	2.10	1.24	1.90	1.85	1.42	1.87
Cr_2O_3 (%, dry weight basis) in wet blue leather after leaching	5.90	6.22		5.06	5.52	

PL_C – Pickle-less control; PL_E –Pickle-less experimental; P_C – Pickle-based control; P_E – Pickle-based experimental.

Table IV

Composite liquor analysis for conventional (C) and experimental (E) chrome tanning systems.[a]

Samples	**COD (mg/L)**	**BOD (mg/L)**	**TS (mg/L)**	**Volume of effluent (L/ton of raw material)**	**Emission load (kg/ton of raw material processed)**		
					COD	**BOD**	**TS**
P_C	16900	5700	13072	1629	27.5	9.3	21.3
P_E	14150	4550	9136	1108	15.7	5.0	10.1
PL_C	14800	5480	12314	1460	21.6	7.9	18.0
PL_E	11900	4050	8104	1193	14.2	4.8	9.7

[a]Composite liquors were collected from chrome tanning up to post tanning

P_C – Pickle-based control; P_E – Pickle-based experimental; PL_C – Pickle-less control; PL_E –Pickle-less experimental.

chrome tanning, neutralization, washing, wet-finishing and fixing obtained from control and experimental processes were mixed together to prepare the composite liquor. COD, BOD and TS are the parameters chosen for analyzing the environmental impact of the spent liquors. The liquors were analyzed for COD/BOD/TS and the emission loads were calculated by multiplying concentration values (mg/l) with the volume of composite effluent (l) per ton of raw skins processed. The data is presented in Table IV. As can be seen, both pickle-based and pickle-less chrome tanning systems in heptane medium provide significant reduction in COD, BOD and TS loads by 34-43, 39-46 and 46-53%, respectively in comparison to water medium. This

Table V
Physical properties of control and experimental crust leathers.

Samples	P_C	P_E	PL_C	PL_E
Tensile strength (N/mm^2)	19.0	17.8	16.1	16.5
Elongation at break (%)	59.1	55.7	58.6	57.9
Tear strength (N/mm)	35.5	43.9	31.5	44.6
Grain crack strength (kg)	31	26	27	25
Grain crack distention (mm)	10.6	8.9	9.5	9.1

P_C – Pickle-based control; P_E – Pickle-based experimental; PL_C – Pickle-less control; PL_E –Pickle-less experimental.

Table VI
Data on the recycling of the spent chrome-heptane liquor in the pickle-based chrome tanning process.

Parameter	First batch	Second batch (1^{st}Recycle)	Third batch (2^{nd} Recycle)
BCS present in total volume of spent chrome-heptane liquor (%)	0.75	0.85	0.91
Amount of BCS added (%)	7	6.25	6.15
Amount of spent chrome-heptane liquor collected (%)	54	56.7	53
Amount of fresh heptane added (%)	100	46	43.3
Images of chrome tanned leather in heptane medium			
Shrinkage temperature (˚C)	108	109	106

could be due to the enhanced uptake of wet-finishing chemicals in the leathers processed through heptane medium owing to high chromium content.

Evaluation of Crust Leathers

The physical properties such as tensile, tear and grain crack strength of control and experimental crust leathers processed through pickle-based and pickle-less chrome tanning in water and heptane medium were analyzed using standard testing methods and the values are presented in Table V. In general, all the strength characteristics of experimental crust leathers are comparable to the values of control leathers. In particular, the tear strength of the leathers chrome tanned in heptane medium is better than that of leathers tanned in water medium. The organoleptic properties evaluated by an experienced tanner on a scale of 0–10 points of control and experimental crust leathers processed through pickle-based and pickle-less chrome tanning in water and heptane medium are shown in Figure 4. It is seen that all the organoleptic properties of the leathers made using the experimental chrome tanning method are comparable to those of leathers made using the conventional chrome tanning process. The general appearance of both control and experimental crust leathers is similar. Scanning electron

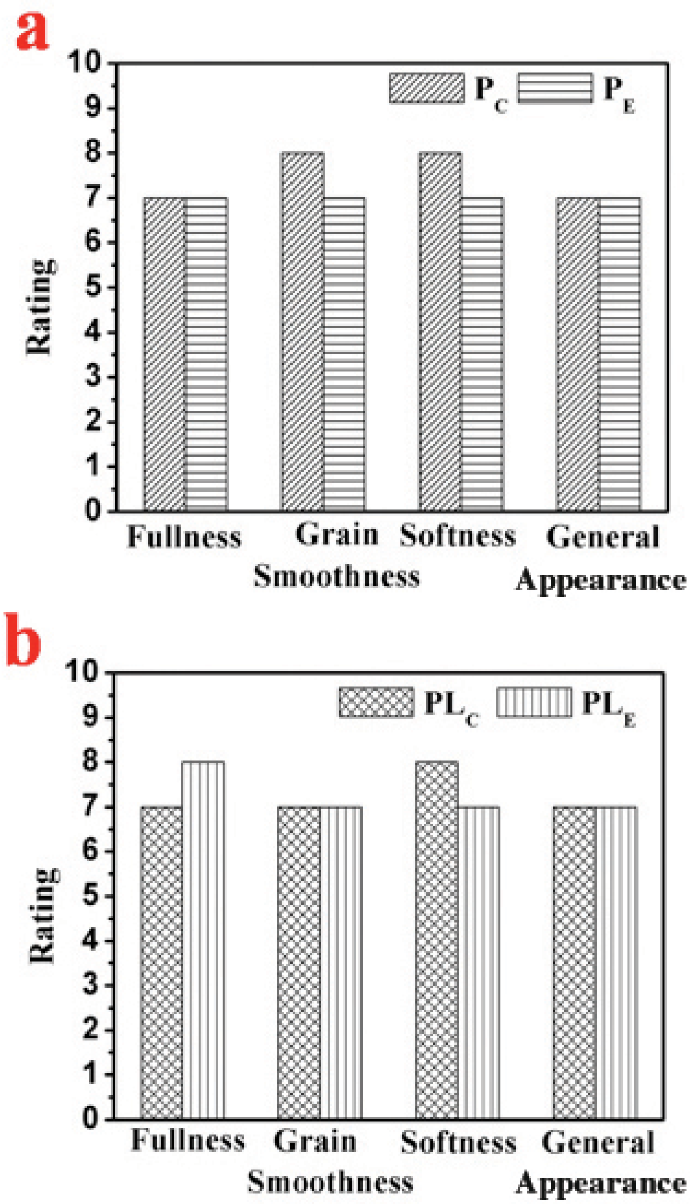

Figure 4. Organoleptic properties of control and experimental crust leathers processed through (a) pickle-based and (b) pickle-less chrome tanning.

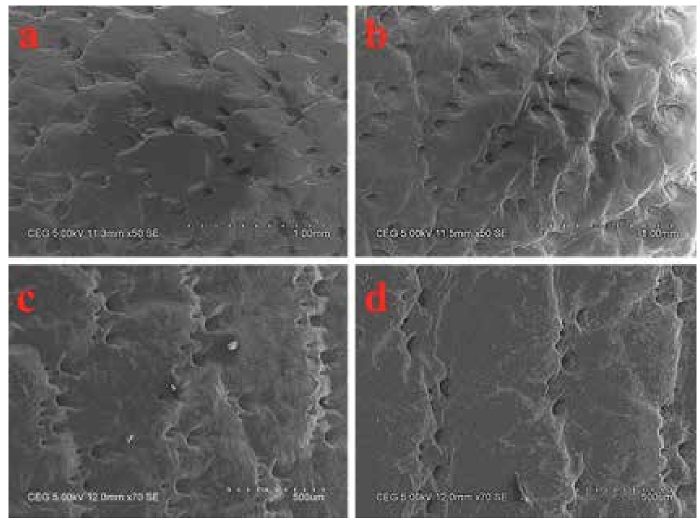

Figure 5. Scanning electron microscopic images showing the grain surface of control and experimental crust leathers from (a) pickle-based chrome tanning in heptane medium (b) pickle-based chrome tanning in water medium (c) pickle-less chrome tanning in heptane medium and (d) pickle-less chrome tanning in water medium.

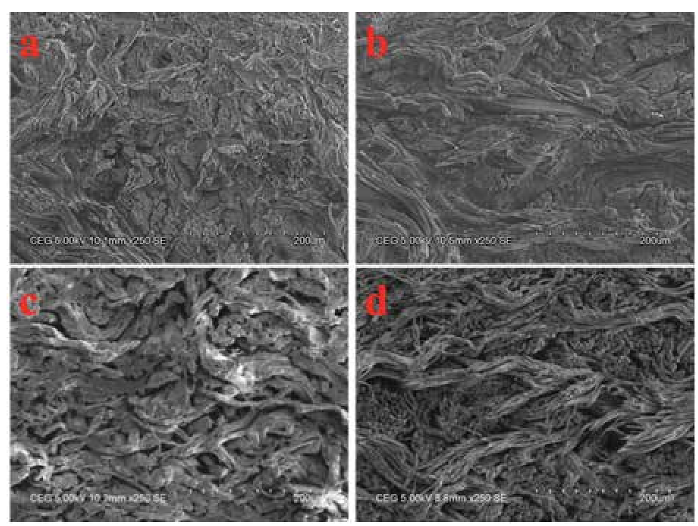

Figure 6. Scanning electron microscopic images showing the cross section of control and experimental crust leathers from (a) pickle-based chrome tanning in heptane medium (b) pickle-based chrome tanning in water medium (c) pickle-less chrome tanning in heptane medium and (d) pickle-less chrome tanning in water medium.

microscopic images showing the grain surface of control and experimental crust leathers processed through pickle-based and pickle-less chrome tanning are displayed in Figure 5a-d. Akin to the observations made at wet blue stage, the grain surface looks clear without any deposition of any foreign particles for both control and experimental leathers. The cross-sectional view of control and experimental crust leathers (Figure 6a-d) exhibit fiber bundles with good splitting and comparable porosity and fiber architecture in both samples. Therefore, these results indicate that the chrome tanning in heptane medium does not significantly affect the physical, organoleptic and structural properties of the final leathers.

Recycling Studies

The data on recycling of spent chrome-heptane liquor for the subsequent batches of pickle-based chrome tanning are given in Table VI. As can be seen, the reuse of spent liquors for the subsequent batches did not significantly affect the quality of leather in terms of appearance, color and thermal stability. As much as 57% of the used heptane can be recovered from each of the chrome tanning batches, which contained nearly 1% of the total BCS employed. This also indirectly demonstrates that the exhaustion of chromium is nearly 85% as already shown. Therefore, it can be determined that it is possible to recycle the spent chrome-heptane liquor up to two times without affecting the quality of the wet blue leathers, which will not only save the environment but also provide cost effectiveness.

Conclusion

In the present of work, chrome tanning process was carried out using heptane employing both pickle-based and pickle-less method. The advantages of the chrome tanning process in heptane medium are better distribution of chromium, comparable organoleptic properties, shrinkage temperature and better exhaustion of chromium in comparison to water mediated conventional chrome tanning process. The amount of leachable chromium is also reduced when compared to chrome tanned leather using water medium. Wet blue leathers post-tanned conventionally in water medium yielded crust leathers with comparable physical, bulk and structural properties. There is a great reduction in pollution loads such as COD, BOD and TS in addition to chromium when the composite liquor comprising chrome tanning to post-tanning was analyzed. Besides, we demonstrate that the used heptane-chrome liquor can be recycled to the subsequent batch without compromising the quality of the wet blue leathers. Nevertheless, a detailed study covering the safety and practical feasibility including the economics of the process need to be carried out before commercial utilization of heptane mediated chrome tanning.

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