Recycling of Spent Chrome Tanning Liquor

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Abstract
Pickling and chrome tanning are the most pollution causing processes in leather industry. In pickling, salt and acids are used to preserve hides and skins. Basic chromium sulphate is used as a pre-tanning agent to convert hides and skins into leather. Only 60 – 70% of the total chrome offer used in tanning process is up-taken by the leather and the rest is discharged in the effluent. In the present study, recycling of chrome tanning liquor was carried out in order to decrease the quantity of chromium discharged in the effluent. The spent chrome tanning liquors were reused 5 times after they had been recharged with the reduced amounts of salt, acids and chrome. Savings in water, salt and chrome were 85%, 33% and 28% respectively. No significant changes were observed in the leather produced using the recycled liquors compared to the leathers produced using the fresh liquor.

Keywords: Recycling, Chrome, Clean Technology.

1. Introduction

In leather industry, raw hides and skins of animals are converted into leather through a series of chemical and mechanical operations. Leather possesses distinctive properties such as toughness, non-flammability, resistance to heat, impermeability to water, and permeability to air and water vapor. These properties make the leather indispensable in many applications especially in footwear and leather goods. Tannery operations can be divided into four categories; Beamhouse, tanning, post tanning and finishing processes. Among these processes, tanning is the most important one. There are many methods of tanning, but the most important and widely used are chrome and vegetable tanning. Chrome tanning process is carried out using Basic Chromium Sulfate (BCS) at the level of 8 - 10% in the tanning process [1].

Chromium (III) has been used widely in tanning for the excellent properties that it renders to the leather along with simplicity of operation. The reported toxicity of chromium compounds coupled with poor uptake of chromium during tanning process has challenged the continued use of this process[2].

Naturally chromium exists in many oxidation states, but Cr(III) and Cr(VI) are of significant concern biologically. Chromium is an essential metal that is involved in the metabolism of glucose in humans and animals, but its hexavalent form is very toxic and carcinogenic [3].

Throughout the world, chrome discharge from tanneries is subject to strict regulations. That notwithstanding, chrome is a component that has to be strictly monitored. The environmental impact of chrome discharged from tanneries has been a subject of extensive scientific and technical dispute. Although the legislative limits on the disposal of solid chrome-
containing waste have been relaxed in some countries, liquid emissions remain strictly regulated throughout the world. Limits on total chrome discharge in effluent vary widely between 0.05 and 10 mg/l for discharges into water bodies (direct discharge) and 1-50 mg/l on discharges into sewage systems (indirect discharge) [4].

Effective management of tannery effluent is the need of the hour. Although a lot of treatment alternatives were assessed to preclude its effect on the environment, neither of them forced out Cr completely. Hence, treatment alternatives are either: complex, energy consuming, expensive or applicable to an indisputable portions of the world due to engineering science or proficient work force requirement. [3]. It has also become increasingly evident that the true scientific solutions to the problem can be achieved through in-plant control measures rather than by using end-of-pipe treatment methodologies [5].

Over the years, treatment of tannery waste-Water put a considerable burden on the total cost of production. After 1980 a very stringent regulation has been imposed on the quality and purity of the waste water that go to the drain. The high amount of money charged for effluent tannery waste-water, lead most of the tanneries to close down with increasingly stringent environmental requirements, it has become necessary to reduce the pollution load in waste-water to a minimum [6].

Recycling operations in a tannery are carried out in order to safe water and chemicals in a process which if not recycled would have been discharged and also to reduce the pollution load in the effluent.[7]

From the total chromium used for tanning only 60% to 70% is utilized, while the rest 30 to 40% remains in the spent tanning liquor, which is normally sent to a wastewater treatment plant.

In practice, there are two ways of chrome recycling methods which are widely practiced: these are direct and indirect recycling. The direct form entails spent float being recycled direct to the chrome tanning processing for re-use. While, the indirect form entails precipitating and separating the chrome from the float containing residual chrome, and then re-dissolving it in acid for re-use [8].

Direct recycling of tanning floats remains the easiest method to apply, recover and reuse chromium salts from tanning operations. After collection and sufficiently fine screening, the floats are controlled and the chromium amounts used in the previous cycle replaced by new chromium salts. In a conventional bovine tanning process, it is estimated that the direct recycling technology can save about 20% of the chromium used in the conventional process [9].

In a study carried out to evaluate the reuse capability of the pickling and chrome tanning liquor. It is found that the addition of 0.2% sulphuric acid and 0.1% formic acid in the old pickling bath and the addition of 5% fresh basic chromium sulphate in the used chrome liquor made the liquors efficient to be reused in the new tanning process without compromising the quality of leather[10].

There are two technological bases for chrome recycling: (i) controlling and adapting the ionic strength of recycled floats so as to avoid acid swelling; and (ii) reaching equilibrium in the chemistry system after several cycles. The recycling with simply complementing the exhausted chromium solutions reduced chromium loss by 25–35%. Grease and solids pre-separation allowed increasing the amount of the cycles.[11]

In this paper, recycling of chrome tanning liquor has been studied. Chrome tanning liquor from the control batch has been successfully recycled for subsequent batches with appropriate replenishments of salt, acid and basic chromium sulphate powder. The objective of this study is to safe water and chemicals and to protect the environment.

2. Materials and Methods

2.1 Materials

Pickled sheep skins of fairly similar size and backbone length and free from physical defects were procured from a local tannery. Chemicals used for tanning and retanning processes were of commercial grade and that used for the analysis of spent liquors were of analytical grade. Normal basic chromium sulphate (25% $\text{Cr}_2\text{O}_3$, 33% basicity) was used as a tanning agent.
2.2 Materials

2.2.1 Tanning Process and Recycling of Spent Liquors

The pickled pelts were divided into 5 batches 10 pieces were used for each batch. The first batch was used as control and the remaining batches were used as experiments. The control batch was tanned using 8% basic chromium sulphate. The spent liquor from the control batch was recovered, screened, sampled, analyzed and reused for the next tanning process after being replenished with the required amounts of salt and water. The formic and sulphuric acids were added till the required pH was reached. After pH adjustment the calculated amount of chrome powder was added. Five cycles have been carried out. Post-tanning processes were carried out common to all experimental and control batches. All tanning and post-tanning experiments were carried out using a temperature, time and speed controlled stainless steel experimental drum 600mm × 1200mm.

2.2.2 Analysis of spent Chrome liquor

The spent liquor from control and experimental tanning processes after each cycle were collected, sampled, screened, filtered and analyzed for salt, chromic oxide contents and pH as per standard procedures [12].

2.2.3 Measurement of Shrinkage Temperature

The hydrothermal stabilities of control and experimental leathers obtained from each cycle were checked by Boiling Test. A small piece of the wet leather was cut off and its shape outlined with a pencil on paper. It was then immersed in water, which was slowly heated with constant stirring until the water boiled. After 2 minutes the sample was removed and its shape was compared with the previously-marked paper outline.[13]

2.2.4. Physical testing of Crust Leathers

The physical properties of the crust leathers from control and experimental leather (cycle 5) such as tensile strength, percentage elongation at break, grain crack strength and tear strength were measured as per standard procedures [12]. The specimens were cut from official position using a clicking machine and conditioned at 20°C ±2°C and 65% ±2% RH over a period of 48hrs. Specimens for tensile and tear strength were cut parallel and perpendicular to the backbone and the thickness of each specimen was measured using a standard thickness gauge at three positions on the grain side and three positions on the flesh side, and then the mean of the six measurements was calculated. The area of cross section of each specimen was calculated by multiplying its width by its thickness. Each value for tensile and tear strength represents the average of four samples (2values along the backbone and 2 values across the backbone). Each value for grain crack strength is the average of three samples.

2.2.5 Hand Evaluation of Crust Leathers

Softness, fullness, smoothness grain tightness (break), and general appearance were evaluated visually and by hand for control and experimental leathers. Three professional tanners graded the leathers on a scale of 0–5 points for each functional property, where 5 indicate (very good) and 1 indicate (poor) property. Values for organoleptic properties are the average of the three assessments.

2.2.6 Chemical Analysis of Crust Leathers

The chemical constituents of crust leathers from control and experimental leathers (cycle 5) such as moisture content, chromic oxide content, oil and fats content, total ash content, water soluble matter, and insoluble ash were determined according to standard procedures [12].
3. Results and Discussion

3.1 Hydrothermal stability of wet-blue

It is usual to check the degree of tannage by measuring the resistance of the leather to hot water – commonly referred to as a Shrinkage or Boiling Test (Ts). A normally well-tanned chrome leather withstands immersion in boiling water (i.e. 100°C) for 2 minutes without shrinking [13]. The shrinkage temperatures of both control and experimental leathers were all pass the boiling test which indicate the completion and effectiveness of chrome tannage this means that, the recycling of chrome liquor did not affect the process.

3.2 Analysis of Spent Chrome Liquor

The analysis results of spent tanning liquors from each cycle were presented in Table 3.1. It has been shown that considerable savings in water and basic chemicals were achieved. Water, chromium and salt were only given to make up the solution as needed, instead of a full amount being added for each fresh float as in the conventional process. Formic and sulphuric acids were added just to reach the desired pH. Impressive savings of 85% in water, 33% in salt, and 28% in chromium have been achieved. The average consumptions based on the fleshed weight of the pelt were 2.2% chrome, 3% NaCl, and 15% water.

Table 1: Analysis of Spent chrome liquor

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>NaCl (g/l)</th>
<th>Cr₂O₃ (g/l)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.0</td>
<td>5.1</td>
<td>3.8</td>
</tr>
<tr>
<td>2</td>
<td>30.0</td>
<td>5.1</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>30.2</td>
<td>5.8</td>
<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td>30.2</td>
<td>5.8</td>
<td>4.0</td>
</tr>
<tr>
<td>5</td>
<td>30.2</td>
<td>5.8</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Table 2: Percentage Chemicals Used for Each Cycle

<table>
<thead>
<tr>
<th>Cycle No.</th>
<th>NaCl %</th>
<th>Chrome powder %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional (control)</td>
<td>10.0</td>
<td>8.00</td>
</tr>
<tr>
<td>1</td>
<td>7.0</td>
<td>5.9</td>
</tr>
<tr>
<td>2</td>
<td>7.0</td>
<td>5.9</td>
</tr>
<tr>
<td>3</td>
<td>7.0</td>
<td>5.7</td>
</tr>
<tr>
<td>4</td>
<td>7.0</td>
<td>5.7</td>
</tr>
<tr>
<td>5</td>
<td>7.0</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Table 3: Comparison of recycling and conventional chrome tanning method

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Average Consumption without recycling (%)</th>
<th>Average Consumption with recycling (%)</th>
<th>saving%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>NaCl</td>
<td>10</td>
<td>7</td>
<td>33</td>
</tr>
<tr>
<td>Chrome powder</td>
<td>8</td>
<td>5.8</td>
<td>28</td>
</tr>
</tbody>
</table>

3.3 Physical properties of Crust Leathers

The leathers obtained were subjected to various quality tests to check their strength properties. The values for physical tests for experimental and control leathers were presented in Table 4. From the table it is obvious that, the strength properties of experimental leathers are comparable to that of control leathers. The high value of tensile strength for control and experimental leathers indicating the good condition of the raw skins. The strength properties of both control and experimental leathers were found to be confirmative to Bureau of Indian Standard (BIS) for chrome tanned upper leathers.
The chemical characteristics of the experimental and control leathers were found to be quite normal. Both control and experimental leathers have good resistance to washing due to the low values of total soluble matter.

### Table 4: Chemical Constituents of Crust Leathers

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Cycle No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>7.1</td>
</tr>
<tr>
<td>Fat content (%)</td>
<td>9.1</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>5.4</td>
</tr>
<tr>
<td>Insoluble ash (%)</td>
<td>2.2</td>
</tr>
<tr>
<td>Water soluble (%)</td>
<td>1.02</td>
</tr>
<tr>
<td>Cr₂O₃ content (%)</td>
<td>4.5</td>
</tr>
</tbody>
</table>

4. Conclusion

In the present study the recycling of the used chrome tanning has successfully been carried out without any significant changing in the quality of final product. The environmental problems can be solve by applying the recycling of the used chrome tanning solutions. Also the production cost can be reduced as there is appreciable savings in chemicals and water used in the process.

Acknowledgments

The authors give their thanks and appreciation to the Ministry of Higher Education and Scientific Research for giving us the opportunity, and fund for this research. Thanks are also due to Sudan University of Science and Technology for their help and support to purchase the equipment for this research and permit to carry out the experimental work at their laboratories.

References


