RECOVERY OF PROTEINS AND CHROMIUM COMPLEXES FROM CHROMIUM – CONTAINING LEATHER WASTE (CCLW)

Gutti, B.1, Omotola, F.1 and Ngala, G.M.2

Abstract

Chromium – Containing Leather Waste (CCLW) constitutes an environmental pollution problem to leather industries disposing the waste by landfill. The waste mainly consists of collagen and chromium III complexes. This work is a design of reactors to recover gelatin, polypeptides and chromium from CCLW. The results of the experiment shows that 68% of protein, based on dry weight of leather scraps, could be recovered. Three reactors with a total volume of 18 m³ was designed to handle 10,431 kg of waste generated from the tanning industries.

1. Introduction

The treatment of Chromium – Containing Leather Waste (CCLW) for the recovery of reusable products is indeed a giant stride towards converting the tanning process to a closed circuit and an environmentally friendly production runs which will drastically slash down the percentage of raw hides/skins lost per year as leather waste. CCLW is a term generally used to qualify leather scraps or chrome shavings produced in post–tanning operations such as trimming, splitting, shaving and buffing processes of leather production. CCLW constitutes the major solid waste generated during the post–tanning operations of leather processing. It is known that only 20% of wet–salted hides/skins are converted into commercial leather, while 20% becomes CCLW and the remainder becomes non-tanned waste or is lost in waste water as fat, soluble proteins and solid suspended pollutants (Alexander et al., 1991). About 18,750 kg of CCLW are generated each day from the Maiduguri leather industry. Disposal of this leather waste is mostly by landfill (Brown et al., 1996). Various researches have been carried out trying to recover or reuse the chromium compounds. Kolomaznik et al. (2008) had worked on how to reuse the waste in NPK fertilizer production, ceramic and glass industry, because of the negative effects the compounds will have on human health. Ammar et al. (2009) had worked on removing with reusing chromium in the tanning process with simple, ecological and economic treatment process and potential valorization of the organic matrix of waste decontaminant. It allows the decontamination of the chromium-containing leather wastes to simplify the recovery of its considerable protein fractions. Thus the need to recover and then convert the waste into valued–added products cannot be overemphasized. Table 1 gives the characteristics of tannery solid wastes.

2. Methodology

A number of techniques have been proposed for the treatment of CCLW by various researchers. Amongst these are: alkali hydrolysis, enzymatic hydrolysis, multi–step alkali hydrolysis and the three–step hydrolysis process (Mu and Zhang, 2003). The three-step hydrolysis method generates no by–
product (secondary waste) and as such forms the basis of the proposed novel CCLW treatment plant
designed in this research work.

Table 1: Characteristics of tannery solid wastes (g/kg)

<table>
<thead>
<tr>
<th>S/No</th>
<th>Constituents</th>
<th>Dustedsalts</th>
<th>Fleshing</th>
<th>Wet trimming and shaving</th>
<th>Drying trimming, shaving and buffing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Moisture</td>
<td>118</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>Proteins</td>
<td>--</td>
<td>236</td>
<td>241</td>
<td>312</td>
</tr>
<tr>
<td>3</td>
<td>Fats</td>
<td>--</td>
<td>190.4</td>
<td>29.78</td>
<td>132</td>
</tr>
<tr>
<td>4</td>
<td>Cr₂O₃</td>
<td>--</td>
<td>--</td>
<td>14.2</td>
<td>26.84</td>
</tr>
<tr>
<td>5</td>
<td>Volatile matter</td>
<td>118</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>Salt</td>
<td>464</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>Lime</td>
<td>--</td>
<td>2.7</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>8</td>
<td>Sulphide</td>
<td>--</td>
<td>1.96</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>


Table 2 gives the analysis of the CCLW used by Mu and Zhang (2003) in their experiments, which gave birth to the three–step hydrolysis process. The CCLW obtained from a commercial pigskin tannery were kept at room temperature and analyzed for pH, moisture, ash, Total Kjeldahl Nitrogen (TKN), chromium and fat. Moisture was determined by heating the sample at 110 °C for 12 hours. Ash in the dried products was determined by heating the sample at 600 °C for 4 hours. TKN was determined by the semi–micro Kjeldahl method. Chromium was determined using a Perkin-Elmer model AA7003 atomic absorption Spectrophotometer. Fat was extracted with chloroform.

Table 2: Analysis of chrome leather waste

<table>
<thead>
<tr>
<th>S/No</th>
<th>Parameter</th>
<th>Measure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PH</td>
<td>4.09 %</td>
</tr>
<tr>
<td>2</td>
<td>Moisture</td>
<td>5 – 10%</td>
</tr>
<tr>
<td>3</td>
<td>Ash&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11.5%</td>
</tr>
<tr>
<td>4</td>
<td>TKN&lt;sup&gt;a, b&lt;/sup&gt;</td>
<td>16.55%</td>
</tr>
<tr>
<td>5</td>
<td>Chrome oxide (Cr₂O₃)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.72%</td>
</tr>
<tr>
<td>6</td>
<td>Fat&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.18%</td>
</tr>
</tbody>
</table>

<sup>a</sup> = Moisture free basis; <sup>b</sup> = Ash – free basis

Data of Tables 1 and 2 indicate that the waste contains about 4% Cr₂O₃ and about 80% protein (the nitrogen content of collagen is 18%). Though the CCLW used in the analysis was obtained from a pigskin tannery it has been found that the results are also applicable to the CCLW of other tanneries processing cattle or goat hides/skins (Mu and Zhang, 2003).

2.2 Treatment of CCLW

The Three – step hydrolysis process

The three–step hydrolysis experiment on CCLW is presented as follows;
In the first step of the experiment 100 g of the CCLW was suspended in water and 2 g of CaO/NaOH was added to increase the alkalinity of the mixture to a pH of 11 ± 0.5. The reaction mixture was stirred at 70 – 80°C for 3.5 hours and then filtered warm to separate the gelatin from chrome sludge. In the second step, 100 g water and 2 g CaO were added to the chrome sludge at 97-99°C for 3-4 hours. Then the mixture was filtered warm through the filter press to separate the collagen hydrolysates from the chrome cake. During the whole process, pH was controlled at 9-10 to maintain optimum alkalinity for avoiding chrome dissolution. In the third step, the chrome cake was dissolved in concentrated sulphuric acid with a pH of 1.0 - 2.0 at 97 – 99°C for 3 - 5 hours. The resultant chromium-containing protein hydrolysate solution was slowly adjusted to the appropriate value with sodium bicarbonate for preparation of re-tanning agents.

The recovered samples from the three-step process were then analyzed for pH, ash and protein as TKN, chromium and calcium. The physical and chemical properties of each product extracted in the three steps (gelatin in step 1, polypeptides in step 2 and chrome cake containing residual proteins) are given in Table 3.

### Table 3: Properties of the recovered product from the three-step process

<table>
<thead>
<tr>
<th>S/No</th>
<th>Sample</th>
<th>pH</th>
<th>Ash&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>Ca&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>Cr</th>
<th>TKN&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Gelatin</td>
<td>6</td>
<td>6.3</td>
<td>0.04</td>
<td>0.015</td>
<td>17.4</td>
</tr>
<tr>
<td>2</td>
<td>Polypeptide</td>
<td>6</td>
<td>8.8</td>
<td>0.12</td>
<td>0.074</td>
<td>16.9</td>
</tr>
<tr>
<td>3</td>
<td>Chromium containing hydrolysate</td>
<td>2</td>
<td>46</td>
<td>--</td>
<td>8.6</td>
<td>10.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> Moisture - free basis;  
<sup>b</sup> Expressed as percentage;  
<sup>c</sup> Ash - free basis

### 2.3 Reactor design of CCLW

The production technology of the proposed process is based on a production capacity of 18, 750 kg waste products per day. Hence we will have an approximate of 3 batches per day. The plant is operated batch wise due to the nature and speed of the reactions involved.

**Basic Data**

Owing to the large quantity of water involved in the reactions, the densities, viscosities and specific heat capacities of all the mixtures (liquors) were taken equal to those of water at 4°C:

- Density, \( \rho = 1000 \text{ kg/m}^3 \)
- Viscosity, \( \mu = 1.567 \times 10^{-3} \text{ Pa.s} \)
- Specific heat capacity, \( C_p = 4.2 \text{ kJ/kg K} \)

**Utilities**

Saturated steam is available for heating at the following conditions:

- Pressure, \( P_s = 8581 \text{ kPa} \)
- Temperature, \( T_s = 300 \text{ °C} \)
- Enthalpy, \( H_s = 2794 \text{ kJ/kg} \)
- Enthalpy of condensate, \( h_s = 1344 \text{ kJ/kg} \)

**R – 1:** Initial temperature of content/mixture, (for all reactors) \( T_o = 20 \text{ °C} \)

**R – 2:** Mass of reactor content = 6100 kg/batch

\[
M_1 \cdot C_p \Delta T = M_s (H_s - h_s)
\]

Where \( M_s \) = mass of reactor content = 6100 kg/batch

\[
6100(4.2 \times 10^{-3})(80 - 20) = M_s(2749 - 1344) \times 10^3
\]

\[
1537200 = (2749 - 1344) M_s \quad M_s = 1094 \text{ kg steam/batch}
\]

**R – 2:** \( M_2 = 3155 \text{ kg/batch, } T_f = 98 \text{ °C} \)

\[
3155(4.2)(78) = M_s(1405)
\]

\[
M_s = 735.64 \text{ kg steam/batch}
\]
R – 3: $M_3 = 1175.8 \text{ kg/batch}, T_f = 98^0 \text{C}$

$1175.8(4.2)(78) = Ms(1405)$
$Ms = 274.16 \text{ kg steam/batch}$

Number of batches treated in each reactor per day is assumed to be one.

The three reactors are basically agitated cylindrical vessels and as such design equations for agitators in Geankoplis (1993) were followed in designing the vessels.

**Reactor R – 1:**

Specifications:
Volume $v$ of reactor = 10 m$^3$
Diameter of reactor, $D_t = \text{height, } H = 2.34 \text{ m}$
Agitator type: three – bladed propeller
Number of baffles: 4
Agitator diameter = $D_a$
Number of revolutions $N = 200 \text{ rpm (3.33rev/s)}$

For standard agitator design from Geankoplis (1993).

$\frac{D_a}{D_t} = 0.4$  \hspace{1cm} (2)

$D_a = 0.4 \times D_t = 0.94 \text{ m}$

For baffles;

$j/D_t = 1/12$  \hspace{1cm} (3)

$j = \frac{2.34}{12} = 0.20 \text{ m}$

Propeller height above reactor bottom $C$:

$C/D_t = 1/3$  \hspace{1cm} (4)

$C = \frac{D_t}{3} = 0.78 \text{ m}$

Propeller Reynolds number:

$N_{Re} = \frac{D_a^2 N \rho}{\mu}$  \hspace{1cm} (5)

$N_{Re} = 0.94^2(3.33)(1000)/1.567 \times 10^{-3}$

$\approx 19 \times 10^5$; Turbulent mixing regime.

From Geankoplis (1993), power number $N_P = 0.4$ for the calculated $N_{Re}$

Agitator/Motor power;

$P = N_P N^2 D_a^5$  \hspace{1cm} (6)

$P = 0.4(1000)(3.33)^3 (0.94)^5 = 10,840 \text{ W}$

Power requirement for $R_1 = 10.84 \text{ kW}$

**Reactor R – 2**

Specifications:
Volume $V$ of reactor = 5 m$^3$
Diameter of reactor, $D_t = \text{height, } H = 1.85 \text{ m}$
Agitator type: three – bladed propeller
Number of baffles: 4
Agitator diameter = $D_a$

$N = 3.33 \text{ rev/s}$

From equation 1

$D_a = 0.4D_t = 0.74 \text{ m}$

From equation 2
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\[ j = \frac{1.85}{12} = 0.15 \text{ m} \] and from equation 3
\[ C = \frac{1.85}{3} = 0.62 \text{ m} \]

Impeller’s Reynolds number
\[ N_{Re} = 0.74^2(3.33)(1000)/1.567 \times 10^{-3} \]
\[ \approx 11 \times 10^5 \]
\[ N_p = 0.4 \]

Driver power, \( P \) from equation 6
\[ P = 0.4(1000)(3.33)^3(0.74)^5 = 3278 \text{ W} \]

Power requirement for \( R - 2 = 3.30 \text{ kW} \)

**Reactor R – 3**

Specifications:
- Volume of \( R - 3, V = 3 \text{ m}^3 \)
- Diameter of reactor, \( D_t = \text{height, } H = 1.56 \text{ m} \)
- Agitator type: three – bladed propeller
- Number of baffles: 4
- Agitator diameter = \( D_a \)
  \[ D_a = 0.4 \times 1.56 = 0.62 \text{ m} \]
- Width of baffles \( j = D_t/12 = 1.56/12 = 0.13 \text{ m} \)
- Propeller height above reactor bottom \( C: \)
  \[ C/D_t = 1/3 \]
  \[ C = \frac{1.56}{3} = 0.52 \text{ m} \]

\[ N_{Re} = 0.62^2 \times 3.33 \times 1000/1.567 \times 10^{-3} = 8.2 \times 10^5 \]
\[ N_p \text{ also} = 0.4 \]
\[ P = 0.4(1000)(3.33)^3(0.62)^5 = 1353 \text{ W} \]

Power requirement of the agitator \( P = 1.35 \text{ kW} \).

**Pump, \( P \):**
- Required flow rate = \( 2.52 \times 10^{-3} \text{ m}^3/\text{s} \)
- Pump power = 0.48 kW

### 2.4 Process description

The raw materials for the process constitute the dry CCLW. The waste is first of all screened to separate stones and other undesired foreign particles from it. Thereafter, the leather scraps are channeled into the size reduction unit (a hammer mill) of capacity 200 kg/h wherein they are crushed into powder to enhance chemical reaction in the next stage. These processes constitute the feed preparation stage of the whole process. The crushed CCLW are then stored temporarily in a tank.

The reactor R-1 is charged with water at a temperature of 20 \(^{\circ}\text{C}\) and as heating is commenced, the feed is charged in (1000 kg/batch) with the stirrer on. Enough base is added only to maintain the pH of the system/mixture at 11. Steam is supplied just to raise the temperature of the reaction mixture to within 70 and 80 \(^{\circ}\text{C}\) for 3 – 4 hours.

The mixture is then passed into the filter press F – 1 to separate gelatin. The filtration is done warm in F – 1 (50 to 60 \(^{\circ}\text{C}\)) so that sol - gel inversion does not occur . The chrome sludge on the other hand is pumped into R–2 for the second stage hydrolysis. More water is added together with CaO to keep the
pH at 9–10. Temperature of R–2 is maintained at 97–99 °C for another 3–4 hours. Thereafter the mixture is withdrawn into the second filter press F–2 for separation of polypeptides solution.

After withdrawing the filtrate, the chrome cake is channelled into R–3 where it is dissolved in concentrated sulphuric acid. The acid hydrolysis also occurs at 97–99 °C and agitation is done for 3–4 hours. After the first hydrolysis the protein yield is about 46.5% while the protein extracted in the second hydrolysis is about 21.5% of the CCLW protein content. Figure 1 shows a typical process flow diagram of the system.

![Figure 1: Three-step hydrolysis process for CCLW](image)

### 3. Results and discussion

Three reactors were designed. Reactor-1 with a capacity of 10 m³ and height of 2.34 m, will function as gelatin extractor and will handle 6100 kg/batch of materials (CCLW, base/alkalis) and 1094 kg/batch of steam. Reactor-2 with a capacity of 5 m³ and height of 1.85 m, will function as polypeptides and chrome extractor and will handle 3155 kg/batch of materials (Chrome sludge containing polypeptides) and 736 kg/batch of steam. Reactor-3 with a capacity of 3 m³ and height of 1.56 m will function as a medium for acidification of chrome cake and will handle 1176 kg/batch of...
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materials (Chrome caked and conc. $\text{H}_2\text{SO}_4$) and 274 kg/batch of steam. The power requirements of the reactors are 10.84 kW, 3.3 kW and 1.35 kW respectively.

The reactors operate in the isothermal well-mixed temperature regime. Steam supply is intermittent (as the need arises) to keep the reactors temperature within the required range. The reactors are lagged to keep heat losses minimal. The material of construction is stainless steel to avoid corrosion and acid attacks. Capacities and dimensions of the reactors are summarized in Table 4, while the specifications are summarized in Table 5.
### Table 4: Design data

<table>
<thead>
<tr>
<th></th>
<th>Reactor 1</th>
<th>Reactor 2</th>
<th>Reactor 3</th>
<th>Pump</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>10 m³</td>
<td>5 m³</td>
<td>3 m³</td>
<td>-</td>
</tr>
<tr>
<td>Height, Dt</td>
<td>2.34 m</td>
<td>1.85 m</td>
<td>1.56 m</td>
<td>-</td>
</tr>
<tr>
<td>Mass of material</td>
<td>6100 kg/batch</td>
<td>3155 kg/batch</td>
<td>1176 kg/batch</td>
<td>-</td>
</tr>
<tr>
<td>Mass of steam</td>
<td>1094 kg/batch</td>
<td>736 kg/batch</td>
<td>274 kg/batch</td>
<td>-</td>
</tr>
<tr>
<td>Agitator type</td>
<td>Three bladed propeller</td>
<td>Three bladed propeller</td>
<td>Three bladed propeller</td>
<td>-</td>
</tr>
<tr>
<td>No. of baffles</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Agitator diameter, Da</td>
<td>0.94 m</td>
<td>0.74 m</td>
<td>0.62 m</td>
<td>-</td>
</tr>
<tr>
<td>No. of revolutions</td>
<td>200 rpm (3.33 rev/s)</td>
<td>200 rpm (3.33 rev/s)</td>
<td>200 rpm (3.33 rev/s)</td>
<td>-</td>
</tr>
<tr>
<td>Width of baffles, j</td>
<td>0.20 m</td>
<td>0.15 m</td>
<td>0.13 m</td>
<td>-</td>
</tr>
<tr>
<td>Propeller height above reactor, C</td>
<td>0.78 m</td>
<td>0.62 m</td>
<td>0.52 m</td>
<td>-</td>
</tr>
<tr>
<td>Power requirement</td>
<td>10.84 kW</td>
<td>3.3 kW</td>
<td>1.35 kW</td>
<td>0.48 kW</td>
</tr>
<tr>
<td>Flow rate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.00252 m³/s</td>
</tr>
</tbody>
</table>

### Table 5: Equipment Specification

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Function</th>
<th>Material handled</th>
<th>Operation</th>
<th>Capacity</th>
<th>Material of Construction</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-1, Jacketed reactor</td>
<td>Gelatin extractor</td>
<td>CCLW and base/alkalis (also water), steam</td>
<td>Batch</td>
<td>10 m³</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>R-2, Jacketed reactor</td>
<td>Polypeptides and chrome extractor</td>
<td>Chrome sludge containing polypeptides, steam</td>
<td>Batch</td>
<td>5 m³</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>R-3, Jacketed reactor</td>
<td>Acidification of chrome cake</td>
<td>Chrome caked conc. H₂SO₄ and steam</td>
<td>Batch</td>
<td>3 m³</td>
<td>Stainless steel</td>
</tr>
</tbody>
</table>
The proposed technology thus, produces no secondary waste and it offers high prospects of converting solid wastes to beneficial use in the leather industry. The gelatin so recovered is a product of commercial value. It could be sold to the glue industry for production of adhesives thereby generating income for the tannery. Gelatin is also used in photography for film production, in food, cosmetics and in textiles industries. It is also used for encapsulation. The recovered products could also be modified for direct use in leather processing. As at the year 2003 researches were being conducted on the three by-products to convert the chromium – containing protein and polypeptides hydrolysates to leather re-tanning agents means of converting the gelatin to leather finishing agent (Heidemann, 1991).

4. Conclusion
Three reactors with a total volume of 18 m$^3$ are designed to handle 10,431 kg of waste generated from the tanning process. Reactor, R-1 with a capacity of 10 m$^3$ is designed to extract the gelatin and it will handle the CCLW and base/alkalis, water and steam. Reactor, R-2 with a capacity of 5 m$^3$ is designed to remove polypeptides and chrome and it will handle the chrome sludge containing polypeptides and steam, while Reactor, R-3 with a capacity of 3 m$^3$ is designed to acidify and handle the chrome cake, concentrated hydrosulphuric acid and steam. The concentration of the recovered gelatin is 13.3 wt% whereas that of the second product (the polypeptides) is 10.8 wt% and the protein extracted is about 21.5% of the CCLW protein content. The operations of the reactors are batch processes. The recovered gelatin could be sold to many industries including tannery for production of adhesives, photography for film production, food, cosmetics and in textile.

References