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

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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 m^3 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–

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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)

		Types of solid waste			
S/No	**Constituents**	Dusted salts	Fleshing	Wet trimming and shaving	Drying trimming, shaving and buffing
1.	Moisture	118	--	--	--
2.	Proteins	--	236	241	312
3.	Fats	--	190.4	29.78	132
4.	Cr_2O_3	--	--	14.2	26.84
5.	Volatile matter	118	--	--	--
6.	Salt	464	--	--	--
7.	Lime	--	2.7	--	--
8.	Sulphide	--	1.96	--	--

Source: Leather Sector Report (Iqbal and Berns, 1998).

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 ^{O}C for 12 hours. Ash in the dried products was determined by heating the sample at 600 ^{O}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

S/No.	Parameter	Measure
1.	PH	4.09 %
2.	Moisture	5 – 10%
3.	Ash[a]	11.5%
4.	TKN[a, b]	16.55%
5.	Chrome oxide (Cr_2O_3)[a]	3.72%
6.	Fat[a]	1.18%

a = Moisture free basis; **b** = Ash – free basis

Data of Tables 1 and 2 indicate that the waste contains about 4% Cr_2O_3 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 2g 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 ^{O}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 ^{0}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 ^{O}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

S/No	Sample	pH	**Ash**$^{a, b}$	**Ca**$^{a, b}$	Cr	**TKN**$^{a, b}$
1	Gelatin	6	6.3	0.04	0.015	17.4
2	Polypeptide	6	8.8	0.12	0.074	16.9
3	Chromium containing hydrolysate	2	46	--	8.6	10.5

^{a}Moisture - free basis; ^{b}Expressed as percentage; ^{c}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 ^{O}C:

Density, ρ = 1000 kg/m^3; Viscosity, μ = 1.567 x 10^{-3} Pa.s; Specific heat capacity, Cp = 4.2 kJ/kg K

Utilities

Saturated steam is available for heating at the following conditions:

Pressure, Ps: 8581 kPa; Temperature, Ts: 300 ^{O}C ; Enthalpy, Hs: 2794 kJ/kg

Enthalpy of condensate, hs: 1344 kJ/kg

R – 1: Initial temperature of content/mixture, (for all reactors) $T_o = 20\ ^{O}C$

Quantity of steam = M_s kg/batch; Desired final temperature, $T_f = 80\ ^{O}C$

Using $M_i\, Cp\, \Delta T = M_s(H_s – h_s)$ *1*

Where M_i = mass of reactor content = 6100kg/batch

$6100(4.2 \times 10^3)(80 - 20) = M_s(2749 – 1344) \times 10^3$

1537200 = (2749 – 1344) Ms $\quad M_s$ = 1094 kg steam/batch

R – 2: M_2 = 3155kg/batch, $T_f = 98^{O}C$

3155(4.2)(78) = Ms(1405)

Ms = 735.64 kg steam/batch

R – 3: M_3 = 1175.8 kg/batch, $T_f = 98^{O}C$
1175.8(4.2)(78) = Ms(1405)
Ms = 274.16 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, Dt = height, H = 2.34 m
Agitator type: three – bladed propeller
Number of baffles: 4
Agitator diameter = Da
Number of revolutions N = 200 rpm (3.33rev/s)
For standard agitator design from Geankoplis (1993).
$Da/Dt = 0.4$ 2
Da = 0.4 Dt = 0.94 m
For baffles;
$j/Dt = 1/12$ 3
j = 2.34/12 = 0.20 m
Propeller height above reactor bottom C:
$C/Dt = 1/3$ 4
C = Dt/3 = 0.78 m
Propeller Reynolds number:
$N_{Re} = Da^2 N\rho/\mu$ 5
$N_{Re} = 094^2(3.33)(1000)/1.567 \times 10^{-3}$
$\cong 19 \times 10^5$; Turbulent mixing regime.
From Geankoplis (1993), power number $N_P = 0.4$ for the calculated N_{Re}
Agitator/Motor power;
$P = N_P \rho N^3 Da^5$ 6
$P = 0.4(1000)(3.33)^3 (0.94)^5 = 10{,}840$ W
Power requirement for R_1 = 10.84 kW

Reactor R – 2
Specifications:
Volume V of reactor = 5 m^3
Diameter of reactor, Dt = height, H = 1.85 m
Agitator type: three – bladed propeller
Number of baffles: 4
Agitator diameter = Da
N = 3.33rev/s
From equation 1
Da = 0.4Dt = 0.74 m
From equation 2

j = 1.85/12 = 0.15 m and from equation 3
C = 1.85/3 = 0.62 m
Impeller's Reynolds number
$N_{Re} = 0.74^2(3.33)\ (1000)/1.567 \times 10^{-3}$
$\cong 11 \times 10^5$
$N_P = 0.4$
Driver power, P from equation 6
$P = 0.4(1000)(3.33)^3\ (0.74)^5 = 3278$ W
Power requirement for R –2 = 3.30 kW

Reactor R – 3
Specifications:
Volume of R – 3, V = 3 m^3
Diameter of reactor, Dt = height, H = 1.56 m
Agitator type: three – bladed propeller
Number of baffles: 4
Agitator diameter = Da
Da = 0.4 x 1.56 = 0.62 m
Width of baffles j = Dt/12 = 1.56/12 = 0.13 m
Propeller height above reactor bottom C:
C/Dt = 1/3 *7*
C = 1.56/3 = 0.52 m
$N_{Re} = 0.62^2 \times 3.33 \times 1000/1.567 \times 10^{-3} = 8.2 \times 10^5$
N_P also = 0.4
$P = 0.4(1000)(3.33)^3\ (0.62)^5 = 1353$ W
Power requirement of the agitator P = 1.35 kW.
Pump, P:
Required flow rate = $2.52 \times 10^{-3}\ m^3/s$
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 ^{O}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 ^{O}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 ^{O}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 ^{O}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 ^{O}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.

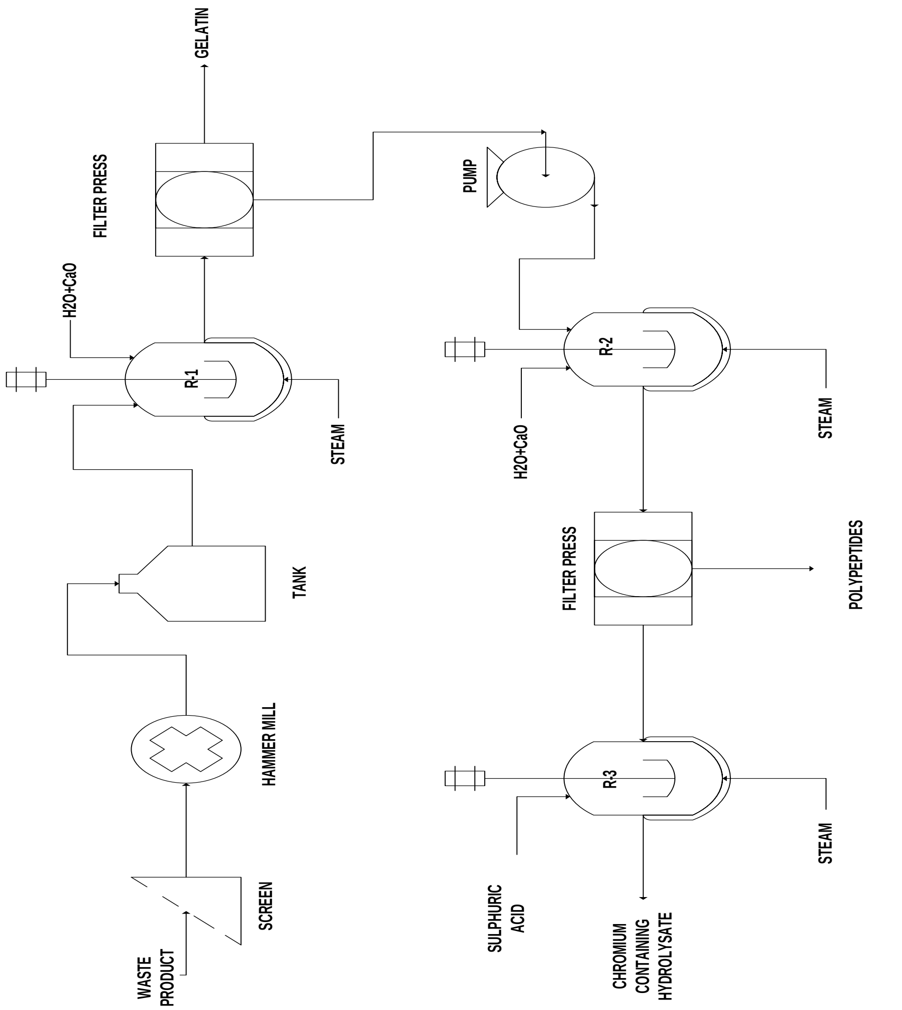

FIGURE 1.0 THREE-STEP HYDROLYSIS PROCESS FOR CCLW (CHROMIUM CONTAINING LEATHER WASTE)

Figure 1: Three-step hydrolysis process for CCLW

3. Results and discussion

Three reactors were designed. Reactor-1 with a capacity of 10 m^3 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 m^3 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 m^3 and height of 1.56 m will function as a medium for acidification of chrome cake and will handle 1176 kg/batch of materials (Chrome caked and conc. H_2SO_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

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

Table 5: Equipment Specification

Reactor	Function	Material handled	Operation	Capacity	Material of Construction
R-1, Jacketed reactor	Gelatin extractor	CCLW and base/alkalis (also water), steam	Batch	10 m^3	Stainless steel
R-2, Jacketed reactor	Polypeptides and chrome extractor	Chrome sludge containing polypeptides, steam	Batch	5m^3	Stainless steel
R-3, Jacketed reactor	Acidification of chrome cake	Chrome caked conc. H_2SO_4 and steam	Batch	3 m^3	Stainless steel

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.

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