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Chrome Tanned Leather Waste Dechroming Optimization for Potential Poultry Feed Additive Source: A Waste to Resources Approach of Feed for Future

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Abstract

In this study chrome tanned leather waste dechroming optimization for potential poultry feed additive source were investigated. Recovery of chrome waste would have environmental and economic benefits and, in this study, the possible application of tannery solid waste as poultry feedstuff additive for poultry growers is investigated. A structured questionnaire was used to collect chrome shaving and got good information about the waste. The elemental analysis of chromium in chrome shaving is around 5.6 mg/kg which satisfies the requirement of poultry feed. The Dechroming rate of 94.82% was achieved for the sample four after treatment by using different chemicals. The higher gelatin solution was 57% w/w in sample four dechromed powder that obtained in the 85-95 °C temperature range. Thermal treatment was used to obtain soluble protein (gelatin) and resulted in a gelatin powder product after drying at 105 °C. The amino acid composition in the isolated protein concentrate was better than the poultry feed such as soybean and wheat. Scanning electron microscope and differential scanning calorimeter were used to analyze the fiber structure and the hydrothermal stability of samples.

Keywords: Chrome waste; Dechroming optimization; Poultry feed; Waste recovery

Introduction

Zero Waste

Leather industry has been considered as one of the extremely polluting industries. There are worries that leather-making action can have adverse influence on the atmosphere [1,2]. Solid wastes produced in leather industries are keratin wastes, skin trimmings, chrome shaving wastes, buffing wastes, and fleshing wastes that contain protein as the main constituent and if this protein is not used properly it will pose problem to the environment. Waste utilization, minimization and reduction concurrently are a powerfully developing matter for sustainable industry growth by engaging a zero-waste concept that comprises reduced consumption, volume reduction and reduced toxicity and recycling [3-6].

There is a need for optimizing the life cycle of the product and reduction of waste and pollution for sustainability. And this issue could be addressed using the life cycle engineering like the discharge, production, process and product [6,7]. Preventive approach can be attained through a potential sustainable and zero waste growth [3,8,9]. Unless the tanner's method discharges zero waste to the environment the environmental burdens will remain an issue and it could be significant to use waste as they develop into co-products [10,11]. Understanding of the science of the bio/chemistry and operations is very important in leather science and this could add value to the by-products by using all the waste materials [10-12]. Processing the raw hides into product comprises water and chemicals produces large amount of waste. For example, for one thousand-kilogram salted hides only two hundred fifty-five-kilogram finished leather could be obtained [3,13-15]. Currently in leather processing chrome tanning is most widely used and that result in chrome containing waste and it is problem to the environment because of the chromium salts. Recently it has been shown that supplemental dietary chromium can be used to solve the effects of the toxicity of vanadium in laying hens and growing as it increases the rate of glucose utilization [3,16-18].

Leather Waste

Leather processing facteries can source adverse changes in the immediate environment and only 255 kg of finished leather (embossed split and grain) is achieved for every 1000 kg wet salted hides processed which means 25.5% of the raw material develops to finished leather) [3,15].

Chrome Tanned Waste

Currently chrome tanning is the major method in leather making, which consequences in a big amount of chrome-containing solid waste and because of large content of environmentally damaging Cr (III) salts, the it is the most environmental problem of tanning production [16,17].

Usually fully tanned leather contains about 4% Cr_2O_3 chrome. Shavings and Chrome split are two major waste streams that must to be handled expertly. There are two methods to the by-products/waste problem that deal with tanners, maximizing the return on by-products and minimizing the quantity of waste generated [2,3].

Sources of Chromium

Naturally occurring chromium compounds in the hexavalent oxidation state are rare and almost all the sources of chromium in the earth's crust are in the trivalent state (Cr^{3+}). Hexavalent chromium (Cr^{6+}) compounds are thus man-made products. Chromium is absorbed primarily in the small intestine and its toxicity is primarily related with exposure to hexavalent chromium compounds. Hexavalent and trivalent chromium compounds act differently in the body. However most of the Cr^{6+} is supposed to be reduced to Cr^{3+} by extracellular fluids before reaching sites of absorption in the small intestine. Information is insufficient on chromium toxicity for poultry. Dietary concentrations of chromium ranging from 3 to 1,000 $CrCl_3$ mg/kg caused effects on growing chicks. Research with poultry has indicated that supplemental dietary chromium can be used to improve some of the toxic effects of vanadium in laying hens and growing chicks. Evidence also has been found that supplemental chromium at 20 mg/kg of diet as $CrCl_3$ rises the rate of glucose exploitation by livers of chicks and poults *in vivo* and *in vitro* [3,16-18].

In Ethiopia, in the basic disposal of tannery solid waste considerable environmental degradation occurs. A rise in the exploitation of traditional and potential feed ingredients by processing industries will lead to the growth of new feedstuffs. The technique of chromium extraction of wet blue leather residues, with consequent attainment of leather waste without chrome, makes this material highly degradable in the rumen and highly digestible in the abomasums, providing it with great nutritional potential. And this study chrome tanned leather waste dechroming optimization for potential poultry feed additive source were investigated with a case example of Ethiopia as recovery of chrome waste would have both environmental and economic benefits.

Materials and Methods

Materials

Chemicals: all chemicals used are analytical grades
1. Sodium Sulfate
2. Sodium Carbonate
3. Calcium Hydroxide
4. Sodium Hydroxide (NaOH, min. assay 98% BDH Chemicals Ltd Poole England) -used to adjust the pH
5. Hydrogen Peroxide
6. Sodium Chloride
7. Sulphuric Acid (H_2SO_4, (98%, England))

Equipments: the equipments used are listed here under
1. Plastic Bags, Knife,
2. Beakers
3. Sieves (mesh size of 2.0 mm, Sortmks-3332, PFEUFFR, Germany)
4. Digital balances (model = Sartorius with 0.01 mg sensitivity, and model = EP214C)
5. Vacuum Filter (model = BN 3 STAATLICH, Berlin)
6. Magnetic stirrer
7. Titration
8. Plastic gloves
9. Funnel

Methods

Chrome shaving survey and collection: Surveying of chrome shaving about ten tanneries were selected for giving us a feedback through the prepared questioner, and from these only four factories were volunteer others were not reactive to give us a feedback due to their own reasons. Chrome containing leather shavings were collected from the tannery of the Habesha Tanning Factory, Bahir Dar Leather Factory plc, Bahir Dar. Ten kilograms of chrome shaving collected (Table 1).

Evaluation of the results of determination of the concentrations of sixteen representatives of PAHs according to US EPA on dust particles PM_{10} taken from Hermanice dump. Prior to the analysis of PAHs on PM_{10} particles, the composition of the mineral phases of the collected dust particle samples was determined. A pyrite content of 0.9% was detected among the detected minerals, which at such a low content is oxidized in the burning material to form iron hydroxides or thermally degraded, and indicates the susceptibility of the deposited material to self-ignition.

Parameters	Methods	Chrome shavings
PH	BS EN ISO,1668:2011	4.4
Moisture content (%)	SLC-201	42.45
Collagen content (%)	IUC-22	80.43
Chrome oxide (%)	BS EN ISO,7396-5:2011	3.72
Fat (%)	BS EN ISO,5896:2008	1.32

Table 1: Characteristics of the chrome shavings

Dechroming step: To increase the surface area grinding of the material was applied without affecting the molecular structure of collagen fibers in order to achieve maximum elimination of chromium from the sample. For optimizing the Dechroming process four samples of Chrome shavings (CS) each of (CS-20 g/100ml) were taken and placed in sodium sulphate (10% w/w), (20%w/w), (30%w/w) and (40%w/w), respectively. To increase the washing effect sodium carbonate (8%w/w) (16%w/w), (24%w/w) and (32%w/w) solution were added and soaked for 30 minutes. And then solutions of (6%w/w), (12%w/w), (18%w/w) and (24%w/w) weight of calcium hydroxide were added for each samples sequentially and stirred for 1 hour. Sodium hydroxide solution (0.1% v/v), (0.2% v/v), (0.3% v/v) and (0.4% v/v) was then added to increase the hydrolysis effect (Table 2).

Time (hr)	Sample 1 (chrome shaving Cr_20_3 %)	Dechroming rate %	Sample 2 (chrome shaving Cr_20_3 %)	Dechroming rate %	Sample 3 (chrome shaving Cr_20_3 %)	Dechroming rate %	Sample 4 (chrome shaving Cr_20_3 %)	Dechroming rate %
0	3.67		3.67		3.67		3.67	
0.5	3.51	4.35	3.49	4.90	2.65	27.79	2.06	43.86
1	3.35	8.71	3.43	6.53	2.44	33.51	1.90	48.22
2	3.01	17.98	3.15	14.16	2.21	39.78	1.73	52.86
3	2.91	20.70	2.49	32.15	1.54	58.03	1.57	57.22
4	2.73	25.61	2.28	37.87	1.41	61.58	1.42	61.30
5	2.46	32.97	2.07	43.59	1.25	65.94	1.22	66.75
6	2.14	41.68	1.53	58.31	1.07	70.84	1.01	72.47
7	1.40	61.85	1.34	63.48	0.53	85.55	0.45	87.73
8	1.21	67.02	1.09	70.29	0.42	88.55	0.31	91.55
24	1.04	71.66	0.52	85.83	0.35	90.46	0.28	92.37
48	0.46	87.46	0.39	89.37	0.29	92.09	0.19	94.82

Table 2: Effect of oxidation time on chrome shaving

The oxidation effect was examined for about (0.5, 1, 2, 3, 4, 5, 6, 7, 8, 24 and 48 hours) of treatment time as it is presented in Table 3 and the water part is detached by filtration. The solutions were also washed three times with sodium sulphate solution and then filtered. The filtered materials were soaked with sodium chloride solution for sample 1(12% w/v), sample 2(18%w/v), sample 3(24%w/v) and sample 4 (30%w/v) and Again the materials were washed sulphuric acid solution (2, 4, 6 and 8%v/v) for acid steeping for 1 hour and the filtered respectively.`

Water (ml)	300			600		
Temperature (°C)	60-70	70-85	85-90	60-70	70-85	85-90
Time (hr)	2	2	2	2	2	2
Extract	I	II	III	IV	V	VI

Table 3: Operating conditions

Next to these activities, the solutions were washed twice with same concentrations of sodium sulphate and sodium chloride solutions and then filtered using muslin cloth. The chromium content (calculated as Cr_2O_3) in, shavings splits and various liquor from the dechroming steps were found by ICP-OES with Dechroming rate (%) = $[Cr_{shav}-Cr_{dech}] / [Cr_{shav}]*100$ and the result is listed below in Table 3. The dechromed materials fiber orientation were investigated using SEM (Digital Microscope VHX-6000 Series) and elemental analysis with EDXA systems. Dechromed shavings (DCS) found from the above tests were suspended in 300ml and 600 ml water with 3% MgO (w/v), 3% $NaHCO_3$ (w/v) to rise the alkalinity to pH 8-9. Alkaline water and dechromed shavings, were fallen at the following investigational conditions. In general, 3-5 extractions are attained in the temperature range 55-95 °C. DCS were investigated by changing three parameters namely temperature, time, and water to materials mass ratio. Liquid protein and an insoluble residue of dechromed shaving were achieved using the above methods and by filtration the water-soluble protein (gelatin) obtained and then concentrated and dried at 105 °C which resulted in a gelatin powder product.

Collagen content and hydroxyproline were determined by using UV-Visible spectrophotometric analysis. The sample was moved into a 250 ml round bottom flask and placed in a heating mantle at 110 °C for 24 hours with 6N HCl for amino acid analysis and was run through an amino acid analyzer.

Scanning Electron Microscopy (SEM): The SEM was employed to study the dechromed materials fiber orientation and the results attained were related against an untanned materials (control).

Thermal treatment for isolation of gelatin: To increase the alkalinity to pH 8-9 the dechromed shavings (DCS) found from the above experimentations were suspended with 3% $NaHCO_3$ (w/v) and 3% MgO (w/v), in 600 and 300 ml water. Alkaline water and dechromed shavings were tumbled at the following experimental conditions. Overall, 3-5 extractions are attained in the temperature range 55-95 °C [3,11]. DCS were investigated by changing three parameters namely temperature, water to materials mass ratio and time.

The extract obtained by the use of above methods described contains an insoluble residue and liquid protein of dechromed shaving. By filtration the water-soluble protein (gelatin) was attained, concentrated, and dried at 105 °C which resulted in a gelatin powder product.

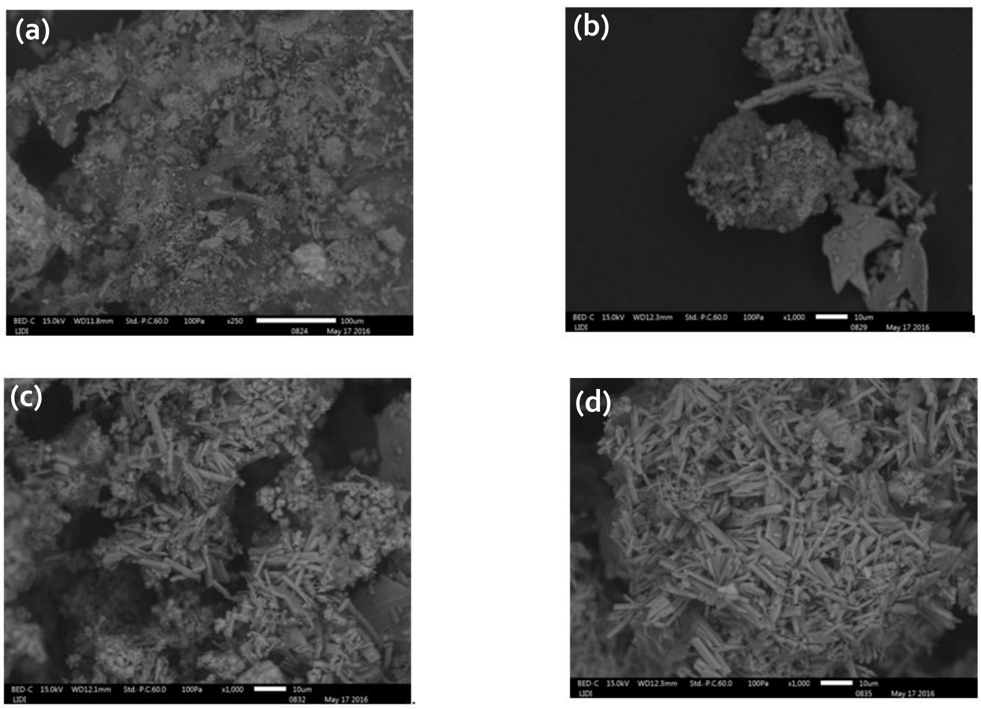
Protein and amino acid analyses: Collagen and hydroxyproline content were determined by using Ultra violet Visible (UV-Vis) spectrophotometric analysis. The sample was transferred into a 250 ml round bottom flask and placed in a heating mantle at 110 °C for 24 hours with 6N HCl for amino acid analysis. The solution was run through an amino acid analyzer (Schimadzu, Japan)

Results and Discussion

During the study it was learnt that the factory studied is facing environmental degradation and public health risk due to uncollected disposal of waste on the boundary of the company streets and burial areas, drainage congestions by indiscriminately dumped waste and contamination of water resources near uncontrolled dumping sites.

In the dechroming step before oxidation one must first treat the tanned leathers with alkali (pH range from 6 to 8) so that the alkali may reach the deepest layers of the leather, creating a sufficient concentration and potentiality of (OH-) between the fibers.

Scanning Electron Microscopy (SEM) images confirm the fiber structure with limited disorientation. There is a decrease of chromium content within the fiber structure; at the end of dechroming it is likely to be untanned hide powder (Figure 1). EDXA is used to confirm qualitatively the decreasing chromium content in the fiber structure. The SEM photos also show that the limited disorientation of the fiber structure and implying there is a reduction in chromium amount in the fiber which is similar to previous study reported somewhere else [3].



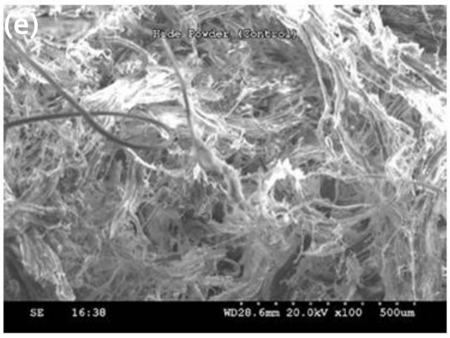


Figure 1: Dechromed powder sample 1, sample 2, sample 3 and sample 4, and control respectively (a, b, c, d, e)

Table 4 shows the total chromium content in the dechromed powder where SPL1: SPL2: SPL3 and SPL4 represent Sample 1, Sample 2, Sample 3, and Sample 4 respectively.

Type of test	Unit	Test methods	Lab design. Code, customer code			
			C-8073,SPL1	C-8074,SPL2	C-8075,SPL3	C-8076,SPL4
Total chromium(as Cr)	mg/kg	ISO 17072-2-2011	80.6	66.4	26.8	5.4

Table 4: Total chromium content in the dechromed powder

Extraction of protein concentrate is carried out by thermal treatment as per operating condition mentioned above (Table 3).

The gelatin solution was increased as the extraction temperature increased (Table 5).

Extract	Water (ml)	Temp. (°C)	Time (hr)	Sample 1	Sample 2	Sample 3	Sample 4
				Gel sol (w/w %)	Gel sol (w/w %)	Gel sol (w/w %)	Gel sol (w/w %)
DSC1	300	60-70	**3**	33	35	38	40
DSC2	300	70-85	**3**	38	43	41	45
DSC3	300	85-95	**3**	45	48	48	53
DSC4	600	60-70	3	29	30	35	40
DSC5	600	70-85	3	40	42	46	50
DSC6	600	85-95	3	47	50	53	57

DSC: Dechromed shaving, Gel sol: Gelatin solution

Table 5: Gelatin Extraction in dechromed shavings

The protein concentrate was analyzed for amino acid and compared with the soybean and wheat (Table 6).

Amino Acids	Isolated Protein Concentrate (%)	Soya bean Meal (%)	Wheat (%)
Threonine	2.98	1.8	0.36
Glycine	12.04	2.0	0.52
Hydroxyproline	11.12	2.3	1.3
Serine	5.13	2.4	0.59
Leucine	1.16	3.6	0.85
Tyrosine	2.18	3.9	1.00
Isoleucine	4.60	2.0	0.41
Histidine	1.91	1.2	0.32
Lysine	2.41	2.8	0.34
Arginine	7.53	3.3	0.59
Alanine	1.85	2.0	0.45
Valine	0.92	2.1	0.53
Methionine	2.71	0.64	0.20

Table 6: Essential Amino Acid (% or dry substance) in different commercially feed products with extracted protein concentrate

Conclusion

This study demonstrates that high crude protein content of the leather residues shows that they can be employed as a protein addition in animal feed. A rise in the use of possible feed elements by processing industries will create to the growth of new feed. And the optimum dechroming rate of 94.82% is achieved after 48-hour oxidation time and by controlling the dechroming step a low level of chrome that could satisfy the requirements for poultry feed was achieved.

Tannery solid waste is however a potentially very vital source of protein once dechromed. Dechroming rate is 94.82% in the sample four after forty-eight hour of oxidation time. Dechroming can be controlled to produce a final product with a low level of chromium and satisfies the requirement for poultry feed. The total chromium content in the dechromed powder is 5.4 mg/kg and satisfactory for the poultry feed requirement. The Essential amino acids concentration in isolated protein is greater than the usual poultry feeds of soybean and wheats. The chemicals used in this vital process do not impinge of the final quality of the product. The sample four dechromed powder gave 57% w/w gelatin solution in the 85-95 °C temperature range.

Recommendation

This study shows how a waste can be changed to a valuable product by adopting a sustainable approach. Further research would needs to be undertaken into these by-products with the aim of establishing their value for a wide range of animal feed.

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