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Towards chrome free chicken – A pilot scale study to remove chromium from leather waste, a source for poultry feed manufacture

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ABSTRACT

Although the leather industry is environmentally important as user of byproduct of the meat industry, it is perceived as a consumer of resources and a producer of pollutants. Only 20% of the raw material waste is converted to leather. There are more than 900 tanneries operating in the 5 districts of Tamilnadu, of which 584 are in Vellore District. The wastes produced from these industries have caused irreversible damage to the surrounding environment. The resultant waste produced in bulk every single day at the tanneries is seen fit to be used as poultry feed for the benefit of both the poultry farmers and tannery operators. It helps the former to buy cheap feed and the latter make money for a product causing disposal problem. A Sinister collusion between tanneries and poultry farmers is posing glare danger to the health and lives of millions of unsuspecting chicken lovers. There were three important by products obtained during the process. The protein, Gelable protein and chromium. Hence by this process it is possible to recover maximum amount of all the value added products thus reusing the product once considered as a waste. Hence from the results it is evident that the hydrolysis of the leather wastes under suitable conditions and in the presence of better hydrolyzing agents can help us in recovering the value added products from the material otherwise considered as a waste.

KEYWORDS

Leather shavings;
Poultry feed;
Enzymatic hydrolysis;
Value added products.

INTRODUCTION

The leather industry is very important, as it is the fourth most export carrying in India. But these industries in India are one of the most seriously affecting pollution sources. The total installed capacity of skins and hides in India has been assessed to be 53.5 million more than 973 tonnes/year of chromium is discharged from the nearly 131 tanneries of Ranipet Industrial area, Tamil Nadu. It cannot be removed by simple methods. (Ranipet, India 5th Most Polluted Town In The World – Blacksmith Institute, US).

A potential consequence of chromium intakes above 200 mg/day is displacement of iron from transferrin. At high levels chromium may compete with iron for transferrin binding and deplete iron levels (Feed international, 1993; WHO, 1988). It is known that only 20% of wet salted hides/skins are converted into commercial leather, while 25% becomes chromium-containing leather waste, and the remainder becomes non-tanned waste or is lost in wastewater as fat, soluble protein and solid suspended pollutants[1].

Pretanned leather shavings, a by-product of the leather tanning industry, are primarily beef skin, which is composed of fibrous proteins such as collagen, elastin, and keratin. Currently, one of the major uses of fiberized leather is in the production of leather board. This product is used primarily in the shoe manufacturing industry as insoles, outsoles, and middle soles. It is also used in the manufacture of leather products such as counters, belts, purses, and wallets.

Collagen can be incorporated in coating materials, in pharmaceutical applications, as an absorbant material for filtering sulphur dioxide and other air pollutants. Protein hydrolysates can be applied in the manufacture of cosmetics. They can also revert to the leather industry, being incorporated at the pretanning stage and contributing to the subsequent better uptake of tanning materials.

Most of these solid wastes apart from dusted salt have secondary uses in the local market; for example, glue manufacturers and poultry feed makers often use this waste (and peptides for use in feeds and fertilizers[2,3,8,11]. However, an important problem with this use is the presence of chromium. The use of chrome-containing solid wastes for poultry feed preparation could cause serious health problems for poultry consumers. Toxic poultry feed a pressing public health concern Poultry feed is being produced through using tannery wastes without necessary treatment and sterilization.

The problem stems primarily from the fact that poultry feed producers are not always using the scientific methods and not going by the health and hygiene standards. Poultry is a fast growing sector, which contributes significantly to the economy. However, the latest finding shows that things are not being handled the way they ought to be in this area.

But acid rain, common across the industrial world, can leach harmless chromium from shavings into ground water and transform it into deadly chromium that causes liver and bladder cancer. An otherwise useful material, the leather waste can be used for the preparation of protein, gelatin and chromium after alkaline hydrolysis with mixture of alkalies and alkaline protease enzyme.

MATERIALS AND METHODS

Analysis of chrome-containing leather waste obtained from a commercial cowshide tannery were kept at room temperature and analyzed for pH, moisture, ash, Total Kjeldahl Nitrogen (TKN), chromium and fat by normal methods. 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[10]. TKN was determined by the semi-micro Kjeldahl method[5]. Total chromium was determined using a Perkin-Elmer model AA7003 atomic absorption spectrophotometer[5]. Fat was extracted with chloroform and estimated[4].

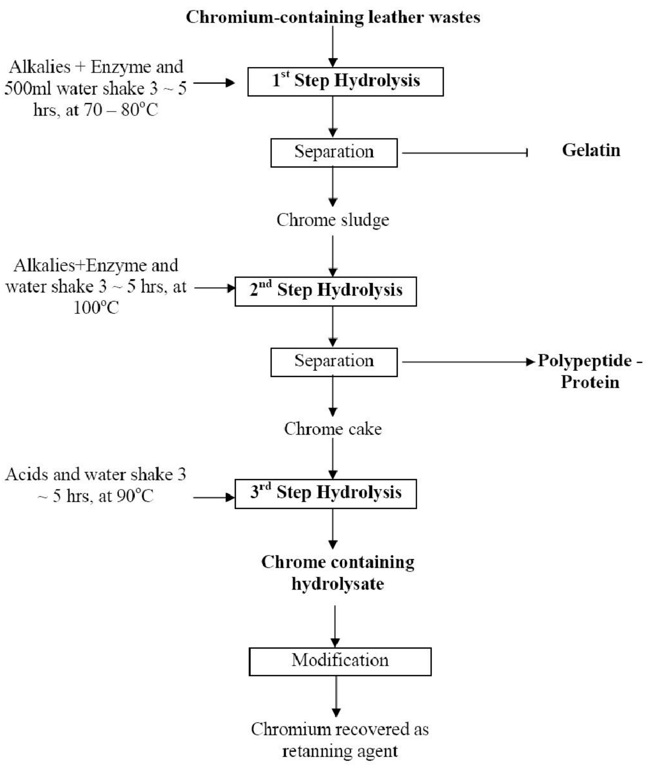
Mixed alkaline hydrolysis of the leather shavings

One hundred grams of leather shavings were shaken in 1 litre of water, and added 20ml each of 5%MgO, 3% NaOH+2% MgO and 3% NaOH 3% MgO at 98°C for 60minutes, 120 minutes, 180minutes, 240 minutes, 300minutes and 360 minutes respectively as described by Taylor et al.[9], without and with the 5 g enzyme alkaline protease, prepared from *Bacillus subtillus* (From The Microbiology department of D.K.M. College, Vellore). Then the samples were filtered warm through Buchner porcelain funnels with Whatman No. 1 filter paper under vacuum condition.

The filtered protein solutions were stored at 4°C, and the protein yield was calculated based on the dry weight of the waste. The remaining chrome sludge was kept at room temperature for further analysis and treatment.

For the separation of various byproducts along with the chromium were completely extracted by following the procedure of Cabeza et al.[6]. Initially 100grams of the chrome shavings was heated with 500ml of water with different proportions of alkalies and heated at 80°C for three hours.

The two fractions were separated and the gelatin fraction was recovered. The chrome sludge was again heated for four hours at 98oC. The fractions were again separated when the protein fraction was obtained. It was dried and recovered. The chrome cake was further hydrolysed with 70% hydrochloric acid. The hydrolysate was then analysed for total chromium using atomic absorption spectroscopy (Varian AAA 220FS).



RESULTS AND DISCUSSION

Increased environmental restrictions and escalating landfill costs have encouraged the leather industry to develop cleaner technology by minimizing wastes generated and maximizing those reused. The leather waste mainly consists of collagen and Cr(III) complexes, which could be treated to give the potential resources of collagen protein and chromium[7]. In past decades, leather researchers have made a lot of effort to study the reuse of leather waste. Before 1970 reports dominantly focused on uses not requiring extensive pretreatment of the tanned wastes, including the manufacture of insulators, building materials, fibrous sheets and shoe soles.

TABLE 1 and Figure 1 show that the leather waste contains an alarmingly high level of total chromium (105 mg/Kg) which when converted to poultry feed is reduced to 50mg/Kg, which may be due to the mixing of corn flour and other ingredients in the feed. Whereas the concentration of chromium seems to be very high both in chicken flesh and liver (such as 40mg/Kg and 103mg/Kg respectively). The bioconcentration of the highly toxic heavy metal in the highly protenious food chicken is really worth taking serious steps. Hence in the present work effort has been made to recover chromium and other different by products of leather waste in a cost effective manner by combining normal alkaline hydrolysis and using enzymes separated from natural microorganisms.

TABLE 1 : Estimation of chromium in various samples

S.No.	Sample	Cr (mg/kg)
1.	Leather waste	105
2.	Poultry feed	50
3.	Chicken - liver	103
4.	Chicken – whole body	40

Values in the table are mean of six individual analysis

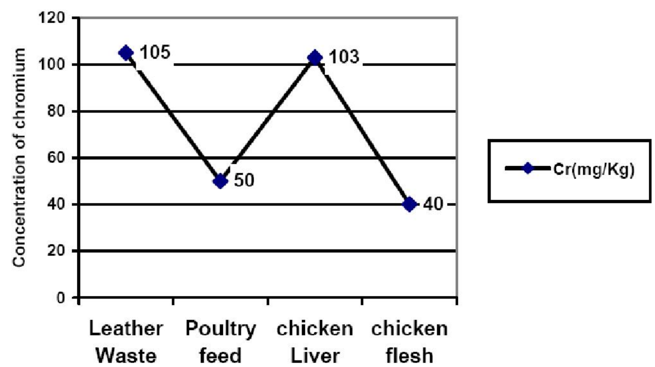


Figure 1 : Estimation of chromium in various samples

TABLE 2 : Analysis of leather waste

Parameters	% of various factors
pH	4.5
Ash %	11.2
Protein %	84
Fat %	0.19
Ca %	0.34
Mg %	0.33
Cr %	17.21
TKN %	16.54

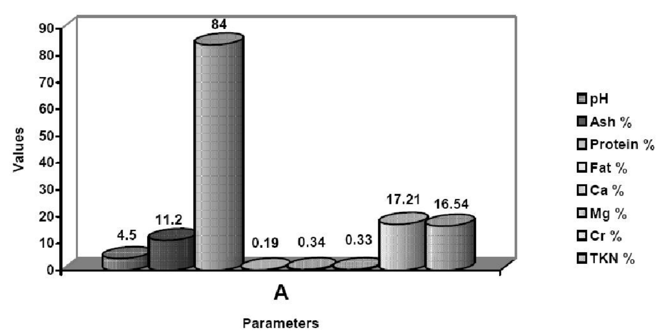


Figure 2 : Analysis of leather waste

TABLE 2 and Figure 2 show the % composition of the various components present in the leather waste collected from Ranipet Industrial area. The major portion of the leather is comprised of protein in the fibrous form as collagen. When this is left into the atmosphere without proper usage they become a pollution problem in the form of dumped land filling, seepage of fat and chromium into the underground water and soil causing damage to the environment.

Hence this work is carried out so that zero waste discharge is made into the environment. Because in this three step process initially gelable protein in the form of gelatin, protein which can be used as a nitrogen source in the form of fertilizer and feed, and the chromium is finally recovered, which can be further used as a retanning agent.

TABLE 3 : Analysis of the products obtained by the alkaline hydrolysis of leather waste

Parameters (%)	A	A+E	B	B+E	C	C+E
Ash	14.32	11.4	14.40	11.55	14.95	11.99
Proteins	67	71	69	74	85	87
Ca	0.34	0.35	0.40	0.82	0.48	1.18
Mg	0.33	4.03	0.08	5.0	0.16	6.73
Cr	4.21	7.76	4.28	11.44	3.99	11.82
N	7.41	14.54	8.40	14.56	8.09	14.13
Fat	0.09	1.37	1.51	3.31	1.79	4.94

A: 3%NaOH and 5% MgO; B: 3% NaOH 5% CaO; C: 3% NaOH +3% MgO+3%CaO; E: Enzyme alkaline protease

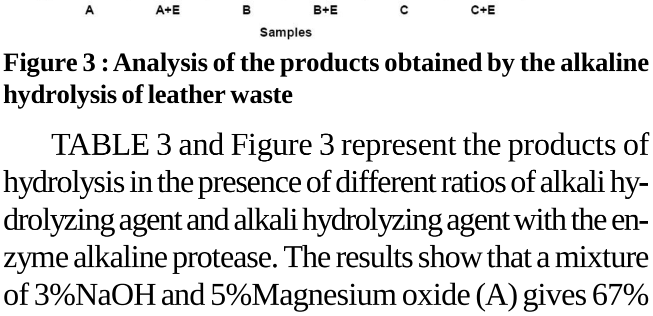


Figure 3 : Analysis of the products obtained by the alkaline hydrolysis of leather waste

TABLE 3 and Figure 3 represent the products of hydrolysis in the presence of different ratios of alkali hydrolyzing agent and alkali hydrolyzing agent with the enzyme alkaline protease. The results show that a mixture of 3%NaOH and 5%Magnesium oxide (A) gives 67% of protein, 4.21% of chromium. Similar experiment with 3%sodium hydroxide and 5% Calcium oxide mixture (B) gives 69% protein and 4.28% of chromium showing that there is better recovery of different products.

At the same time, the hydrolyzing agents A and B show not much difference in their hydrolyzing efficiencies. Whereas C shows a higher percentage of recovery of different products including total chromium (8.99). But when the same hydrolysis was conducted with alkali in the presence of enzyme all the results were improved. There were three important by products obtained during the process. The protein, Gelable protein and chromium. Hence by this process it is possible to recover maximum amount of all the value added products thus reusing the product once considered as a waste.

A Sinister collusion between tanneries and poultry farmers is posing glare danger to the health and lives of millions of unsuspecting chicken lovers. During the production of chrome–tanned leather, chromium is assumed to be incorporated into the leather with at least 3 types of interactions. Most important is the chromium that is complexed with collagen to give leather its characteristic properties. Other interactions would include nonproductive binding of chrome to collagen and adsorption of chromium by the collagen matrix.

One area of considerate interest is the use of enzymes to liberate a protein rich product and chromium from Cr-containing wastes. There has been significant interest in the use of these protein rich solutions as fertilizers, detergents and animal feed. The "precautionary principle" in the context of the municipal law means - where there are threats of serious and irreversible damage, lack of scientific certainty should not be used as a reason for postponing measure to prevent environmental degradation.

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