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6024 Telegraph Road
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ENZYMIC TREATMENT OF CHROMIUM WASTE GENERATED IN THE LEATHER INDUSTRY

Abstract

In the United States, almost 56,000 metric tons of chromium-containing solid waste is generated by the leather industry each year, and approximately ten times this amount is generated world-wide. Continued disposal of this waste product is becoming a serious concern, for landfills are reluctant to accept this solid waste even though the chromium in it exists in the non-toxic +3 oxidation state. This presentation will describe a method in which the chromium-containing waste is treated with a proteolytic enzyme at moderate temperatures and for a short period of time to achieve separation of the chromium from the soluble hydrolyzed protein as a recoverable solid. The isolated chromium can be chemically treated and recycled into the tanning process. The protein hydrolyzate solution, practically devoid of chromium, could be used as a fertilizer, animal feed, or simply treated as sanitary sewage.

Introduction

During the processing of hides and skins to leather, a solid by-product known as chrome shavings is generated. Although this waste product has been acceptable for landfills, there is growing concern that chromium in these shavings could possibly be converted to a toxic state. Landfills are therefore becoming increasingly reluctant to accept this waste. Researchers at ERRC developed a process that can help the tanning industry in solving this potentially difficult waste disposal problem. In this process, the chrome shavings are treated with alkaline proteolytic enzymes at moderate temperatures for a short period of time. The process is unique because the pH at which the reaction takes place (8.3 to 10.5) prevents the chromium from going into solution, thus averting the poisoning of the enzyme by the chromium and enabling the recovery of chromium as $\text{Cr}(\text{OH})_3$ by filtration. The resulting protein solution may have commercial use as a feed or a fertilizer or could be discarded as sanitary sewage. The isolated chromium cake has the potential to be recycled into the tanning process by treatment with sulfuric acid. The tanning industry has begun collaborative efforts with ERRC to assess the process on a commercial scale.

It has been documented in the literature (1-12) that chromium-containing waste can be treated enzymically. The waste has to be pretreated to denature the collagen. The methods developed at this laboratory demonstrated that the collagen may be denatured in the presence of alkali at moderate temperatures, and thus the direct addition of the enzyme to shavings already subjected to moderate pretreatment temperatures may be made. Maintenance of these temperatures throughout the entire digestion process eliminates the need to cool the reaction mixture.

In preliminary investigations using calcium hydroxide to control the pH (9-12), we achieved 78% solubilization of the shavings when we used 6% (based on wet weight of shavings) of an alkaline proteolytic enzyme for hydrolysis. It has been documented in the literature that shavings can be treated at 300 °C and at 150 atm. in the presence of magnesium oxide for the purpose of chromium recovery (13), or hydrolyzed at 100 °C with sodium hydroxide, when magnesium oxide or calcium oxide are present (14). Precipitation of the chromium, in an industrial recycling system, can be carried out using magnesium oxide as well as other alkaline agents (such as sodium hydroxide). In our experiments using magnesium oxide in conjunction with these other alkaline agents (15-16) at more moderate temperatures, we achieved higher solubilization of protein with lower amounts of enzyme than previously reported, thus making the treatment more cost-effective.

Experimental

Materials

Chromium-containing leather waste was obtained from commercial tanneries. Sample A shavings came from a conventional chrome tannage. Sample B shavings came from a tannage in which a high exhaust chrome treatment had been used in order to reduce the chromium in the effluent. Sample C shavings came from a tannage in which the final pH was more acidic (pH 3.6) than other chrome offal investigated (pH 3.8-4.2).

Alcalase[®] (alkaline protease) was obtained from Novo Nordisk Bioindustrials, Inc. (Danbury, CT). It is a proteolytic enzyme with optimal activity at pH 8.3-9.0 and 55-65 °C. It is supplied both as a granular solid (adsorbed onto an inert carrier) - standardized to contain 2.0 AU/g (Anson Units/g), and as a liquid standardized to contain 2.5 AU/g.

Procedure

Eleven kg (25 pounds) of each of the shavings samples (A, B & C) were pretreated at 67-69 °C for two hours. Bench type experiments determined the best pretreatment for each individual sample prior to the pilot scale runs. Thus, Sample A was pretreated with 5% magnesium oxide (all percentages are based on the wet weight of the shavings), and Sample B with 3% NaOH and 2% magnesium oxide. After several preliminary bench experiments, it was found that Sample C needed to be treated with 6% magnesium oxide. Because of its acidity, another portion of this sample was pretreated with 3% NaOH and 3% magnesium oxide. Three percent Alcalase[®] was added in three feeds to each of the four reactions, over a three hour period. Upon completion of the digestion, the sample was pumped from the reaction vessel and allowed to settle overnight. The protein hydrolyzate layer was decanted and the settled chromium layer was filtered through Whatman #1 filter paper. An aliquot of each protein layer was stored at 4 °C. The unwashed chrome cake was collected and it, too, was stored at 4 °C.

Results and Discussion

Preliminary experiments on the enzymic treatment of chrome shavings used calcium hydroxide for pH adjustment. In these experiments, the initial pH of the reaction, or the holding pH, was about 10.5. As the enzymic reaction proceeded, the pH fell to about 8.3. These reactions were carried out at temperatures that ranged from 55 to 75 °C, with optimal reaction temperature at about 60-63 °C. Under these reaction conditions, 6% enzyme was needed to achieve the highest solubility (defined as the hydrolysis of the denatured collagen away from the insoluble chromium hydroxide), about 78%.

We felt that the solubility could be improved and at the same time the amount of enzyme could be reduced. Magnesium oxide is similar in its chemistry to calcium oxide and calcium hydroxide. It has a very low solubility in water at 25 °C, but differs from calcium oxide in that the solubility increases slightly with an increase in temperature. The main objective was to make the treatment more cost effective by reducing the amount of enzyme needed, at the same time retaining or improving the efficiency of the reaction. In the experiments in which we used 5-6% magnesium oxide, we achieved 80% solubility when only 1% enzyme was used. Sodium hydroxide, one of several chemicals that are used to recover chromium when chromium recycling is used in the tannery, was found to be effective in improving the efficiency of the enzymic reaction when used in conjunction with magnesium oxide.

Not all chromium-containing leather waste is the same. Tanneries use different types of processes to tan

the leather. These differences are introduced not only to affect the properties of the tanned leather, but also, in some cases, to allow high chrome exhaustion for the purpose of reducing the chromium load in the effluent. We had to adjust the protocol for the preliminary pretreatment of these shavings to achieve optimal solubility. The commercial value of this process depends not only on the savings from decreased landfill fees, but also on the value of the reaction products. Thus, it is important to know the chemical composition of the isolated chrome cakes and the protein hydrolyzate.

The chrome shavings from each of the tanneries were analyzed for moisture, ash, chromium, nitrogen, fat, calcium, and magnesium (Table 1). The chemical composition of the recovered chrome cakes from each treatment is shown in Table 2. The fat contents reflect the amount of fat found in the shavings originally. The fat content in Sample B may also reflect the compounds that had been used in the high exhaust chrome treatment. These cakes were not washed during filtration; the nitrogen content reflects the hydrolyzed protein that remains and is dependent on the efficiency of the filtration process. The chromic oxide content reflects the amount of chrome in the original shavings as well as the presence of other salts in the cakes. The magnesium contents reflect the amount of magnesium used in the pretreatments. The value for calcium found in the cakes may reflect the approximately 1% calcium impurity in the magnesium oxide.

In preparation for chrome recycling, repeated washing of the cakes decreased the nitrogen content to about 2 to 2.3%. Vacuum filtration on an industrial scale might reduce the nitrogen content even further.

We subjected the isolated protein hydrolyzate to analyses for chromium, Total Kjeldahl Nitrogen (TKN), total solids and ash (Table 3). Data for samples A, B, C1 and C2 show that the chromium content is less than 1 ppm. The TKN averages about 11000 ppm and the total solids is 72000 ppm, with a total ash of about 8000 ppm.

The hydrolyzate was freeze dried and the dried sample was analyzed for TKN, ash, amino acid profile and molecular weight distribution. The nitrogen content of the dried protein ranges from 13.8% to 15.0% and the ash content ranges from 9.7 to 18.9% (Table 3). This ash content not only reflects the pretreatment but also the ash content of the original shaving samples. Amino acid profiles of the protein hydrolyzates are quite similar to those of collagen.

At present, we are performing experiments to further clarify the enzymic reactions. We are interested in the effect of time, temperature, and enzyme concentration on the molecular weight distribution of the products of protein hydrolysis. Preliminary treatments on other types of solid chrome-containing tannery waste—trimmings of blue stock and even of finished leather—have been carried out successfully; this is an area in which there might be some interest.

CONCLUSION

Various alkalinity-inducing agents can be used to maintain pH in a range suitable for enzymic hydrolysis of chrome shavings. We have shown that magnesium oxide, alone or in combination with sodium hydroxide and other alkaline agents, will increase the efficiency of the solubilization of and—at the same time—substantially reduce the amount of enzyme needed, thus making the treatment more cost effective. Selection from these various alkalinity-inducing agents will enable each tannery to tailor the process to conform to its particular procedure for recycling soluble chrome from its waste streams. We have shown that chromium-containing leather waste from a variety of sources can be enzymically treated following an appropriate pretreatment step. The chemical composition of the isolated products will depend on the type of treatment and on the composition of the original chromium-containing leather waste product. These findings are the subject of a patent (10).

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TABLE 1
ANALYSES OF CHROME SHAVINGS

Parameter% ^a	A	B	C
Moisture	53.51	53.47	51.47
Ash ^b	14.32	8.40	14.95
Chromium ^c	4.21	4.28	3.99
TKN ^b	14.54	14.56	14.13
Fat ^b	0.09	1.51	1.79
Calcium ^b	0.34	0.40	0.48
Magnesium ^b	0.33	0.08	0.16

^a N = 3.

^b Moisture free basis.

^c Expressed as Chromic Oxide (MFB).

TABLE 2
ANALYSES OF CHROME CAKES

Parameter% ^a	A	B	C1	C2
Moisture	85.42	85.54	82.93	82.53
Ash ^b	35.45	32.55	34.14	36.99
Chromium ^c	7.76	11.82	8.74	11.44
TKN ^b	7.51	8.40	6.66	8.09
Fat ^b	1.37	6.31	4.26	4.93
Calcium ^b	0.35	0.82	0.75	1.18
Magnesium ^b	9.96	5.00	9.47	6.73

^a N = 3.

^b Moisture free basis.

^c Expressed as Chromic Oxide (MFB).

TABLE 3
ANALYSES OF PROTEIN HYDROLYZATES

Solubilization with		
1% Enzyme	(%)	80
Protein Hydrolyzate (Liquid) ^a		
Chromium	(AV)	< 1
TKN	(AV)	11000
Total Solids	(AV)	72000
Total Ash	(AV)	8000
Protein Hydrolyzate (Dried) ^b		
TKN		13.8-15.0
Ash		9.7-18.9

^a Expressed in PPM.

^b Expressed as percent.