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ISOLATION & CHARACTERIZATION OF VALUE-ADDED BY-PRODUCTS

from Chromium-Containing Leather Waste

In the United States, over 50,000 metric tons of chromium-containing solid waste, produced from tanning of hides and skins, is generated by the leather industry each year, and approximately 10 times this amount is generated worldwide. Continued disposal of this waste product is becoming a serious concern, for landfills are increasingly reluctant to accept this solid waste even though the chromium in this waste exists in the non-toxic +3 oxidation state.

Chromium-containing leather waste may be treated or modified by a variety of methods to make value-added by-products[1].Alkaline hydrolysis has been one of the most investigated procedures for the purpose of chrome recovery and isolation of a protein fraction. Studies have been done using sodium hydroxide with pressure, and sodium carbonate, sodium hydroxide and calcium hydroxide combinations.

Several investigators have hydrolyzed the products with sulfuric acid, hydrochloric acid and organic acids. Others have carried out hydrolysis with acrylic and methacrylic acids and the resulting hydrolysate was copolymerized with vinyl monomers to give fillers for leathers.

The hydrolysates from these reactions have been used to make ampholytic detergents, fodder, surfactant production, glues, fertilizer, coagulants for natural rubber and leveling agents for leather dyeing. They have been used as a protein binder for controlling flowability and setting of gypsum and phosphogypsum. From acid hydrolysis, amino acids were recovered for food supplements, for retanning and filling of leather, and also to make fatliquors and as germination stimulants. They have been treated with methylolamines for fixation of acid chrome dyes for leather. It has been suggested that the hydrolysates could be used for the stiffening of corrugated paperboard.

Chromium has been recovered by wet air oxidation, peroxide treatments and incinerations at a variety of temperatures. Chromium in the toxic +6 oxidation state would be generated in these reactions and a reduction step would be needed.

Reaction of the chromium-containing waste product with monomers and polymers has been carried out by a number of investigators. The leather scraps have been reacted with polyisocyanates to make insulators and building materials. The substrate has been grafted with methylmethacrylate and with hydrophilic acrylates. It has been polymerized to make molded products fillers for leather, leather substitutes, formed into sheets to make insoles and to make polymer blends.

The recovered chrome may also be used in contents and mortars. The waste product has been autoclaved and used as feed, in the manufacture of composite sheets, and for the wetting, refining and cleaning of fur products. Leather substitutes have been made by a papermaking method and have also been used in paper substitutes. Applications have been described for use as a component in elastomer mixtures. Several researchers have detanned the chrome product for the purpose of gelatin preparation and others have been able to isolate collagen and collagen fibers.

There have been relatively few references to the enzymic treatment of the solid waste. In the described methods, either the waste is pretreated at 90°C or higher to denature the collagen, or enzymes that have activity at a neutral or acid pH are used with subsequent solubility of the chromium. The methods developed at this laboratory demonstrated that the collagen may be denatured in the presence of alkali at moderate pretreatment temperatures may be made[2]. Maintenance of these temperatures throughout the entire digestion process eliminates the need to cool the reaction mixture. 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 chromium and enabling the recovery of chromium as $CR(OH)_3$ by filtration.

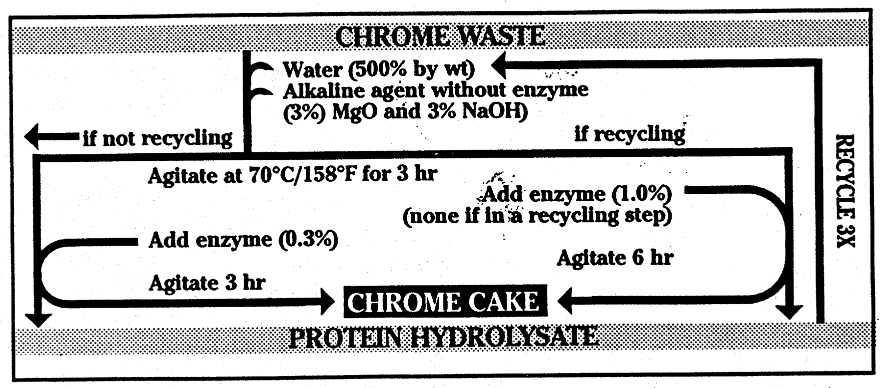
In our preliminary investigations using calcium hydroxide to control the pH, 78% solubilization of the shavings was achieved when 6% (based on wet weight of shavings) of an alkaline proteolytic enzyme was used for hydrolysis. When magnesium oxide was used in conjunction with other alkaline agents, higher solubilization of protein was achieved with lower amounts of enzyme than previously reported, thus making the treatment more cost-effective. In the experiments in which 5–6% magnesium oxide was used, 80% solubility was achieved 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 reaction when used in conjunction with magnesium oxide. As shown in Figure 1, by increasing the pretreatment parameters, we are able to use even less enzyme, and possibly can recycle the enzyme several times.

We demonstrated that tanned full splits and trimmings could be enzymically hydrolyzed. In this treatment, the alkali pretreatment time was extended to three hours and the temperature was increased to 70–72°C. The structure of the hides was so totally disrupted that upon addition of the enzyme, the samples were digested. We decided to apply this extended holding time and higher temperature to chrome shavings and giving a recyclable chromium product. Thus, the amount of enzyme that was suggested previously had been reduced considerably.

We investigated the recycling of the protein solution containing the enzyme. The enzyme did not denature after being subjected to the high temperatures and pHs, and we found that we could successfully recycle the protein solution and enzyme, not once, but four times. Eventually, the inorganic concentration became quite high, and the enzyme lost its activity. It is possible that the activity is inhibited by the inorganic compounds. An initial 1% concentration of the enzyme is recommended if one is recycling.

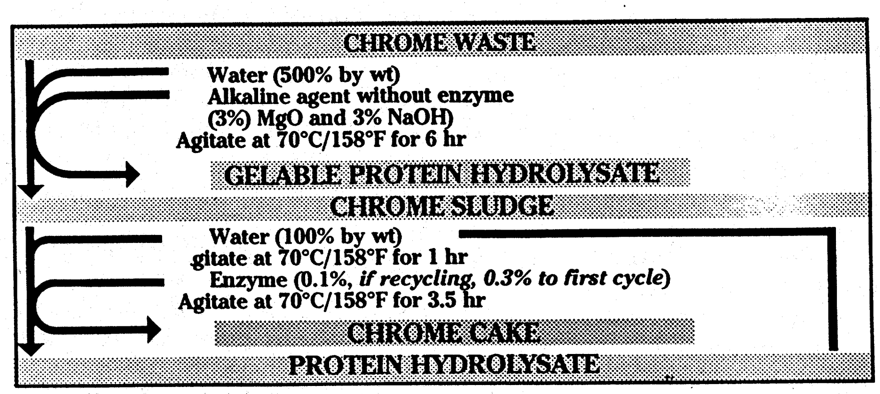
The next important step in the investigations would be obtaining a higher molecular weight protein than was previously isolated. The original one-step process gave a recyclable chromium product but also gave a low molecular weight protein hydrolysate with only limited commercial value as a fertilizer. The overall economic return from such a process would only be attractive if landfill fees were exorbitant or if landfilling were prohibited outright. Even though it was demonstrated that this protein solution and enzyme could be recycled in order to reduce the cost of the process, a higher return from a better quality by-product would be desirable.

FIGURE 1
Example of application of U.S. Patent 5,094,946



Extraction of gelatin from chromium leather waste has been described in the literature. A considerable amount of chromium sludge remains after this extraction, however, and disposal of this sludge is necessary. We developed a new two-step process that allows a gelable protein to be isolated in the first step and a lower molecular weight, hydrolyzed protein after enzymic treatment of the remaining chrome sludge(3). A recyclable chromium product is also obtained. Figure 2 is a flow diagram of the new process and illustrates one of the many alkalinity-inducing combinations that can be used to extract the gelable protein. After isolation of the protein product by filtration, the chrome sludge is prepared for enzymic hydrolysis. The pH is measured and adjusted if necessary for optimal enzyme activity and the alkaline protease is added. The reaction is carried out for 3.5 hours. The protein hydrolysate solution can be recycled, and a 0.3% initial feed of enzyme is recommended. If one has whole splits or large trimmings, chipping or grinding is recommended before the first step is carried out. These substrates have been dissolved in their intact state, with 1% enzyme or less, but the protein product is low molecular weight.

FIGURE 2
Example of U.S. Patent 5,271,912 (CIP of 5,094,946)



The effect of magnesium oxide, alone and in combination with varying amounts of sodium hydroxide, sodium carbonate, potassium hydroxide and potassium carbonate, on the chemical and physical properties of the gelable and hydrolyzed protein products has been investigated(4). Careful control of the concentrations of the alkalinity-inducing agents will give the optimal pH range for enzyme hydrolysis and the optimal range for gelable protein extraction. Also the pH of the reaction should not fall below 8.5, for then there would be the risk of solubilizing the chromium. Shavings from different tannery processes have different pH values, ranging from 3.50 to 4.20. The shavings being used in these experiments had a pH range of 3.95–4.00. The concentrations of alkalis to be added were arrived at experimentally in small bench trials prior to larger scale runs.

The chemical and physical properties of the extracted gelable protein will vary depending on the combinations of the abovementioned alkali treatments that are used. The percent total solids in the solutions can range from 1.75 to 4% depending on the choice of alkali. The chromium content of the protein products can range from 50–126 ppm. These gelable protein solutions are freeze dried; the moisture content ranges from 4 to 13%, and the ash content ranges from 8.9 to 21%. Molecular weight distribution ranges from 75,000 to over 200,000 depending on alkali treatment that is used. The Bloom values, or gel strengths, range from 80 to 150. Possible uses of the gelable protein fractions include graft polymerized products, in wastewater treatment, encapsulation, powdered filler for skid resistant tires and in thermal printing materials.

The chemical properties of the hydrolyzed protein products will vary depending on the choice of alkali. The percent total solids of the solutions ranges from 6.00 to 9.50%. The chromium content ranges from five to 50 ppm. The protein molecular weight distribution ranges from 10,000 to 20,000, and these values are much higher than those protein products isolated in the original process and reflect the small amount of enzyme used in the digestion. The total ash content of the hydrolyzed protein products (3.30–7.70%) is much lower than those found in the original process, due to the fact that the bulk of the inorganic materials is extracted with the gel. Possible uses for the hydrolysates include fertilizer and adhesives.

It has been reported in the literature that the ash content of a good gel should be between 0–3%. The ash content of our samples ranged from 8.9–21% on a moisture-free basis (MFB). As shown in a previous publication, these ashes contain magnesium and calcium ions as well as the more soluble sodium and potassium salts. This ash content reflects not only the ash content of the original shavings, but also the type of alkali used to extract the gel. Typically, in commercial gelatin preparation, the solutions are passed through ion-exchange columns to lower the ash content. The gelable solutions were passed through mixed bed ion-exchange columns of two different compositions. The ash content of the treated samples of gelable proteins was reduced to 0.40–0.50%, which is within the criteria set for gelatin. Both resins worked equally well.

Would there be a market for these protein products? According to the Chemical Marketing Reporter, from March, 1992 to March, 1994, approximately 4.3 million pounds of gelatin were imported into the United States. During that same period, approximately two million pounds of hide glue and approximately 330,000 pounds of photographic gelatin were imported.

A cost and return estimate of the described treatments has been calculated. The cost of chemicals, energy, labor, and equipment and the return from chrome cake, savings on landfilling, and the recovered protein were factored into the equation. It was found that one should realize a significant return from the total chrome-containing solid waste generated from each cattlehide, when using the technology of the newer two-step process and recycling the enzyme-containing solution twice. The new treatment is more profitable and this is influenced by the return on the gelable protein. Recycling the enzyme will increase profits slightly in the two-step treatment, but will definitely improve the cost effectiveness of the original one-step treatment. The savings are mainly the result of lowered costs of evaporation.

Presently, the waste from finished leather is still being accepted by landfills. There is a concern, however that in the near future it will be rejected. If finished leather waste is prohibited from being dumped into landfills, residues from retanning, coloring, fatliquoring and finishing would have to be extracted and treated or the finished leather would have to be reused in other products.

In conclusion, high-quality gelable and hydrolyzed protein products can be isolated from treatment of chromium leather waste. This study has shown that a variety of alkali inducing agents can be used to treat the waste, depending on the desired composition of the end product or compatibility with the chemicals used in chrome recycling in the tannery system. The chemical composition of the original chromium waste product also contributes to the chemical makeup of the protein products. A higher percent of the ash is extracted with the gelable protein, and if this ash is too high for the desired end product, it can be removed by ion-exchange resins. Finally, it has been shown that, based on the import data, a market is available in this country for these types of products.♦

References

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