6134

Enzymes assist recovery of chrome and high-value protein from shavings

In the United States, almost 56,000 metric tonnes of chromium-containing solid waste is generated by the leather industry each year and approximately ten times this amount is generated world-wide. Environmental concerns and escalating landfill costs are becoming increasingly serious problems to the leather industry and alternative disposal methods are needed. Members of the Research Liaison Committee of the American Leather Chemists Association urged the scientists at the Eastern Regional Research Center (ERRC) to look into possible treatments of this waste. As a result, two processes were developed that can help the leather industry solve this potentially difficult waste disposal problem. Success by the ERRC team, in fact, has inspired the tanning industry to look seriously at these processes and others as well, all in order to divert their waste from landfilling.

Digestion of chrome leather wastes

In the first ERRC process (U.S. Patent 5,094,946), the chrome waste is 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 chromium and enabling the easy recovery of chromium as $Cr(OH)_3$ by filtration. The resulting protein solution may have commercial use as a fetiliser. The isolated chromium cake has the potential to be recycled into the tanning process by treatment with sulphuric acid.

It has been documented that chromium-containing waste can be treated enzymatically but only after pretreatment 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 may be made to shavings already subjected to moderate pretreatment temperatures. 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, 78% solubilisation 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 solubilisation of protein was achieved with lower amounts of enzyme (0.3%) than previously reported, thus making the treatment more cost-effective.

Two step process for gelable protein products

More recently, it was found that, if a two-step process is used, a gelable protein product can be obtained that will provide a higher economic return. In this process (U.S. Patent 5,271,912), the chromium waste is treated with alkaline agents for six hours at 70–72°C and then filtered to recover a gelable protein. The chromium-containing sludge that remains after filtration is then treated with the bacterial enzyme as in the original process, resulting in an easily-filtered, protein hydrolysate fraction and a chromium cake that can be chemically treated and subsequently recycled. The recovered protein fractions, practically devoid of chromium, have potential utility in a wide range of products, including adhesives, cosmetics, films and fertiliser. Future research will be directed towards the utilisation and modification of the isolated protein products.

This research has been recognised by various awards from the United States government, industry and professional societies. The Prize Paper Award of the American Leather Chemists Association allowed this research to be presented before the IULTCS in Barcelona in 1991. Initial interest in the United States has led to several industrial-scale trials and enquiries over non-exclusive licensing of this technology.

Potential uses for protein products

These products are potential proteinaceous feedstocks that have not been previously available at such a low cost. Other potential uses include gelatin-copolymer finishes for leather and as a culture medium for preparation of gelatinase-containing composition. The hydrolised protein products from the one-step process can be used in the preparation of fertilisers, detergents, animal feed, surfactants, finishing agents for textiles, fillers and finishing agents for leather, metal-protein complexes for tanning and retanning of leather and plant growth stimulators. The gelable protein products can be used in the preparation of adhesives, films, encapsulated products, protein plastics, high moisture-absorption products, protein-macromolecule reaction products (biogradeable polymers). ◆