Industrial applications of keratins – A review

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Keratin, a fibrous protein forming main structural constituent of feather, hair, wool, horn, hoof etc., is abundantly available as a by-product from poultry, slaughterhouse, tanning and fur processing industry. Keratins though find applications in food, pharmaceutical, cosmetic and fertilizer industry, considerable amount of these products is wasted repeatedly. Keratins are difficult to degradation and their disposal leads to environmental problems. Research is being done globally to utilize these wastes. Keratin hydrolysates find potential application in leather tanning industry.

Keywords: Fibrous protein, Keratin, Leather tanning industry

Introduction

India has a large livestock population, which produce annually: goatskins, 82; sheep skins, 30; cattle hides, 23; and buffalo hides, 28 million1. World production of bovine and ovine skins during 2000 was 1,192 million pieces2. Feathers constitute up to 8-10% of total chicken weight and it is estimated that several million tons of feathers are produced annually. Bovine and ovine hair is obtained as a by-product from the tanneries during hair-saving unhairing process and it is estimated that about 5% of dry hair is recovered based on the raw hide weight3,4. But still most of the tanneries are following hair-burning process, which destroy the hair completely and contribute high amount of COD, BOD, TDS etc., to the effluent5-8. Microbial proteases offer potential solution to remove the hair completely from the raw skins9-12.

An enormous quantity of keratins in the form of hairs, feathers, horns and hoofs are wasted each year13. Keratins are broadly classified as hard (5% sulfur) and soft (1% sulfur) keratins. Keratin is mechanically robust and chemically unreactive due to tight packing of protein chain in the form of α-helix or β-sheet into a super coiled polypeptide chain crosslinked with disulfide bonds. In horns, hoofs and hair, keratin is in the form of α-keratin, whereas in feathers it is in the form of β-keratin14-17. Feather (90% keratin) is used as animal feedstuff in the form of feather meal18-21. Acid, alkali or enzymes hydrolyze keratin and hydrolysates have number of applications22-27. Cosmetics based on keratin preparations have been reported for the treatment of human hair and skin28-33. Keratinous materials are used as additive in the preparation of concrete and ceramics34,35. Sulfur bound amino acid solution is used to prepare organic fertilizer, which enhances plant metabolism36. Fire fighting composition is prepared from a solution of organic colloid derived from the hydrolysis of horns and hoofs37. Oxidization of keratinous materials cleaves and oxidizes some of the disulfide linkages to form water-soluble peptides and this material is used as a wound healing agent38. An attempt has been made for the first time in Central Leather Research Institute (CLRI), Chennai to utilize keratin wastes successfully in leather tanning processes39,40,92-95,102,103. Successful attempts have been made to convert keratinous wastes like poultry feathers, animal hair, horns and hoofs into keratin hydrolysate (KH) by controlled alkali hydrolysis. KH has been successfully employed in leather processing particularly during chrome tanning and rechroming operations to enhance the uptake of chromium salt by leather. KH is also successfully employed in filling cum retanning operation in leather processing. The process of KH preparation was upscaled in CLRI pilot plant and technology was transferred to a company for commercial exploitation.
Recently, authors at CLRI subjected raw horns and hoofs of slaughtered cattle and buffaloes collected from the local slaughterhouse at Chennai to high steam pressure (40 psi) in a rendering plant (FMC, Australia) for 3 h (raw horn: water ratio: 100:30 w/v). The resulting material (Fig. 1) was dried in a dryer (BHL, Ahmedabad) and pulverized in pulverizer (FMC, Australia) to get horn meal (60%).

**Approaches to Convert Keratin Protein into Keratin Hydrolysate**

**Hydrothermal Treatment**

Hydrothermal process usually employs high steam pressure (10-15 psi) and/or high temperature (80-140°C) in the presence of acid (HCl, H₂SO₄, HCOOH etc.) or alkali (NaOH, KOH, Na₂CO₃, K₂CO₃, NaSiO₂ etc.) or acid oralkali at the boiling temperature for over 2-3 h opens disulfide linkages of keratin and yields water soluble polypeptides, oligopeptides or even amino acids. The effect of change in pressure, temperature, chemicals and pH during thermo-chemical treatment has been studied to analyze the nutritional value of feather meal. Main drawback in hydrothermal process is that hydrolysis may result in partial or even complete destruction of amino acids, which contain peptides with varying molecular weight and nutritional improvement. These methods leads to losses of essential amino acids (lysine, methionine and tryptophan) and causes the formation of non-nutritive amino acids (lysinoalanine, lanthionine, etc). Merits and demerits of alkali versus acid hydrolysis have been reported.

**Microbial Treatment**

Microbial conversion of keratin wastes is a potential technique for degradation and utilization of keratin as a hydrolysate in terms of cost-effective and environmentally benign processing. Presence of disulfide bonds in keratins hinders their degradation by proteolytic enzymes (trypsin, pepsin and papain), which can be efficiently degraded by soil microorganisms, actinomycetes, bacteria and fungi by synthesis of keratinolytic proteases-keratinases. Keratinases are robust enzymes with a wide temperature and pH activity range and are largely serine or metalloproteases. Keratinases attack keratin residues (feather, wool, steam hydrolyzed horn powder etc.) and convert them into degradative and cost effective products. Application of keratinase-producing microorganisms is being explored in feed, fertilizer, detergent, leather and pharmaceutical industries where there is great need for materials derived from alternative raw materials specifically animal wastes derived from meat processing plants, poultry units, marine and slaughter houses.
Applications of Keratin Hydrolysate in Leather Processing Industry

Keratin Hydrolysate in Tanning

In leather processing, tanning converts putrescible skin collagen into stable leather. At present, chromium sulfate is widely used world over as a tanning agent due to its versatile nature to produce different types of leathers with required properties and uses. But this tanning system is under increased pressure from the green groups due to its polluting and toxic nature. One of the constraints reported in conventional chrome tanning practices is the exhaustion of Cr in the tanning bath, which does not exceed 60-65% in commercial tanneries. Due to this, very large quantity of chromium is discharged into the effluent causing environmental pollution. The discharge limit of chromium in the waste stream should not exceed 2.0 ppm in most of the countries necessitating treatment of discharge in Common Effluent Treatment Plant (CETP) before it let out for usage. This leads to increase in cost of leather processed in tanneries. Hence, CLRI studies conducted to improve exhaustion of Cr in tanning bath by using KH prepared from poultry feathers and tannery hairs were carried out. KH (2-3%) was used in chrome tanning (based on skin weight) and the exhaustion of chromium in tanning bath could be more than 90%. KH prepared from horn meal by acid hydrolysis (using HCl) and microbial hydrolysis (using Bacillus subtilis strain) could also be successfully employed in chrome tanning process to improve exhaustion. The reaction of water-soluble keratin peptides in chrome tanning involves two-step reaction. Initially, low molecular weight peptides react with chromium. In second stage, collagen in leather reacts both with free chromium and chromium-keratin complex. Fixation of keratin complex in leather enhances further uptake of chromium resulting into enhanced uptake of chromium by leather. Fixation of KH generates additional carboxylic groups that have high affinity for chromium. In second stage, collagen in leather reacts both with free chromium and chromium-keratin complex. Fixation of keratin complex in leather enhances further uptake of chromium resulting into enhanced uptake of chromium by leather. Fixation of KH generates additional carboxylic groups that have high affinity for chromium.

Keratin Hydrolysate in Retanning

Fibre structure of hide/skin is not uniform throughout the entire area and it is most common to fill the empty nature of chrome tanned leathers by retanning to improve the required properties of leathers, which are intended for making foot wear, garments, gloves, furniture and automotive upholstery etc. Today several developments are taking place in the field of retanning such as phenol formaldehyde and naphthalene formaldehyde condensates, melamine, dicyandiamide and carbodiimide based syntans, polymers of various types, such as acrylates, urethanes and melamine resins. Most of these retanning agents are still suspected in their application due to release of high COD, TDS, free phenol and free formaldehyde. Protein based retanning agents offer better prospects as they fill loose areas such as belly, flanks and poor substance materials without contributing much load to tannery effluent. Chicken feathers and hairs can be converted into water soluble peptides using lime and sodium hydroxide at elevated temperature and pressure in an autoclave and hydrolysate has been successfully employed as a retanning-cum-filling agent in leather processing. KH has selective filling action, upgrades the poor substance skins and it can be used along with other retanning agents. Besides, the use of KH in retanning process influences lubricating effect that enhances grain smoothness and softness characteristics of leathers.

Conclusions

This review provides base material towards the establishment of environmentally friendly technology for the treatment of keratin wastes and throws light on conversion of non-edible slaughterhouse and tannery waste (hair, feather, horn and wool) into value-added products. The use of KH in leather processing has two-fold advantage. Initially, bio waste is converted into KH, which is used as exhaustive aid in chrome tanning to reduce the pollution load, and finally it is used as filler-cum-retanning agent to replace existing retanning-cum-filling material used by the leather industry.

References

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