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Management and utilization of Keratin Waste– A review

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ABSTRACT

Keratin is a major complex structural protein present in hair, wool, home, hoops, feathers and nails of animals. It is considered as an environmental pollutant because of its slow degradation and produced mostly at both domestic and industrial levels. So beneficial utilization and management go these keratin-based waste has a significant importance. Out of many traditional and new approaches to breakdown keratin, the use of natural soil keratinophilic microbes is widely studied because of nontoxic and useful byproducts produced. These keratin-based products have a widespread application in medical, animal feed, fertiliser, biomedical uses and many other types of industries. In the present review various strategies for hydrolysis of keratin from the organic waste have been described and use of natural keratin in different industries have also been explored.

Keywords— *Keratin, environmental pollutant, keratinophilic microbes, industrial application*

1. INTRODUCTION

Keratin is an insoluble protein found in the outer parts of the body of animals (mainly in the epidermis) and helps to prevent the loss of body fluids [1,2]. It has a complex structure, with disulfide bonds, hydrogen bonding, shydrophobic interactions and extremely high molecular weight because of which it has high durability [3]. There are two types of keratin - Alpha keratin (found in the epithelia of all vertebrates) and Beta keratin (present in reptiles and birds) [4,5]. Currently, millions of tons of keratin containing waste is produced because of increasing urbanization, food industries especially the meat market, slaughter house and wool industry produces. These proteins constitute keratin by-products have from 2–5% Sulphur, 15 to 18% nitrogen, 3.20% mineral elements and 1.27% fat and 90% of proteins [6,7].

Bird feathers, mainly chicken feathers are the most common waste product of keratin, produced in poultry slaughter houses. Other sources include goatskins, sheepskins, cattle hides and buffalo hides; skin and appendages including nails, hair, feathers, wool, hooves, scales and stratum corneum etc are the richest source of keratin [6,8]. Increasing amount of keratin waste is creating an environmental impact by causing pollution in many ways. At a worldwide scale, around 8.5 billion tons of poultry feather is generated annually, and these are disposed in the landfills which directs to the environmental pollution and leading to the deterioration of a valuable resource [9,10]. Keratin waste is generated from the meat industry (slaughterhouses) in the form of chicken feathers, beaks, mixture of bones, organs and hard tissues in very large quantity. It causes problems of acidification of soils, eutrophication and decreased species diversity. Also, the main disposal option is incineration, producing huge amounts of ashes the valorization of which becomes a major concern [11]. Leather tannery industries discharge the wastes including keratin protein waste such as hair, horns and hoofs and cause serious health problems as well as pollute the air, soil, and water [12]. Human hair waste is also yet another source of keratin waste, which accumulates due to slow degradation property and chokes up the drainage system. If these hair and other keratin waste are burnt for disposal, it causes relapse of foul odor and toxic gases such as ammonia, carbonyl sulphides, hydrogen sulphides, Sulphur dioxide, phenols, nitriles, pyroles, and pyridines [13].

The tremendous volume of keratin waste is creating a serious solid waste problem in many countries and its efficient management id crucial. the traditional disposal methods for these keratin wastes include incineration, landfilling, composting, and mechanical grinding, but these methods are also restricted because of enormous production of harmful gases and poses the risk to the environment [14]. Thus there is a need to have an environment friendly keratin waste management and utilisation system for domestic and industrial sources.

This paper explores and assesses various uses of keratin waste from the perspective of expanding its management and utilisation as a resource and applying it to the benefit of the environment.

2. KERATIN FROM THE POULTRY INDUSTRY

Poultry industry is one of the largest industries and contributes to a large proportion of solid waste generation which includes the slow degrading keratin in chicken feather waste. Every bird is estimated to have around 125g of feather which brings the worldwide production of feather waste up to 3000 tons per week. This amount is enough to cause environmental problems considering the pollution to soil and ground water sources as burning this waste releases sulfur dioxide [15]. Thus, alternative industrial uses of this waste will not only reduce the environmental impact and health hazards but also increase the value of feathers. Feathers are a good source of keratin (around 90%)

Composed of ordered α-helix or β-sheets and about 7% cysteine that forms sulfur-sulfur bonds with other molecules. These linkages give strength and stiffness to keratin in the solid state. Feathers contains around 50% fibers and 50% quills. Feathers have been modified to transform them into films using compression molding, casting, or extrusion techniques by various methods like surface grafting of synthetic polymers or by blending with plasticizer [16]. Thus, application of these feather waste to different industries is an excellent way of its utilization and management.

These feathers have been analyzed to be used as Cement reinforcement. Study showed that it is possible to use chicken feather as reinforcement in cement bonded composites upto 10% feather content which have been observed to be similar in strength and stiffness properties to commercial wood-fibre cement boards. Increasing the feather percentage above 10% showed major reduction of manufacturing operating expense and decreased dimensional stability. Potential use of feathers in cement reinforcement could help the poultry industry by reducing waste disposal cost [17].

By pressing the feather fibres into thin mats and coating with commercial soybean oil preparations a desired dielectric constant can be achieved thus turning them into circuit boards. These resulting boards were tested for their qualities like rigidity and thermal expansion and other attributes important in applications like aerospace, electronics, farming equipment, defense etc. Studies have shown that feathers have a dielectric constant of 1.6 which is almost half of silicon dioxide (3.8-4.2) and thus electrons on the feather board can move twice as fast as traditional boards. It also has a coefficient of thermal expansion similar to the traditional boards and hence can be used on industrial scale [18].

Another application of feathers is in development of bioplastics. The development of plastics from renewable and biodegradable sources has seen a rise as compared to the petroleum-based plastics which present many concerns related to sustainability and environmental pollution. To compete with these petroleum-based plastics, the bioplastics must have comparable performance measures like cost and mechanical properties. Recently the focus has been shifted to protein-based bioplastics. Poultry feather quill is a good source of keratin as it is made of 90% protein. Feathers can be processed into thermoplastic resins by extrusion processing and by mixing them with plasticizers like ethylene glycol, glycerol etc [19].

Also, research is carried out to develop chicken feather keratin nanoparticles to be used as a hemostatic agent and has many biomedical applications like keratin-based carriers for drug delivery and incorporate in wound dressing and keratin-based hydrogels.

3. HUMAN HAIR WASTE

Being rich in protein, Human hair is considered one of the highest nitrogen containing organic biomaterial. Also, it is rich in carbon, sulfur and other nutrients essential for plant growth. Atmospheric decomposition of hair is very slow, but moisture and keratinolytic fungi present in soil, animal manure, and sewage sludge can degrade hair within a few months. Human hair, because of its protein content, is a good source of amino acid and it is estimated that 1 kg hair can produce 20 liters amino acid. The hair is heated at very high temperature (about 400-500 degree Celsius) when it turns into liquid, which is then mixed with water to prepare the crude mixture of amino acid solution. Like other fertilizer, amino acid solution mixed with water is sprayed on plants. Amino acid acts as natural stimulant and hair has different types of amino acid including lysine which is very good for legume growth. These amino acid-based organic fertilizers can thus be made available to farmers at a cheaper rate and the pollution caused by hair waste is also nullified [20,21].

The Scientists at Kerala Agricultural University have also stated that liquified hair after few thermochemical treatments gives a solution which is rich in Nitrogen (approximately 9000ppm) with potassium and phosphorous in lesser quantities. The liquid fertilizer made from hair was applied as foliar spray on Okra plants and they were found to have more vigorous growth and early flowering than the plants treated with normal fertiliser package [22].

Also in some experiments, Liquid nitrogenous fertilizer was synthesized using waste human hair as the raw material. Potassium hydroxide (KOH) and Tetramethylammonium hydroxide (TMAH) were used as the non-recoverable solvents for diffusion controlled reductive cleavage of hair protein, out of which KOH extract proved to be more efficient since KOH was better for dissolving hair and extraction of nitrogen in the forms of ammonium and nitrate ions compared to TMAH. For comparative analysis, these extracts were used parallel to plants growing with Nitrogen-Phosphorus-Potassium, NPK (15-15-15), fertilizer on the growth and yield of a short cycle crop, spinach (Spinacia oleracea L). The results showed prominent growth of spinach in KOH extract hair fertilizer as compared to the NPK and TMAH extracts [23,24].

It has also been reported that experiments on horticulture plants show that direct application of human hair to soil provides the necessary plant nutrients for over two to three cropping seasons [25].

A company named SmartGrow has popularized the fertilizer use of human hair in the USA by selling it in the form of hair mats for potted plants. Small entrepreneurs in the USA are also promoting hair as fertilizer by packaging it in various user-friendly forms such as in tea bags [26].

The hair-based fertilizers not only serve as a cheaper source of plant nutrient, they also act as soil conditioners. The high amino acid and protein content in these fertilizers enhance bacterial growth and the soil flora is increased. It is also found that Bacterial growth was approximately thrice than that was seen in the non-fertilized farm field soil. The soil-intrinsic bacteria were increased as per the viable cell count, and more diversified. Increase in the rhizosphere bacterial community in the farm field soil, gives an indication that the hair hydrolyzate makes the farm field soil nutritional for bacterial growth [27,28].

Experiments on Hot pepper plants treated with hair extract solution showed increase in size of the plant and an increased diversity of soil-intrinsic bacteria, which significantly reduces the spread of a wilt disease in these plants caused by the bacterium Ralstonia solanacearum. Long term impacts of this use, however, need to be assessed [29].

As Oil Spill Adsorbent - The number of oil spillage accidents have tremendously gone up with the increasing demands of petroleum products. The Gulf War, Deepwater Horizon, IXTOC Oil Spill in Gulf of Mexico and the Atlantic Empress to name a few, have had massive adverse impacts on natural ecosystems, and in turn leads to environmental degradation. During an oil spill, in order to minimise the damage, large quantities of adsorbent plastic, polypropylene and other types of plastic polymers are released into the site of spillage. This inturn cause plastic accumulation and is even more hazardous [31].

The selection of an inexpensive, high hydrophobicity, high oil adsorption capacity, good reusability, readily available, high abrasion resistance and non-toxic oil sorbent is important in cleaning up these spills. Researchers suggested that waste hair could be a cheap alternative to the synthetic plastics that are currently used to clean up after oil spills. Human hair is naturally adsorbent and can soak up three to nine times its weight in oil [31].

Basic adsorption works on the following principle: oil molecules get diffused into surface of the sorbent, they are trapped in the sorbent structure as a result of capillary action, agglomeration into the porous sorbent structure of oil droplets.[32]

Human hair (50-100 um) is naturally a bio-sorbent. It is made of dead cells that are formed of lipid, 65-90% proteins like keratin and cysteine, cuticle, trace elements, water, cortex and medulla. The cuticle gets its water repellent property due to its hydrophicity. Multiple peptide bonds, CO- and NH- groups make hydrogen bonds between adjacent molecules on the human follicle surface, giving it a very porous cortex [33]. Hair and oil have a relatively higher adhesive force than hair and water, hence hair selectively and effectively absorbs oil in presence of water [32].

The capacity of human hair to adsorb crude oil, vegetable oil and diesel fuel was investigated by Peter Rawland and Akpevwe Idogun. Human hair showed a maximum adsorption capacity of 7470 mg/g, and was shown to perform better than other conventional adsorbents like peat moss, rice husks, organoclay and activated carbon. The mode of action for adsorption by human hair was chemisorption exothermic method which was investigated by Langmuir and Freundlich adsorption isotherm models.[33] Waste hair is a good material for adsorbing spilled oil that comes into direct contact with it. Approximately 50% of the adsorbed oil can be recovered from the oil-soaked hair by pressing it [32].

As insulation of superconducting material - Human hair has shown good dielectric strength at room temperature and a feeble increase at 77 K. The dielectric strength of human hair/epoxy was found to be 118.99 kV/cm. Human hair had a breakdown voltage of 21.91kV and breakdown strength of 52.92 kV/cm at room temperature, whereas at cryogenic temperature it had a breakdown voltage of 46.36 kV. Insulation systems that are cryogenic need to be made of complex composite material to ensure that effective control of electrical stress. Since superconductivity needs to be introduced into the electrical power supplies, insulation with high sustenance to such a system is required. Especially for high voltage equipment, the integrity of insulation system is of utmost relevance. Natural fiber composites incorporating hair as a composite material were investigated, and concluded to be effective mediums for cryogenic applications [34].

As reinforcement of construction materials - Human hair has high tensile strength and high friction coefficient and has been used for reinforcing clay-based constructions. This clay-based material is used for plastering house walls, making wheels, etc. in rural areas of the country. Adding hair to such material reduces the risk of cracking and increases the life of such constructions. Researches have proved that hair addition has increased the structural strength as well as thermal insulation capacity of such constructions [35]. Another advantage of hair reinforcement is that it increases compressive strength of cement by three times. It also reduces cracking in cement usually caused by plastic shrinkage. This property has improved the structure resilience and this process is useful in high pressure application industries [36].

For removing Phenols, Aldehydes, Dyes, Heavy metal pollutants from water - Human hair has a tendency to absorb several chemicals from aqueous solutions. Research has shown that hair can absorb several elements like phenol, heavy metals like mercury, cadmium, etc. from the aqueous solutions. To increase the absorption by hair, it is recommended to treat it with alkali to enhance the absorption [37]. Also, human hair in its powdered state has very good absorptive property and partially burnt hair has selective absorption property for various chemical elements and heavy metals. The cost factor can be reduced to a very high extent by using hair as an absorbent. However, disposal of hair becomes a difficult task [38]. Researches have made it possible for recovery of chemical substances from human hair after absorption but still researchers are working on obtaining a fine procedure for safe disposal or recovery of human hair [39].

4. CONVERSION OF KERATIN TO KERATIN HYDROLYSATE

To improve the degradation rate of keratin, approaches like hydrothermal process, chemical methods and microbial methods are being tested. Hydrothermal method uses high temperature (80–140°C) and high steam pressure (10–15 psi) with the addition of acids or bases for the degradation of keratin wastes. The main drawback of this method is partial or complete degradation of amino acids, rendering the byproduct of this treatment with no nutritional value [40]. Chemical treatment includes use of acid, or other chemicals which hydrolyses the keratin protein but this method increases the emission of certain gases like CO, SO_2 into the environment and causes respiratory diseases, cardiovascular diseases, and cancer, among other illnesses [41]. The microbial method of degradation of keratin waste is more efficient than hydrothermal and chemical degradation, resulting in more useful and toxin-free product. the use of keratinophilic microorganisms having keratinise enzymes convert keratin waste into the nutrient-rich animal feed. Microbial keratin degradation follows the sequence of adhesion, colonization, amplification of keratinase pursued by the breakdown and deprivation of the substrate [42]. Keratinolysis comprises two major actions, i.e., sulfitolysis (breakdown of disulfide bonds) and proteolysis (proteolytic attack) by keratinolytic proteases (keratinases) based on the complexity nature of keratin[43]. These keratinophilic microbes include *Chrysosporium, Microsporum, Trichophyton, Aspergillus, Fusarium,* and *Uncinocarpus* [44]. The gram positive bacteria - *Bacillus, Microbacterium, Lysobacter*, *Nesternokia* and *Kocuria* and gram negative bacteria - *Vibrio*, and *Xanthomonas* and *Chryseobacterium* also have shown efficient keratinolytic properties in soil [45]. 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 [46]. These keratin hydrolysates are having a wide application in leather processing industries for tanning and retanning [46,47]. Other application of keratin, keratin extracts and keratin hydrolysates include - Development of protein fibers and 2Dand 3D scaffolds for tissue engineering, preparation of firefighting composition, to explore structural and biological properties of self-assembled keratins, keratin film for drug delivery system, bio-composites or composite fabrication, thermoplastic films for packaging of food, making of flame retardant and some other medicinal uses [48-52].

5. CONCLUSION

Though keratin in a biodegradable waste, the slow hydrolysis property and resistance to the common breakdown process make it a hazardous waste because of which it tends to accumulate in the environment causing environmental pollution. Many harmful effects of these waste have been reported and its efficient management is important. All the literature survey has revealed that keratin is an important component for the production of a number of value-added products. The hydrolysis of keratin waste followed by its reconversion into commercially used product, will not only save the ecosystem from large amount of sludge but will also economically boost up different industries mentioned in this review. Also following the sustainable and environment friendly method of microbial biodegradation of these wastes is beneficial. Large scale implementation of these uses, however, requires several environmental, social, and economic considerations.

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