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Biodegradability of leathers through anaerobic pathway

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Abstract

Leather processing generates huge amounts of both solid and liquid wastes. The management of solid wastes, especially tanned leather waste, is a challenging problem faced by tanners. Hence, studies on biodegradability of leather become imperative. In this present work, biodegradability of untanned, chrome tanned and vegetable tanned leather under anaerobic conditions has been addressed. Two different sources of anaerobes have been used for this purpose. The effect of detanning as a pretreatment method before subjecting the leather to biodegradation has also been studied. It has been found that vegetable tanned leather leads to more gas production than chrome tanned leather. Mixed anaerobic isolates when employed as an inoculum are able to degrade the soluble organics of vegetable tanned material and thus exhibit an increased level of gas production during the initial days, compared to the results of the treatments that received the anaerobic sludge. With chrome tanned materials, there was not much change in the volume of the gas produced from the two different sources. It has been found that detanning tends to improve the biodegradability of both types of leathers.
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1. Introduction

Implementation of cleaner technologies in the leather sector considerably reduces the pollution load generated from tanneries. However, solid leather wastes generated from leather processing units, leather garment manufacturing units, footwear manufacturing industries and the unused leather garments, are generally disposed off in the dumpsite and render the solid waste management system highly inactive because of the non-biodegradability of the tanned leather. During the processing of leather, tanning is one of the unit operations in which the tanning agents react with the collagen matrix, stabilizing the protein and collagen; thereby the leather acquires resistance towards chemical, thermal, and microbiological degradation. Chrome tanning, the most important tanning method used to obtain light, inexpensive leathers of high thermal and bacterial resistance, uses basic chromium sulfate as the tanning agent. The other tanning agent, which is popularly used, is based on vegetable tannins. Collagen molecules of the skin/hide interact with chromium at least in three ways. The most important is the chromium, which has coordinate covalent interaction with collagen to give leather its characteristic properties. Other interactions include nonproductive binding of chrome to collagen and adsorption of chromium onto the collagen matrix. As reported by Brown and Taylor (2003), only 2% chromium is simply adsorbed and has little effect on stability and about 7–10% chromium is providing stability, i.e., thermal stability, and 40% chromium appears to be bound to collagen, but no longer crosslinked.

With regard to the polyphenolics binding to collagen, four mechanisms for interaction between polyphenolics and proteins have been postulated, including covalent interactions, ionic interactions (Pierpoint, 1969), hydrogen

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bonding interactions (Loomis, 1974) or hydrophobic interactions. As studied by Bo et al. (2001), the interactions between proanthocyanidins and collagen involve primarily hydrogen bonding between the amide carbonyl and phenolic hydroxyl (Hagerman and Klucher, 1986). Proline, an amino acid with carbonyl oxygen adjacent to secondary amine nitrogen is a very good hydrogen bond acceptor, thus, strong hydrogen bonds were exhibited by collagen with polyphenolics. Since collagen has a helical structure, it enhances the accessibility of the peptide backbone for the purpose of hydrogen bonding. Hydrogen bond formation by stabilizing the collagen fibers is responsible for the increase in the denaturation temperature of the tanned leather (Hagerman, 1980; Creighton, 1980; Hagerman and Butler, 1981).

With regard to the production of tanned leather, Europe stands first with 25% of the leather production, generating about 170,000 ton of tanned leather wastes annually with 43,000 ton from the footwear sector. Thus, disposal of leather waste, especially tanned leather waste, is a serious problem. The conventional methods followed such as land co-disposal and incineration have certain demerits and are not practicable for the disposal of tanned leather wastes. In the land co-disposal method, leaching of Cr^{3+} from the tanned leather wastes to groundwater due to acid rain limits the dumping process. Conversion of Cr^{3+} to Cr^{6+}, which is a well known carcinogen, is possible during incineration. Emissions of NOx are unavoidable due to the presence of 0.21–0.7% nitrogen in the leather waste. The nitrogen content of leather is mainly in the form of amino acid. Heidemann (1993) study demonstrated that pyrolysis of amino acids at 850 °C was highly controlled by their molecular structure. Alanine and alpha amino butyric acid are the two amino acids completely converted to gases during pyrolysis. Amino acids with functional groups reduce the efficiency of pyrolysis, and it was observed that only a 60–70% breakdown occurred with serine and lysine. Generation of HCN and NH_3 during incinerations contribute towards air pollution. In addition to the nitrogen present in the tanned leather, chromium compound also contributes heavily to air pollution. At low incineration temperatures, 300–600 °C, soluble hexavalent chromium is produced as long as small quantities of alkali and carbonates are present. The incineration of leather waste at normal temperatures of 760–980 °C and normal pH values of 6–9 produces predominantly trivalent chromium in ash. Rai et al. (1989) affirmed that between pH 6.3 and 11.5, the dominant chromium species is Cr^{3+} while at pH >11.5 the dominant species is Cr^{6+}. Thus, these two technologies are discouraged, as they are not untangling the solid waste disposal problem in eco-friendly manner. Thus, the importance for setting up a task force for developing a technology for the disposal of tanned leather solid waste becomes eminent. Moreover, the current environmental regulations demand energy recovery from solid wastes, which consists of digesting the solid wastes through anaerobic process to recover chemical energy and fuel energy. The main advantages of this process are: (i) decontaminating the waste with the production of biogas; and (ii) production of nutrient enriched effluents for agricultural purposes (Gnanamani and Kasturi Bai, 1992). This technology employs bacteria with low yield co-efficient and low decay co-efficiency that allow the process to sustain with low production of sludge. However, anaerobic digestion is less efficient to degrade low molecular weight phenolic and polyphenolic compounds such as tannins and lipids. They exert inhibitory effects on various microflora involved in the digestion process (Hamdi, 1996; Borja et al., 1995; Beccari et al., 1996) and thus tend to persist in the digesters and be released along with the digested effluents. As reported by Borja et al. (1998), some biological and chemical pretreatment methods reduce the toxic nature of these phenolics, especially tannins, in the anaerobic digester. Becari et al. (2002) observed that more promising results were achieved by integrating the active microflora having the ability to degrade the low molecular weight compounds and further degradation of the metabolites by anaerobic species. Hence, the present study aims to assess the feasibility of anaerobic digestion technology of untanned, chrome tanned and vegetable tanned wastes and detanned chrome and vegetable wastes using two different sources.

2. Materials and methods

2.1. Materials

For evaluation of anaerobic biodegradability of leather wastes, untanned (delimed pelt), chrome tanned, and vegetable tanned samples were collected from a tannery located in Chennai, India.

2.2. Isolation of anaerobic bacterial species

Anaerobic bacterial species were isolated from anaerobic sludge collected from the upflow anaerobic sludge blanket (UASB) treating tannery wastewater and also from the sludge obtained from the sewage treatment plant treating domestic wastewater. Isolations were made according to the standard procedures summarized by Cappuccino and Sherman (1996) using beef heart infusion, 5 g; tryptose, 10 g; sodium chloride, 5 g; distilled water, 1000 ml; pH 7.3. Growth of the anaerobic organism was assessed based on hemolysis. Sub-culturing of the isolated species was performed and the pure cultures thus obtained were maintained in the Horsemeat agar media containing sodium thioglycollate 45%. About five pure isolates were obtained from anaerobic sludge from tannery wastewater and anaerobically digested sewage sludge. These isolates were named as AO1–AO5. These isolated organisms were further subjected to gram staining in accordance with the procedures of Bergy's Manual of determinative bacteriology (1994).

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