Journal of Hazardous Materials 163 (2009) 207–212

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Sulphates for skin preservation—A novel approach to reduce tannery effluent salinity hazards

Padma S. Vankar*, Ashish Kr. Dwivedi

Facility for Ecological and Analytical Testing, Indian Institute of Technology, Kanpur 208 016, India

ARTICLE INFO

Article history:
Received 5 January 2008
Received in revised form 8 April 2008
Accepted 20 June 2008
Available online 1 July 2008

Keywords:
Buffalo hide
Ecological hazards
Scanning electron micrographs
Sodium sulphate

ABSTRACT

In tanneries microorganisms are able to find environment suitable for their growth. Raw hide of buffalo and other animals like goat that are economically important, are an ideal source of nutrients for bacterial and fungal growth. In the past, preservatives like sodium chloride provided effective protection to fresh hides however the ill effect of their excessive use was not evaluated. But recently concern over potential ecological hazards has become more deliberate and sodium chloride features lot of disadvantages in agriculture as most of the tannery effluent is flown in agricultural fields in India. After rigorous laboratory experimentation on moisture content, SEM of hide, pure sodium sulphate as well as sodium sulphate in addition with sodium chloride (i.e. 10% w/w and 20% w/w) proved as most preferable option for curing of buffalo hide which gives effective preservation. Pollution load studies put forward sodium sulphate as an effective curing agent for buffalo hide to apply at industrial scale also.

1. Introduction

Raw hides are the most valuable by product of meat industry and most of those hides are converted into leather. Skins of cow, goat, sheep and buffalo are found to be most useful and widely available hence utilized in leather making. This is evident that buffalos occupies the important place in Indian rural economy and are major source of agriculture-based products like milk and meat also. After death or slaughtering buffalo skins are preserved and supplied to the leather industries where they are processed into finished leather articles.

1.1. Raw hide deterioration, preservation and hazards of traditional preservatives

Autolysis of raw hides is a spontaneous process responsibly done by the microorganisms. Many practical experiences have indicated that this simplified assumption was not completely accurate. In the last few years the role of halophilic bacteria has become more realistically appraised in the hide curing and storage process [1]. However simple salt NaCl perfectly preserve raw hides at its best. Salt curing acts to preserve hides in double manner. Firstly it combines with moisture for removal of water from the hide and secondly it lowers the water activity of remaining moisture. Salt packs are historically the first method for hide preservation. In this process the first hide is placed on a bed of salt, is then covered with salt and the next hide is placed on top. This process is repeated until the stack is several feet high. It requires about a pound of salt per pound of hide to do a thorough job of curing. The process is much slower and takes as much as 30 days to complete [2,3]. Bacteria cannot live in the presence of certain chemical treatments. There are two classes of chemical treatments for bacteria, bacteristats that limit the growth of microorganisms at whatever stage they are in and bactericides that kill the organisms outright. Both these types of materials are, at best, useful for short-term preservation [4]. NaCl is bacteriostatic compound which have good binding compatibility with collagen fiber of buffalo skin hence dehydrates skin rapidly so the growth of microorganism is inhibited due to lack of appropriate moisture content available in raw hide. Beside these properties of NaCl, there are several disadvantages found in form of increase in salinity. The dry matter yield at maturity of plant tops decreased with increasing salinity of irrigation water [5]. An observation in greenhouse experiment irrigation with sea water undiluted or diluted with an equal volume of fresh water, reduced plant height, grain yield and straw yield of spring barley and oats [6]. It was reported that reduction in growth, yield components, grain yield and 1000 grain weight produced by irrigation with diluted sea water varied among 13 barley cultivars [7]. Hence to replace NaCl from traditional skin curing process, lot of scientific efforts have been attempted on laboratory scale and also on industrial level. Initial studies were concentrated on determination of efficiency of experimental alternatives. Treated

* Corresponding author. Tel.: +91 512 2597844; fax: +91 512 2597436.
E-mail address: psv@iitk.ac.in (P.S. Vankar).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.06.090

hides/skins were monitored periodically for physical changes like smell and hair slip, which are indications for putrefaction [8] Further several other analytical parameters like moisture content, volatile nitrogen, bacterial colony count, hydro thermal characterization, physical strength and properties and pollution load analysis, were included for the study of the goodness of the curing agent.

Numerous compounds and combinations were scrutinized for experimentation to preserve skin efficiently and to decrease pollution load from final effluent. Boric acid [9], boric acid in combination with NaCl [10], potassium chloride [11], sodium meta-bisulphite (SMBS) with acetic acid [12], Salt-less preservation by the use of neem oil (1%) with alcohol could also preserve the skin but the leather quality is affected [13]. Short-term preservation of hide/skin with hypo at an offer level of 5% on hide weight could preserve the skin/hide for 10 days [14]. Silica gel was also found to be a good dehydratant comparatively to the NaCl [15]. Eventually abovementioned and other practiced hide curing methods were standardized in laboratory and not cost effective for Indian scenario of leather industry.

Curing alone contributes 40–50% total dissolved solid (TDS) in final effluent so curing agent should follow the criteria of pollution control, i.e. less chloride (Cl^-) ion concentration and also in reach of flayers and slaughterhouses belongs basically to rural India because they use NaCl due to its economic feasibility and availability. Sodium sulphate was used as curing agent alone and in combinations due to having similar properties as like of NaCl but not has chloride in the formulation and proved better for goat skin preservation. In our previous work sodium sulphate was opted experimentally as initiative to find an alternative to sodium chloride, thus we optimized curing against sodium chloride and showed remarkable differences. Firstly, in reduction of the quantity used for curing, hence sodium sulphate referred as novel became cost comparative in term of Indian leather industries requirement. It was observed in our earlier work that the quantity of sodium chloride required for curing of goat skin was nearly half of weight of hide, but sodium sulphate showed same curing level only with the use of one-fifth the quantity of the hide weight [16].

Buffalo hides are somewhat different in physicochemical and structural properties from goat skin so the affectivity of sodium sulphate was also been tested against the numerous parameters for buffalo hide which found to be equally efficient as it was proved on goat skin.

2. Materials and methods

2.1. Materials

2.1.1. Buffalo hides/skins

Freshly flayered two buffalo skins 16 kg each of weight and area of approximately 20 ft^2 were purchased from local slaughterhouse near Indian Institute of Technology, Kanpur used in study.

2.1.2. Sodium sulphate

Commercial grade sodium sulphate white in color, were purchased from Neha Chemicals an authorized stockist of laboratory chemicals and Grasim Industries in Kanpur region.

2.1.3. Sodium chloride

Commercial NaCl purchased from outlet known for supply in slaughterhouses and hometown flayer community which have purity of 60–70% and grey in color.

2.2. Methods

Two freshly flayed buffalo hides were purchased from local slaughterhouse, and were treated with experimental salt and control salt. Experimental salt was prepared by mixing NaCl in two ratios, i.e. 10% and 20% of total weight used for curing with Na_2SO_4 hence the two ratios were prepared for experimentation 90:10 and 80:20 (Na_2SO_4:NaCl). One hide was cut into two equal halves and treated with the two ratios, i.e. 90:10 and 80:20 (Na_2SO_4:NaCl). Out of the four hide halves of about 8 kg each, three were treated with pure sodium sulphate and combination of sodium sulphate:sodium chloride separately, so three halves were treated with experimental salt [ratios of 90:10 and 80:20 (Na_2SO_4:NaCl) and pure sodium sulphate] and rest one half piece of hide was treated with control salt (sodium chloride). For sodium chloride treatment 4.5 kg of salt was used as tradition and for experimental salt [ratios of 90:10 and 80:20 (Na_2SO_4: NaCl) and pure sodium sulphate] about 900 g (rationally one-fifth of sodium chloride mediated curing quantity) was utilized. When lesser quantities of both experimental salt mixtures and controlled salt were used the hide samples started deteriorating very fast even at 30–35 °C (as an attempt for reducing pollution load, but it failed). The skin halves were folded and kept at ambient temperature of 30–35 °C. These were monitored periodically for putrification, hair slip and physical changes like odor that are indication of auto proteolysis. The experimental skin halves were kept for 21 days (3 weeks). Efficiency of curing with both experimental and control salt was systematically assessed by analysis of treated skin halves for change in moisture content, total extractable nitrogen content, bacterial colony count. Scanning electron micrographs are taken after treatment of experimental salt and control salt at different intensifying zooms, i.e. 250× and 1500×. Method for pollution analysis adopted for biochemical oxygen demand (BOD), chemical oxygen demand (COD), TDS, total suspended solid (TSS) and chloride ion content in effluent.

2.2.1. Determination of moisture content

Skins were preserved with experimental salt and control salt, were unhaired without disturbing the moisture content and weighed. After each period of experimentation the moisture content of skin pieces was determined by using the procedure outlined in [17].

2.2.2. Determination of nitrogen content

Cured samples of known weight (5 g) were cut from the experimental and control-treated skins, mixed with distilled water in 1:10 w/v, and shaken well in a bottle for 3 h at 30–35 rpm. The liquid was then filtered through a filter paper, digested and the amount of nitrogen was determined using the kjeldahl method [17].

2.2.3. Determination of bacterial count

Bacterial colony count determines the number of bacterial colonies present in per gram of medium at different preservation duration after curing with experimental salt mixtures and control salt. 5 g preserved skin pieces were weighed and soaked in 50 ml sterile water; the skin extract was prepared by shaking it in the arbitral shaker at 200 rpm for 30 min. 1 ml of liquid in which skin pieces had been soaked was taken in 9 ml of sterile water and shaken well to get uniform suspension of the bacteria. A volume of 0.1 ml of the resulting diluted solution was taken in sterile petri plates, and molten nutrient agar at 40 °C was poured and shaken gently to obtain uniform distribution of the bacteria. The plates were incubated at 37 °C for 48 h and colony forming units were determined by serial dilution method [18].