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Delimiting water in the chromium-induced stabilization of collagen

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ABSTRACT

Industrial processes, such as stabilization of skin matrix using chromium, often consume huge quantity of water resulting in depletion of globally demanded valuable resource. Nevertheless, water is essential for the hydrolysis, diffusion, distribution and fixation of chromium in the collagen matrix. Although greener and sustainable solutions for this industrially important process can be obtained through the use of green solvent such as ethanol, probing the minimum quantity of water required for the chromium-induced stabilization of collagen matrix is defied for several years. Here, we show that a minimum of 55–65% internal water content within the collagen matrix is necessary for making chrome tanned leathers through lyophilization technique. The amount and distribution of chromium in the leather decreases as a linear function of internal water content in the skin matrix (from 65 to 15%) with increasing lyophilization time as demonstrated through optical and electron microscopic analyses coupled with energy dispersive x-ray microanalysis.

1. Introduction

Stabilization of collagen matrix, tanning, involves complex processing of skins and hides to prepare leather and other biomaterials (Covington, 1997). Chrome tanning is the widely used technique for making leather. This process requires water as an important component in its manufacturing practice. Basic chromium sulphate (BCS) used conventionally for tanning dissolves in the process water, hydrolyzes and form several hydroxyl-bridged (olated) polynuclear complexes (Rao et al., 1997). It is known that these chromium molecules stabilize collagen through coordinate covalent interactions (Sykes, 1956). Water is essential for the aforementioned reactions as well as medium for diffusion of chromium into the skins and hides (Rao et al., 2003). However, the use of water in large quantities for leather processing has come under severe scrutiny as the availability of water is being drastically depleted (Saravanabhavan et al., 2004). Although several methods have been attempted to reduce the consumption of water for tanning such as recycling of process streams after filtration, process innovation, product innovation etc., (Olle et al., 2013; Morera et al., 2011; Suresh et al., 2001; Aravindhan et al., 2007; Kanagaraj et al., 2008; Saravanabhavan et al., 2004; Sunder et al., 2002) the use of water in chrome tanning is still very common. It has been projected that 1.8 billion people will live in countries or regions with absolute water scarcity by 2025 AD (www.un.org, 2002) thereby positioning water management as a global challenge (Bagatin et al., 2014). The developing world is projected to have much higher growth in total water demand than the developed world, and about 93% of the additional demand will occur in developing countries such as India (Cai and Rosegrant, 2002). Access to safe drinking water is one of the basic human rights and essential for healthy life (Khan et al., 2013). It is therefore imperative to develop a tanning technique with zero water usage. Such an approach can be made without employing water through green chemistry principles for the long term sustenance of leather manufacture. Although several studies have been reported for carrying out chrome tanning in organic solvents (Chagne et al., 1993; Maire, 1976; Ushakoff, 1957), the question of "What is the minimum quantity of water required for chrome tanning?" is still unanswered with a methodical study. Since the role of water for chromium tanning is well known, the answer to this lingering question is of importance both in terms of fundamental understanding as well as development of waterless chromium-induced collagen stabilization technologies.

It is well known that skins and hides possess about 65 wt.% water in varying degrees of freedom such as bound (structural) and free water (Bienkiewicz, 1990). The free water can be removed from skins/hides easily by mechanical pressure or freeze drying or

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dehydration. Lyophilization (freeze drying) is a convenient technique for the removal of excess water from hides and skin. In this study, freeze drying was employed to remove water to the desired levels in order to understand the role of water in the chromium-induced stabilization of collagen as a function of time and moisture content. The different amounts of moisture present within the skin matrix after desired periods of freeze drying was beneficially utilized for chromium tanning in the presence of a green solvent, ethanol, (Alfonsi et al., 2008) as medium. Both conventional pickle-based as well as pickle-free chromium tanning processes (Legesse et al., 2002) were examined in non-aqueous medium. The tanned leathers were characterized for their hydrothermal stability, chromium uptake, distribution and leaching.

2. Experimental section

2.1. Preparation of skin matrix

Wet salted goat skins with larger area (0.46 ± 0.09 m^2) were chosen as raw material and soaked, dehaired, relimed, delimed and pickled following conventional leather processing procedures (Saravanabhavan et al., 2003). The pelts after deliming and pickling were cut in to small square pieces of 10 × 10 cm^2 size and used for subsequent experiments. For enabling the pickle-less chrome tanning, the pH of delimed pelt was adjusted to 5.5 ± 0.5 using 0.5% formic acid on the weight of the pelt (Legesse et al., 2002). The chemicals used for leather processing were of commercial grade. Chemicals used for the analysis were of analytical grade.

2.2. Lyophilization

Lyophilization was used for the removal of water present in the skin matrix without affecting the structure of collagen. The delimed and pickled pelts were frozen at −40 °C and lyophilized for 1, 2 and 3 h duration to remove moisture from the pelts. The weight of the samples after lyophilization for different duration was noted down.

2.3. Determination of moisture content

The internal moisture content of the delimed and pickled pelts was determined after lyophilization for different time intervals (1, 2 and 3 h). Lyophilized samples after different time intervals were accurately weighed and analyzed for moisture content in the hot air-oven for 4 h at 103 ± 2 °C (Clesceri et al., 1989). Triplicate measurements were carried out for each experiment and the average values were calculated.

2.4. Chrome tanning process in ethanol medium

Lyophilized samples of delimed and pickled pelts were tanned using basic chromium sulfate salt. Delimed and pickled pelts were separately treated with 7% BCS (percentage based on pelt weight) in stainless steel drums with ethanol (100% w/v) as a medium following pickle-less and pickle-based chrome tanning procedures, respectively. In the case of pickle-based chrome tanning, after ascertaining the penetration of chromium after 1 h, the pH was found to be 3.0 ± 0.2. In the subsequent basification step, pH of the tanning bath was increased to 3.8 ± 0.2 using 1% sodium formate for 10 min drumming followed by the addition of 1% sodium bicarbonate in 3 installments at 10 min interval and finally drumming for 90 min. In the case of pickle-less chrome tanning (Legesse et al., 2002), lyophilized and pH adjusted delimed pelt was drummed with 7% BCS in ethanol (100% w/v) medium for 3 h. After ascertaining the penetration of chromium, the pH was found to be 4.0 ± 0.2. The total duration of both pickle-based and pickle-less chrome tanning was around 3 h.

2.5. Determination of shrinkage temperature (T_s) and chromium oxide content in tanned leathers

The shrinkage tester, SATRA STD 114 apparatus (SATRA STD 114), was used for determining the shrinkage temperature of tanned leathers with samples of 1 × 2 cm^2. The tanned leathers were analyzed for chromium as per standard procedure (IUC 8, 1998) using a UV-Visible spectrophotometer (UV 1800, Shimadzu). Triplicate measurements were carried out for each experiment and the average values were calculated.

2.6. Analysis of leachable chromium

Known weight of chrome tanned leather was placed in a beaker with 20 ml of distilled water and ethanol separately. The leathers were agitated in a shaker at low rpm for 3 h. The solution was analyzed for chromium content using alkaline peroxide procedure. Concentration of chromium was determined at 372 nm using a UV-visible spectrophotometer (UV 1800, Shimadzu). The amount of chromium was then calculated using molar absorption coefficient (ε) value of 4.8 × 10^3 $M^{-1}cm^{-1}$ after incorporating the dilution factors. Triplicate measurements were carried out for each experiment and the average values were calculated. Chromium leached from Cr-tanned leather sample (% Cr_2O_3) was calculated by dividing the amount of chromium in the leachate by the amount of chromium in the chrome tanned leather sample and multiplying by 100.

2.7. Scanning electron microscopic and energy dispersive X-ray analysis (EDAX) of leather samples

The tanned leather samples were dehydrated gradually using acetone and methanol as per standard procedure (Echlin, 1971). Excess solvent on the leathers was removed by placing them between filter papers. The samples were then cut into specimens of uniform thickness and coated with gold using Edwards E306 sputter coater. Quanta 200 FEG (FEI) scanning electron microscope equipped with energy dispersive X-ray analyzer was used for the analysis. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 30 kV in high vacuum with different lower and higher magnification levels.

3. Results and discussion

In order to find out the minimum quantity of water required for the stabilization of collagen using chromium salts, two different skin substrates were chosen namely delimed and pickled pelts (after the removal of hair and other unwanted biological materials such as globular proteins, proteoglycans, fat, flesh etc). The chosen substrates allow the stabilization of collagen using pickle-less and pickle-based chrome tanning techniques, respectively. For enabling the pickle-less chrome tanning, the pH of delimed pelt was adjusted to 5.5 ± 0.5 using formic acid prior to lyophilization. Pickled pelts were lyophilized as such without any pretreatment. Table 1 shows the amount of moisture present in the delimed and pickled pelts after lyophilization as a function of time. It is seen that the delimed pelts contain around 65, 45 and 18% moisture after first, second and third hour of lyophilization, respectively. While the picked pelts contained around 55, 40 and 13% moisture when lyophilized under similar duration. The lyophilized pelts were chrome tanned using 7% BCS salt. Ethanol was used as a medium for tanning instead of water. Basification (formation of coordinate

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