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A novel chrome tanning process for minimization of total dissolved solids and chromium in effluents

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ABSTRACT

Presence of chlorides and chromium in the tannery effluents are serious environmental concerns of leather making. Elimination or minimization of these is active area of global leather research. Treatment system for removal of chlorides from effluents is very expensive and affects seriously the viability of the tanning industry. Long lasting and convincing solution to the problem rests on development of a common salt free tanning system with high chromium exhaustion levels. Common salt, also known as sodium chloride, is most responsible for the salinity in tannery effluents. In this context a new common salt free tanning process has been developed to overcome the stated problems of industrial leather making. The new process affords use of less chromium tanning agents apart from completely eliminating use of common salt in tanning. The reduction in specific consumption of chromium (ton of equivalent chromium per ton of pelts treated) for tanning in the prescribed method provides significant economic benefits to the new process. Substantial reduction of Total Dissolved Solids (TDS) reduction in effluents has been achieved by adopting the new process. The process essentially is based on modification of the reactants activity to ensure high uptake of tanning material. The process also affords uniform distribution of chromium in the leather. The chemical, physical and microscopical analyses indicate comparable leather properties processed by new method when assessed along with conventionally processed leathers. The innovation which has been commercially implemented provides an economical and simple solution to a century old problem.

1. Introduction

Leather processing technology has evolved naturally from a traditional practice to an industrial activity. Environmental challenges to leather processing arise from both the nature and the quantum of wastes discharged. The industrial leather making process generates substantial quantities of solid, liquid (especially inorganic solids) and gaseous wastes (Sundar et al., 2001; Sundar and Muralidharan, 2009). Processing of one metric ton of rawhide results in 200 kg of tanned leather, 190–350 kg of non tanned waste, 200–250 kg of tanned leather waste, and 50,000 kg of wastewater (Sundar et al., 2011a).

Chromium has been the dominant tanning agent for the better part of the century, and now accounts for approximately 85% of leathers produced globally. This is largely due to its ability to impart high strength and comfort properties compared to other tanning systems. An extensive worldwide research has been carried out on alternative tannages, but no satisfactory replacement for chromium has emerged until now (Sundar et al., 2011b). Conventionally, prior to the chrome tanning process, the pH of hides and skins is lowered to about 2.5–3.0 by use of an acid reagent by a process known as 'pickling'. Lowering of pH helps in the facile penetration of the mineral tanning agent into the fibrous protein substance, the constitutive structure, of hides and skins. Common salt is added to negate the effect of swelling of animal tissues caused by acid addition, which would otherwise make the leather physically unstable. Chrome tanning salt forms aqua hydro complex during hydration and undergoes hydrolysis liberating acid. This acid binding to skin protein causes swelling and leads to reduction in tear and grain crack strength apart from imparting undesirable feel to the leather. Hence common salt is conventionally used during tanning for suppressing acid swelling (Gustavson, 1956). While addition of the common salt in the above process helps in retaining the strength and quality of leather, it leads to high amount of chlorides and TDS with respect to pollution standards for the industrial effluents discharged into environmental receptors after tanning. Conventional tanning necessitates use and discharge of about 8–10% of common salt on the weight of hides and skins,

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resulting in high salinity of tannery effluents apart from large quantities of unfixed chromium (Aslan, 2009; Sundar et al., 2002). The uncontrolled release of chromium containing tannery effluent in natural water bodies increases environmental pollution concerns and health risks (Khan, 2001; Kimbrough et al., 1999). Therefore, whatever method is used to reduce the amount of Cr salts in the final discharge, it will portend chromium as a potentially toxic source to the environment (Mwinyihija, 2010). Chromium released into the air, water and soil can be transported among the various environmental media through various intermedia transport processes where chromium can be taken up by human and other ecological receptors (Murugesan et al., 2012; Mwinyihija et al., 2006).

Extensive research has been carried out on avoidance or elimination of the common salt during tanning (Li et al., 2009). Use of non-swelling acids (naphthalene sulfonic acid condensates) during pH change, pickle liquor recycling and modification of the tanning material have been attempted earlier. However these methods altered the characteristics of the leather and hence did not gain user acceptance and are not being commercially adopted (Krishnamoorthy et al., 2013; Morera et al., 2007). One of the commercially acceptable methods of controlling the total discharge of neutral salts as well as chromium is the reuse of spent chrome liquor in pickling. The high salinity of spent chrome liquor enables its direct reuse in pickle bath. But the collection of spent chrome liquor for recycle and reuse is cumbersome (Cassano et al., 2001; Morera et al., 2011). Number of additives based on dicarboxylic acids, silicates, polyacrylates, ozazolidines which increase the exhaustion of chromium have been attempted for use in tanning but in spite of many claims, most of the additives cause non-uniform distribution of chromium inside leather and while the deposition of the salts on surface of the leather also occur sometimes (Rao et al., 2003; Suresh et al., 2001). In-process changes have not resulted as commercially viable technologies until now (Kanagaraj et al., 2008; Sivakumar et al., 2005). End of pipe treatment to meet the discharge norms have also been not successful or viable (Munz et al., 1997).

While the treated tannery effluents have TDS value of about 7000–10,000 ppm, the standard for the TDS in the treated effluent is prescribed as 2100 ppm in many countries (Moretton et al., 1992). Reverse osmosis and mechanical evaporation system generate clean water but the massive energy use and the enormous quantities of unwanted mixed salts reject generated makes the system unsustainable (Sreeram and Ramasami, 2003). Even though treatment methodologies such as membrane separation (ultra filtration) are being employed by tanneries, generation of solid wastes in the form of rejects pose serious problems (Alves and Pinho, 2000; Viero et al., 2002).

Therefore, long lasting solution to overcome the TDS problems in leather processing would be to eliminate the use of common salt through process innovations (Sundar and Muralidharan, 2004). Pickle free chrome tanning at elevated pH, around 5.0–5.5, has been attempted already (Sundar and Muralidharan, 2002).

The new process developed affords tanning at high pH, thereby avoiding need for addition of acid and common salt for lowering the pH of hide or skin as being practiced conventionally. At high pH the reactivity of collagen, the leather making protein and that of chromium tanning agent is higher, providing an opportunity for reducing the tanning salt in leather processing (Sundar and Muralidharan, 2008). The process also ensures in-situ neutralisation of the acid liberated through hydrolysis of chromium tanning salts.

2. Materials and methods

Ten delimed cow hides (at pH 8.0–8.5) processed as per conventional process were cut into two halves with left half and right half sides taken for experimental and conventional trials respectively. Commercial grade basic chromium sulphate (BCS), Formic acid (~95% purity) Sodium formate (~95% purity) and sodium bicarbonate (~95% purity) were used for the tanning studies. Shrinkage temperature and Stratigraphic chrome distribution in tanned leather were analysed by official methods of analysis (SLTC, 1996).

2.1. Details of experiments

The left half of the delimed pelts meant for experimental were treated with an aqueous solution of (0.2% *w/w*) formic acid to attain pH 5.0–5.5. Then float (water) less chrome tanning method was followed with addition of 3% *(w/w)* BCS with 0.5% Sodium Acetate and drumming for 1 h followed by addition of 3% *(w/w)* BCS and further drumming for another hour. After the complete penetration of chromium throughout the cross section of the pelt, the drum was fed with 100% water followed by addition of 1% sodium bicarbonate in six instalments for 60 min. The pH of the leather was found to be 4.0 at the completion of tanning. Any drastic changes in pH make the grain surface of the leathers harsh and rough, so gradual

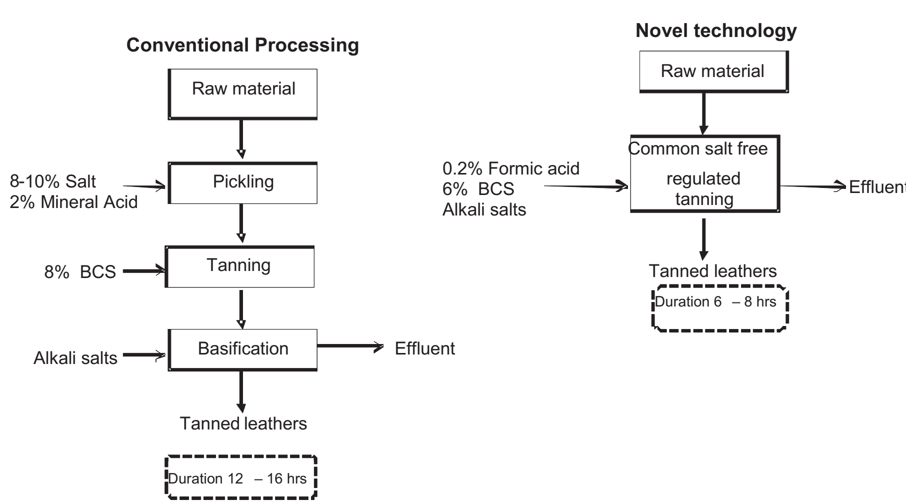

Fig. 1. Flowchart diagram of the experimental (on right) and conventional (on left) methods.