Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Green remediation of sulfide in oxidative dehairing of skin and correlation by mathematical model: An eco-friendly approach

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ARTICLE INFO

Article history:
Received 11 September 2015
Received in revised form 7 December 2015
Accepted 17 December 2015
Available online 29 December 2015

Keywords:
Oxidative dehairing
Sodium percarbonate
Mathematical modeling
Reduction of pollution loads
Replacement of hazardous chemical of sodium sulfide

ABSTRACT

The dehairing of goat skin using sodium percarbonate has been attempted in place of conventional dehairing using lime and sodium sulfide. Conventional dehairing generates huge pollution loads to the maximum level in leather processing. The present method is very simple that dehairs the goat skin with the help of 5% sodium percarbonate at an optimum level in combination with 4% sodium hydroxide and replaces hazardous material like sodium sulfide. The complete dehairing was achieved in 16 h duration. The pollution loads in terms of BOD, COD, Total Dissolved Solids (TDS), and Total Suspended Solids (TSS) were reduced up to the level of 56.3, 62.5, 68.1, and 52% in comparison with the control sample. Reduction of TOC values has been noticed. The advantage of the method lies with the fact that the processing time for leather making is considerably reduced by skipping reliming and deliming unit processes. A mechanistic mathematical model describing the diffusion reaction phenomena of dehairing agent through pores of skin has been developed that supports monolayer adsorption by Langmuir isotherm. Thermo gravimetric analysis and differential scanning calorimetry results explain that the present unit operation is dominated by exothermic process. Experimental samples show improved uptake of color with comparable leather qualities.

1. Introduction

Leather industry is one of the major polluting industries that received negative image due to severe environmental pollution problems. Leather processing involves many unit operations which generates huge amount of pollutants. Many researchers (Muthusubramanian and Mitra, 2006) have presented technologies concerning enzymatic soaking (Morera et al., 2013), dehairing (Saravanan et al., 2014), pickle free tanning process improved chrome tanning process (Guo et al., 2006; Li et al., 2009; Ma et al., 2014a,b; Morera et al., 2011; Sundar et al., 2002) and techniques for utilization of solid wastes (Hu et al., 2010). But, these do not provide holistic approach and do not aim for cleaner production. Hence there is a need for viable and sustainable technologies through eco-friendly means in every unit operations, especially dehairing where limited attention has been given for waste management. Thus there is a need for commercial viable technology for the sustainability of leather industry (Dixit et al., 2014).

Dehairing is one of the important operations in leather making where the hair is removed by using lime and sodium sulfide in the conventional process. Dehairing is responsible mostly for untidiness and contributes about 60–70% of the total pollution load in leather processing. A significant amount of BOD, COD and TSS are generated in this operation. Sodium sulfide is said to be toxic and hazardous as

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http://dx.doi.org/10.1016/j.psep.2015.12.005
0957-5820/

it produces H_2S through NaHS as intermediate in aqueous medium. Thus there is a need to replace this hazardous chemical whose extensive use bears unfavorable consequences on environment and affects the soil, air and water bodies and also reduces the efficacy of effluent treatment plants. Moreover, the conventional method is time consuming and alters collagen matrix of skins. Consequently it is worthwhile to look for alternative dehairing process, which will completely replace the lime and sodium sulfide that will augment in maintain green environment (Crispim and Mota, 2003; Annapurna Raju et al., 1996).

Enzymatic dehairing is an alternative to conventional dehairing process as proposed by many researchers. In the enzymatic dehairing of the skin, the root of hair is broken by a selective proteolytic enzyme that cleaves the peptide bonds that surrounds the basement membrane of the hair bulb which constitutes mainly proteoglycans, such as, glycosaminoglycans and dermatan sulfate, thereby, removing hair very safely. Dehairing is achieved rapidly in enzymatic method than conventional process (Cantera et al., 2003, 2004).

Senthilvelan et al. (2012) presented enzymatic unhairing by using protease enzyme to replace sulfide. This enzyme was obtained from *Bacillus* sp. that showed optimum activity at pH 11.0, at temperature of 45 °C and duration 16 h. This yielded complete dehairing through the use of protease at 2%. This method relinquished the pollution loads with BOD, COD, TSS, and TDS at the level of 62.8, 79.0, 88.2, and 82.5%, respectively in comparison with the conventional process. The product leather resulted in comparable strength properties and showed enhanced color properties.

From other literature it is known that dehairing of goat skins using proteolytic enzyme isolated from *Aspergillus tamarii* through solid state fermentation showed similar results where the dehairing was achieved in an incubation period of 18 h. This method resulted in reducing the pollution load to BOD (50%), COD (40%), and TDS (20%) (Dayanandan et al., 2003; Kanagaraj, 2009). According to another method it is possible to replace sulfide completely by alkaline protease obtained from *Vibrio metschnikovii* NG155, at pH 10, temperature 65 °C that effectively removes hair. In addition to that better physiochemical properties of dyed crust and lesser pollution load in dehairing process were achieved in leather processing. Dettmer et al. (2012, 2013) reviewed use of enzymes in leather processing to improve and optimize process and to produce good quality of leather. But, the limitation of the enzymatic method is that the maintenance and dependence of the process on different parameters like, pH, temperature and activity of enzyme. The method cannot be universally accepted as the environmental temperature is a barrier (George et al., 2014).

As an alternative to these methods, oxidative dehairing with the help of oxidative agents was suggested (Gehring et al., 2003; Shi et al., 2003). Number of oxidative chemicals like calcium peroxide (Gehring et al., 2003), alkaline peroxide (Marmer and Dudley, 2004; Richardson et al., 2000, 2003), magnesium peroxide and potassium peroxymonosulfate have been experimented in dehairing to replace sodium sulfide in the conventional dehairing (Marmer and Dudley, 2004, 2005). Literature reports that combination of 4% hydrogen peroxide with enzyme at the level of 100–300 U g/l is a viable method for unhairing process to replace lime and sulfide from the conventional method for producing better quality leather (Marmer and Dudley, 2005). It has been found from literature that several commercial enzyme formulations were available in combination with hydrosulfide and peroxides for better results. These reports indicate that activity of enzyme is stabilized by the addition of hydrosulfide through activity measurements; thus, peroxide augments the activation effect (Andrioli and Gutteres, 2014).

Oxidative agent alone with the help of calcium peroxide rapidly dehairs cattle hide satisfactorily as that of sodium sulfide. Calcium peroxide is applied at the level of 5–15% (w/w) at (pH 13) to get complete dehairing at a reaction temperature of 45 °C (Gehring et al., 2003). Other dehairing methods using alkaline sodium perborate with alkaline hydrogen peroxide amended with either potassium cyanate or urea can able to remove the hair completely (Marmer and Dudley, 2005; Wei et al., 2010). It has been concluded that leather produced from the chemicals showed similar physical properties as that of lime and sulfide one. Dehairing using urea and dicyandiamide may have negative effects on the qualities of leather because of toxicity and degree of reactivity with collagen matrix (Marsal et al., 2002, 2003; McKillop and Sanderson, 1995).

Oxidative dehairing using sodium percarbonate and sodium hydroxide was also proposed by Marmer and Dudley (2004). Though complete dehairing is possible by the oxidative unhairing methods, the amount of chemicals/recipe and operating conditions/parameters are not optimized. A mathematical modeling may be helpful to understand the mechanism of dehairing and to optimize the said conditions and recipe for commercial exploitation of the process. Hence, the objective of this work is to develop cleaner oxidative dehairing of skins and to formulate a mathematical model to understand the process through experimental design and optimization. The main aim of the present investigation is to demonstrate the dehairing with the help of sodium percarbonate and sodium hydroxide and to study the various effects during dehairing and in leather. This process can be commercially exploited for sustainability and cleaner production of leather units.

2. Experimental

2.1. Materials

Fresh goat skins weighing, 1 kg/skin, were procured immediately after flaying from local abattoir. Other reagents namely sodium percarbonate and sodium hydroxide for the experiments were collected from Sigma-Aldrich, Mumbai, India of laboratory reagent grade. Matlab V2012b was used to solve mathematical model for the dehairing experiment.

2.2. Dehairing studies

Oxidative dehairing was carried out with the help of sodium percarbonate and sodium hydroxide. Initially, the salted skins were cut into halves and left sides were used for experiments while the right sides were used for control. Totally five dehairing experiments were carried out using fixed level of 5% sodium percarbonate along with varying levels of 1, 2, 3, 4, and 5% of sodium hydroxide and 200% of water. The skins were dipped in the bath containing the above reagents and cooled air was circulated to expedite the oxidation process by maintaining temperature constant at 37 °C for a period of 16 h. Two control experiments were carried out; one with lime (10%), sodium sulfide (2%), and water (200%). Another control experiment was performed with 5% sodium percarbonate along with