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Hide unhairing: achieving lower pollution loads, decreased wastewater toxicity and solid waste reduction

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ABSTRACT

This study aims to diminish the pollution being discharged into wastewaters through changes in the unhairing process. To this aim, we are replacing a reductive hair degrading process with a process which combines a reductive hair degrading process with an oxidative hair degrading process. Hydrogen peroxide is used to decrease the supply of sulfide as unhairing chemical. As a result, commercially acceptable leather regarding both costs and quality is obtained and significant reductions in the contaminant load of the wastewater being discharged are observed. Results indicate that wastewater conductivity is cut by 26%, suspended solids decrease by 75%, observable sulfide disappears, while the amount of chromium being absorbed by the hides is increased. This leads to considerable savings in the chromium salt offer in hide tanning and, consequently, a decrease in the amount chromium in the wastewater.

1. Introduction

Chemically speaking, tanning means stabilizing a protein called collagen, which is the main constituent of the skin. The tanning process may be divided into several stages. The beamhouse procedures are cleaning operations that prepare the hides for the subsequent leather making process. Beamhouse involves high water consumption and is considered as highly polluting. Actually, this is the stage that generates the most polluted wastewaters (Saravanabhan et al., 2006) and most solid waste (Kanagaraj et al., 2015). According to data published by the International Union of Leather Technologists and Chemists Societies (IULTCS, 2008), the beamhouse stage uses about 60% of all the water consumed in the whole tanning process and generates about 75% of the chemical oxygen demand (COD), 80% of suspended solids (SS), and 100% of sulfide (S^{2-}).

These data are an average assuming good practices in working conditions. According to the Food and Agriculture Organization of the United Nations (FAO, 2013), yearly world production of cattle hides, expressed in wet salted weight, approaches 6.5 Mt. This means that each year beamhouse operations worldwide approximately consume 104 Mm^3 of water. Likewise, approximately 0.91 Mt of COD, 0.036 Mt SS and 0.62 Mt of S^{2-} are generated. These figures are actually lower than the real ones especially for two reasons. First, numerous tanneries are located in countries where environmental laws are practically nonexistent, which suggests that the import figures are actually higher. Second, besides tanned cowhides, also other types of skins are being tanned worldwide (sheep, pigs, reptiles, etc.), although to a much lesser extent. In fact, cowhides account for approximately 75% of total world leather. All in all, the figures above suggest that the pollution generated during the beamhouse stage may be considered a major environmental problem.

Unhairing, one of the operations during the beamhouse stage, consists in removing the hair or wool off the hides and skins. The reagents conventionally being used during this operation are sodium sulfide and/or sodium hydrosulfide and lime. After a reductive reaction, the joint action of hydrosulfide (HS^-) and hydroxyl (OH^-) ions causes the disruption of the disulfide bridges of hair cystine, thus transforming it into cysteine and obtaining the subsequent hydrolysis of keratin (hair protein). Eq. (1) shows one of the possible mechanisms of this reaction.

$$-S-S- + 2^{-}SR \rightarrow -S-S-R + R-S-S- \quad (1)$$

The hydrolysis of keratin influences the characteristics of the effluent resulting from the unhairing process, and therefore its COD and Total Kjeldahl Nitrogen (TKN) values are considerably high. The

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presence of hydrosulfide and sulfide ions is also a major challenge, especially due to the possibility of transformation into hydrogen sulfide (Black et al., 2013). Over the years there have been numerous poisonings and even fatalities due to inhalation of hydrogen sulfide. Theoretically, hydrogen sulfide production should be avoided by maintaining the pH of the float at a certain level, as the chemical reaction below shows in Eq. (2).

$$HS^- + H_2O \leftrightarrow H_2S\uparrow + OH^- \quad (2)$$

Unfortunately though, production of hydrogen sulfide has not always been avoided.

Besides, sulfide and hydrosulfide ions are not completely removed from the hides, which is also major drawback. The next step after unhairing is the fleshing operation, in which a large amount of solid waste is generated. The fleshings contain sulfides and this increases the difficulty and cost of their recovery for glue, gelatin or cosmetic production (Bayramoglu et al., 2014).

In the last decades numerous studies (Vidal et al., 2004; Sengil et al., 2009; Haydar and Aziz, 2009) have been carried out to try to minimize the environmental impact of unhairing. One of the systems to reduce pollutant loads from residual floats and thus facilitate their subsequent treatment is to implement the hair recovery process (Frendrup, 2000; Valeika et al., 2009; Galarza et al., 2010). This process consists of two parts: First the shaft of the hair is protected with lime against the attack of sodium sulfide. This operation is called immunization and involves the formation of compounds such as lanthionine (see Fig. 1) and other similar compounds. As a result, only the hair root undergoes hydrolyzation, whereas the shaft of the hair separates from the hide without hydrolyzing, and COD and TKN values are significantly reduced in the wastewater float. Subsequently, the hair root must be hydrolyzed by adding more sodium sulfide. This system is used on an industrial scale and its main problem is the presence of sulfides in waste floats and in unhaired hides.

Another line of research is based on the use of hydrogen peroxide as an unhairing agent instead of sodium sulfide/hydrosulfide (Bronco et al., 2005; Morera et al., 2008; Andrioli and Gutterres, 2014). Hydrogen peroxide, at pH values close to 13, is capable of hydrolyzing the hair through an oxidative reaction. The oxidative attack of the S–S bond is due to the formation of peroxy anion from hydrogen peroxide (Eq. (3)).

$$H_2O_2 \leftrightarrow HOO^- + H^+ \quad (3)$$

Research has also been conducted to explore the possibility of performing this type of unhairing by immunizing the hair first in order to minimize the pollution load from wastewater floats. The environmental impact of this practice has been evaluated by performing a life cycle assessment (LCA) (Castiello et al., 2008). This system reduces the pollution discharged and eliminates sulfides in the wastewater. However, further research is needed to implement it in the industry.

The use of enzyme products to replace sodium sulfide as an unhairing agent is an old practice (Heidemann, 1993). The problem is that the enzymes used to date, besides attacking the hair, do also attack the collagen, thus damaging the surface of the hides. Of course, this considerably diminishes the commercial value of hides and therefore is an impediment to the industrial application of this system. However, numerous researchers are currently exploring the behavior of various unhairing enzymes on the hides under different conditions of pH, temperature, concentration, etc. (Thangam et al., 2001; Jian et al., 2011; Dettmer et al., 2012).

In short, there are various lines of research open to explore the replacement of sodium sulfide as unhairing agent. So far though, an effective, inexpensive product that may be applied at an industrial scale has not yet been found.

Our work has studied the possibility of modifying the reductive unhairing process with hair recovery (using lime, sodium sulfide and sodium hydrosulfide), combining it with an oxidative unhairing (using hydrogen peroxide) to obtain less polluted wastewater. Moreover, the new process is less toxic due to sulfide removal.

Specifically our studies aim to eliminate the use of sodium sulfide to hydrolyze the hair root, replacing it with hydrogen peroxide, as well as examine the consequences of this change in the discharged wastewater. The anticipated improvement in wastewater quality should not compromise the physical properties of the leather required for the manufacture of consumer goods.

2. Materials and methods

2.1. Materials

Part of the laboratory tests were carried out using 0.40 m in diameter and 0.15 m wide stainless steel drums, Inoxvic brand. The rest of the laboratory tests and the pilot plan tests were carried out using 1 m in diameter and 0.4 m wide stainless steel drums, Olcina brand. Drums are cylindrical vessels that rotate around an axle (Fig. 2).

The chemicals and the machinery used in the beamhouse operations were those normally used in the leather industry: Sodium hydroxide (50% w/w), lime (95% w/w), sodium hydrosulfide (70%

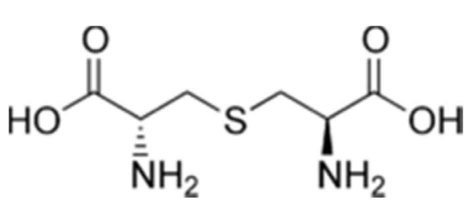

Fig. 1. Lanthionine structure.

Fig. 2. Pilot plant drum.