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Review

Carbon dioxide deliming in leather production: a literature review

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ABSTRACT

In this article, carbon dioxide deliming development in leather process was comprehensively reviewed. Based on carbon dioxide properties and its solubility in water, carbon dioxide deliming principle and mass transfer were analyzed, respectively. It was creative to propose reuse of carbon dioxide with available absorption and desorption technology which reduces occupational safety risk, regenerates new resource and leads to a cleaner production. Additionally this review provided the possible ways forwards of this technology. This review aims to give an overview of fundamentals, process optimization, occupational safety and possible ways forwards of carbon dioxide deliming in leather, and to provide useful information to researchers and engineers in this field.

1. Introduction

Leather production is a common industry in the world. The major raw materials for leather making are hides and skins of bovines, buffaloes, goats, sheep and pigs. The term of skin is used for the integument of smaller animals and term of hide is for animal body surface more than 1 square meter in area and several millimeters in thickness. Beamhouse process conventionally refers to soaking and liming where beams were employed to better flesh hides and skins. The tasks are to remove components such as elastin, collagen, keratin, hemoglobin, proteoglycans and lipids and to keep only the collagen which will be later tanned into leather (Heidemann, 1993). Currently, beamhouse work industrially includes soaking, liming, deliming, bating, picking and tanning (Covington, 2009). Beamhouse processes, their purposes and resultant appearances are shown in Fig. 1. After depilation at the beginning of liming, hide or skin is also called pelt. Deliming is a process after liming to remove mechanically depositing lime or chemically bound lime by conversion into readily soluble salts. The most typical deliming agent is ammonium sulfate or ammonium chloride. Limed pelts can also be delimed in carbon dioxide oversaturated bath. This deliming process is called carbon dioxide deliming (CDD) in leather field.

Leather production plays an important economic role in light industry of China. The turnover of leather and their articles in China reached approximately 600 billion US dollars in 2009. However, leather manufacture employs a wide range of chemicals, and as result, brings more and more environmental challenges. Typically, 35–40 tons of wastewater with different chemicals is generated in order to turn 1 ton raw hide into leather (Li et al., 2010). It was reported round 100 million tons wastewater was discharged annually from tanneries in China (Duan, 2000). Efforts from researchers and scholars insistently provides solution to reduce leather pollution (Li et al., 2009, 2010; Mariliz et al., 2010; Hu et al., 2011; Dettmer et al., 2013; Krishnamoorthy et al., 2013; Saran et al., 2013; Bacardit et al., 2014; Saravanan et al., 2014; Lofrano et al., 2013; Almeida et al., 2013). Ammonium Nitrogen (NH_3-N) is one of the key leather pollutants. It was calculated as approximately 6 kg along all processed when 1 ton raw hides was put into production with conventional deliming process (UNIDO, 2000). It was also reported that 78% NH_3-N of the total emission comes from conventional ammonium salt deliming process (Wang et al., 2011).

Occupationally long-term contact with ammonia gas (NH_3) has potential to hepatic encephalopathy (Abraham and Maria, 2009) and methemoglobinemia (Julio et al., 2006).

NH_3-N exists in aqueous solution in forms of ammonium ion (NH_4^+) and un-ionized ammonia (free NH_3). At pH of 7 and temperature of 25 °C, free ammonia amounts for only 0.6% of total NH_3-N, while at pH of 9.5 and temperature of 30 °C, this figure climbs to 72% (Hellinga et al., 1999; van Hulle et al., 2007). Free ammonia is more active substrate providing nutrient for autotrophic bacteria in

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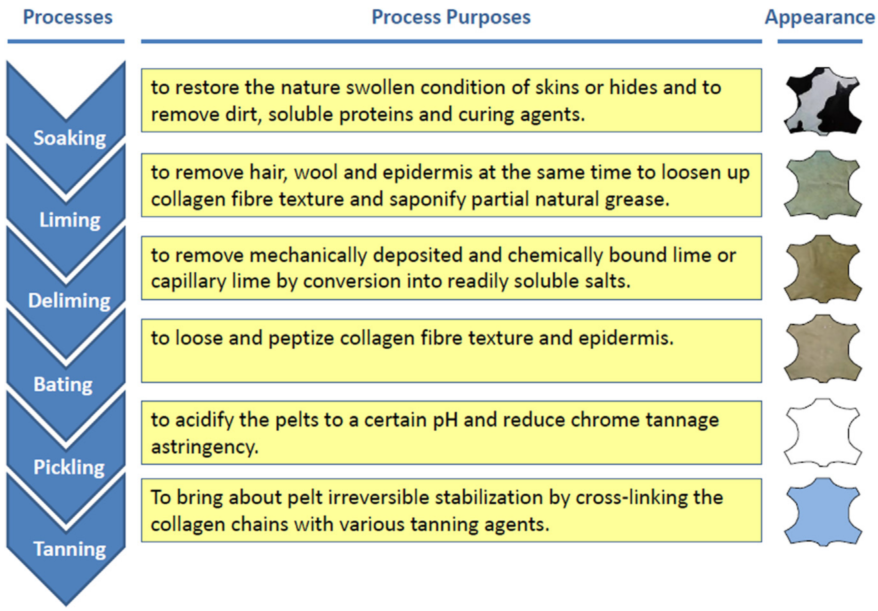

Fig. 1. The processes of beamhouse work of leather production.

surface water and other ecosystem and buffering anaerobic digestion system (Paredes et al., 2007). It is reported that ammonia concentration has direct relation to microbial activity as shown in Table 1.

When NH_3-N is discharged into and diluted in water body, it provides nutrient for autotrophic bacteria and most plant species which augments them growth and in return stimulates wildlife production. It also leads to serious environmental problem for aquatic life (Effler et al., 1990). The eutrophication cause by NH_3-N breaks the ecological balance in lakes and rivers directly indicated by the overgrowth of algae, death of aqueous life and different dissolved oxygen distribution along the vertical depth (Smith, 2009). Ammonia in water is chemically oxidized by dissolved oxygen, resulting in decrease and depletion of dissolved oxygen in aqueous solution. On the surface of water, there is more dissolved oxygen caused by activity of algae. Already low concentration of 0.2 g/L is toxic to many forms of aqueous life, invertebrate and vertebrate species, including human beings (Kadlec and Knight, 1996). The guide discharge level of 0.05 mg/L NH_3-N was suggested by the Council of European Union.

Biological and physicochemical effluent treatment methods are the conventionally used strategies for NH_3-N removal. Physicochemical processes include air stripping (Marttinen et al., 2002), ion exchange (Jorgensen and Weatherley, 2003; Wang and Peng, 2010), membrane separation (Palma et al., 2002), and chemical precipitation (Renou et al., 2008). Chemical precipitation with magnesium ammonium phosphate or air stripping is feasible but much more expensive than conventional biological treatment (Siegrist, 1996). The traditional biological convention consists of nitrification and denitrification. Aerobic treatment is economical but needs big instruction space and long time for treatment due to low microbial activity and yield. This method is not effective for tannery wastewater due to high concentration load and the presence of inhibiting substance to bacteria (Murat et al., 2002) and shortage of carbon sources for denitrification. SHARON is presented as 25% of the oxygen and 40% of the carbon demand compared with nitrification and denitrification. However, an external electron donor such as methanol and an effective aeration system are still necessary (Hellinga et al., 1998). Anaerobic ammonium oxidation (Anammox) was discovered over 50% of the oxygen to be saved and no organic carbon source is needed under anoxic conditions with nitrite as the electron acceptor (Mulder et al., 1995). Anammox experiments showed a very low growth rate (Strous et al., 1999). Additional challenge of this process is long time and bacterial cells retention of start-up. In conclusion, NH_3-N prevention is a better solution for leather cleaner production.

Table 1
Ammonia concentration and the effect to microbial activity (Berge et al., 2005).

Concentration of ammonia (mg/L)	Effect to microbial activity
50–100	Beneficial in anaerobic degradation
200–1000	Detrimental
1500–3000	Inhibitory particularly at higher pH
More than 5800	Toxic to some microorganisms

Concerning the global awareness and economic stress to the leather pollution, leather industry is being driven for cleaner, economically and environmentally sustainable solutions. Research of ammonium free deliming is never stopped with fast penetration, stable pH and low cost. Magnesium sulfate or its combination with sulfuric acid substituted ammonium salt in leather deliming (Koopmann, 1982; Taylor et al., 1988). NH_3-N in effluent was reduced to 8% of original level. Magnesium lactate delimed pelts had better performance, however, the cost made it unfeasible for production (Kolomaznik et al., 1996). Weak acids such as boric acid, acetic acid and citric acid were applied on sheep skins deliming with achievement of NH_3-N reduction from 77% to 95% (Colak and Kilic, 2008). The deliming experiment with formic acid, sulfosalicylic acid, citrate acid, Nylon acid, gluconic acid and other nitrogen-free materials showed that not only could remove the pollution caused by ammonia nitrogen in the deliming wastewater and greatly reduce the S^{2-} in the wastewater, but also could effectively reduce COD_{Cr} and BOD_5 of the deliming effluent (Cai and Li, 2012). The deliming values and buffer capacities should be further improved. Boric acid is more promising on application performance on leather (Zeng et al., 2011). However, more recently, boric acid was added on the candidate list of Substance of Very High Concern (SVHC). In EU, it started to be banned in 2011 from REACh.

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