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Review

Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review

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HIGHLIGHTS

- Wastewater characteristics depend on the chemicals used in tannery processes.
- In plant control is the best option to minimize water consumption and chemicals use.
- Emerging treatment technologies are in advance as treatment of tannery wastewaters.

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ABSTRACT

Although the leather tanning industry is known to be one of the leading economic sectors in many countries, there has been an increasing environmental concern regarding the release of various recalcitrant pollutants in tannery wastewater. It has been shown that biological processes are presently known as the most environmental friendly but inefficient for removal of recalcitrant organics and micro-pollutants in tannery wastewater. Hence emerging technologies such as advanced oxidation processes and membrane processes have been attempted as integrative to biological treatment for this sense. This paper, as the-state-of-the-art, attempts to revise the over world trends of treatment technologies and advances for pollution prevention from tannery chemicals and wastewater. It can be elucidated that according to less extent advances in wastewater minimization as well as in leather production technology and chemicals substitution, biological and chemical treatment processes have been progressively studied. However, there has not been a full scale application yet of those emerging technologies using advanced oxidation although some of them proved good achievements to remove xenobiotics present in tannery wastewater. It can be noted that advanced oxidation technologies integrated with biological processes will remain in the agenda of the decision makers and water sector to apply the best prevention solution for the future tanneries.

Contents

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1. Introduction

Leather tanning is a wide common industry all over the world. It is known to be one of the most important industries in Mediterranean countries (Insel et al., 2009; Mannucci et al., 2010). Because of their complex wastewater characteristics leather tanneries are generally located in so called *organized industrial districts*. In Italy tanneries, represented by about 1400 tanneries, are sited in four main poles: Veneto, Toscana, Lombardia and Campania regions (Fig. 1a); they transform raw or wet-blue skins into products used for various purposes. The value of production weighs for 17% of worldwide production and for 62% considering only the European Union. In terms of trade, it has been calculated that nearly one out of three skins traded between international operators is of Italian origin (UNIC, 2013). A proportional distribution of the leather tanneries in Italy and in EU countries is shown in Fig. 1b.

Tanneries represent an important economic field also in developing countries as in the cases of Turkey, China, India, Pakistan Brazil and Ethiopia (Orhon et al., 1999; Leta et al., 2004; Lefebvre et al., 2006; Banu and Kaliappan, 2007).

Currently the aqueous streams of each exhausted bath of tanning process are mixed all together in balancing tanks and pre-treated before biological treatment (Cassano et al., 2001; Dogruel et al., 2006; Lofrano et al., 2006). However the mixture of many compounds used in the process can be released into the environment because they even remain after conventional treatment and negatively affect organisms (Kumar et al., 2008; Siqueira et al., 2011) and environment (Meriç et al., 2005; Oral et al., 2007; Shakir et al., 2012; Alvarez-Bernal et al., 2006; Tigini et al., 2011) or may inhibit nitrification process (Jochimsen and Jekel, 1997; Szpyrkowicz et al., 2001). The effluent of leather tanneries was associated to a huge foaming problem on surface waters too (Schilling et al., 2012).

The high concentrations of pollutants with low biodegradability in tannery wastewater represent a serious and actual technological and environmental challenge (Di Iaconi et al., 2002; Schrank et al., 2009). Much research has addressed this aim over the past decade highlighting the promising role of a special class of oxidation techniques defined as advanced oxidation processes (AOPs) to treat tannery wastewater and synthetic and natural tanning materials (Szpyrkowicz et al., 2001; Dantas et al., 2003; Dogruel et al., 2004; Schrank et al., 2005; Pokrywiecki Sauer et al., 2006; Kurt et al., 2007; Preethi et al., 2009; Di Iaconi et al., 2010; Lofrano et al., 2007a,b, 2010a,b). Thus, the leather industry is being pressured to search cleaner, economically as well as environmentally sustainable wastewater treatment technologies (Suresh et al., 2001; Sundarapandiyan et al., 2010; Krishnamoorthy et al., 2012).

This paper presents the state-of-the art of chemical minimization and treatment technologies applied to leather wastewater. An introduction of the common production technologies, water consumption and wastewater characteristics is first presented and accordingly wastewater treatment options are compared, taking into account several criteria. Additionally the greening production and advances in treatment technology is discussed.

2. Tannery industry

2.1. Leather production and chemicals used

The tanning process aims to transform skins in stable and imputrescible products namely leather (Fig. 2). There are four major groups of sub-processes required to make finished leather: beamhouse operation, tanyard processes, retanning and finishing (U.S. EPA, 1986; Tunay et al., 1995; Cooman et al., 2003). However for each end product, the tanning process is different and the kind and amount of waste produced may vary in a wide range (Tunay et al., 1995; Ates et al., 1997) (Fig. 3). Traditionally most of tannery industries process all kind of leathers, thus starting from dehairing to retanning processes. However in some cases only pre-pickled leather is processed with a retanning process. Table 1 shows a typical retanning bath procedure applied for production of clothing leathers in a large leather tannery district, Southern Italy. A similar procedure was reported by Saravanbahavan et al. (2004) and by Basaran et al. (2008) for Indian and Turkish leather tanneries respectively.

Acids, alkalis, chromium salts, tannins, solvents, sulphides, dyes, auxiliaries, and many others compounds which are used in the transformation of raw or semi-pickled skins into commercial goods, are not completely fixed by skins and remain in the effluent. For instance the present commercial chrome tanning method gives rise to only about 50–70% chromium uptake (Saravanbahavan et al., 2004). During retanning procedures, synthetic tannins (Syntan), oils and resins are added to form softer leather at varying doses (Lofrano et al., 2008). One of the refractory groups of chemicals in tannery effluents derives mainly from tannins (Di Iaconi et al., 2010). Syntans are characterized by complex chemical structures, because they are composed of an extended set of chemicals such as phenol-, naphthalene-, formaldehyde- and melamine-based syntans, and acrylic resins (De Nicola et al., 2007; Lofrano et al., 2007a; Munz et al., 2009). Among syntans, the ones based on sulfonated naphthalenes and their formaldehyde condensates play a primary role, for volumes and quantity used in leather tanning industry (Munz et al., 2009). According to Fig. 4, the oils cover the greater COD equivalents compared to the resins and syntans. The BOD_5/COD ratio of syntans was also lower than other compounds (Lofrano et al., 2007a). However it is worth to notice as no one of these