Process Safety and Environmental Protection 95 (2015) 195–201

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Removal of chromium from tanning wastewater and its reuse

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ARTICLE INFO

Article history:
Received 10 September 2014
Received in revised form 3 March 2015
Accepted 6 March 2015
Available online 14 March 2015

Keywords:
Chrome
Wastewater
Reuse
Chemical precipitation
Electrocoagulation
Cost comparison

ABSTRACT

The chromium (Cr) used in the manufacture of leather from hides has well-known adverse effects when inappropriately disposed in the environment. The tanneries use large quantities of water for processing hides. The recovery of Cr from the wastewater produced in the tanning step is an environmentally friendly and economically viable alternative avoiding the disposal of large amount of Cr-containing sludge in industrial hazardous waste landfills. This work aims at studying the removal of the Cr from the tanning wastewater through chemical precipitation (CP) and electrocoagulation (EC) techniques and its reuse in tanning process. In the CP experiments, efficient Cr removal from wastewater samples was achieved, with up to 99.74% removal efficiencies. In the EC experiments, three different electrode materials, Al, Cu, and Fe were tested. The highest removal efficiency of 97.76% was obtained with Al electrodes by conducting electrolysis at 3.0 V for 110 min. This was followed by Fe electrodes and Cu electrodes, which showed removal efficiencies of 90.27% (at 2.5 V) and 69.91% (at 2.0 V), respectively, for an electrolysis of 100 min. The recovered Cr was reused as a tanning agent in leather processing, where good crossing of Cr was reached in leathers tanned with the liquors prepared from the sludge, and the pH and ash content values were measured. While the hides tanned with the Cr-containing liquor recovered by CP and by EC with Cu electrodes showed good hydrothermal stability and Cr content above 2.5% Cr_2O_3, the hides tanned with Cr-containing liquors recovered by chemical precipitation and by EC conducted with Fe and Cu electrodes showed contents of Cr according to technical specifications. However, the Cr samples obtained with the iron electrode showed a dark coloration due to oxidation of the iron. It can be concluded that the tanning process with Cr recovered by CP and by EC with Cu electrodes showed the best results.

1. Introduction

Various environmental concerns are associated with the leather industry due to the generation of high quantities of solid and liquid wastes as well as gaseous emissions and unpleasant odors (Andrioli et al., 2015) during the manufacturing process. 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., 2011). The tanning process in Brazil and worldwide is of great economic importance. Brazil has the second largest herd overall and the largest marketable herd in the world, consisting of approximately 210 million heads of cattle. The country is also the second largest producer and exporter of leather and aims at achieving excellence in the industry with investments, qualification, and technology (ABQTIC, 2013).

The processing of hides involves three main phases, namely beamhouse, tanning, and finishing, which are further subdivided into several steps. Beamhouse operations are mainly responsible of cleaning the hide and preparing it for subsequent tanning steps. Therefore, the beamhouse process, carried out in the conventional manner, is

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http://dx.doi.org/10.1016/j.psep.2015.03.007

responsible for producing 70% of the total pollution arising from leather processing (Li et al., 2010).

"A large amount of chemicals are added in leather processing. Each of these operations gives rise to characteristic pollutant loads, as high biological oxygen demand (BOD), high chemical oxygen demand (COD) and high concentrations of suspended solids, organic nitrogen, sulfide and chromium (Thorstensen, 1997).

Rao et al. (2003) and Gutterres et al. (2015) characterized the parameters of tannery wastewaters in all process operations finding the following values for tanning wastewaters: pH (2.5–3.0), BOD (350–800), COD (1000–2500), total solids (25,000–60,000), dissolved solids (24,000–57,500), suspended solids (1000–2500), chlorides (15,000–25,000) and total chromium (2000–5000)".

Roughly 3% of the reserves of chromium are used for the manufacture of tanning salts, dyestuffs and raw materials for chromium-plated surfaces or pharmaceuticals, of which leather accounts for 1–2%. The use of chromium for leather tanning has no significant impact on the world's chrome reserves. However, a recycling concept of chromium for leather would be an interesting and realistic approach which should be considered and addressed, at least in countries with high consumption (Tegtmeyer and Rabe, 2014).

It is possible to recycle the tanning wastewater, passing them through a sieve, do a chromium solution analysis and replenish the amount of chromium salt and chemical inputs required for the process. Tests were conducted on an industrial scale for reuse of tanning wastewaters in a tannery in Brazil (Aquim, 2009; Aquim and Gutterres, 2012). Before the tanning wastewaters were recycled the pH value, the concentration of Cr_2O_3 and the content of oils and greases were measured. It was possible to reduce the supply of salt (sodium chloride) in tests through recycling. As the recycled wastewaters already contained a certain amount of salt (necessary to avoid the swelling of the hide) 3.0–4.5% of sodium chloride was added in relation to the mass of hides, while usually 5.5% of sodium chloride is added to a new processing water. In the recycling of tanning wastewaters the supply of chromium, was reduced from 5.5 to 4.0%. Water reuse in tanning not only saves clean water but also proposes reusing a wastewater that would be handled and disposed of to the environment; thus the use of this input is maximized. The proposed direct reuse of chrome baths is even more important because chromium is a chemical of great environmental impact (Aquim, 2009)".

The global leather industry is increasing attention for treating liquid effluents and providing adequate endpoints for the sludge and residues generated in the processes. Conventional tanning necessitates use and discharge of about 8–10% of common salt on the weight of hides and skins, resulting in high salinity of tannery effluents apart from large quantities of unfixed chromium (Aslan, 2009 and Sundar et al., 2002). Considering the level of Cr in the wastewater, the development of appropriate techniques to recover and recycle the residual Cr is relevant (Gutterres and Mella, 2014). The uncontrolled release of chromium containing tannery effluent in natural water bodies increases environmental pollution concerns and health risks (Khan, 2001 and Kimbrough et al., 1999). Residues containing Cr are classified as dangerous in Brazil and must be disposed of in dangerous industrial residues landfills. This applies to wet-blue leather shavings and trimmings, semi-finished and finished leather cuts, and the sludge generated in wastewater treatment plants (Gutterres and Mella, 2014).

Many methods are used to remove heavy metals from wastewater e.g., chemical precipitation, ion exchange, adsorption, reverse osmosis, coagulation–flocculation, electrocoagulation, flotation, membrane filtration, etc. (Fu and Qi, 2011; Kurniawan et al., 2006).

Chemical precipitation (CP) is widely used for heavy metal removal from inorganic wastewater (Kurniawan et al., 2006). By adjusting the pH to basic conditions using an alkali, the dissolved metal ions are converted into an insoluble solid. In the case of Cr, chromium (III) hydroxide ($Cr(OH)_3$) is precipitated.

Another technique for wastewater treatment is by electrocoagulation (EC), where a sacrificial anode undergoes oxidation, releasing metal ions, and the hydrolysis of water takes place at the cathode, resulting in the formation of hydroxyl ions. Metal ions combine with the hydroxyl ions to form metal hydroxide compounds that favor the formation of flocs by destabilizing the suspended particles. The resulting flocs can be separated from the liquid by flotation or sedimentation depending on their density (Bensadok et al., 2007).

The most preferable electrode materials in electrochemical coagulation are Al or Fe (Mollah et al., 2004), creating a unique chemical/physical environment, which allows destabilization of the pollutant matter and its subsequent coagulation and flotation, thus avoiding addition of another coagulant agent (Espinoza-Quiñones et al., 2009).

Until now, little attention has being paid to other metals such as copper (Montero-Ocampo et al., 2007). Indeed, a recent study found that the use of copper electrodes increased arsenite removal to 99.6% without any secondary contamination (Ali et al., 2013).

In the electrocoagulation (EC), to release the coagulating agent, the metal ions and hydroxyl radicals, a potential difference has to be applied to the electrodes. As the sacrificial anode corrodes, the active cation is released to the solution (Wimmer, 2007).

Using copper as constituent material of the electrode, the following reactions occur, according to Eqs. (1)–(4):Anodic reaction:

$$Cu_{(s)} \rightarrow Cu^{2+}{}_{(aq)} + 2e^- \quad (1)$$

Cathodic reactions:

$$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-{}_{(aq)} + H_{2(g)} \quad (2)$$

Overall reaction:

$$Cu_{(s)} + 2H_2O_{(l)} \rightarrow Cu(OH)_{2(s)} + H_{2(g)} \quad (3)$$

The formation of chrome complex occurs:

$$Cu(OH)_{2(s)} + CrSO_4OH \rightarrow Cr(OH)_3 + CrSO_4 \quad (4)$$

After these processes, the $Cr(OH)_3$ is redissolved with the controlled addition of a strong acid. The Cr so obtained can be reused as an input in the tanning process.

This work aims at studying the removal of Cr present in the tanning wastewater through CP and EC techniques and its reuse in the tanning process. After its recovery from wastewater, the Cr recovered is tested as a tanning agent in leather processing, and is verified the economic viability of these processes.

2. Materials and methods

2.1. *Analysis of wastewater*

The tanning wastewater was collected directly (without any pretreatment) from the tanning drum of a tannery that performs beamhouse and tanning operations, processing 500 hides/day and generating a total average effluent flow of 200 m^3/day in addition to 60 m^3/day of Cr-containing wastewater. This wastewater was filtered with glass wool before the experiments, according to NBR 13336 (NBR, 1995) standards, to remove the suspended solids (shavings and fats).

The pH and the electrical conductivity of the raw and treated wastewater were determined. The analyses of biological oxidation demand (BOD) and chemical oxygen demand (COD) were carried out by the titration method and sulfides were analyzed using a spectrophotometer. The total amount of Cr in the wastewater was determined according to the ABNT NBR 13341 (2010) standard.

2.2. *Chromium recovery by CP and EC*

The CP tests were performed with the same sample; 1000 mL of effluent were added in each of the 12 vats of the jar test