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RECENT ADVANCES IN LEATHER TANNERY WASTEWATER TREATMENT

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Abstract: *The tannery industry is one of the most important economic sectors in many countries, representing an important economic field also in developing countries. Leather tannery industry is water intensive and originates highly polluted wastewater that contain various micropollutants raising environmental and health concerns. Tannery wastewater is difficult to treat biologically because of complex characteristics like high salinity e high content of xenobiotics compounds. After conventional treatment (i.e., chromium precipitation–primary sedimentation–biological oxidation–secondary sedimentation), effluents still do not meet the required limits, at least for some parameters such as BOD, COD, salinity, ammonia and surfactants. The leather industry is being pressured to search cleaner, economically as well as environmentally friendly wastewater treatment technologies alternative or integrative to the conventional treatment in order to face the challenge of sustainability. The most spread approach to manage tannery wastewater is the steam segregation before conveying wastewaters to in treatment plants that typically include pre-treatment, mechanical and physico-chemical treatment, biological treatment, and treatment of the generated sludge. Thus proper treatment technologies are needed to handle tannery wastewater to remove effectively the environmental benign pollutants. However among various processes applied or proposed the sustainable technologies are emerging concern. 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.*

Key words: *Leather tannery, leather tannery wastewater, sustainability, innovative treatment technologies, BOD, COD*

1. INTRODUCTION

The tannery industry is one of the most important economic sectors in many countries, representing an important economic field also in developing countries [1]. Currently it is condidered that the environmental impact of the leather industry is equivalent to the pollution generated by 1000–4000 citizens for each ton of animal hide treated [2]. The concerns related to effluents originated from this industry are mainly due to severe toxic effects caused by the mixture of many compounds used in the process that can be released to the environment because they even remain after conventional treatment [3],[4], [5] or may inhibit nitrification process as well [6].

The leather industry is being pressured to search cleaner, economically as well as environmentally friendly wastewater treatment technologies alternative or integrative to the conventional treatment in order to face the challenge of sustainability [1]. This paper reviewes the recent advances in leather tannery wastewater treatment, discussing their main findings.

2. WATER USE AND WASTEWATER CHARATERISTICS

Tannery wastewater production varies in wide range (10–100 m^3 per ton hide) depending on the raw material, the finishing products and the production processes. The streams released from several process units present very different characteristics [7]. For instance the beamhouse wastewater is characterized by an alkaline pH and the tanning effluent by a very acidic pH as well as high COD. The exhausted bath of the soaking contains excrements, salts and chemical additives. Degreasing steps are characterized by organic solvents [8,], [9]. In the dyeing step azo dyes are released [10].

3. TANNERY WASTEWATER TREATMENT

The most spread approach to manage tannery wastewater is the steam segregation before conveying wastewaters to in treatment plants that typically include pre-treatment, mechanical and physico-chemical treatment, biological treatment, and treatment of the generated sludge. In otherwords, stream segregation is the initial step in implementing in-plant controls. Due to the difference in wastewater characteristics from beamhouse (high pH, and sulfides), tanning and retanning (low pH and chromium) operations, more efficient control could be achieved trough the use of a treatment process specifically designed for the related pollutant [8],[10].

Various physiochemical techniques used for wastewater treatment can be applied to tannery wastewater (to the entire process or to separated streams in the process) including advanced oxidation processes [1]. However those processes needs to be properly calibrated in order to avoiding an excessive sludge production.

Tannery wastewater is difficult to treat biologically because of complex characteristics like high salinity e high content of xenobiotics compounds. After conventional treatment (i.e., chromium precipitation–primary sedimentation–biological oxidation–secondary sedimentation), effluents still do not meet the required limits, at least for some parameters such as BOD, COD, salinity, ammonia and surfactants [1,3,6].

4. ADVANCED WASTEWATER TREATMENT TECHNOLOGIES

The rising need of reducing the impacts and increasing resilience of water uses require a new wastewater management strategy that includes: i) the development of innovative wastewater technologies able to lead to the reuse or recycling of spent liquors and the recovery of materials; ii) the optimization of the water-energy nexus in this sector.

For instance the low pH, relatively high temperature (43–45 °C) and the high presence of aromatic compounds, especially in the streams of retanning baths make them attractive to use Fenton and Photo-Fenton processes [11], [12].

The use of high performance materials for tannery wastewater treatment has been recently investigated. De Martino et al. [13] reported a 99.9% Cr^{3+} removal and a decreasing of COD from 13.17 g L^{-1} to 8.70 g L^{-1} in tanney wastewater treated by using an on an organo-mineral complexes adsorbent tested the potential use of plasma-sprayed photocatalytic TiO2 coatings in tannery wastewater treatment, reporting a decreasing of TOC and colour under acidic conditions. A cobalt oxide doped nanoporous activated carbon (Co-NPAC) has synthesized and used as a heterogeneous catalyst for the Fenton oxidation of organic dye chemicals used in tannery process by.

The solid waste productions represent a further aspect in the sustainability assessement of tannery wastewater treatment. Therefore their reuse should be promoted in a sustainable wastewater management. In a recent study carried out in a pilot-scale tannery drum, solid waste from tanneries, i.e., chromium-tanned leather shaving waste, was used as the adsorbent reaching 86.6% dye removal form effluents generated through a wet end process [10].

Finally Souza et al. [2] demonstrated the feasibility of energy recovery through the photocatalytic conversion of sulfide-rich tannery sludge into hydrogen using CdS as a photocatalyst, platinum as a co-catalyst and visible light.

Table 1 gives a cumulative comparison approach to the the innovative technologies searched in tannery wastewater management.

Table 1. *Evaluation of innovative technologies proposed/applied for tannery wastewater management*

Process	Matrix	Innovation	Objectives	Scale	Main findings	Ref.
Photocatalytic hydrogen production	Sludge	Sludge was treated photocatalytically with visible light irradiation, under anaerobic conditions, using CdS as a photo- catalyst and Pt as co-catalyst	Energy recovery	Laboratory	The tannery sludge concentration and pH were the most important factors in producing the highest hydrogen levels. The strong interaction between these two factors was associated with the consumption of hydrogensulfide ions during the reaction. In contrast, the Pt content and mass of CdS were less relevant factors.	[2]
Adsorption	Dyeing wastewater	Wastewater was treated by using solid waste from tanneries, i.e., chromium-tanned leather shavingwaste as adsorbent	Optimizing adsorption parameters	Pilot	86.04% dye removal and 16.05 mg g−1adsorption capacity of the adsorbent at equilibrium, predictedby the pseudo-second-order model	[10]

Adsoprtion	Wastewater	Wastewater was treated with an organo-mineral complex, named LDH–HP, obtained in turn by sorption of polymerin, the humic acid-like fraction occurring in olive oil mill wastewater, on a layered double hydroxide (LDH) of magnesium and aluminium with carbonate in the interlayer.	Removing Cr3+ from tannery	Laboratory	This process allows the complete removal of Cr3+ from wastewater and also the abatement of chemical oxygen demand, indicating to be a very promising purification process for an industrial application	[13]
Fenton oxidation (FO)	Dyeing wastewater	Wastewater was treated by Fenton oxidation using a cobalt oxide doped nanoporous activated carbon (Co-NPAC) prepared from rice husk	Enhancing removal of refractory organics in tannery dyeing wastewater	Laboratory	The maximum percentage of COD removal was found to be 77%	[15]
Photocatalysis	Methylene blue dye in aqueous solution.	Application of plasma-sprayed TiO2 coatings	Enhancing photocatlysis performance	Laboratory	The findings showed that there was a clear organic matter mineralisation and colour removal by photo-catalysis beyond the photolysis effect under acidic pH.	[14]
Biological treatment +FO	Wet –blue wastewater	Integrated Anoxic/Oxic (A/O) and Fenton of oxidation	Removal of organic pollutants	Laboratory	In the A/O process, the suitable OLR was at least up to 0.8 kg COD m_3 d_1. In the Fenton for post-treatment the highest predicted COD removal percentage was 55.87%.	[16]

5. CONCLUSIONS

The ongoing development of advanced treatment systems may facilitate the whole wastewater processes promoting its reuse inside the industrial water cycle. Most of these technologies are still at lab scale therefore the costs related to full scale application can not be estimated.

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