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Comparative study of electrochemical water treatment processes for a tannery wastewater effluent

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ABSTRACT

Comparison of tannery wastewater treatment results of electrocoagulation (EC), electro-oxidation (EOx), electro-Fenton (EF) and photoelectro-Fenton (PEF) processes using two current densities was performed and employed no only to assess the best electrochemical approach but also to have elements to suggest a combined and cost effective process. In this way, iron plates were used as the anode and cathode in the EC tests. For the EOx process, a boron-doped diamond (BDD) thin-film electrode was used as the anode, and an iron plate was employed as the cathode. For the EF and PEF treatments, both electrodes were of BDD and H_2O_2 was produced by O_2 reduction at the cathode surface. Electrolytic trials were carried out in stirred open tank reactors containing 250 mL of wastewater applying either 65 or 111 mA cm^{-2}. In PEF trials, the wastewater was irradiated using a 6 W UVA light source. The characterization of the sludge generated in the EC process showed that it was not dangerous for the environment. Total Organic Carbon (TOC) removal values were larger at the highest density. Higher mineralization on the other hand, was found in EF and PEF when the concentration of Fe^{2+} was 3.0 instead 1.0 mM. Comparison of the methods revealed that their efficiency to remove the organic pollutant increased in the order EOx < EC ~ EF < PEF after 180 min of electrolysis. Furthermore, the information obtained from the study, also allowed designing a combined strategy aimed to produce an effluent suitable for discharge. The combination of EC followed by PEF was also studied. The results showed that the EC/PEF treatment gave higher organic removal than EC and was more economic than PEF, being able to yield 90% TOC reduction of the tannery wastewater.

1. Introduction

Tannery wastewaters generated from different industries contain high amounts of organic and inorganic pollutants and therefore need appropriate remediation before discharge. The accumulation of these contaminant species in the aqueous bodies leads to adverse effects on human life and on the environment. The tannery industry is one of the most important economic sectors in many countries such as Mexico, where in the zone of León Guanajato, for example, more than 200 leather industries are located. Every year, the tannery industry produces more than 300 million tons of wastewater and 64,320 t of sludge in the world [1]. These wastewaters contain ammonia, sulfides, heavy metal ions and many organic compounds including different azo dyes, which result from hides and skins and from the addition of reagents during the different operations made on these materials [2,3]. To minimize the environmental problem, alternative approaches to treat wastewater of tannery effluents are needed.

1.1. Electrocoagulation process (EC)

In this context, different reports have demonstrated that electrocoagulation (EC) can be used to successfully decontaminate effluents with different organic contaminants. In this process, organics can be separated by coagulation with metal hydroxide precipitates, mainly with $Fe(OH)_3$, that is continuously formed in the contaminated solution by chemical oxidation of the iron anode. The reactions involved for the production of $Fe(OH)_3$ are shown in Eqs. (1)–(3) [4]:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$2Fe^{2+} + 5H_2O + 1/2O_2 \rightarrow 2Fe(OH)_3 + 4H^+ \quad (2)$$

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$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (3)$$

At the cathode, hydrogen evolution takes place as shown by Eq. (4) [5,6]:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (4)$$

1.2. Electrochemical advanced oxidation processes (EAOPs)

On the other hand, EAOPs have been suggested as an attractive alternative for wastewater treatment [4,7–9]. Among these processes, electro-oxidation (EOx) and indirect electrochemical methods based on Fenton's reaction chemistry with electrochemical H_2O_2 production (such as electro-Fenton (EF) and photoelectro-Fenton (PEF)) are the most promising. In these environmentally friendly methods, free hydroxyl radicals (·OH) are produced in situ as the main oxidizing species. ·OH has a high standard reduction potential (E° = 2.80 V *vs* SHE) that makes albeit capable of non-selectively reaction with organics to give hydroxylated or dehydrogenated derivatives until their complete mineralization to CO_2, water and inorganic ions is achieved [10].

1.3. Electro-oxidation (EOx)

In EOx, on the other hand, organic pollutants are degraded in an electrolytic cell by physi-sorbed M(·OH) formed as intermediate from water oxidation to O_2 at the surface of a high O_2-overvoltage anode M, as shown by Eq. (5) [11–13]:

$$M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \quad (5)$$

The recent use of a BDD electrode in EOx has received great attention for wastewater treatment [14]. This anode material possesses technologically important characteristics such as an inert surface with low adsorption properties, remarkable corrosion stability and an extremely wide potential window in aqueous medium, resulting in the production of reactive BDD(·OH) in much larger extent than other common anodes [13,15]. This has been confirmed from the total mineralization achieved for several organic compounds in aqueous medium using EOx that employ BDD anodes [16–21].

1.4. Electro-Fenton (EF)

Indirect electrochemical methods such as EF and PEF are currently being developed for the removal of organic pollutants in acidic wastewaters. These processes are carried out in an electrolytic cell where H_2O_2 is continuously supplied to the contaminated solution from the two-electron reduction of O_2 at reticulated vitreous carbon [22], carbon-felt [23] carbon-polytetrafluoroethylene (PTFE) O_2-diffusion [24,26] and recently, BDD [27,28] cathodes (see Eq. (6)):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (6)$$

In the EF process, a small quantity of Fe^{2+} is added to the solution to react with the electro-generated H_2O_2 to yield the strong oxidant ·OH and Fe^{3+} by means of the Fenton's reaction [29]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (7)$$

Reaction (7) is propagated from Fe^{2+} regeneration that takes place by reduction of Fe^{3+} at the cathode [30] and/or by reaction with H_2O_2 [31] (it is not catalytic since Fe^{2+} actually transforms into Fe^{3+}).

1.5. Photoelectro-Fenton (PEF)

The PEF process involves the simultaneous radiation with UV light, like UVA light of λ_{max} = 360 nm, of the solution treated by EF [8,10,32,33]. UV radiation improves the degradation rate of organics due to different effects such as: (i) the photolysis of $Fe(OH)^{2+}$, the predominant species from pH 2.5 to 4.0, regenerating Fe^{2+} and producing more ·OH as shown by Eq. (8) and (ii) the photodecarboxylation of Fe(III)-carboxylate complexes, as exemplified for Fe(III)-oxalate complexes with n = 1, 2 and 3 in Eq. (9).

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \cdot OH \quad (8)$$

$$2Fe(C_2O_4)_n^{(3-2n)} + h\nu \rightarrow 2Fe^{2+} + (2n-1)C_2O_4^{2-} + 2CO_2 \quad (9)$$

In general, some papers have described the treatment of tannery wastewaters by coagulation–flocculation [34,35], ozonation [36,37], and electrochemical techniques such as EC [5,6,38], EOx with Pt-Ir [2], graphite [39], DSA [40] and BDD and SnO_2-Sb [41], photoelectro-oxidation [42,43], photoelectrocatalysis [44], EF with iron electrodes and H_2O_2 addition [45], as well as combined systems like electrocoagulation/adsorption [46,47] and photo-Fenton/electrocoagulation [48]. However, to the best of our knowledge, the application of EAOPs with a BDD anode and its combination with EC for the remediation of this kind of wastewaters have not been reported. Table 1 presents several reviews for different conditions of tannery wastewater treatment using several oxidation processes.

The aim of this work is therefore to study the comparative degradation of a tannery wastewater by EC using stirred tank reactor equipped with Fe/Fe (anode/cathode) electrodes, by EOx using a BDD/Fe stirred tank reactor and by EF and PEF using a BDD/BDD stirred tank reactor. The effect of applied current density on the mineralization rate of these methods was examined. The influence of Fe^{2+} concentration on the EF and PEF treatments was also evaluated. From the comparison of results, the combination of EC followed by PEF (the most potent EAOP) was suggested as a feasible combination for wastewater treatment rendering the effluent suitable for discharge.

2. Experimental

2.1. Sampling and characterization of tannery wastewater

The tannery wastewater used in this study was an effluent provided from a local industry of León Guanajuato (Mexico). A primary settling storage allowed an important reduction of total suspended solids (TSS). Samples were collected in polypropylene bottles and stored in a refrigerator at (279 K) until use. The effluent was characterized by a total organic carbon (TOC) content near 1800 mg L^{-1}, a TSS of about 500 mg L^{-1}, a conductivity of 6.3–9.1 mS cm^{-1} and pH close to 4, as can be seen in Table 2.

2.2. Chemicals and analysis procedures

Analytical grade sulfuric acid and heptahydrated ferrous sulfate were supplied by Baker. Sodium hydroxide was purchased from Karal. The solution pH was determined with an Extech 407227 pH-meter. Wastewater mineralization was monitored using TOC decay which in turn was measured using a Shimadzu TOC-L analyzer. The accuracy of these measurements was ±1% by injecting 50 μL aliquots into the analyzer. Before analysis, samples were withdrawn from the solutions treated by EC and EOx, and filtered with 0.45 μm PTFE filters purchased from Whatman. In contrast, samples obtained during the EF and PEF trials were alkalinized to pH 8 to stop the degradation process and further, filtered with