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Performance evaluation of an integrated photo-Fenton – Electrocoagulation process applied to pollutant removal from tannery effluent in batch system

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HIGHLIGHTS

- ▶ Integrated processes were applied to remove pollutants from tannery effluents.
- ▶ Both photo-Fenton and electrocoagulation processes were optimized and integrated.
- ▶ A sludge yield reduction was studied searching a minimum environmental impact.
- ▶ A minimum H_2O_2 content was investigated to drive an efficient low-cost treatment.
- ▶ High pollutant removals were attained with values below the allowed environmental limits.

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ABSTRACT

The treatment of tannery industrial effluent (TIE) by integrating the widely used photo-Fenton and electrocoagulation (EC) processes was investigated. The optimization of the photo-Fenton process by using solar irradiation was made performing a full 3^3 factorial experimental design. An irradiation time of 120 min for the photo-Fenton reaction was more favorable to pollutant removal in acidic medium using Fe^{2+} concentrations ranging from 0.4 to 0.5 g L^{-1} and H_2O_2 concentrations ranging from 15 to 30 g L^{-1}. Nonetheless, a reduction in sludge production and a minimum residual content of hydrogen peroxide were attained within 540 min of irradiation time, with 0.4 g L^{-1} Fe^{2+} and 15 g L^{-1} H_2O_2 initial concentrations, with almost the same efficiency of COD, color, and turbidity removal obtained under the optimal experimental conditions. When the pretreated TIE samples were submitted to an EC process, the results of inorganic pollutants removal were better than with the conventional method (use of a combination of filtration, chemical coagulation, and sedimentation processes). In addition, the application of the integrated photo-Fenton and EC process for TIE treatment is cheaper than the conventional one. All the results showed that the integrated photo-Fenton and EC process could be applied as an efficient low-cost alternative treatment for the removal of organic and inorganic pollutants from tannery industrial effluent with a low environmental impact.

1. Introduction

The increasing standard of drinking water supply and the very severe environmental regulations regarding wastewater discharge have required innovative wastewater treatment technologies. Due to their high toxicity, tannery wastewaters containing a complex mixture of organic and inorganic pollutants are strictly regulated and must be treated before being discharged into water bodies. These substances are derived from the hides and skins themselves and from the addition of reagents during the leather tanning process [1,2]. Classical physicochemical and biological processes are often inadequate to completely remove pollutants from tannery wastewaters [3]. For this reason, more efficient methods such as electrochemical or advanced oxidation processes have been proposed.

Advanced oxidation processes (AOPs) have the great advantage of degrading pollutants by introducing highly oxidizing species, such as hydroxyl radicals. Among the AOPs, the most widely used techniques are Fenton and photo-Fenton reactions [4,5]. A series of advantages and disadvantages of AOPs have been earlier discussed by Huang et al. [6], suggesting that methods like Fenton process are the most promising technologies for the treatment of wastewaters. The photo-Fenton process has been applied to the treatment of tannery [1,2], food processing [7], wood processing wastewaters [8], and landfill leachate [9], as well as pharmaceutical pollutants [10], organic compounds [11], and dyes [12–15].

Based on the electrocoagulation (EC) advantages, many studies on wastewater treatment have been reported in order to remove a wide range of organic and inorganic pollutants and to ensure good

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quality effluent before its discharge into aquatic environment [16]. The EC technology has been widely applied to the treatment of effluents from tannery [17,18], textile [19,20], and agro-food industries [21], as well as to heavy metal removal [22,23]. In addition, a combination of EC and electro-oxidation techniques with ionizing radiation was proposed as a reliable method for the treatment of highly colored and polluted industrial wastewater [24]. An integrated EC-ozone process has been also applied to improve the wastewater quality [25].

A study of an integrated tannery effluent treatment system in batch mode based on the application of both widely used photo-Fenton and electrocoagulation techniques was carried out. A full 3^3 factorial experimental design with a 3D response analysis was applied to the photo-Fenton process data. Effects of irradiation time, initial pH, and Fenton reagent concentration were analyzed. The production of sludge and the amount of residual H_2O_2 were also analyzed. After the tannery effluent treatment by the photo-Fenton process, the EC treatment was performed under the optimal EC experimental conditions. An operational cost analysis was performed in order to show the economic viability of treatment systems based on the integration of photo-Fenton and EC processes.

2. Materials and methods

2.1. Sampling and chemicals

An amount of 50 L of raw tannery effluent was weekly collected from an equalization tank of a non-treated tannery industrial effluent (TIE), which is a by-product of the leather finishing process in a factory located in Toledo, Paraná (Brazil). A slight variability on their physico-chemical properties of the real tannery effluent samples was observed during collections from the equalization tank. Besides, these variations are not greater than 20% within two months of sample collection. In order to maintain a representativeness of the raw tannery effluent, all collected samples were mixed in an equalization tank, providing a homogenized non-treated TIE before experiments and stored according to the standard methodologies recommended by the American Public Health Association [26].

All chemicals used were of analytical-reagent grade. A 100-mL standard solution (Combicheck 20, Merck) containing a COD concentration of 750 mg L^{-1}, which is traceable to NIST, was used without dilution instead of the sample solution for checking the quality of the photometric measurement system, as well as to identify sample-dependent effects on the COD results. In addition, a 100-mL multielement atomic spectroscopy standard solution, prepared with high purity salts and nitric acid (70002, Fluka), was used in order to obtain the sensibility curves of the SR-TXRF (Synchrotron Radiation Total Reflection X-ray Fluorescence) spectrometer for K and L series X-rays and determine the element concentrations in TIE samples. For SR-TXRF analysis, a 2 mL aliquot of each TIE sample was taken and 20 μL of a standard solution (1.0 g Ga L^{-1}) was added as an internal standard. An aliquot of 5 μL was deposited on a pre-cleaned acrylic disk and dried at room temperature. The same procedure was repeated for the multi-elemental standards at five different concentrations. All the disk-samples were prepared in triplicate, except for the standard samples, which were prepared in quintuplicate.

2.2. Photo-Fenton and electrocoagulation reactors

In order to perform the pollutant removal from TIE samples in batch system, photo-Fenton reactors consisting of magnetically stirred 500 mL vessels were exposed to the external environment for 5 h of solar irradiation on non-cloudy days, during the summer. As reported by the Technological Institute of Meteorology of the Brazilian Parana State [27], a mean solar irradiation of approximately 1.13 MJ m^{-2} h^{-1} was measured at the nearest meteorological station from Toledo city.

As reported in a previous work [18], the electrocoagulation (EC) experimental condition for TIE treatment using a pair of aluminum electrodes might be set at 68 mA cm^{-2}, with initial solution pH of 8.3 and interelectrode distance of 4 cm, for optimal performance. Based on this information, a laboratory-scale EC reactor consisting of a 1.5 L cylindrical glass container, a pair of aluminum plates (7.5 cm × 12.12 cm × 0.17 cm) with a 4.0 cm gap between them, and a 150 rpm magnetic agitation system was used. The aluminum electrodes were dipped into the beaker containing 800 mL of the TIE effluent. The aluminum plates were partially immersed (approx. 7.8 cm) in the effluent, resulting in an active electrode surface area of 58.8 cm^2. The aluminum electrodes were operated in a mono-polar mode and were connected to terminals of direct current power supply (Instrutemp DC Power Supply, FA 1030) that provided the stabilized currents and voltages, ranging from 0 to 10 A, and from 0 to 30 V, respectively.

2.3. Photo-Fenton and electrocoagulation experiments

A detailed study was really performed on the integration of both EC and photo-Fenton processes in order to minimize the amount of final sludge yielded. From preliminary tests (data not shown), it was observed that applying in first place the photo-Fenton process a mineralization of organic matter is obtained but with a high residual amount of dissolved iron. Then, applying the EC process a good performance on the removal of suspended and dissolved matters was achieved, resulting in a significant lower amount of final sludge than that obtained in an inversion on the integration of EC and photo-Fenton processes, as first and second stages, respectively.

Photo-Fenton experiments were carried out using different hydrogen peroxide and ferrous ion concentrations, and different initial pH values. The iron salt was mixed with the tannery effluent solution before the addition of hydrogen peroxide. The pH value of all samples was adjusted with H_2SO_4 and NaOH solutions. The reaction mixture inside the cell, consisting of 200 mL of TIE sample and a precise amount of Fenton reagent, was magnetically stirred. From previous photo-Fenton tests, 120 min of solar irradiation was enough to evaluate the influence of each reactor operation parameter (ROP) on pollutant removal. The three ROPs, namely concentrations of Fe^{2+} and H_2O_2, and initial pH, were labeled as q_1, q_2, and q_3, respectively.

For a statistical analysis and modeling of the optimization procedure, planned photo-Fenton experiments based on the Response Surface Methodology (RSM) were carried out [28,29].

Considering a combination of two-levels and one point at the center of each experimental region, a full 3^3 factorial experimental design (FED) was applied to optimize the photo-Fenton reactor conditions. From previous photo-Fenton tests, the ranges of 0.25–0.5 g L^{-1}, 15–30 g L^{-1}, and 3–7 for Fe^{2+} and H_2O_2 concentrations, and initial pH values, respectively, were considered for FED analysis, under 300 rpm controlled stirring and 120 min of solar irradiation in batch mode. Besides, a most-frequently used second-order polynomial model, described by Eq. (1), was applied to model the photo-Fenton experimental data. A set of response variables (R) such as removal of COD and total suspended solids was used in order to optimize the performance of the photo-Fenton reactor. An optimized variable response in 3D graphical representation was obtained by applying the Lagrange criteria [30]. By application of ANOVA with a 95% confidence level ($p < 0.05$), all modeled variable responses were tested for their statistical significance.