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Enhancing electro-Fenton-based tertiary treatment for tannery effluent via Response Surface Methodology

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Abstract This study focuses on improving advanced oxidation methods as a final treatment for tannery wastewater. The goal was to find the best conditions for an electrochemical peroxidation (ECP) process that removes COD and color from tannery effluents at neutral pH, while reducing costs by avoiding chemicals that increase salinity effluent. Using an experimental design (CCD-RSM), the effects of current, treatment time, and hydrogen peroxide levels were tested. The best results were achieved with 36 mA/cm² current, 19.7 minutes of treatment, and 9.9 g/L of H_2O_2, removing 74% of COD and 96% of color. Adding UV-C light in photo-electrochemical and photolysis processes did not significantly improve removal and increased energy use. This study offers a new approach to remove hard-to-treat COD from tannery wastewater, overcoming limitations of traditional electro-Fenton methods. Future work should focus on making the process more sustainable for large-scale use.

Keywords: CCD-RSM, tertiary treatment, wastewater treatment, electrochemical advanced oxidation, recalcitrant COD

1. Introduction

Thanks to the high quality of its finished leathers, the Italian tannery industry is a global leader. However, each stage of leather manufacturing consumes significant amounts of reagents and water, producing large volumes of highly saline wastewater that require treatment. In this context, conventional biological treatments are ineffective against persistent organic pollutants, making the implementation of advanced treatment processes in WWTPs essential.

Electrochemical advanced oxidation processes (EAOPs) facilitate the degradation of recalcitrant compounds that are resistant to conventional treatment methods by applying an electric current. In the conventional electro-Fenton process, the utilization of ferrous salts (e.g., $FeCl_2$, $FeSO_4$) in combination with acidifying agents (e.g., HCl, H_2SO_4) results in elevated concentrations of chloride and sulphate ions in the treated effluent, potentially impacting its quality. In contrast, the electrochemical peroxidation (ECP) process uses a sacrificial iron anode to generate Fe^{2+} ions in solution, supporting Fenton-like reactions for pollutant removal.

Based on previous research (Pasciucco et al., 2024), this study optimized the ECP process for tannery wastewater treatment using CCD-RSM to maximize COD and color removal and improve cost-efficiency by replacing pure iron electrodes with mild steel ones (Pasciucco et al., 2025).

2. Materials and methods

Samples of tannery wastewater were taken from the secondary treatment effluent at Aquarno WWTP in Tuscany, Italy (Table 1).

Experiments were performed in a 300 mL batch reactor with stainless steel electrodes (25 cm² area, 3.5 cm apart). The ECP process was tested and compared with photolysis and photo-electrochemical peroxidation to assess the effect of UV-C light on COD removal.

All tests used the same reactor setup and conditions.

Table 1. Secondary tannery sample characterization.

Parameter (mg/L)	Value	Limit value*
pH	7.7±0.1	5.5-9.5
COD	380.3 ± 16.9	160
TOC	119.3 ± 4.4	-
TSS	65.3 ± 24.8	80
TN	39.9 ± 10	-
NO_3^--N	19.4 ± 13.7	20
NO_2^--N	0.2 ± 0.04	0.6
NH_4^+-N	0.5 ± 0.2	15
Cl-	3363.7 ± 42	1200
SO_4^{2-}	1992 ± 31	1000

* Limit values set according to Italian Legislative Decree 152/2006

Using Minitab 18, two central composite designs (CCDs) were performed to optimize the ECP process for COD and color removal. The first CCD, based on preliminary tests, involved 20 experiments varying current density (10–30 mA/cm²), H_2O_2 concentration (1.8–7 g/L), and electrolysis time (30–90 minutes). Following initial results, a second CCD with 13 experiments fixed the current and focused on refining H_2O_2 concentration (5–15 g/L) and electrolysis time (20–30 minutes) to identify optimal conditions.

3. Results and discussion

3.1 Effect of independent variables on COD and color removal

A first CCD-RSM was conducted to study the effects of H_2O_2 concentration, current density, and electrolysis time. The R^2 values for COD and color removal were 99.67% and 82.08%, respectively, showing a strong agreement between predicted and experimental results.

Furthermore, ANOVA results showed that H_2O_2 concentration, current density and their interactions significantly influenced COD removal. Notably, current density had the strongest impact, with the lowest P-value. This can be explained by the fact that high current densities enhance the dissolution of iron ions into solution, which react with H_2O_2 to produce hydroxyl radicals and iron hydroxides under alkaline conditions, enabling contaminant removal through oxidation and electrocoagulation. However, the first CCD-RSM step was unable to identify the region of peak process efficiency.

Thus, a second CCD-RSM was carried out with H_2O_2 concentration and electrolysis time as variables, while the current density was fixed at the optimal 36 mA/cm².

Figure 1 presents contour plots for COD (1a) and color removal (1b). Electrolysis time had little impact on COD removal but significantly affected color removal (1b). For COD (fig. 1a), removal efficiency decreased with increasing H_2O_2 concentration, reaching a maximum above 81%, probably due to scavenging effects at high H_2O_2 levels. Similar results were reported by Kumar et al. (2018), who found that excessive H_2O_2 reduced COD removal but did not impact color removal. As a result, the optimal conditions for both COD and color removal were determined to be 9.9 g/L of H_2O_2 and 19.7 minutes of electrolysis time.

3.2 Effect of UV-C light

The optimized ECP conditions were tested in photo-electrochemical peroxidation (PECP) and photolysis. UV-C light irradiation did not notably enhance removal efficiency but increased energy consumption. In this study, using a sacrificial iron anode caused continuous iron ion dissolution, producing dark brown sludge under alkaline conditions as electrolysis time increased. The constant mixing kept the sludge suspended, causing UV-C irradiation to be absorbed by iron precipitates, which limited its effectiveness.

4. Conclusions

Using CCD-RSM, key parameters were optimized to enhance COD and color removal, achieving 74% and 96% efficiency. Current density played a major role via Fenton reaction mechanisms. Switching to stainless steel electrodes and shorter times reduced costs to 0.18 €/L. Future work should prioritize renewable energy for sustainability.

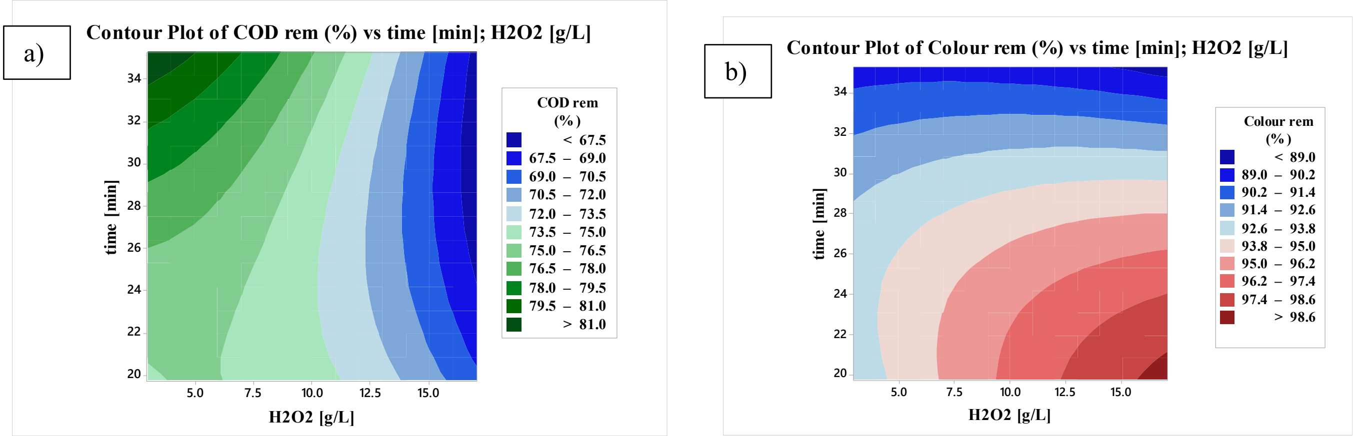

Figure 1. COD (a) and color (b) removal contour plots.

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