



# A Fenton-based approach at neutral and un-conditioned pH for recalcitrant COD removal in tannery wastewater: Experimental test and sludge characterization

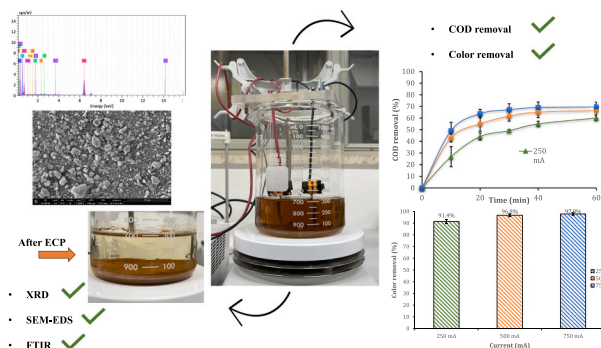
Erika Pasciucco, Francesco Pasciucco, Renato Iannelli, Isabella Pecorini\*

Department of Energy, Systems, Territory and Construction Engineering, University of Pisa, Via C.F. Gabba 22, Pisa, Tuscany 56122, Italy

## HIGHLIGHTS

- A Fenton-based approach was tested on tannery wastewater without changing the pH.
- The electrochemical peroxidation treatment removed up to 60 % of recalcitrant COD.
- The electrocoagulation process played a key role in removing color and COD.
- A current of 500 mA was considered the best trade-off in treatment implementation.
- The formed precipitate was made of iron oxides and can promote recovery processes.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The combination of raw animal skin manufacturing processes involves the use of large amounts of chemicals, resulting in the generation of complex and highly polluted tannery wastewater. In this context, the high concentration of chloride in tannery wastewater represents a crucial bottleneck. Indeed, sodium chloride, commonly used in tannery industry to prevent skin rot, increases the concentration of chlorides up to 50 %. At the same time, most of the advanced oxidation processes usually employed in tannery wastewater treatment to remove recalcitrant COD involve the use of conditioning agents, thus increasing the overall concentration of chlorides in the treated effluent. The aim of this study was to evaluate the electrochemical peroxidation process (ECP) efficiency in the treatment of tannery wastewater without changing pH, to improve Fenton technology by avoiding the use of chemicals. The influence of different electric currents on COD and color removal was investigated. The characterization of the produced sludge was conducted through FTIR, SEM and XRD analysis, exploring the morphology and composition of precipitate, depending on the applied current. Although an electrical current of 750 mA yields the highest COD and color removal efficiency (69.7 % and 97.8 %, respectively), 500 mA can be considered the best compromise because of energy consumptions. Iron oxides and hydroxides were generated during the ECP process, playing the role of coagulants through the absorption of organic and inorganic contaminants. The consumption of energy increased as a function of time and applied current; however, cost analysis

\* Corresponding author.

E-mail addresses: [erika.pasciucco@phd.unipi.it](mailto:erika.pasciucco@phd.unipi.it) (E. Pasciucco), [francesco.pasciucco@phd.unipi.it](mailto:francesco.pasciucco@phd.unipi.it) (F. Pasciucco), [renato.iannelli@unipi.it](mailto:renato.iannelli@unipi.it) (R. Iannelli), [isabella.pecorini@unipi.it](mailto:isabella.pecorini@unipi.it) (I. Pecorini).

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showed that the electrodes contributed the most to the total cost of the process. In authors' knowledge, the application of ECP process as a tertiary treatment for the removal of recalcitrant COD in tannery wastewater represents a novelty in the literature and the results obtained can be considered as the basis for scaling up the process in future research.

## 1. Introduction

In many countries, tannery industry is one of the most important economic sectors. Despite this, it represents a growing environmental issue (Vilardi et al., 2018).

The combination of raw animal skin manufacturing processes involves the use of large amounts of chemicals, resulting in the generation of complex and highly polluted wastewater (Korpe and Rao, 2021). As a result, tannery wastewater treatment, in compliance with required standards in terms of COD, BOD, total suspended solids (TSS), total chromium, sulphates, etc., involves multiple biological and chemical processes before discharge (Zhao and Chen, 2019).

In particular, the salinity of tannery waste is mainly related to the traditional methods of preservation, pickling and chrome tanning (Sundar and Muralidharan, 2019). However, sodium chloride, commonly used to prevent skin rot, increases the concentration of chlorides up to 50 % and the amount of TSS up to 40 % (J. et al., 2020). Because of that, serious environmental problem can arise, as a higher concentration of chlorides modifies the ionic composition of water with important consequences on aquatic life. In addition, the reuse of water with high salinity for irrigation purposes is limited (Uddin et al., 2022).

Conventional tannery wastewater treatment processes include aerobic treatments, anaerobic treatments, oxidation methods and chemical precipitation (Korpe and Rao, 2021; Kurt et al., 2007). In general, conventional biological processes are well-known and more sustainable from both an environmental and economic point of view compared to chemical oxidation, but are unable to remove recalcitrant and non-biodegradable compounds. Furthermore, high concentrations of pollutants with low biodegradability can hinder biological treatments, requiring the need for physical-chemical ones; however, these processes imply high energy and chemical consumptions (Lofrano et al., 2013).

In recent years, there has been growing interest in advanced oxidation methods (AOPs) for wastewater treatment. All these processes exploit the formation of the hydroxyl radical ( $\cdot\text{OH}$ ,  $E^0 = 2.8 \text{ V vs SHE}$ ), a powerful oxidant able to remove a wide range of pollutants (Lofrano et al., 2013). In this context, electrochemical advanced oxidation processes (EAOPs), such as electro-Fenton (EF), seem to be the most promising alternative to remove recalcitrant and toxic compounds that cannot be oxidized by conventional technologies due to their high removal efficiency, ease of operation and environmental sustainability (Isarain-Chávez et al., 2014).

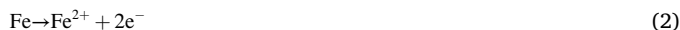
The EF process is based on the Fenton reaction (Eq. (1)), where  $\text{Fe}^{2+}$  reacts with  $\text{H}_2\text{O}_2$  to form the hydroxyl radical. However, although the EF process has the advantage of generating  $\text{H}_2\text{O}_2$  in situ, it generally involves the use of compounds such as  $\text{FeCl}_2$  or  $\text{FeSO}_4$  as the main source of iron, thus increasing the overall concentration of chlorides or sulphates in the treated effluent.



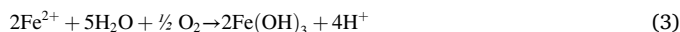
Regarding chlorides, the most common removal methods used in tannery wastewater treatment plants (WWTPs) are reverse osmosis, electro osmosis and ion exchange. Nevertheless, due to the high levels of organics, suspended solid and neutral salt in tannery effluent, these technologies cannot be used directly (Zhao and Chen, 2019). Furthermore, the costs associated with these processes would be difficult to afford (Hernández-Francisco et al., 2017).

Electrochemical peroxidation (ECP) is a Fenton-based process, consisting of a sacrificial iron anode able to generate ferrous ions in the aqueous medium according to Eq. (2) (Brillas et al., 2009; Nidheesh

et al., 2018).



As the reaction goes on, excess iron precipitates as ferric hydroxide (Eq. (3)); therefore, ECP combines electrochemistry with the electrocoagulation process (EC) in order to exploit both the action of hydroxyl radical and the adsorption by ferric hydroxides for heavy metal and organic compound removal (Nidheesh, 2018; Venu et al., 2014).



Compared to classical EF approach, the ECP process uses less  $\text{H}_2\text{O}_2$  and produces less sludge (Casado, 2019).

Until now, the ECP process has been applied for COD removal from textile wastewater (Ghanbari and Moradi, 2015), landfill leachate (Lu et al., 2023) and pharmaceutical wastewater (Yazdanbakhsh et al., 2015). In all of the studies cited above, a COD removal efficiency above 80 % was achieved within 60 min of electrolysis. According to Ghanbari and Moradi (2015), the ECP process results in a high process yield with lower energy consumption (3.38 kWh/kg COD removed) compared to electro-Fenton (EF), electrocoagulation (EC) and peroxi-coagulation (PC) processes. Similarly, Lu et al. (2023) highlighted that, compared to electrocoagulation/electro-Fenton process, the application of the ECP process followed by electro-Fenton provided better results (COD and nitrogen removal increased by 36.9 % and 34.5 %, respectively) while resulting in a lower cost (32 % less). In addition, among the several Fenton-based technologies, Farhadi et al. (2012) described the ECP process as the best alternative for the treatment of pharmaceutical wastewater.

As the Fenton-based processes perform best at pH 3, most of the studies in the literature tested the ECP process in acidic medium. However, common conditioning agents used to modify pH (e.g., HCl,  $\text{H}_2\text{SO}_4$ ) also contribute to the final concentration of chlorides and sulphates. In contrast, Lu et al. (2023) demonstrated that ECP performs better at pH 9 in the treatment of landfill leachate.

Therefore, the aim of this study was to evaluate the efficiency of the ECP process in the removal of recalcitrant COD in tannery wastewater without changing initial pH (7.7), in order to improve Fenton technology by reducing the use of chemicals and the presence of undesired residues in the treated effluent.

In authors' knowledge, the application of ECP process as a tertiary treatment for the removal of recalcitrant COD in tannery wastewater represents a novelty in the literature. Indeed, most of the previous studies tested this technology for the removal of biodegradable COD in different type of wastewater. Furthermore, the efficiency of the ECP process at neutral and unconditioned pH was not investigated for our purpose.

## 2. Materials and method

### 2.1. Case study description and study objective

The tannery district of Santa Croce sull'Arno is located in central Italy (Tuscany) and represents one of the main industrial hubs in this field at an Italian and international level, including >450 companies. As a consequence of the industrial processes, tannery wastewater, produced from the district and collected in two large centralized WWTPs, contains high pollution level and must be properly treated in order to encourage water reuse and resource recovery (Pasciucco et al., 2023a, 2023b).

In Aquarno WWTP, both tannery wastewater from the industrial

district and municipal wastewater from the surrounding urban centers are treated by means of two separate treatment lines. Specifically, municipal wastewater is treated using an activated sludge system, while the industrial treatment line for tannery wastewater is composed of three main sections as follows.

In the first section, after preliminary treatments of fine screening and sand removal, tannery wastewater is pre-oxidized and then homogenized. The pre-oxidation is essential to reduce the concentration of sulfides entering the plant, which can generate toxic effects for microorganism in subsequent biological treatments, and reduce the formation of hydrogen sulphides (H<sub>2</sub>S), which is produced by sulfides in condition of pH < 9. Afterwards, homogenized wastewater undergoes a first stage of biological activated sludge oxidation and sedimentation of primary sludge.

Wastewater from the first section is sent to the second treatment stage, consisting of denitrification, biological oxidation and sedimentation of secondary sludge. Finally, in the third and last stage, two further treatments are carried out, in order to reduce residual and recalcitrant COD, namely Fenton process and clariflocculation using polyelectrolyte.

Fenton process involves the reaction of Fenton's reagent (iron salt in Fe<sup>2+</sup> form) with hydrogen peroxide resulting in the generation of hydroxyl radical. In the case-study plant, chlorine-based chemical agents are widely used for process implementation, thus increasing the content of chlorides in the effluents.

Indeed, the treatment is performed by dosing hydrogen peroxide (as oxidant) and ferrous chloride (as catalyst) in an acidic environment, which is obtained by using hydrochloric acid (at the end of the process, the pH is brought back to neutral values by dosing lime).

In this context, the use of ferrous sulphate as a catalyst would represent a possible solution to avoid the use of chlorine-based reagents. However, the addition of ferrous sulphate would increase the overall concentration of sulphate ions in the secondary effluent, which is beyond the limit parameter value of the required standards (see Table 1).

Therefore, the aim of this study was to investigate an alternative advanced oxidation treatment to the Fenton process, capable of reducing residual and recalcitrant COD without use of chlorine-based chemical agents.

## 2.2. Sample characterization

Tannery wastewater samples were collected at the Aquarno WWTP and stored in a refrigerator at 4 °C before the experiments. In order to evaluate the efficiency of an alternative process to the classic Fenton, the wastewater to be treated was sampled at the end of the second treatment section (before undergoing the Fenton process), as described above. The characteristics of samples in terms of pH, conductivity, chemical oxygen demand (COD), total organic carbon (TOC), total suspended solids (TSS), total nitrogen (TN), nitrate-N (NO<sub>3</sub><sup>-</sup>-N), nitrite-N (NO<sub>2</sub><sup>-</sup>-N),

**Table 1**  
Characterization of the sample.

Parameter	Value	Limit parameter value <sup>a</sup>
pH	7.7 ± 0.04	5.5–9.5
Conductivity (mS)	13.84 ± 0.02	–
COD (mg/L)	380 ± 8.5	160
TOC (mg/L)	118.7 ± 25.8	–
TSS (mg/L)	50 ± 1.4	80
TN (mg/L)	31.4 ± 4.2	–
NO <sub>3</sub> <sup>-</sup> -N (mg/L)	10.1 ± 2.1	20
NO <sub>2</sub> <sup>-</sup> -N (mg/L)	0.12 ± 0.03	0.6
NH <sub>4</sub> <sup>+</sup> -N (mg/L)	0.5 ± 0.1	15
Cl <sup>-</sup> (mg/L)	3411 ± 14.0	1200
SO <sub>4</sub> <sup>2-</sup> (mg/L)	1961 ± 21.9	1000

<sup>a</sup> Limit concentration established according to the Italian Legislation Decree 152/2006.

ammonium-N (NH<sub>4</sub><sup>+</sup>-N), chlorides (Cl<sup>-</sup>) and sulphates (SO<sub>4</sub><sup>2-</sup>) are shown in Table 1, showing threshold concentrations of each parameter according to the Italian Legislative Decree 152/2006. The samples were dark brown in color and highly concentrated in COD, chlorides and sulphates, thus requiring more stringent treatments to comply with regulatory standards.

## 2.3. Electrochemical set-up

The ECP process was conducted in an electrochemical reactor, consisting of a glass cylindrical cell containing 300 mL of tannery effluent. The electrodes were placed inside the reactor at 3.5 cm from each other. Both electrodes (5 cm × 5 cm, 3 mm thickness) were made of iron (99.5 % purity) and provided by GoodFellow Cambridge Ltd. The experiments were carried out using a DC power generator EA-PSI 9080–60 DT 1500 W with voltage and current ranges of 0–84 V and 0–3 A, respectively. All tests were performed in the same conditions of room temperature (25 ± 2 °C) and 240 rpm mixing by using a magnetic stirrer, which was used instead of a mechanical stirrer due to the working volume operated. After each use, the electrodes were cleaned with deionized water and sandpaper.

## 2.4. Experimental procedure and chemicals

The ECP experiments were performed on three replicates at the natural pH of tannery samples (7.7), to avoid the use of chemicals and conditioning agents (e.g., HCl, H<sub>2</sub>SO<sub>4</sub>) which contribute to the increase in the overall concentration of chlorides and sulfates. The influence of the applied electrical current was evaluated at 250, 500 and 750 mA. Based on literature data (Lu et al., 2023), 1.5 mL of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 % w/w) was added into the reactor. The residual concentration of H<sub>2</sub>O<sub>2</sub> was measured with peroxide chemical test strips (Sigma-Aldrich). Samples were taken at regular 10-min intervals: 0, 10, 20, 30, 60 min. Although the residual concentration of H<sub>2</sub>O<sub>2</sub> was equal to 0 mg/L after 60 min of electrolysis, excess hydrogen peroxide can distort the COD measurement (Teng et al., 2020); therefore, the samples were mixed with MnO<sub>2</sub> 99.9 % for 10 min to remove the excess of H<sub>2</sub>O<sub>2</sub>. Each sample was passed through a 0.45 μm filter before analysis.

## 2.5. Analytical methods

pH and conductivity were measured using a pH meter PC 700 by Eutech Instruments.

Chemical oxygen demand (COD) was analyzed using Hach spectrometer DR3900 with potassium dichromate oxidation method. The COD removal efficiencies were calculated according to Eq. (4):

$$COD\ removal\ (\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad (4)$$

where C<sub>0</sub> and C<sub>f</sub> are the initial and final concentration (mg/L) of COD, respectively.

The color removal efficiency was evaluated at 520 nm using Evolution 201 Thermo Scientific UV–Vis spectrophotometer according to Eq. (5):

$$color\ removal\ (\%) = \frac{Abs_0 - Abs_f}{Abs_0} \times 100 \quad (5)$$

where Abs<sub>0</sub> and Abs<sub>f</sub> are the initial and final absorbance, respectively.

Color and COD removal analysis were based on the Standard Methods of the American Public Health Association (APHA, 2005).

The theoretical amount of dissolved iron from the anode was calculated according to Faraday's law (Eq. (6)):

$$C_{Fe} = \frac{M \times I \times t}{nF} \quad (6)$$

where  $C_{Fe}$  is the concentration of  $Fe^{2+}$  (g/L),  $M$  is the molecular weight of iron (55.85 g/mol),  $I$  is the applied current (A),  $t$  is the reaction time (s),  $n$  is the number of electron and  $F$  is the Faraday constant (96,485C/mol). The amount of  $Fe^{2+}$  released from anode was calculated from the weight loss of the electrode.

The energy consumption per kWh/g COD was calculated according to the following equation (Liu et al., 2022):

$$\text{Energy consumption} = \frac{E_{cell} \times I \times t}{V \times \Delta(COD)} \quad (7)$$

where  $E_{cell}$  is the average cell voltage (V),  $I$  is the applied current (A),  $t$  is the reaction time (h),  $V$  is the volume of treated sample (L) and  $\Delta(COD)$  is the concentration of COD removed (mg/L).

The overall cost of ECP process, including the consumption of electrodes, energy cost and chemical consumption was calculated according to Eq. (8)

$$\text{Total cost} = \frac{\text{Energy cost (€)} + \text{Chemical cost (€)} + \text{Electrode consumption (€)}}{\text{Volume of treated sample (L)}} \quad (8)$$

## 2.6. Data analysis

The results obtained in terms of COD removal as a function of the applied current were compared by one-way analysis of variance (ANOVA) followed by the post hoc Tukey-test. Previously, the normality of the data and the homogeneity of the variances were verified by Shapiro-Wilk and Levene tests, respectively (Ribeiro et al., 2023). The null hypothesis (data are normal distributed and variances are equal) cannot be rejected for both tests; therefore, ANOVA and Tukey tests can be performed. The  $p$ -values for the normality and homoscedasticity tests were 0.931 and 0.715, respectively (Parra-Enciso et al., 2022).

For this study, the electric current was considered as the independent variable, while the COD removed as a dependent one. All tests were conducted with the level of statistical significance set at  $p < 0.05$  (Pecorini et al., 2016).

## 2.7. Sludge characterization

Sludge produced from the ECP process was analyzed through Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis, to investigate the morphology and composition of the precipitate. At the end of the experiment, the sludge formed was centrifugated and dried in an oven at 105°C for 24 h. X-ray powder diffraction patterns were collected using a Bruker D2 Phaser diffractometer operating at 30 kV and 10 mA in  $\theta$ - $\theta$  scan mode with Ni-filtered  $CuK\alpha$  radiation and equipped with a one-dimensional Lynxeye detector. Scanning electron microscope (SEM) with Energy Dispersive Spectroscopy (EDS) investigations were conducted using FEI Quanta 450 FEG operated at 15 kV. For SEM analysis, the powdered sample was deposited on special aluminum stubs using double-sided graphite tape. Images were acquired in high vacuum (SE) mode at different magnitude range. Spectrum GX spectroscopy (Perkin Elmer) was used for collecting FTIR spectra in the range of 4000 to 400  $cm^{-1}$  at 4  $cm^{-1}$  scanning resolution. FTIR spectroscopy was carried out on KBr pellets, thus 5 mg of sample was mixed with KBr in a 1:5 ratio.

## 3. Results and discussion

### 3.1. Effect of the current on COD removal

The rate of the electrochemical reaction is significantly affected by current density (Yazdanbakhsh et al., 2015). In this study, the influence of electric current on COD removal efficiency was evaluated by varying the current from 250 to 750 mA. The results are shown in Fig. 1. As can

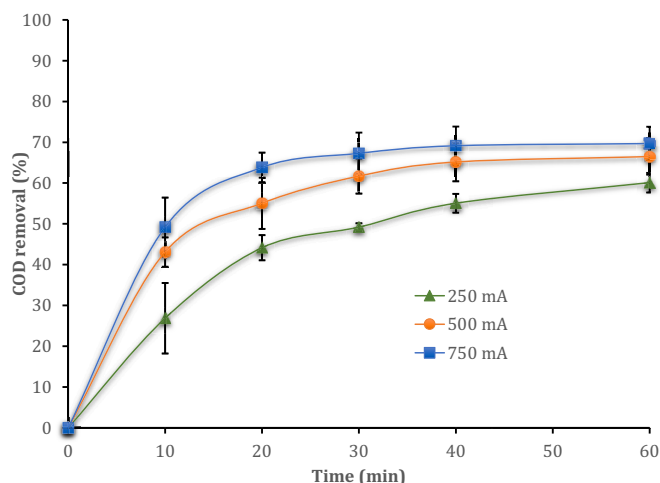


Fig. 1. Effect of current on COD removal during ECP process.

be seen, the increase in the applied current from 250 mA to 750 mA resulted in greater COD removal. Consequently, the required voltage increased with the current applied (Fig. S1). According to Faraday's law (Eq. (6)), the increase in the applied current promoted the dissolution of  $Fe^{2+}$  ions from the sacrificial anode, with a consequent increase in the production of hydroxyl radicals for pollutants removal. However, despite the higher removal yields, high current densities can lead to undesirable effects: first, high currents accelerate the phenomena of corrosion and poisoning of the electrode due to the adsorption of iron oxides on the surface layer (Panizza and Cerisola, 2009); second, the increase in current promotes side reactions of  $\cdot OH$  consumption with a decrease in the efficiency of the process (Ren et al., 2018; Yang et al., 2014):



In this study, the greatest COD removal (69.7 %) was achieved at 750 mA after 60 min of ECP, compared to a removal of 66.5 % and 60.1 % at 500 mA and 250 mA at the end of the electrolysis, respectively. Therefore, the results highlighted that both organics and inorganics compounds were removed by ECP. Although Fenton-based processes showed better performance at low pH (Brillas, 2020), a COD removal percentage equal to or  $>60\%$  was achieved without changing the natural pH of the wastewater in all experiments performed in this study. According to other authors, an efficient COD removal in alkaline environment is mainly related to the formation of iron hydroxides ( $Fe(OH)_n$ ) in neutral pH conditions, which on the one hand contribute to the removal of COD through an electrocoagulation process, on the other hand exploit the formed  $Fe(OH)_n$  complexes as heterogeneous catalysts for Fenton reaction (Deng et al., 2019; Olvera-Vargas et al., 2019).

This allows  $H_2O_2$  to be activated even in basic medium without changing the pH, thus avoiding the consumption of conditioning agents and increasing the pH application range (Zhang et al., 2022).

In effluents with high concentrations of chlorine ions, anodic oxidation promotes the formation of active chlorine on the anode surface (Eq. (10)), thus playing a key role in disinfection process (X. Chen et al., 2023; Z. Chen et al., 2023); indeed, its reaction into the water in alkaline environment leads to the generation of hypochlorite, which is able to remove organic compounds close to the anode (Eqs. (11)–(12)) (Scialdone et al., 2009).



Compared to the hydroxyl radical ( $\cdot OH$ ,  $E_0 = 2.67$ ), chlorine gas has



a lower redox potential ( $\text{Cl}_2|\text{Cl}^-$ ,  $E_0 = 1.36$ ), which favors the production of active chlorine and chlorine by-products. Moreover, indirect oxidation by chlorinated by-products is more effective than direct oxidation, hence the presence of available chlorine contributes significantly to the COD removal.

On the other hand, the generation of chlorinated by-products represents a crucial bottleneck, due to the suspected carcinogenic and mutagenic effects. Consequently, the presence of chlorinated by-products to be treated limits the field of application of electrochemical advanced oxidation processes for the decontamination of wastewater with high chloride concentrations (Feng et al., 2023). However, the oxidation of chlorides at the anode strictly depends on the electrode material.

In particular, when the anodes are made of iron, it is challenging to produce active chlorine due to the low electrocatalytic activity of the iron electrode towards active chlorine. As mentioned by other authors (Deng et al., 2019), iron anode's linear sweep voltammetry (LSV) curve showed that as the anodic potential increases above 0.5 V, the anode current keeps constant, thus suggesting that the release of iron ions is the main process of electron transfer. Similarly, in our study, the use of an iron anode prevented the formation of active chlorine, which did not provide support in the removal of COD.

Excluding pH among the variables that influence the ECP process, the results obtained at 500 and 750 mA showed a similar trend, with a slightly lower COD removal efficiency in the first 30 min at 500 mA. However, in both cases, the COD concentration decreased by >50 % after 30–40 min of electrolysis. As a result, the ECP process obtained a final COD concentration complying with the Italian discharge Standard.

Therefore, based on the experimental results, a current of 500 mA and a treatment duration of 30 min can be considered as the optimal conditions for an efficient COD removal.

### 3.2. Statistical analysis

The one-way ANOVA statistical analysis was conducted in order to identify significant differences between the concentrations of COD at different current ranges (250, 500 and 750 mA, respectively). The significance of the model can be evaluated based on P and F values, where P is the probability of the response of the independent variable to the dependent one and F is the Fischer's value. In general, a better fit between the model and the experimental data is obtained when the F-value is high (>1), and the P one is low (< 0.05). If the P-value is less than the established level ( $P < 0.05$ ) there are significant statistical differences between data, whereas a P-value >0.05 suggests that there are not significant differences. In this case, the one-way ANOVA test showed a P-value <0.05 and a F-value >1, which meant a significant statistical difference between the experimental results (Table 2). In order to understand which groups differed from each other, the post-hoc Tukey-test was performed. According to the results, there was an important difference between data collected at 250 and 500 mA (groups A and B, respectively) and results obtained at 250 and 750 mA (groups A and C, respectively), with a P-value <0.05 in both cases (0.004 and 0.001, respectively). In contrast, the Tukey test showed no significant differences between groups B and C ( $P = 0.787$ ). Groups that were statistical significantly different ( $P < 0.05$ ) were indicated with different letters in Table 2.

**Table 2**

One-way ANOVA comparison between COD removal results at 250 mA (group A), 500 mA (group B) and 750 mA (group C).

Groups	Source of variation	SS	Df	MS	F	P-value	Remark
A <sup>a</sup> , B <sup>b</sup> , C <sup>b</sup>	Between groups	32,191.92578	2	16,095.96289	9.5054694	0.00039	Significant
	Within groups	71,120.15333	42	1693.336984			
	Total	103,312.0791	44				

SS: sum of square; df: degree of freedom; MS: square of mean; F: factor.

Groups that were statistical significantly different were indicated with different letters ('a' and 'b').

### 3.3. Color removal efficiency

Decolorization efficiency was investigated at the electrical current of 250, 500 and 750 mA after 60 min of electrolysis. Color removal was measured in the 24 h following the end of the process, to ensure an efficient separation between clarified solution and precipitate. The electrical current played a key role in the formation of hydroxyl radicals and iron hydroxides. The influence of the current on decolorization is shown in Fig. 2. As can be observed, as the current increased from 250 to 750 mA, color removal increased from 91.4 % to 97.8 %. A greater decolorization efficiency at higher electrical current can be explained with an increase in iron species, resulting in increased production of both  $\cdot\text{OH}$  and Fe(II)/Fe(III) hydroxides available for dyes removal from tannery wastewater (Martínez-Huitle and Brillas, 2009).

In fact, it was observed that an increase in the current from 250 to 750 mA corresponded to a progressive amount of the precipitate and iron ions released from the anode (Tables S1 and S2): the concentration of sludge increased from  $16.68 \pm 2.81$  to  $25.01 \pm 1.72$  g/L, whereas the amount of iron released ranged from  $1.03 \pm 0.03$  to  $3.10 \pm 0.08$  g/L, respectively.

pH is another important parameter that influences the color removal efficiency of the process. However, the natural pH of the tannery samples used in this study is reported in the literature as optimal pH value for the generation of iron hydroxides, suggesting that the EC process contributed more to color removal by determining the efficiency of the ECP process. Furthermore, according to Brillas and Casado (2002), pH increased with electrolysis time, which promoted the formation of Fe(OH)<sub>n</sub>.

The change in pH with electrolysis time is shown in Fig. S2.

Considering our results, although the electrical current of 750 mA achieved the highest color removal efficiency (97.8 %), an electrical current of 500 mA (where a decolorization efficiency of 96.8 % was obtained) can be considered a best compromise in view of the lower energy consumption.

### 3.4. Sludge analysis

The iron oxides and hydroxides produced during the ECP process played the role of coagulants through the adsorption of organic and inorganic contaminants (Isarain-Chávez et al., 2014; Rezgui et al., 2022). However, the intensity of the electrical current affected the amount of sludge produced, as well as the morphology and composition of the sample.

XRD analysis was performed to characterize the crystalline structure of the sludge. The XRD patterns of the precipitate at 250, 500 and 750 mA are shown in Fig. 3. In all three cases, the precipitate's pattern showed an amorphous or weakly crystalline character. In particular, the sludge collected at 250 mA showed a single characteristic peak at  $2\theta = 29.57^\circ$ , assigned to the presence of  $\text{CaCO}_3$ . Conversely, the XRD patterns at 500 and 750 mA showed peaks at  $2\theta = 30.58^\circ, 35.79^\circ, 43.48^\circ, 54.12^\circ, 57.47^\circ, 63.20^\circ$  and  $30.46^\circ, 35.76^\circ, 43.60^\circ, 54.01^\circ, 57.59^\circ, 63.17^\circ$ , respectively. The peaks at  $2\theta = 30.58^\circ$  and  $30.46^\circ$  confirmed the presence of carbonate, which precipitates in alkaline conditions; however, the XRD analysis showed that the precipitate collected at 500 and 750 mA was a mixture of iron oxides, primarily hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) (Han et al., 2016; Yang et al., 2018).

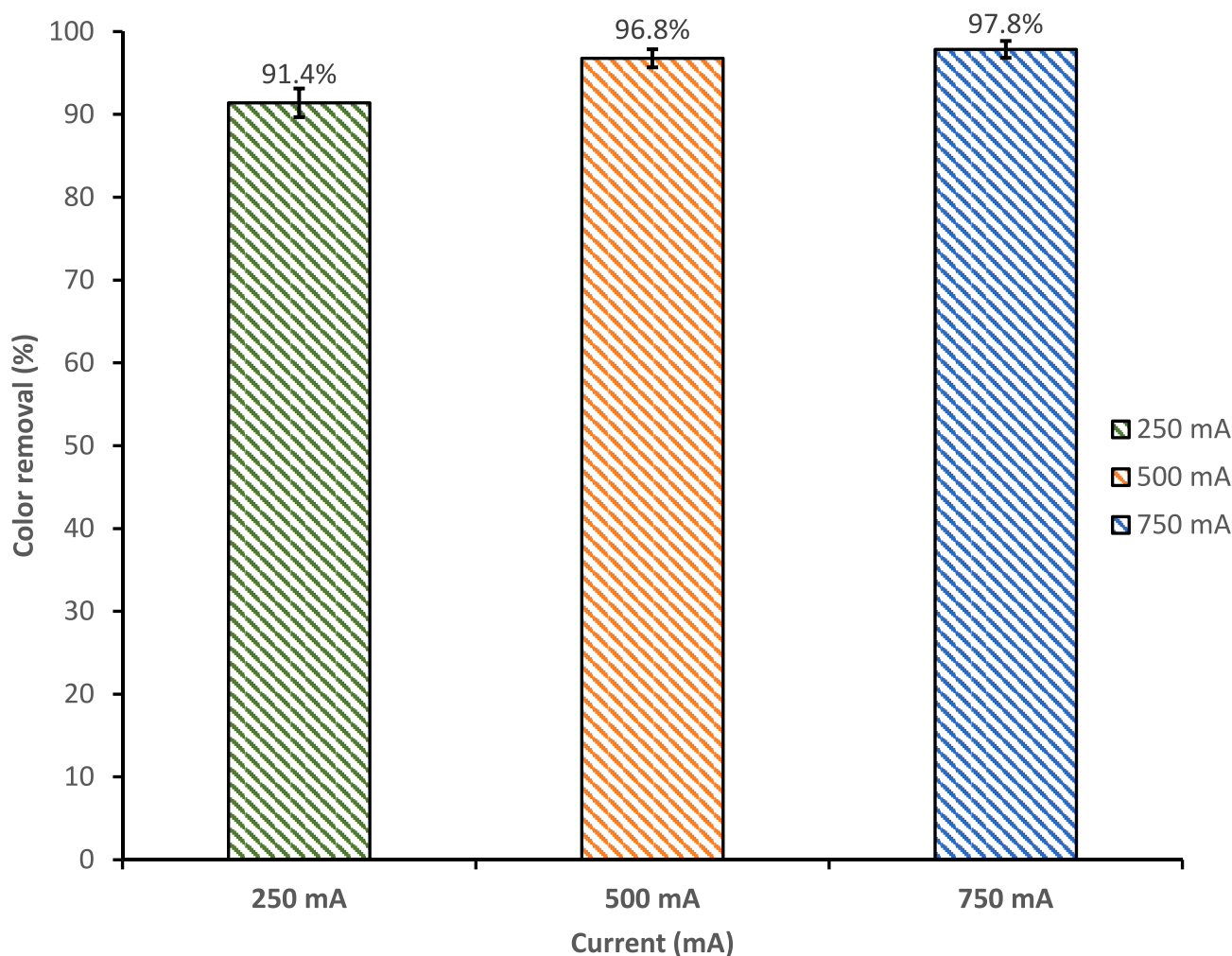


Fig. 2. Effect of current on color removal during ECP process.

SEM images were collected at different magnitude range (Fig. S3). Fig. 4 (3000 $\times$  of magnitude, 40  $\mu$ m of diameter size) showed that as the current increased the size of precipitants decreased, resulting in a gradual breakdown of the precipitates during the electrolysis time. Furthermore, the structure of precipitate appeared compact at lower currents, while it seemed porous at higher electrical current values. Nevertheless, the composition of samples resulted homogeneous throughout the applied current range. An EDS analysis was conducted to identify the presence of different metals within the spinel structure of hematite and magnetite.

Fig. 5 revealed the presence in traces of many elements as Ca, Na, Cl, S in the precipitates collected at different current values (Tables S3, S4 and S5), whereas iron and oxygen were the most abundant elements. However, the presence of sodium chloride used to prevent skin was confirmed by the presence of both Na and Cl in the sludge.

On the other hand, the presence of sulfur was consistent with the high concentration of sulphates in the sample treated, due to the use chemicals such as sulfuric acid ( $H_2SO_4$ ) during pickling process. The presence of carbon, instead, indicated the removal of organic component by EC (Villalobos-Lara et al., 2021).

FTIR spectra of the precipitate formed at various current values are shown in Fig. 6. The broad band at 3400  $cm^{-1}$  corresponds to the stretching of O—H group (Zaini et al., 2013).

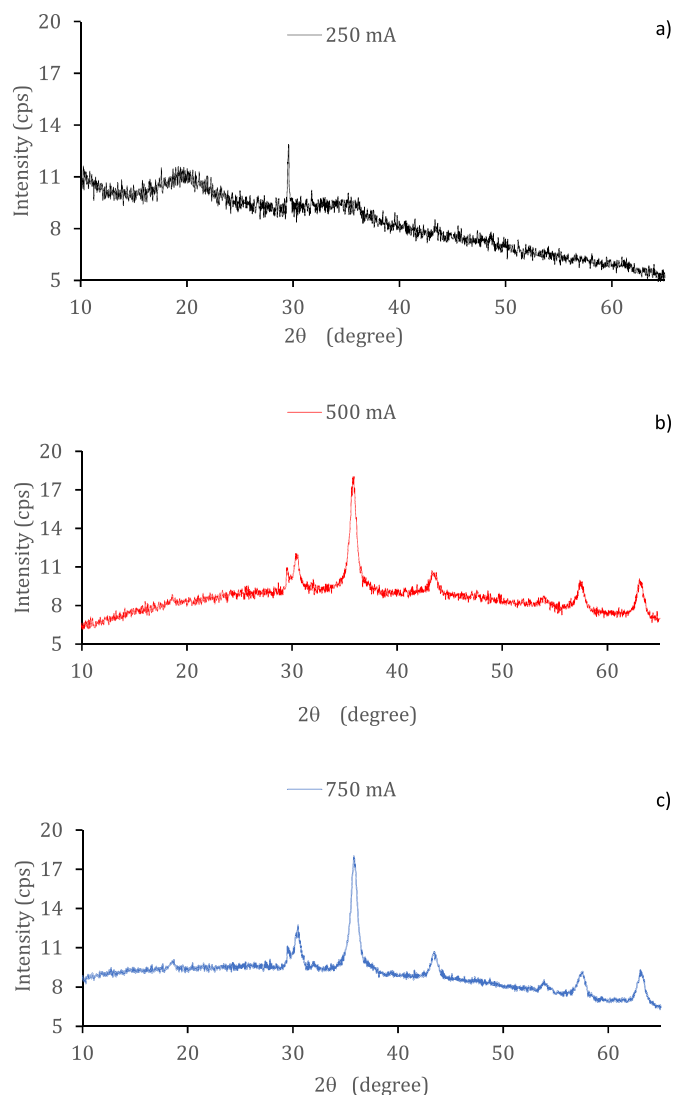
Although weak in intensity, at 500 and 750 mA two peaks close to 2850 and 2920  $cm^{-1}$  were observed, due to the symmetric and asymmetric C—H stretching of methylene groups, respectively (Zhang et al., 2019).

The band near 1630  $cm^{-1}$  corresponded to the bending of O—H bond, while the C=C stretching of the aromatic ring at 1493.8  $cm^{-1}$  was observed only for the sample at 250 mA (Akyol et al., 2013). The band at 1384  $cm^{-1}$  was associated to the N—O stretching of nitrate (Nidheesh and Gandhimathi, 2014). The signals included in the region near 1200–1000  $cm^{-1}$  of the spectrum were due to the C—O vibration (X. Chen et al., 2023). In addition, the weakly intense bands around 700 and 872  $cm^{-1}$  showed in the spectrum collected at 250 mA (Fig. S4) resulted from in-plane and out-of-plane deformation vibrations of the planar  $CO_3$ , which was consistent with the presence of carbonate observed in the XRD analysis (Tatzber et al., 2007).

The absorption peaks in the region of the spectrum between 634 and 440  $cm^{-1}$  corresponded to Fe—O vibrations in iron oxide (Wang et al., 2017).

### 3.5. Energy consumption and costs analysis

The energy consumption per kWh/g COD was calculated according to Eq. (7) as a function of electrolysis time. The results reported in Fig. 7 showed a general increase in electricity consumption over time when the electric current intensity increased from 250 to 750 mA. In particular, the energy consumption at 250 mA was equal to 0.013 kWh/g COD after 60 min of electrolysis; conversely, in the cases at 500 and 750 mA, the energy consumptions increased to 0.036 and 0.073 kWh/g COD, respectively. However, although an electrical current of 750 mA allowed achieving higher COD removal yields, the energy consumption was about 2 times higher than the process at 500 mA.



**Fig. 3.** XRD analysis of sludge produced at a) 250 mA, b) 500 mA and c) 750 mA.

The total cost, including energy, chemical and electrode consumption costs were also calculated according to Eq. (8) (Olvera-Vargas et al., 2019). The results obtained at different current range are shown in Table 3. Specifically, the energy consumption was calculated based on the average price of electricity in Italy (0.11 €/kWh, approximately), and was established according to ARERA reports (Regulatory Authority for Energy, Networks and the Environment). The iron electrode consumption was calculated according to Eq. (6), while chemicals costs were estimated based on the  $H_2O_2$  30 % w/w consumed during the process. Calculation details are summarized in Table S6.

As can be observed, the costs of the ECP process increased with the applied current. However, in all cases electrode consumption provided the largest contribution to the overall cost.

### 3.6. Literature comparison

Nowadays, advanced oxidation processes (AOPs) represent a promising alternative for the tertiary treatment of industrial effluents. Sivagami et al. (2018) compared Fenton's reagent and ozonation process for the treatment of real tannery wastewater. The COD removal efficiency via ozonation process was higher than Fenton treatment, with a reduction of 40–50 % in the secondary effluent. In addition, the authors demonstrated that the combination of different processes (coagulation

and aeration followed by ozonation) led to higher yields (80–90 % reduction of COD). However, it is important to highlight some critical aspects: first, the use of ozone in wastewater treatment is challenging due to its low solubility and stability in water and high production costs (Mehrzouei et al., 2015); second, in most of the literature studies dealing with Fenton process, the pH was set at 3, which was considered the best working condition. The need to reduce costs and chemical consumption associated with Fenton technology has driven research towards the use of alternative metal catalysts. Ribeiro et al. (2022a, 2022b) tested manganese, copper, and cobalt as co-catalysts in homogeneous Fenton and photo-Fenton processes of real pulp bleaching wastewater. The authors emphasized that partial replacement of iron with transition metals increased the color removal efficiency, while the greatest COD reduction (63.3 %) was achieved when the molar ratio  $Fe^{2+}/Cu^{2+}$  was 75:25 via Fenton process. Despite this, strictly acidic conditions are required to improve catalytic activity; whereas, the use of heterogeneous catalysts has several advantages, including the ability to work in milder pH conditions and increased reuse options due to their ease of separation from wastewater.

For instance, Ribeiro et al. (2022b) presented a circular solution for the removal of recalcitrant pollutants from pulp bleaching wastewater based on the use of residual iron dust from metallurgical industry, where a reduction of 36.4 % of COD was achieved.

To improve the removal of absorbable organic halides (AOX) from pulp bleaching wastewater, Ribeiro et al. (2023) investigated the role of granulated biomass fly ash coupled with Fenton process. Although a sequential Fenton/granulated biomass fly ash treatment provided remarkable results (60–70 % of AOX removed), COD removal did not exceed 15 %.

A heterogeneous Fenton approach was also applied for the treatment of tannery wastewater, using a mixed-iron coated olive stone bio-sorbent particles as catalyst within fixed-bed columns in series (Vilardi et al., 2018). In this case, the combination of coating olive and  $H_2O_2$  resulted in a COD removal efficiency equal to 58.4 %.

Recently, electrochemical advanced oxidation processes are suggested for the treatment of wastewater containing refractory organics, due to the capacity to generate highly reactive species through the application of electric current, thus avoiding the consumption of chemicals. In this context, the ECP process has been applied for the treatment of wastewater with different characteristics. Kumar et al. (2018) performed a modified peroxi-coagulation process for the treatment of composite wastewater where iron plates were used both as anode and cathode. The experimental results showed a COD and color removal efficiency of 77.7 % and 97 %, respectively, under optimal conditions (pH 3, 60 min of electrolysis, 1 V of voltage, 50 mM of  $H_2O_2$ ).

In a recent study conducted by Lu et al. (2023) the performance of the ECP process was investigated after the addition of 2.5 mL of hydrogen peroxide at different pH (3–11) and current density (10–50  $mA\ cm^{-2}$ ), in order to improve the treatment of old landfill leachate. Contrary to other research, a greater COD removal was reached in alkaline condition. Although high current density allowed fast pollution removal, 95.9 % of COD was removed after 60 min of electrolysis, pH equal to 9 and a current density of 30  $mA\ cm^{-2}$ ; whereas, varying the pH to 3 the COD removal efficiency was lowered to 60 %.

About tannery wastewater treatment, an electrochemical batch reactor with two iron electrodes was used by Kurt et al. (2007) under different pH conditions and  $H_2O_2$  concentrations. The results highlighted that the greatest COD removal (73 %) was reached after 40 min of electrolysis at pH 3 when the concentration of  $H_2O_2$  was equal to 1670 mg/L and the electrical power was maintained at 15 W.

Under the same conditions of  $H_2O_2$  and current, at pH 7.2 the removal of COD reached a maximum efficiency of 60 % in 12 min of electrolysis. According to the authors, although the ECP process performed better at pH 3, it involved the consumption of conditioning agents to reduce pH, making the system exposed to corrosion. Therefore, if the concentration limits set for the discharge are reached, working at



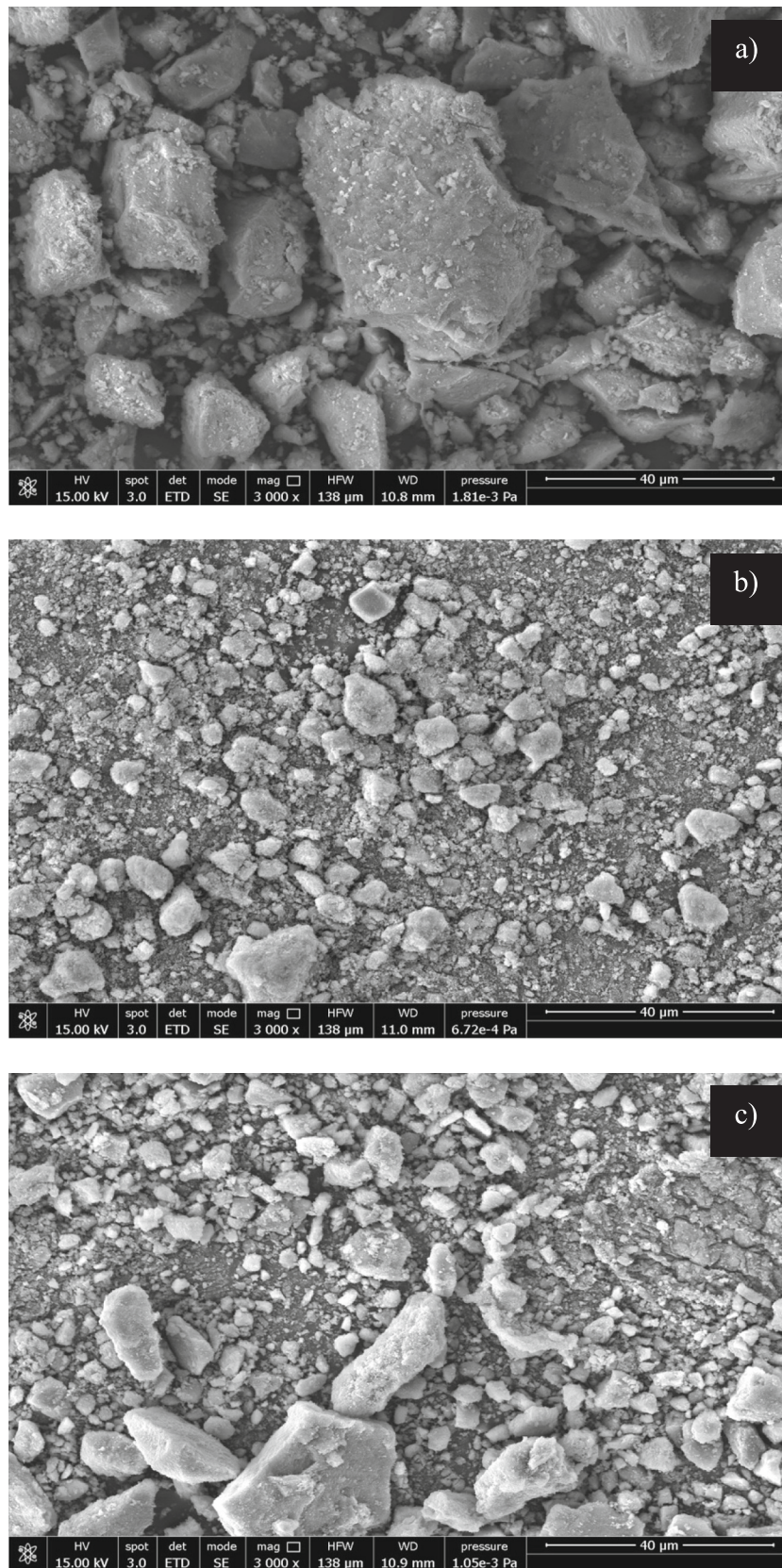


Fig. 4. SEM images collected at different electrical current: a) 250 mA, b) 500 mA and c) 750 mA.



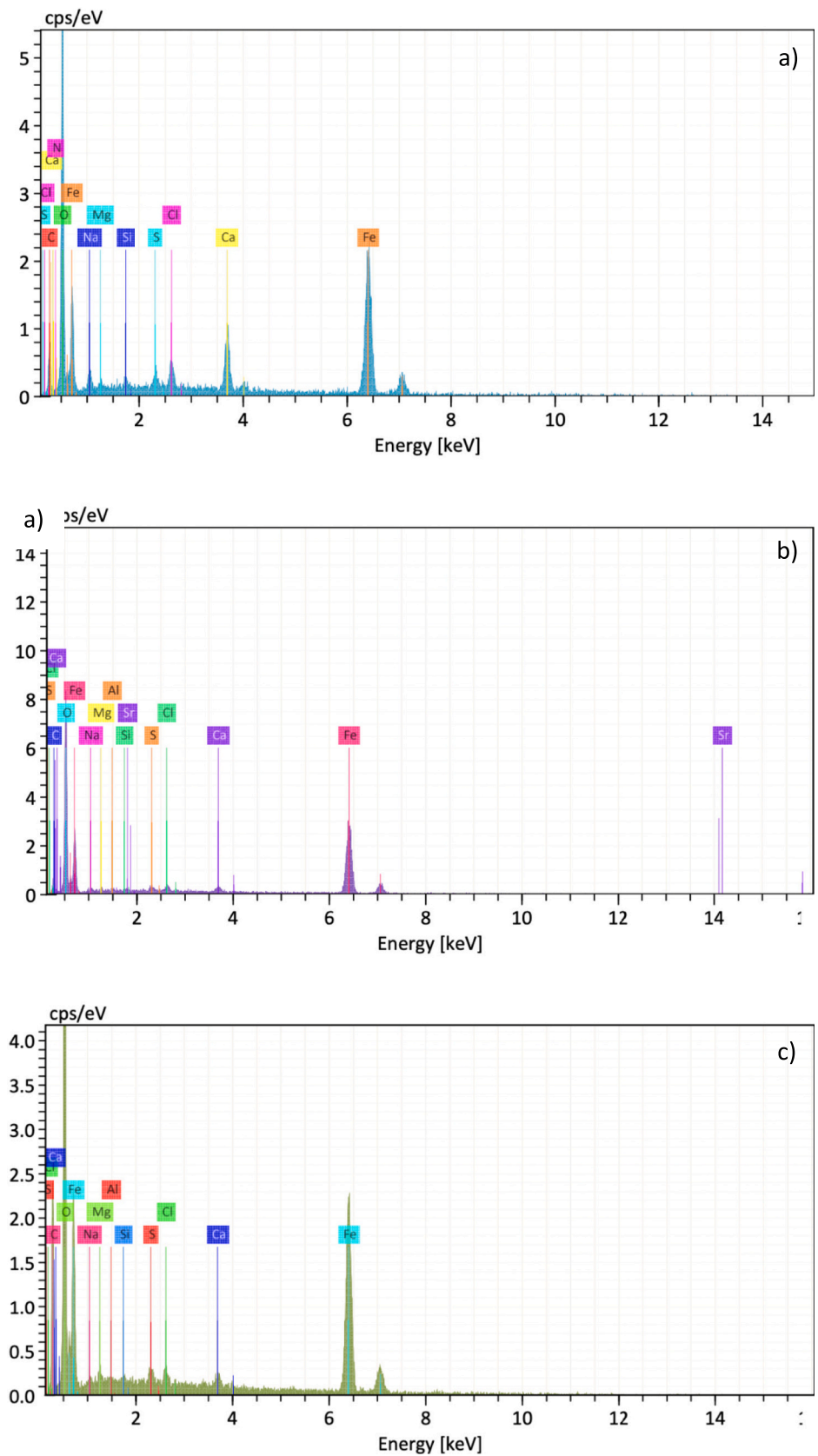


Fig. 5. EDS spectra of the sludge collected at a) 250 mA, b) 500 mA and c) 750 mA.

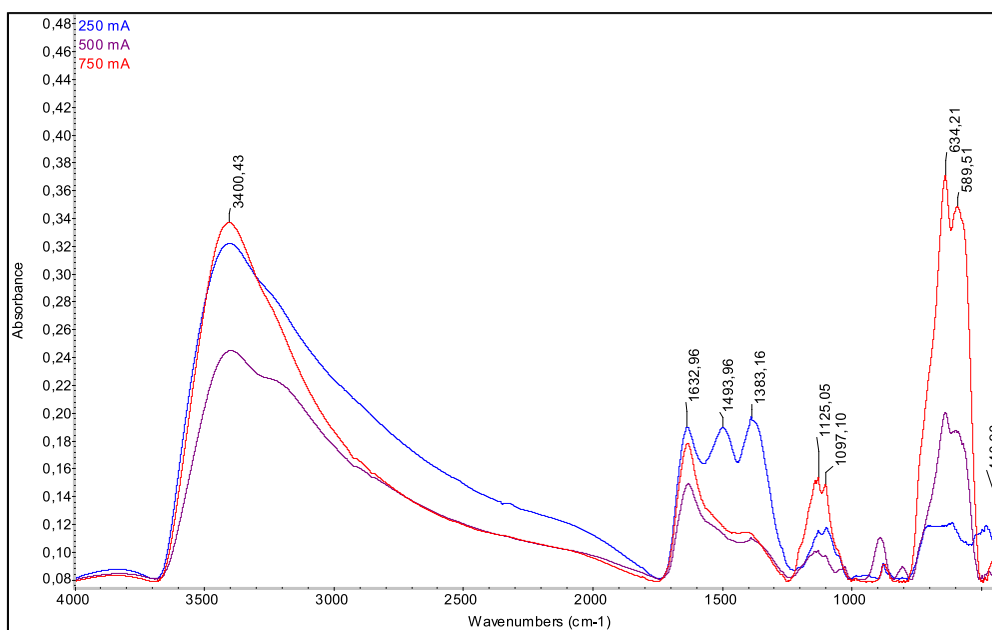


Fig. 6. FTIR spectra of sludge precipitated as a function of electrical current.

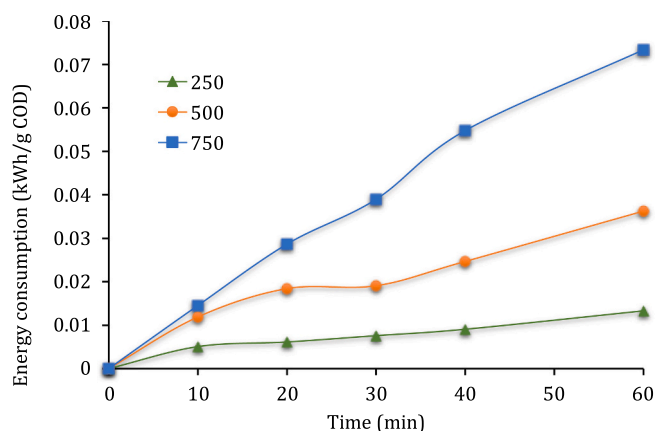


Fig. 7. Energy consumption per kWh/g COD during ECP process.

Table 3

Total costs of the ECP process.

Current applied (mA)	Costs			
	Energy (€)	Chemicals (€)	Electrode (€)	Total cost (€/L)
250	0.0001	0.045	1.00	3.47
500	0.0003	0.045	1.99	6.79
750	0.0006	0.045	2.99	10.11

neutral pH is the preferred option.

Comparing these results with those presented in our study, it should be considered that our work aimed at the removal of recalcitrant COD, which explains a lower removal efficiency when compared with the removal of biodegradable COD via ECP.

On the other hand, according to other authors, the high energy consumption makes the electrochemical processes low cost-effective when employed for the treatment of raw tannery wastewater, while their application as tertiary or refinement treatments makes them economically competitive (Lofrano et al., 2013).

### 3.7. Future perspective

The results obtained in this study highlighted how the ECP process can obtain an efficient removal of recalcitrant COD, meeting the standards established by the Italian law for discharge. However, cost analysis highlighted that the consumption of electrodes contributed the most to the overall cost of the process.

For this reason, it may be interesting to test the efficiency of the ECP process using less expensive mild steel electrodes. At the same time, a scaling up of the process can be performed, in order to optimize the concentration of  $H_2O_2$  and evaluate the removal efficiency of the process with respect to sulphates and chlorides.

Further considerations concern the pH at which the process takes place, since this study showed that the ECP treatment provides satisfactory results even at the initial pH of the sample. Compared to a classic Fenton process, working at neutral pH has the advantage of avoiding the consumption of conditioning agents, which are required both to conduct the process and bring the pH back close to neutral at the end of the treatment. Anyway, it must be taken into account that alkaline conditions lead to the formation of sludge.

An important environmental risk is represented by increasing sludge generation because of the challenges related to the treatment and disposal of sludge (Priyanka and Saravanakumar, 2024).

At the current state of knowledge, strategies for the recovery and valorization of tannery sludge include the conversion into biochar, catalyst and bioenergy production (Pasciucco et al., 2023c) (Moktadir et al., 2023). Furthermore, the high content of heavy metals in tannery sludge poses a challenge for a safety reuse, particularly related to the presence of chromium and the potential risk of conversion to the hexavalent carcinogenic forms during waste management (Kanagaraj et al., 2015).

However, the sludge characterization carried out in this study did not show the presence of heavy metals such as chromium in the precipitate, thus increasing its potential reuse options (Pasciucco et al., 2021).

Recent advances exploit the pyrolysis process to obtain, biochar or activated carbon from tannery sludge, in addition to bio-oil and syngas (Castagnoli et al., 2022). In this context, a recent study (Rossi et al., 2023) investigated the use of pyrolyzed tannery sludge as an adsorbent for the removal of volatile organic compounds emitted during leather finishing operations. The authors conducted pyrolysis experiments at

different temperatures (750–850 °C) and durations (6–60 min) to determine the ideal operating parameters for developing BET specific surface area. The results highlighted that a high surface area of 127 m<sup>2</sup>/g was obtained at 850 °C for 6 min, which was the best compromise in terms of textural characteristic, pyrolysis time and sorption capacity. This draws attention to new possible alternatives for the reuse of the precipitate in a circular economy perspective.

#### 4. Conclusion

In this study, a Fenton-based approach was tested for recalcitrant COD removal in tannery wastewater at neutral and un-conditioned pH, avoiding the addition of chemicals as source of iron. Laboratory-scale tests were performed applying different currents (250, 500 and 750 mA) for 60 min of electrolysis, showing that the process represents a promising alternative to the classic Fenton process. Specifically, COD and color removal efficiencies increased as the applied current increased, ranging from 60.1 to 69.7 % and 91.4–97.8 %, respectively. FTIR, SEM and XRD analyses highlighted that the applied current affected the morphology and composition of the sludge generated during process. Future efforts in this field should try to improve the economic and environmental sustainability of electrochemical processes by reducing the use of chemicals, optimizing the consumption of energy, implementing resource recovery from sludge, and testing recycled materials for electrodes.

#### CRedit authorship contribution statement

**Erika Pasciucco:** Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Francesco Pasciucco:** Writing – review & editing, Visualization, Investigation, Data curation. **Renato Iannelli:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Funding acquisition, Conceptualization. **Isabella Pecorini:** Writing – review & editing, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.172070>.

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