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Evaluation of pollutant load removal efficiency and toxicity in tannery wastewater treated by ion exchange–adsorption, hydrodynamic cavitation–ozonation, and electrocoagulation

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ABSTRACT

The tanning industry generates complex effluents with high organic load, salts, sulfides, nitrogen compounds, and chromium; therefore, the evaluation of their treatment should not be limited to physicochemical parameters. In this study, the efficiency of three technologies applied to a previously pretreated composite tannery effluent was compared: ion exchange–adsorption using natural zeolites (T-ZE), electrocoagulation (T-EC), and hydrodynamic cavitation coupled with ozonation (T-HCO). BOD, COD, TSS, ammoniacal nitrogen, sulfides, chlorides, and metals were determined, and toxicity was evaluated through an acute bioassay using *Lactuca sativa*. Natural zeolite showed the best performance in the removal of COD, TSS, ammoniacal nitrogen, and a high reduction of total chromium; however, its toxicity level was similar to that of the initial sample. Electrocoagulation achieved the highest chromium removal and a high reduction of TSS, but did not produce a significant ecotoxicological improvement. In contrast, hydrodynamic cavitation with ozonation showed the lowest residual toxicity and the highest removal of sulfides and BOD. However, none of the treatments applied individually was able to simultaneously optimize physicochemical quality and effluent detoxification; moreover, all treated samples at 100% concentration maintained marked phytotoxicity. These findings demonstrate that the removal of regulated contaminants does not necessarily translate into a proportional reduction in toxicity and support the need to incorporate bioassays into the selection and scale-up of treatment technologies, as well as to evaluate hybrid treatment approaches.

Keywords: phytotoxicity, *Lactuca sativa*, tannery wastewater, zeolite, electrocoagulation, hydrodynamic cavitation.

INTRODUCTION

The tanning industry generates effluents with a high pollutant load, which require treatment to comply with current environmental regulations before discharge into sewer systems or receiving water bodies. Traditionally, the evaluation of treatment technologies has focused on the removal of regulated physicochemical parameters; however, the residual toxicity of treated effluents is not always considered as a complementary performance criterion. This toxicity may be associated with both persistent contaminants and physical, chemical, or biological transformations

occurring during or after treatment. In this context, technologies such as ion exchange–adsorption using natural zeolites, hydrodynamic cavitation, and electrocoagulation have been evaluated as alternatives to improve the quality of tannery effluents (Aguilar-Ascon et al., 2024; Barra-Hinojosa et al., 2024).

Natural zeolites are crystalline aluminosilicates with a three-dimensional structure formed by SiO_4 and AlO_4 tetrahedra, generating a porous network with internal channels and cavities. In zeolites, the partial substitution of Si^{4+} by Al^{3+} within the tetrahedral framework generates a structural negative charge, which is compensated by exchangeable cations located in the channels and cavities (Díaz, 2017; Ivan et al., 2013). This characteristic provides a high ion-exchange and adsorption capacity (Mansouri et al., 2013), enabling their application in the removal of various contaminants present in wastewater. Furthermore, their properties can be modified through chemical treatments that alter the cationic composition, surface characteristics, or pore accessibility, thereby improving their affinity for specific contaminants.

Zeolites have been applied to the treatment of tannery effluents, particularly due to their ability to remove chromium, hexavalent chromium, and ammoniacal nitrogen. The zeolite types evaluated include mainly clinoptilolite and mordenite. Some studies have conducted adsorption tests using synthetic chromium solutions to evaluate the adsorption capacity of zeolites (Carvalho et al., 2022; Covarrubias et al., 2008; Misaelides, 2011). In the study conducted by Barra-Hinojosa et al. (2024), the effectiveness of Neonite zeolite was evaluated for the treatment of composite tannery effluents and tanning effluents (chrome tanning bath), where under optimal conditions maximum removals exceeding 90% were achieved for many of the parameters evaluated in the composite effluent, as well as a chromium removal efficiency of 97% in the chrome bath.

Cavitation is a physical phenomenon involving the formation, growth, and collapse of cavities or microbubbles within a liquid. During collapse, extreme local conditions of pressure and temperature are generated, as well as regions of high energy density that promote the formation of reactive species such as hydroxyl radicals (•OH), hydrogen radicals (•H), hydroperoxyl radicals (HO_2•), and hydrogen peroxide (H_2O_2) (Gogate et al., 2006). These species may contribute to the oxidation and degradation of contaminants present in water (Rajoriya et al., 2016). In the case of hydrodynamic cavitation, cavity generation occurs through constriction devices such as orifice plates or Venturi systems, which induce abrupt pressure changes in the fluid flow. In addition, this process can be coupled with ozonation to intensify the generation of oxidizing species and improve contaminant removal in complex aqueous matrices.

Saxena et al. (2018) evaluated the treatment of tannery wastewater using hydrodynamic cavitation alone and coupled with ozone, hydrogen peroxide, and the Fenton reagent. Hydrodynamic cavitation alone achieved reductions of 14.46% in COD, 12.60% in total organic carbon, 10.01% in total dissolved solids, and 34.82% in total suspended solids under an optimal inlet pressure of 500 kPa for 120 min. However, coupling with the Fenton process was the most efficient alternative, achieving maximum reductions of 50.20% in COD and 32.41% in total organic carbon using an $FeSO_4 \cdot 7H_2O/H_2O_2$ ratio of 1:3 (w/w). Likewise, Devakirubai et al. (2025) evaluated hydrodynamic cavitation and its combination with ozonation as an advanced treatment for secondary tannery effluents, highlighting its potential for total suspended solids removal and improvement of treated effluent quality. These studies demonstrate that hydrodynamic cavitation can be intensified through complementary oxidative processes; however, its performance varies according to the type of effluent, target parameters, and operating conditions.

Electrocoagulation is a physicochemical technology based on the application of electric current between metallic electrodes, commonly aluminum or iron, to generate coagulant species *in situ* capable of removing contaminants from wastewater (Chen, 2004; Mollah et al., 2001; Moussa et al., 2017). In systems employing aluminum electrodes, anodic dissolution releases Al^{3+} ions, which hydrolyze in the aqueous medium and form monomeric, polymeric, and amorphous aluminum hydroxide species, such as $Al(OH)_3$, promoting contaminant removal through charge neutralization, adsorption, coprecipitation, and floc formation (Hakizimana et al., 2017; Mollah et al., 2001). Simultaneously, water reduction occurs at the cathode, generating hydrogen microbubbles that can facilitate the flotation of formed flocs and their subsequent separation by sedimentation, flotation, or filtration (Butler et al., 2011; Chen, 2004; Holt et al., 2005).

This technology has been applied to the treatment of tannery wastewater due to its ability to

remove solids, organic matter, color, and metals such as chromium, although its efficiency depends on operational variables including electrode material, pH, current density, electrolysis time, and the characteristics of the treated matrix (Feng et al., 2007; Villalobos-Lara et al., 2021). Deghles and Kurt (2016) optimized the treatment of raw tannery wastewater by electrocoagulation using aluminum electrodes, achieving removals of 64.4% COD, 99% total chromium, and 88% color under optimal conditions of 50 mA/cm², pH 7, and 25 min of electrolysis. Similarly, Thirugnanasambandham and Sivakumar (2016) applied electrocoagulation with stainless steel electrodes to reduce color, oils and grease, and COD in tannery wastewater, achieving removals of approximately 92%, 95%, and 80%, respectively. In studies focused on chromium removal, Aguilar-Ascon et al. (2019) reported a 99% removal of total chromium from raw tannery wastewater using electrocoagulation with aluminum electrodes, whereas Genawi et al. (2020) achieved a maximum chromium removal of 100% using iron electrodes at 13 mA/cm², pH 7, and an initial concentration of 750 ppm. These studies demonstrate the effectiveness of electrocoagulation for tannery wastewater treatment; however, its performance depends on electrode material, pH, current density, electrolysis time, and the characteristics of the treated matrix.

The incorporation of bioassays into the evaluation of treated effluents has gained increasing relevance because the removal of conventional physicochemical parameters does not necessarily imply a proportional reduction in residual toxicity. This approach is related to the concept of "whole effluent toxicity", in which the biological response integrates the combined effects of contaminants present in the matrix, including regulated substances, unmonitored compounds, transformation products, and interactions among effluent components (U.S. Environmental Protection Agency [U.S. EPA], 2025). In tannery wastewater, this approach is particularly important due to the simultaneous presence of organic matter, sulfides, salts, nitrogen compounds, chromium, and other metals, whose interactions may influence toxicity even after treatment. In this context, Thirugnanasambandham and Sivakumar (2016) evaluated the removal of ecotoxicological components from tannery wastewater by electrocoagulation, highlighting the need to consider not only the reduction of conventional contaminants but also the biological response of the treated effluent. Similarly, Jallouli et al. (2020) investigated tannery wastewater treated by electrocoagulation, UV photolysis, and a sequential electrocoagulation–UV process, reporting high COD removal and a reduction in phytotoxicity evaluated through germination assays with Hordeum vulgare. These studies demonstrate that bioassays provide complementary information for assessing the environmental safety of treated effluents and allow the identification of residual effects that may not be evident through physicochemical characterization alone.

Studies conducted on other industrial matrices also support this need. Palácio et al. (2009), while evaluating textile effluents treated by electrocoagulation, reported that prolonged treatment times could increase toxicity despite the removal of COD and color, demonstrating that process intensification does not always result in greater detoxification. Likewise, Moraes and Bidoia (2015) evaluated synthetic textile effluents treated by electrochemical processes using different organisms, including *Lactuca sativa*, and observed lower toxicity in treated effluents compared with untreated effluents. Furthermore, (Van den Berg et al., 2020) compared aluminum-based coagulation–flocculation and chitosan-based treatments applied to domestic wastewater previously treated with microalgae, observing inhibition of *L. sativa* germination, although with lower toxic effects in the chitosan treatment. Collectively, these studies demonstrate that ecotoxicological assessment makes it possible to distinguish between physicochemical removal and actual detoxification. However, studies comparing, within the same real tannery wastewater matrix, the physicochemical efficiency and residual toxicity of individual technologies such as adsorption with natural zeolites, electrocoagulation, and hydrodynamic cavitation coupled with ozonation remain limited. This gap justifies the need to simultaneously evaluate contaminant removal and the phytotoxic response of treated effluents through bioassays using sensitive organisms such as *Lactuca sativa*.

Therefore, although technologies such as adsorption and ion exchange using natural zeolites, electrocoagulation, and hydrodynamic cavitation coupled with ozonation have demonstrated the ability to remove contaminants present in tannery wastewater, their performance is generally assessed primarily in terms of physicochemical parameter reduction and regulatory compliance.

However, physicochemical improvement of the effluent does not necessarily imply a proportional reduction in residual toxicity, particularly in complex matrices such as tannery wastewater, which is characterized by the simultaneous presence of organic matter, sulfides, salts, nitrogen compounds, chromium, and other metals. In this context, comparative evidence regarding the relationship between contaminant removal efficiency and the ecotoxicological response of real tannery effluents treated by individual technologies under the same evaluation matrix remains limited.

Accordingly, the objective of the present study was to compare, using the same pretreated real tannery wastewater matrix, the performance of ion exchange–adsorption with natural zeolites, electrocoagulation, and hydrodynamic cavitation coupled with ozonation in terms of pollutant load removal and reduction of residual toxicity in treated effluents. To this end, the effluents were characterized through conventional physicochemical parameters, and their acute phytotoxicity was evaluated using a *Lactuca sativa* bioassay, in order to determine whether the physicochemical improvement achieved by each technology translates into effective effluent detoxification.

MATERIALS AND METHODS

Materials and reagents

For the adsorption treatment, Neonite® zeolite type Neonite-MO-1 was used. This zeolite is characterized by its high pollutant removal capacity in effluents with different characteristics (Barra-Hinojosa et al., 2024).

For the acute toxicity assay, lettuce seeds (*Lactuca sativa*) of the cultivar Long Pale Green Romaine Lettuce (BATLLE S.A.) were used, as they exhibit a high germination rate. The following analytical-grade reagents were used for the bioassay: potassium chloride (reagent grade), sodium hydrogen carbonate (reagent grade, ACS, ISO), and anhydrous magnesium sulfate (extra pure, obtained from Scharlau®), as well as calcium sulfate dihydrate and zinc sulfate heptahydrate (obtained from EMSURE®).

Wastewater sampling

The wastewater samples used in the present study were generated at the Tannery Pilot Plant of the CITEccal Lima. The following wastewater samples were collected: A composite tannery effluent sample generated from aliquots proportional to the water consumption of each stage of the bovine hide tanning process, including soaking, liming, deliming, degreasing, rinsing, pickling, and tanning. This sample constituted the raw sample effluent (RSE). A sample obtained after pretreatment by aeration and sedimentation of coarse solids (PTE), this is the sample from which the treatments described in the following sections were applied. A wastewater sample treated by ion exchange–adsorption using natural zeolites (T-ZE). A wastewater sample treated by electrocoagulation (T-EC). And finally, a wastewater sample treated by hydrodynamic cavitation coupled with ozonation (T-HCO). Treated wastewater samples were collected in triplicate and stored at low temperature. Details regarding the application of each treatment are described in the following sections.

Pretreatment

A pretreatment step was applied to the wastewater, consisting of sample aeration for a period of 10 min (Bagastyo et al., 2023), combined with the sedimentation of coarse solids.

Wastewater treatment

The pretreated effluent (PTE) was independently treated in triplicate by ion exchange–adsorption using natural zeolites (T-ZE), electrocoagulation (T-EC), and hydrodynamic cavitation coupled with ozonation (T-HCO).

Electrocoagulation treatment (T-EC)

A batch reactor with dimensions of 30 × 20 × 25 cm (length, width, and height, respectively), with a volume of 15 L was used. A total of eight aluminum electrodes were installed to operate as anodes and cathodes, each with dimensions of 10 × 10 cm, with a separation of 2 cm between them (Aguilar-Ascon et al., Electric current was supplied by a power source capable of delivering a voltage range of 0–24 V and a current intensity range of 0–10 A. The experimental trials were conducted at a current intensity of 5 A and a treatment time of 20 min, the current density applied was 6.25 mA/cm^2 considering both active faces of the anodic electrodes.

At the end of the treatment, and after 5 min of sedimentation, treated wastewater samples by T-EC were collected for physicochemical analyses. Figure 1 represents the electrocoagulation system.

Treatment using natural zeolites (T-ZE)

In the present study, the treatment by adsorption using natural zeolites was carried out under the optimal operating conditions identified by Barra et al. (2024), who developed a treatment process based on the application of Neonite zeolite. The optimal treatment conditions consisted of a zeolite concentration of 4 g/L, agitation at 300 rpm for 11 min, and sedimentation for 10 min to promote phase separation. The treated wastewater obtained under these conditions was designated as T-ZE, a representation of this treatment process is depicted in Figure 2.

Hydrodynamic cavitation coupled with ozonation treatment (T-HCO)

The hydrodynamic cavitation coupled with ozonation treatment was performed in a recirculation system consisting of a 25 L cylindrical tank, a multistage recirculation pump, a filtration unit, a Venturi-type cavitation device, and an ozone generator. For each experimental run, 20 L of pretreated wastewater were processed. Effluent recirculation was achieved using a pump with a nominal capacity of 4 m^3/h and a maximum pressure of 4 bar, connected to a 2 inch suction line in order to provide the hydraulic conditions required for cavitation generation. The Venturi device, manufactured from stainless steel, consisted of a converging section, a throat, and a diverging section. This configuration allows a local pressure drop in the fluid to conditions close to the vapor pressure, promoting cavity formation followed by their collapse during pressure recovery.

Ozonation was integrated into the recirculation system through an ozone generator with a nominal capacity of 1000 mg/h, supplied with air by an auxiliary compressor operating at 60 L/min. Ozone was introduced into the hydraulic line through silicone and PVC Venturi-type connections in order to enhance its transfer to the wastewater during recirculation.

The wastewater was processed for 120 min under continuous recirculation. The recirculation pump operated at an effective flow rate of approximately 2 m^3/h, while ozonation was applied continuously at the maximum generator capacity of 1000 mg/h. Considering the treated volume of 20 L, the wastewater theoretically passed through the hydraulic circuit approximately 200 times during the treatment period. The Venturi device had a rectangular throat (2 × 4 mm^2, 5 mm length), and the hydraulic system operated with an inlet pressure of 4 bar and an outlet pressure of −0.5 bar, providing the pressure differential required for the generation of an intense cavitation regime. Based on the nominal hydraulic conditions and assuming that the effective recirculation flow passed entirely through the Venturi throat, the cavitation number was theoretically estimated to be approximately 0.02. This value should be regarded only as an approximate hydraulic indicator because the effective flow rate through the Venturi throat was not directly measured (Figure 3).

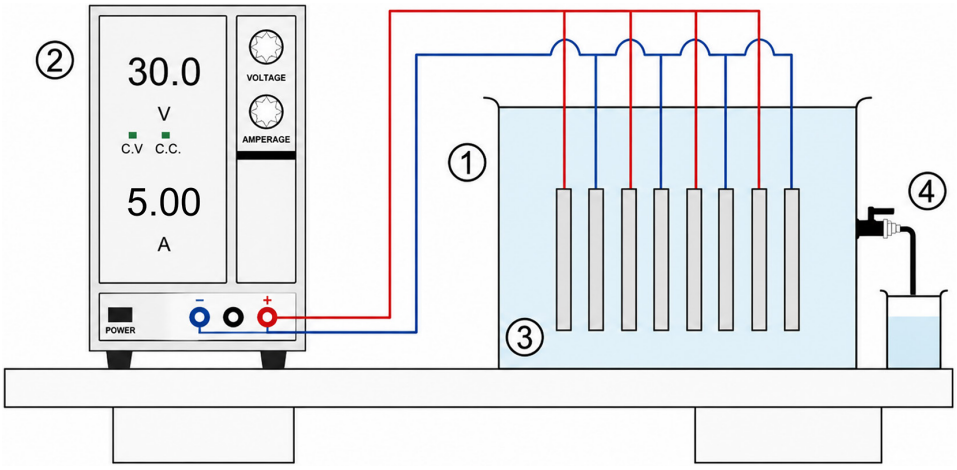

Figure 1. Electrocoagulation system for the treatment of effluents. (1) Electrocoagulation reactor. (2) Power supply. (3) Aluminum electrodes. (4) Sample collector

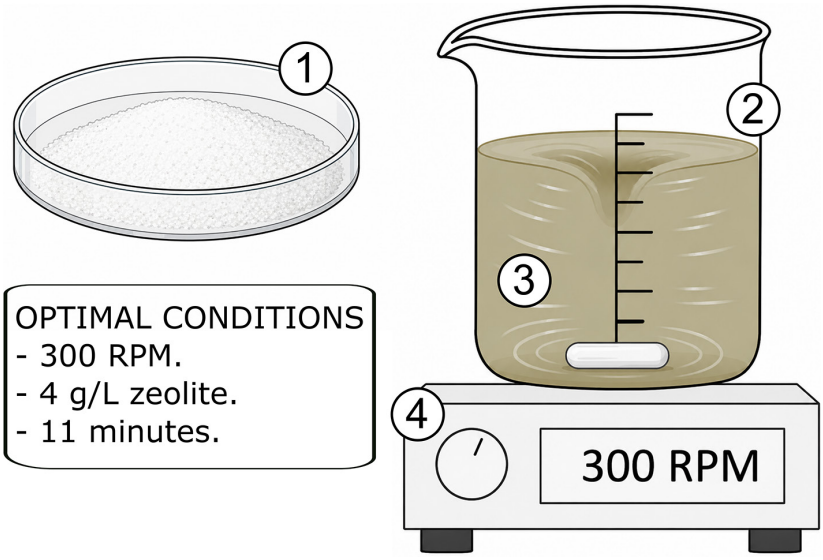

Figure 2. Adsorption treatment of effluents applying zeolites: (1) zeolite neonite, (2) adsorption process recipient, (3) tannery wastewater, (4) magnetic stirrer

Physicochemical parameter analysis

The samples were analyzed to determine biochemical oxygen demand (BOD) (SMEWW-APHA-AWWA-WEF Part 5210 B, 23rd Ed., 2017. BOD: 5-Day BOD Test), chemical oxygen demand (COD) (SMEWW-APHA-AWWA-WEF Part 5220 D, 23rd Ed., 2017. Chemical oxygen demand, closed reflux, colorimetric method), total suspended solids (TSS) (SMEWW-APHA-AWWA-WEF Part 2540-D, 23rd Ed., 2017. Solids: Total Suspended Solids Dried at 103–105 °C), fats (ASTM D3921-96 (Reapproved 2011). Standard Test Method for Oil and Grease and Petroleum Hydrocarbons in Water), ammonia (SMEWW-APHA-AWWA-WEF Part 4500-NH_3-D, 23rd Ed., 2017. Nitrogen (Ammonia), Ammonia-Selective Electrode Method, 2019), sulfides (SMEWW-APHA-AWWA-WEF Part 4500-S^{2-}-I, 23rd Ed., 2017. Sulfide. Distillation, Methylene Blue Flow Injection Analysis Method), chlorides (EPA 300.0 Rev. 2.1, 1993. Determination of Inorganic Anions by Ion Chromatography), and total metals (EPA Method 200.8 Rev. 5.4, 1994. Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma–Mass Spectrometry).

Acute toxicity assay with *Lactuca sativa*

The bioassay was conducted according to the procedure described by Aguilar-Ascón et al. (2024). The negative control, or reconstituted hard water (RHW), was prepared by dissolving 2.4 g of $MgSO_4$, 3.24 g of $NaHCO_3$, 0.16 g of KCl, and 2.4 g of $CaSO_4 \cdot 2H_2O$ in 20 L of distilled water. For the positive control, used to evaluate a reference contaminant, a 500 mg/L $ZnSO_4$ solution was prepared in RHW, from which 10%, 20%, 30%, 40%, and 50% dilutions were prepared with RHW in 100 mL volumetric flasks. Wastewater samples were diluted in RHW at concentrations of 1%, 3%, 10%, 30%, 70%, and 100%.

Lettuce seeds were sown in 10-cm diameter Petri dishes in triplicate, placing 20 seeds per dish and adding 3 mL of each test solution according to the distribution shown in Figure 4. The Petri dishes were then placed inside hermetically sealed bags and incubated at 22 ± 2 °C (VELP incubator, Model FTC 90I) in darkness for 120 h.

Based on the germination and seedling growth results obtained in each Petri dish, the absolute germination (AG) and germination index (GI) were calculated according to Equations 1 and 2, respectively. Toxicity levels according to the GI are presented in Table 1.

$$AG = \frac{N_{germ}}{N_{seed}} \quad (1)$$

$$GI = \frac{N_{germ}}{N_{cont}} \times \frac{RL_{germ}}{RL_{cont}} \quad (2)$$

where: EC50 is the median effective concentration, which is calculated by a linear regression model applied to the dose response curve derived from radicle length

data, allowing the determination of the concentration at which 50% of germination in *Lactuca sativa* seeds was inhibited. N_{seed} is the total amount of seeds sown by Petri dish, N_{germ} is the average amount of germinated seeds, N_{cont} is the amount of germinated seeds in the negative control, RL_{cont} is the average root length in the negative control, RL_{germ} is the average amount of root length in each sample.

Statistical analysis

Outlier identification for data cleaning was performed using the interquartile range (IQR) method. Differences among Petri dishes and concentrations in the Lactuca sativa bioassay were evaluated using the Kruskal–Wallis test, which compares the medians of more than two independent groups. Subsequently, multiple comparisons among groups were conducted using the Conover–Iman test with Holm correction. Both tests were performed at a significance level of 5% ($\alpha = 0.05$). In addition, principal component analysis (PCA) and correlation analysis were performed to explore the relationship between the physicochemical characterization results and the toxicity assay outcomes.

All analyses were implemented in R software version 4.4.2 (R Core Team, 2024) using

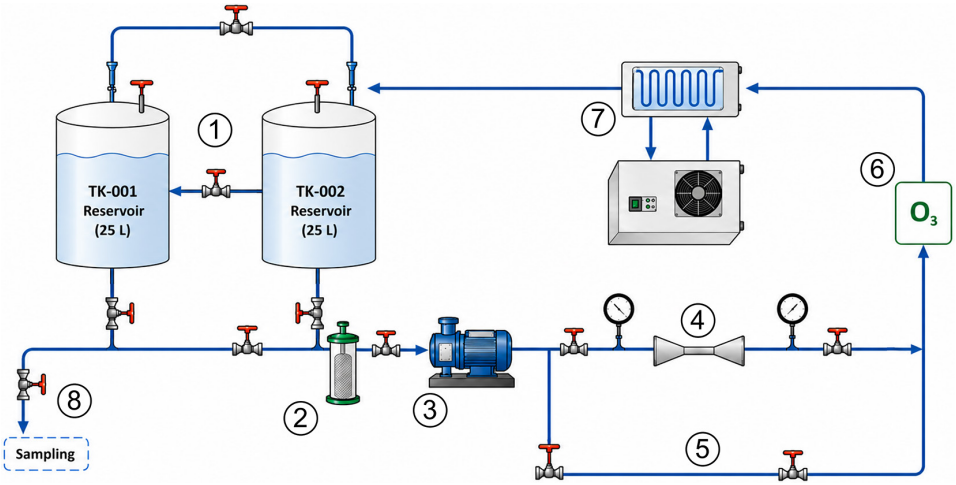

Figure 3. Hydrodynamic cavitation coupled with ozonation system: (1) 25 L cylindrical tanks, (2) filtration unit, (3) recirculation pump, (4) Venturi-type cavitation device, (5) free-flow line, (6) ozonation generator, (7) cooling circuit system, (8) sampling point

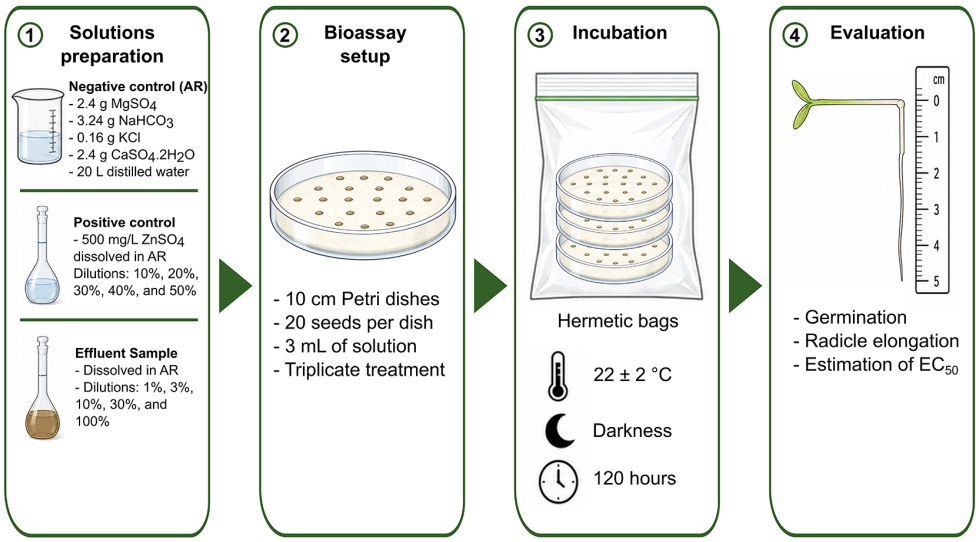

Figure 4. Preparation of the bioassay with *Lactuca sativa* seeds

Table 1. Germination index classification and hazard classification system by toxic units

GI	Germination index classification
GI = 0	Total inhibition
0.0 < GI < 0.4	Significant inhibition
0.4 ≤ GI < 0.8	Slight inhibition
0.8 ≤ GI < 1.2	No significant effect
1.2 ≤ GI	Stimulation effect

the packages 'readr', 'plyr', 'tidyr', 'tidyverse', 'car', 'FSA', 'PMCMRplus', 'FactoMineR', 'ggplot2', 'ggrepel', 'dplyr', and 'ggcorrplot'.

RESULTS AND DISCUSSION

Wastewater characterization and treatment

Table 2 presents the characterization results of the RSE, PTE, T-ZE, T-EC, and T-HCO wastewater samples, together with a comparison against the environmental regulatory limits established by the maximum admissible values (VMAs) for wastewater discharges into sewer systems. Additionally, the results were compared with the environmental quality standards (ECAs) established for vegetable irrigation, which were used as reference values for substances that may affect the normal growth of plant species such as lettuce seedlings.

Pollutant load removal by treatment

T-ZE achieved the highest COD removal with respect to the pretreated effluent, with an average efficiency of 48.36 ± 1.33%, followed by T-HCO, with 40.61 ± 2.62%, and T-EC, with 33.78 ± 3.15%. Despite this reduction, residual COD concentrations remained above the VMA of 1000 mg/L in all treatments, indicating that the partial decrease in oxidizable load was insufficient to achieve regulatory compliance.

Previous studies have reported higher COD removal efficiencies through adsorption processes applied to tannery wastewater. Omer et al. (2017) obtained a COD removal efficiency of 65.32% using clinoptilolite, from an estimated initial COD concentration of approximately 1860 mg/L. Nigam et al. (2019), using tea waste as an adsorbent, reported a COD reduction of 74.8% from an initial concentration of 8500 mg/L. Likewise, Baskaran et al. (2024) achieved a maximum COD removal of 88.19% using palm husk powder, although the optimization assay was conducted with diluted effluent under an optimal initial COD concentration of 1013.40 mg/L, derived from a raw effluent containing 9600 mg/L COD. However, these comparisons should be interpreted with caution due to differences in experimental conditions, including the initial COD concentration, the use of dilution, adsorbent type and dosage, pH, and contact time. In particular, some studies employed adsorbent dosages as high as 30 g/L and extended contact times, whereas the present study applied a dosage of 4 g/L for 11 min to a real composite tannery effluent characterized by a complex matrix with high salinity and pollutant load.

The efficiency of zeolites largely depends on their structure, surface modifications, and the nature of the target contaminant (Bresolin et al., 2024). The zeolite used in this study consists predominantly of clinoptilolite, with calcite as an associated mineral (Barra-Hinojosa et al., 2024). Scientific literature indicates that the adsorptive properties of clinoptilolite are related to its aluminosilicate composition and the presence of exchangeable cations. For organic compounds in water, zeolites with higher Si/Al ratios generally exhibit better performance due to their lower hydrophilicity, greater relative hydrophobicity, and reduced competition with water molecules for adsorption sites. In these cases, micropore volume, pore size, and channel accessibility are also determining factors (Grifasi et al., 2024; Jiang et al., 2018). This is consistent with the results obtained in the present study, where the removal of metallic species such as chromium was substantially greater than that observed for COD.

It should be noted that COD does not represent a single molecule, but rather a complex mixture of organic compounds present in the effluent. In tannery wastewater, this fraction may include soluble and colloidal organic matter, fats, proteins, tanning compounds, and other dissolved constituents (Zhao et al., 2022). Therefore, COD removal depends not only on the availability of adsorption sites, but also on the ability of the different species to access the pores and exhibit chemical affinity for the adsorbent surface (Jiang et al., 2018). In this regard, the moderate COD removal observed in the present study may be explained, at least in part, by the complex nature of the remaining organic matter and by the inherent

Table 2. Wastewater characterization results.

Parameter	BOD (mg/L)	COD (mg/L)	TSS (mg/L)	Ammonia (mg/L)	Sulfides (mg/L)	Total chromium (mg/L)	Aluminum (mg/L)	Chlorides (mg/L)
VMA*	500.00	1000.00	500.00	30.00	5.00	10.00	5.00	500.00
RSE	1221.30	3071.20	1490.00	120.10	121.84	37.24	18.74	3433.48
PTE	997.50	2567.90	288.00	106.80	93.98	16.86	7.19	3620.58
T-ZE1	357.00	1288.10	15.00	75.80	16.14	0.17	0.73	3790.38
T-ZE2	790.00	1335.80	17.00	81.30	23.17	0.14	0.43	3798.16
T-ZE3	781.30	1354.40	14.00	71.30	0.00	0.14	0.47	3779.80
T-EC1	723.80	1793.90	42.00	195.00	24.50	0.00	10.02	3533.18
T-EC2	765.00	1656.80	46.00	271.00	31.40	0.00	8.60	3458.02
T-EC3	690.00	1651.00	54.00	118.00	45.30	0.00	9.99	3545.86
T-HCO1	508.50	1542.60	132.00	215.00	1.07	11.44	2.25	2824.04
T-HCO2	577.50	1582.00	278.00	181.00	1.06	29.86	14.56	2876.76
T-HCO3	435.50	1450.90	195.00	157.00	0.69	18.26	4.05	2722.89

Note: *VMA: Valores Máximos Admisibles para descargas a fuentes de alcantarillado – Decreto Supremo – N° 010-2019-VIVIENDA.

limitations of natural clinoptilolite in efficiently adsorbing heterogeneous organic mixtures.

T-EC exhibited an average COD removal of 33.78 ± 3.15%, a value lower than those reported in other studies on tannery wastewater, where efficiencies of approximately 68–70% and even greater than 90% have been achieved under optimized conditions of pH, current density, electrolysis time, and reactor configuration (Bhagawati et al., 2024; Feng et al., 2007; Villalobos-Lara et al., 2021). Chemically, this process relies on the in situ generation of metallic coagulant species and the formation of hydroxide/oxyhydroxide flocs capable of removing contaminants through adsorption, charge neutralization, coprecipitation, and sweep flocculation (Tegladza et al., 2021). pH is a critical variable because it controls the speciation of these coagulants. Under highly acidic conditions, floc formation is less favorable, whereas under neutral or slightly alkaline conditions, particularly when aluminum electrodes are used, amorphous $Al(OH)_3$ species predominate and are associated with higher treatment efficiency. In strongly alkaline media, however, soluble species such as $Al(OH)_4^-$ become more abundant, reducing process effectiveness (Al-Marri et al., 2023; Holt et al., 2002; Tegladza et al., 2021).

Given that the wastewater pH remained close to 8.2, the limited COD removal observed in this study does not appear to be primarily explained by unfavorable pH conditions for electrocoagulation. Rather, this behavior is likely associated with the complex nature of the residual organic matter present in the effluent, as well as with operational conditions such as electrolysis time, current density, and the effective generation of coagulant species (Elabbas et al., 2016). In this context, the greater effectiveness of electrocoagulation in the removal of total chromium and TSS may be attributed to the fact that these correspond to species that are more readily precipitated, colloidal, or adsorbable, unlike COD, which represents a more heterogeneous and partially dissolved mixture of oxidizable compounds (Karahan et al., 2008; Tegladza et al., 2021).

T-HCO achieved a COD removal efficiency of 40.61 ± 2.62%, reducing the concentration from 2567.90 mg/L to 1525.17 ± 67.27 mg/L. Although this result demonstrates a moderate oxidative effect, it was insufficient to meet the MAV of 1000 mg/L. Previous studies have investigated similar applications using different effluent types, pollutant loads, and treatment conditions. A performance comparable to that obtained in the present study has been reported for HC + O_3 systems applied to real industrial wastewater (38.7%), although lower than that observed in alternative configurations such as HC + H_2O_2 + O_3 (60.8%) and optimized ozonation processes for tannery wastewater, where COD removals of up to 92% have been reported (Preethi et al., 2009; Thanekar and Gogate, 2019). From a chemical perspective, the HC + O_3 combination promotes the degradation of organic compounds through cavity collapse, the generation of high-energy microenvironments, and the enhancement of ozone mass transfer and decomposition

into more reactive oxidizing species, particularly hydroxyl radicals (•OH). Nevertheless, the efficiency observed in this study was likely limited by the complexity of the effluent, whose COD represents a heterogeneous mixture of oxidizable organic and inorganic compounds characteristic of the tanning industry (Zhao et al., 2022).

Regarding BOD, T-HCO achieved the highest removal efficiency, with an average value of 49.16 ± 7.12%, followed by T-ZE, with 35.56 ± 24.81%, and T-EC, with 27.19 ± 3.77%. Furthermore, the final concentrations obtained through T-HCO were the closest to the MAV of 500 mg/L, suggesting a greater capacity of this treatment to reduce the biodegradable fraction of the residual organic load. Although evidence regarding BOD removal by HC + O_3 systems applied to tannery wastewater remains limited, this combination may promote the oxidation of organic compounds through enhanced ozone mass transfer and the generation of reactive species, particularly hydroxyl radicals (Thanekar and Gogate, 2019; B. Wang et al., 2022).

The performance of T-EC with respect to BOD was lower than that reported in studies conducted under optimized conditions. Aguilar-Ascón et al. (2019) achieved a BOD removal efficiency of 69.2% in tannery wastewater treated by electrocoagulation using a Box–Behnken design. Likewise, Bhagawati et al. (2024) reported BOD removals ranging from 87.57% to 90.86% in tannery wastewater treated by electrocoagulation using flat and perforated aluminum and iron electrodes at pH 9 and a treatment time of 90 min. In comparison, the average BOD removal obtained in the present study was 27.19 ± 3.77%.

The BOD removal achieved through T-ZE was 35.56 ± 24.81%, from an initial concentration of 997.50 mg/L after pretreatment. This performance was lower than that reported in previous studies using zeolitic materials for tannery wastewater treatment under optimized conditions. Omer et al. (2017) reported a BOD removal of up to 75% using natural clinoptilolite at a dosage of 3 g per 100 mL of effluent, equivalent to 30 g/L, at pH 9 and a contact time of 30 min, from an estimated initial BOD concentration of approximately 560 mg/L. Similarly, Barra-Hinojosa et al. (2024) achieved a BOD removal efficiency of 93.11% in a composite tannery effluent treated with Neonite, reducing the concentration from 1106.30 to 76.20 mg/L under optimal conditions of 4.73 g/L adsorbent and 12.17 min of agitation at an initial pH close to 7.8.

In comparison, the present study applied a natural zeolite dosage of 4 g/L, with agitation at 300 rpm for 11 min and sedimentation for 10 min to promote phase separation. Although these conditions are similar to those reported for Neonite by Barra-Hinojosa et al. (2024), the lower efficiency observed may be mainly associated with the initial condition of the treated matrix. In this case, the zeolite was applied to a wastewater sample that had already undergone pretreatment, with an initial BOD concentration of 997.50 mg/L. Consequently, the remaining biodegradable fraction may have exhibited lower affinity for the adsorbent surface or may have consisted of more soluble, dispersed, or difficult-to-retain organic compounds. Furthermore, the presence of salts, nitrogen compounds, sulfides, and other constituents characteristic of tannery wastewater may have generated competition for active sites or limited access to the pores and channels of clinoptilolite. Taken together, these results suggest that BOD removal by zeolite depends not only on dosage, pH, or contact time, but also on the composition of the residual organic matter after pretreatment and its affinity for the adsorbent material.

With respect to TSS, T-ZE achieved the highest removal efficiency (94.68 ± 0.53%), followed by T-EC (83.56 ± 2.12%), whereas T-HCO exhibited a much lower and more variable removal efficiency (29.98 ± 25.43%). It should be noted that pretreatment had already reduced this parameter to 288 mg/L, a value below the VMA of 500 mg/L.

The observed behavior is consistent with the nature of each process. T-EC may promote the retention of particles and colloids through surface adsorption, electrostatic interactions, ion exchange, and physical retention associated with its porous structure, whereas electrocoagulation promotes the formation of amorphous metallic hydroxides capable of removing suspended solids through charge neutralization, coprecipitation, and sweep flocculation (Tegladza et al., 2021; S. Wang and Peng, 2010).

In contrast, the lower efficiency and greater variability observed for TSS removal by hydrodynamic cavitation coupled with ozonation may be attributed to the fact that this treatment does not primarily function as a solid–liquid separation stage, but rather as a process for the partial oxidation of the remaining matrix. Previous studies have reported that the HC + O_3 combination can improve TSS removal in tannery wastewater (Devakirubai et al., 2025); however, its performance

depends on the optimization of variables such as inlet pressure, ozone dosage, and reactor hydrodynamics (B. Wang et al., 2022).

Regarding ammonia, T-Z was the only technology that achieved removal relative to the pretreated effluent, with an average efficiency of 28.71 ± 4.69%, reducing the concentration from 106.8 mg/L to 76.13 ± 5.01 mg/L. In contrast, both T-EC and T-HCO showed apparent increases in ammoniacal nitrogen concentration. These results indicate that ammoniacal nitrogen, originating from the use of ammonium salts as well as from the hydrolysis of proteins and other nitrogen-containing compounds during beamhouse operations, was a difficult parameter to remove from the matrix evaluated in this study.

The higher removal efficiency achieved by zeolite is associated with the nature of clinoptilolite, since NH_4^+ removal in this material occurs primarily through ion exchange and adsorption onto active sites within the aluminosilicate structure (Adam et al., 2023; Chen, 2004; Wasielewski et al., 2018). Considering that the wastewater pH was approximately 8.2, ammoniacal nitrogen remains predominantly in the NH_4^+ form, as the NH_4^+/NH_3 equilibrium has a pKa of approximately 9.25. Under these conditions described by Wasielewski et al. (2018), removal by clinoptilolite is chemically favorable because NH_4^+ is the exchangeable species, that study also described clinoptilolite as an effective ion exchanger for ammonium in concentrated solutions, while Han et al. (2021) identified it as one of the most widely used adsorbents for NH_4^+/NH_3 removal from wastewater. Reports on the application of clinoptilolite to tannery wastewater are limited; however, the review by Grifasi et al. (2024) highlights its versatility for industrial and municipal wastewater purification, whereas Wasielewski et al. (2018) described it as an effective adsorbent/ion exchanger for ammonium in synthetic waters with high ammonium loads. Nevertheless, in the present study, the VMA of 30 mg/L was not achieved.

In electrocoagulation, NH_4-N removal has generally been reported as moderate. For example, Feng et al. (2007) reported a removal efficiency of 43.1% in tannery wastewater. Electrocoagulation generates aluminum coagulant species that primarily remove other contaminants, whereas ammonium reduction depends largely on the OH^- generated at the cathode, which promotes the conversion of NH_4^+ into NH_3. Once formed, NH_3 may be removed through volatilization. This behavior is favored at elevated pH values. Given that the wastewater evaluated in the present study had a pH of approximately 8.2, the limited ammoniacal nitrogen removal suggests that electrocoagulation did not generate a sufficiently alkaline environment to markedly promote the NH_4^+/NH_3 conversion (Kuntke et al., 2018).

The increase in ammoniacal nitrogen observed after T-EC may reflect the generation of NH_4^+ from other nitrogen-containing species present in tannery wastewater. In this type of effluent, ammoniacal nitrogen originates primarily from the deliming and bating stages due to the use of ammonium salts, but it may also be generated through the decomposition and hydrolysis of proteins during soaking, washing, and liming operations. These compounds may subsequently be transformed into NH_4^+ during wastewater treatment (Aguilar-Ascon et al., 2024; Y. Wang et al., 2012).

Hydrodynamic cavitation can also promote ammoniacal nitrogen removal; however, the best results have been reported in systems combined with aeration and supplemental oxygenation, optimized cavitation devices, and longer operating times, where removal efficiencies exceeding 80% have been achieved in certain wastewater matrices (Patil et al., 2021). Nevertheless, ozonation of real wastewater matrices not only degrades organic matter but may also modify nitrogen speciation, transforming dissolved organic nitrogen into inorganic compounds such as ammonium and nitrate (Lai et al., 2017), which could explain the increase in ammoniacal nitrogen observed in the present study.

A different behavior was observed for sulfides. Hydrodynamic cavitation coupled with ozonation (T-HCO) achieved the highest removal efficiency, with 99.00 ± 0.23%, reducing the concentration from 93.98 mg/L to 0.94 ± 0.22 mg/L and thereby complying with the MAV of 5 mg/L. Natural zeolite (T-ZE) also achieved a high removal efficiency of 86.06 ± 12.64%, resulting in an average final concentration of 13.10 ± 11.88 mg/L, whereas electrocoagulation (T-EC) exhibited a lower removal efficiency of 64.11 ± 11.27% and did not meet the regulatory standard.

The high sulfide removal observed in T-HCO is likely associated with the strong reactivity of sulfide species toward ozone. In aqueous systems, sulfide oxidation by ozone occurs primarily through oxygen atom transfer reactions, with high reaction rate constants for H_2S and, particularly, for deprotonated sulfide species. This behavior

explains the rapid transformation of sulfides under oxidative conditions. In addition, this process may involve progressive oxidation toward sulfur species with higher oxidation states, ultimately yielding sulfate as the final product under sufficient ozonation conditions (von Gunten, 2003). Furthermore, coupling with hydrodynamic cavitation may intensify the process by enhancing ozone mass transfer and promoting the generation of secondary oxidizing species, such as hydroxyl radicals, thereby contributing to the high removal efficiency observed.

Likewise, considering that the wastewater pH was approximately 8.2, HS^- would be the predominant sulfur species (Prokkola et al., 2020). In the case of zeolites, the observed sulfide removal cannot be directly explained by ion exchange, as occurs with NH_4^+, because natural zeolites exhibit little or no affinity for anions due to their negatively charged framework (Faghihian and Bowman, 2005). Sulfide removal was more likely associated with surface adsorption, retention of sulfur-containing colloidal species, or interactions with cations present within the mineral structure (Karimi and Azadmehr, 2017).

In electrocoagulation, sulfide removal has been reported to depend strongly on electrode material. Feng et al. (2007) demonstrated that, in tannery wastewater, mild steel electrodes were considerably more effective than aluminum electrodes for sulfide removal, achieving efficiencies greater than 90% through the formation of characteristic black iron sulfide precipitates. In the comparative study conducted by Demertzis et al. (2016), sulfide removal using aluminum electrodes was low and very slow (<6%), whereas iron electrodes achieved rapid and nearly complete removal. The interaction of sulfides with aluminum electrodes is likely associated more with adsorption onto $Al(OH)_3$ than with direct and efficient chemical precipitation of HS^-.

This behavior is also consistent with the residual aluminum concentrations observed in the treated samples. While a reduction in aluminum concentration was observed from RSE to PTE, and T-ZE further reduced aluminum levels below the regulatory limit, T-EC exhibited aluminum concentrations higher than those measured in PTE in all three replicates. This increase may be related to the anodic dissolution of aluminum during electrocoagulation, since the electrode material itself serves as the source of coagulant species within the system (Krupińska, 2020). Therefore, although electrocoagulation with aluminum electrodes promotes the formation of metallic hydroxides capable of removing suspended solids and part of the pollutant load, its performance toward sulfides may be lower than that achieved with iron electrodes and may additionally increase residual aluminum concentrations in the treated effluent.

With respect to total chromium, natural zeolite (T-ZE) and electrocoagulation (T-EC) were the most effective technologies. T-ZE reduced chromium concentration from 16.86 mg/L in the pretreated effluent to 0.15 ± 0.02 mg/L, corresponding to a removal efficiency of 99.11 ± 0.10%. Electrocoagulation achieved non-detectable chromium concentrations, thereby complying with the VMA of 5 mg/L.

In chrome tanning processes, the metallic contaminant originates primarily from chromium salts, particularly basic chromium sulfate; therefore, most of the chromium present in the effluent occurs as Cr(III) (Akihisa, 2008; Vasquez et al., 2024). In this context, clinoptilolite and other natural zeolites may promote Cr(III) removal through ion exchange and adsorption onto the aluminosilicate matrix (Barros et al., 2004; Covarrubias et al., 2005), whereas electrocoagulation removes chromium through anodic dissolution and the in situ generation of metallic hydroxides and insoluble chromium compounds, followed by precipitation, coprecipitation, and cosedimentation of the metal (Genawi et al., 2020; Theodosis-Nobelos and Rekka, 2022). The performance of T-ZE is consistent with previous tannery studies in which Neonite achieved chromium removals exceeding 98% in composite effluents and up to 99.95% under optimized conditions (Barra-Hinojosa et al., 2024). Likewise, other natural and modified zeolites have demonstrated the capacity to reduce chromium concentrations in tannery wastewater to permissible levels (Ayele et al., 2018; Covarrubias et al., 2005).

Regarding electrocoagulation, the results are consistent with previous studies. Genawi et al. (2020) reported chromium removal efficiencies of up to 100% using iron electrodes in real tannery wastewater. Similarly, Elabbas et al. (2016) and Villalobos-Lara et al. (2021) reported Cr(III) removal efficiencies greater than 90% using aluminum electrodes.

Unlike T-ZE and T-EC, T-HCO is primarily an oxidation process rather than a metal separation technology. Moreover, evidence indicates that ozone and hydroxyl radicals may oxidize Cr(III)

to Cr(VI) under alkaline conditions, suggesting that a strongly oxidative system may alter chromium speciation without necessarily decreasing total chromium concentration. This aspect warrants further investigation in future studies (Gogolev and Shilov, 2014).

In the case of chlorides, hydrodynamic cavitation coupled with ozonation (T-HCO) was the only technology that achieved removal relative to the pretreated effluent, with an average removal efficiency of 22.45%; however, the final concentrations did not reach the levels proposed by Mogollon et al. (2020).

Chlorides are a highly soluble and non-biodegradable anions, making its removal particularly challenging. Effective pathways reported for chloride removal from water primarily include specific chemical precipitation, adsorbents or ion exchangers designed for anion removal, oxidation under particular conditions, and, most notably, membrane-based processes such as nanofiltration, reverse osmosis, and electrodialysis (Li et al., 2022).

Clinoptilolite is a cation-exchange material. For anion removal, the literature indicates that zeolite surfaces generally require modification, for example through the use of cationic surfactants, in order to transform the inherently negative surface into a positively charged one capable of retaining anions. Consequently, substantial chloride removal would not be expected from the zeolite used in the present study (Rodríguez-Iznaga et al., 2022).

In electrocoagulation systems employing aluminum electrodes, chlorides generally behave more as supporting electrolytes than as contaminants effectively removed by the process. They can increase conductivity, reduce anodic passivation, and promote anodic dissolution; however, these effects do not imply substantial removal of Cl^- from the aqueous phase (Huang et al., 2020).

On the other hand, an apparent decrease in chlorides observed in T-HCO systems may reflect chemical transformation rather than actual removal of total chlorine species. Studies on ozonation and advanced oxidation processes in chloride-containing matrices indicate that chloride tends to participate in oxidation chemistry, for example through the transformation of hydroxyl radicals into reactive chlorine species or the formation of other oxychlorinated compounds (Grebel et al., 2010), rather than being effectively removed from the system. Therefore, the apparent reduction in chloride concentration observed in this treatment should be interpreted with caution, and further investigation is needed to clarify the mechanisms involved in chloride transformation and removal.

Acute toxicity bioassay with *Lactuca sativa*

The negative control achieved a germination rate of 100.0% (≥ 90.0%), and the coefficient of variation was 18.25% (≤ 30.0%). These results demonstrate the quality of the seeds and their high representativeness, while also supporting the validity of the phytotoxicity results obtained in the present study (Cardoso et al., 2024; Cavalheri et al., 2023; Escoto-Valerio et al., 2007). The results of the acute toxicity bioassay using Lactuca sativa seeds are presented in Table 3 and Figure 5. A decrease in toxicity was observed in the treated samples relative to the initial wastewater sample, particularly in PTE and in those treated by T-EC and T-HCO.

Based on the EC50 values, the raw sample effluent (RSE) exhibited an EC50 of 10.41%, the pretreated effluent (PTE) an EC50 of 22.63%, electrocoagulation-treated samples (T-EC) 16.70 ± 2.15%, zeolite-treated samples (T-ZE) 10.56 ± 2.22%, and hydrodynamic cavitation coupled with ozonation-treated samples (T-HCO) 41.48 ± 3.61%. These results indicate that all treatments maintained the effluent within a condition of acute toxicity, although T-HCO exhibited the lowest residual toxicity, whereas T-ZE remained very close to the untreated effluent.

Pretreatment resulted in a substantial decrease in toxicity, as evidenced by the increase in EC50 from 10.41 to 22.63%. This behavior may be associated with the removal of coarse solids and the reduction of the pollutant load present in the wastewater sample. Regarding the germination index, both RSE and PTE exhibited slight inhibition at the concentrations where germination and seedling growth occurred, indicating that although toxicity decreased after pretreatment, both samples still displayed similar toxicity characteristics.

However, the subsequent behavior of each treatment differed. T-HCO exhibited the highest EC50, which is consistent with its superior performance in sulfide removal and its higher BOD removal efficiency. In contrast, although T-ZE achieved substantial reductions in total chromium, TSS, and part of the COD and BOD, its EC50 value of 10.56 ± 2.22% was practically equivalent to that of the untreated effluent. T-EC achieved high removal efficiencies for total chromium and TSS, but the reduction in toxicity was lower than

Table 3. Results of the toxicity assay with Lactuca sativa seeds

Samples	Volume of sample in relation to control hard water volume (%)												EC_{50}
	1		3		10		30		70		100		
	GA	IG	GA	IG	GA	IG	GA	IG	GA	IG	GA	IG	
RSE	0.93	0.74	0.92	0.58	0.95	0.50	1.00	0.59	0.00	0.00	0.00	0.00	10.41
PTE	1.00	0.63	0.98	0.58	1.00	0.55	0.98	0.46	0.00	0.00	0.00	0.00	22.63
T-EC1	1.00	0.71	0.95	0.64	0.98	0.34	0.95	0.15	0.00	0.00	0.00	0.00	18.27
T-EC2	1.00	0.67	1.00	0.52	1.00	0.28	0.80	0.24	0.00	0.00	0.00	0.00	14.25
T-EC3	0.95	0.66	0.98	0.62	0.93	0.52	1.00	0.22	0.00	0.00	0.00	0.00	17.57
T-ZE1	0.98	0.91	0.98	0.77	0.98	0.49	1.00	0.33	0.00	0.00	0.00	0.00	8.20
T-ZE2	0.98	0.87	0.98	0.63	1.00	0.46	1.00	0.25	0.00	0.00	0.00	0.00	10.87
T-ZE3	0.97	0.80	0.98	0.66	1.00	0.61	1.00	0.31	0.00	0.00	0.00	0.00	12.61
T-HCO1	1.00	0.87	0.98	0.90	1.00	0.72	1.00	0.62	0.98	0.13	0.00	0.00	37.37
T-HCO2	1.00	0.96	1.00	0.83	1.00	0.70	1.00	0.65	1.00	0.27	0.00	0.00	42.28
T-HCO3	1.00	1.00	1.00	0.86	1.00	0.71	1.00	0.63	1.00	0.28	0.00	0.00	44.16

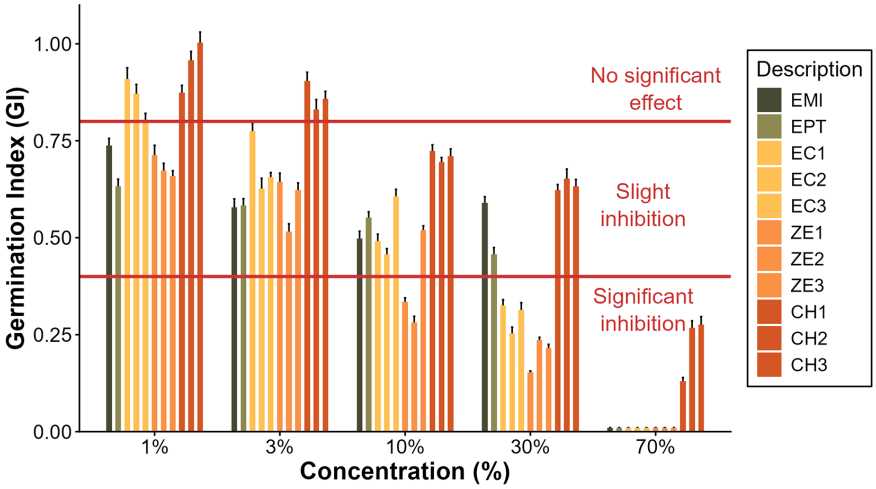

Figure 5. Germination index results of the acute toxicity test with *L. sativa*

that obtained with T-HCO. This suggests that, although highly effective in removing metallic and particulate species, dissolved toxic fractions capable of inhibiting root growth remained in the treated effluent, probably associated with residual sulfides, ammoniacal nitrogen, salts, and soluble organic compounds.

When evaluating the different concentrations, T-HCO exhibited no significant effects (GI > 0.80) at lower concentrations (1% and 3%), whereas T-EC and T-ZE displayed a behavior similar to that of RSE and PTE and even showed greater toxicity at higher concentrations. This finding helps explain why its EC50 was comparable to that of the untreated samples. At a concentration of 70%, only the samples treated by T-HCO maintained nearly complete germination (AG = 0.98–1.00), although GI values remained low (0.13–0.28), corresponding to the category of significant inhibition, indicating that root elongation was more sensitive than germination. Conversely, all samples at 100% concentration caused complete inhibition of germination and root growth (AG = 0; GI = 0), demonstrating that even after treatment, the effluents remained markedly phytotoxic.

Considering the differences in pollutant load removal capacity and phytotoxicity expressed in the samples, correlation analysis and main effects analysis were applied to evaluate the association between the presence of compounds in the effluents and the identified toxicity. Figure 6 presents the principal component analysis developed using pollutant load and toxicity data for the effluent samples evaluated in the present study.

PC1 mainly separated the samples with high organic, sulfur, and metal loads. The variables with the highest contribution to this axis were COD (18.36%), TSS (18.35%), sulfides (14.52%), chromium (14.32%), aluminum (12.87%), and BOD (11.98%). Meanwhile, EC50 and parameters that appeared not to contribute to toxicity were located at the opposite end. The RSE and PTE samples were positioned on the side associated with higher pollutant load, whereas the treated samples were aligned toward EC50, indicating a decrease in their toxicity.

PC2, in turn, represented the samples that showed a greater reduction in toxicity after treatment, but also some parameters that may lead to a misleading interpretation regarding their effect on toxicity. The variables with the highest contribution were chlorides (30.28%), EC50 (28.79%), ammonia (9.33%), zinc (8.44%), BOD (7.86%), and chromium (7.21%). The samples treated by T-HCO were associated with lower toxicity, being located close to EC50, whereas the samples treated by T-EC and T-ZE were positioned on the negative side of PC2. The opposition observed between EC50 and chlorides is due to the fact that the samples treated by T-EC and T-ZE, despite reductions in pollutant load and toxicity, maintained high chloride concentrations, which generated this relationship and could be one of the causes of the higher toxicity observed in these samples. On the other hand, the proximity of ammonia to EC50 is related to the content observed in the samples treated by T-HCO. The correct interpretation is not that ammonia is associated with lower toxicity, but rather that in the samples showing lower toxicity, the ammonia content could have caused the toxicity.

In tannery wastewater, toxicity is usually multicomponent because the matrix simultaneously contains organic matter, sulfides, chlorides, nitrogen compounds, and chromium, among other contaminants. Therefore, the biological response does not necessarily follow the same pattern as the physicochemical removal of an individual parameter. Although the zeolite treatment was highly effective in removing total chromium and TSS, and also partially reduced ammoniacal nitrogen, BOD, COD, and sulfides, the treated effluent maintained a considerable residual load of dissolved compounds, especially chlorides and a still elevated organic fraction, including ammoniacal nitrogen. This suggests that the removal of metallic and particulate species was not sufficient to eliminate the factors that most affected germination and root growth (Cotman et al., 2004).

An important aspect to consider is the aluminum content, which in the present study was associated with higher toxicity levels. Treatment with zeolite reduced the concentration of this metal below the values established in the regulation. In contrast, the samples treated by electrocoagulation showed aluminum concentrations above the standard, which could be related to the use of aluminum electrodes as part of the process. Likewise, sample T-HCO2 shifted toward the higher toxicity region, associated with an elevated aluminum concentration; however, this behavior should be interpreted as an outlier, since the other samples treated by hydrodynamic cavitation coupled with ozonation showed aluminum concentrations below the regulatory value.

Another point to highlight is the increase in ammoniacal nitrogen concentration in the electrocoagulation and hydrodynamic cavitation

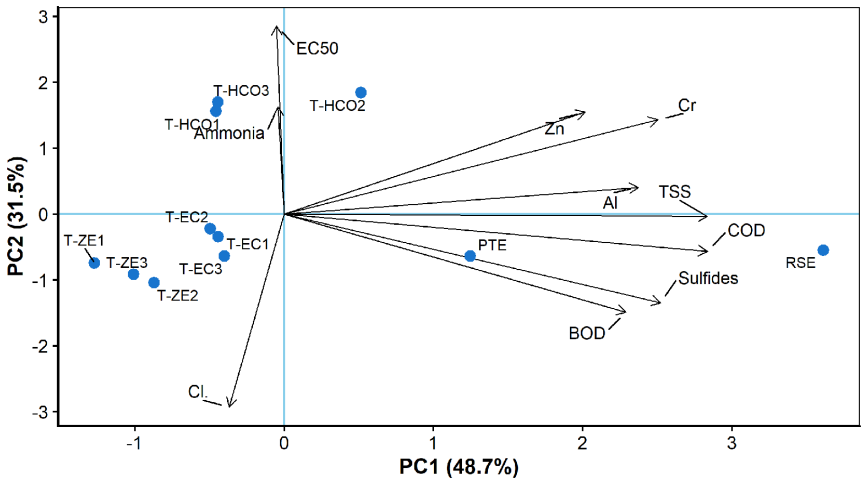

Figure 6. Principal component analysis (PCA) for the treated effluent and toxicity results

coupled with ozonation treatments. In the study conducted by Aguilar et al. (2024), an increase in ammoniacal nitrogen concentration was also observed in samples treated by electrocoagulation and electrocoagulation plus ozonation. This indicates that the applied treatments may enable the generation of ammoniacal nitrogen from other nitrogen-based substances present in the effluents, due to the collagenous matrix of hides.

However, in the cavitation treatment, where the greatest increase in ammoniacal nitrogen content was observed, lower toxicity was evidenced. This is relevant because, in plant systems, NH_4^+ can aggravate salt stress by promoting the overaccumulation of Cl^- in tissues, intensifying growth inhibition. This could explain the increase in toxicity of the treated effluents, but also the lower toxicity observed in T-HCO, since this treatment achieved a significant decrease in chloride concentration (Liu et al., 2020).

Likewise, T-HCO was the most effective treatment for sulfide removal. The importance of this result is reinforced by considering that sulfide is a potent phytotoxic compound, capable of severely affecting plant metabolism and cellular respiration. In fact, it has been reported to inhibit cytochrome c oxidase and alter multiple physiological processes in plants (Lamers et al., 2013).

Additionally, despite the complete removal of total chromium and the significant reduction in TSS achieved by electrocoagulation, the residual toxicity remained very close to that of the pretreated effluent. This response is consistent with previous studies on tannery wastewater treated by electrocoagulation and ozonation, in which toxicity was observed to persist despite improvements in several physicochemical parameters, due to the incomplete removal of the pollutant load and the possible presence of recalcitrant or residual toxic compounds (Aguilar-Ascon et al., 2024).

These findings are further supported by the toxicity results obtained for the adsorption treatment, which were comparable to those of the raw effluent. Although this treatment achieved highly significant removal of organic matter and metals, sulfides, ammoniacal nitrogen, and chlorides persisted, and these compounds may be responsible for the high phytotoxicity observed. Further studies are required, including the evaluation of treated effluents using other bioindicators, in order to comprehensively establish the efficiency of treatment technologies beyond conventional physicochemical parameters.

In the case of chlorides, the results indicate that this parameter constitutes a persistent limitation of the treatment system, and its removal requires an additional treatment stage specifically designed for anion removal or desalination, such as anion exchange, modified adsorbent materials, or membrane processes, which should be further investigated.

Opportunities and future implications

The differential performance of the evaluated technologies indicates that they should not be interpreted as mutually exclusive processes, but rather as stages with complementary functions within an integrated treatment system. T-ZE achieved the highest removal of COD, TSS, ammoniacal nitrogen, total chromium, and aluminum, confirming its relevance for reducing physicochemical load, cationic species, and suspended solids. However, its limited ecotoxicological improvement demonstrates that the reduction of these parameters was not sufficient to ensure effective detoxification. T-EC was highly efficient in the removal of total chromium and TSS; nevertheless, the residual toxicity observed, together with the increase in aluminum and ammoniacal nitrogen, suggests that this process, when applied individually, does not completely eliminate the factors associated with ecotoxicological risk. In contrast, T-HCO achieved the lowest residual toxicity and the highest removal of sulfides and BOD, supporting the role of the oxidative transformation of sulfur-containing species and biodegradable organic fractions in reducing the phytotoxicity observed, the main observations of the results are recapitulated in Table 4.

In this context, the findings support the evaluation of hybrid treatment systems. The results obtained suggest that an initial electrocoagulation stage may be suitable for the removal of suspended solids and total chromium, reducing matrix complexity and improving the performance of subsequent treatments. Thereafter, the application of ion exchange–adsorption using natural zeolite or hydrodynamic cavitation coupled with ozonation is proposed as a second treatment stage, in order to determine which of these processes provides a greater reduction in sulfides, organic load, ammoniacal nitrogen, and residual toxicity. Furthermore, future studies may evaluate configurations integrating all three technologies to determine whether their complementary mechanisms of separation, oxidation, and adsorption can simultaneously

Table 4. Principal results from the treatments processes

Treatment	Treatment strengths	Ecotoxicological response	Identified limitations	Proposed role in the hybrid treatment system
T-ZE	High capacity for the removal of total chromium, TSS, and part of the organic and nitrogen load. It also promoted the reduction of residual aluminum.	Residual toxicity remained similar to that of the raw effluent, indicating that the reduction of metals and solids did not translate into an equivalent decrease in phytotoxicity.	Persistence of sulfides, chlorides, ammoniacal nitrogen, and dissolved organic fractions associated with residual toxicity.	Complementary polishing stage, particularly for the removal of metals and compounds susceptible to adsorption or ion exchange.
T-EC	High efficiency in the removal of total chromium and suspended solids, promoting the separation of metallic and particulate species.	Produced a limited reduction in toxicity, maintaining an ecotoxicological response similar to that of the pretreated effluent.	Persistence of dissolved compounds associated with toxicity, increase in ammoniacal nitrogen, and presence of residual aluminum generated during the process.	Primary treatment stage for the removal of suspended solids and metals, facilitating wastewater conditioning prior to subsequent treatment processes.
T-HCO	Highest capacity for sulfide removal and reduction of the biodegradable fraction of the organic load. It was also the only treatment that achieved an appreciable reduction in chlorides.	Presented the lowest residual toxicity and the highest EC50, demonstrating the greatest detoxification potential among the evaluated technologies.	Limited capacity for metal removal, variable suspended solids removal, and persistence of ammoniacal nitrogen and dissolved salts.	Oxidation and detoxification stage focused on the reduction of sulfur-containing compounds and residual organic matter, preferably following a solids and metals removal stage.

improve compliance with physicochemical parameters and reduce effluent toxicity.

CONCLUSIONS

The evaluated technologies improved tannery wastewater quality to different extents. Natural zeolite showed the best performance in the removal of COD, TSS, and ammoniacal nitrogen, as well as a high reduction in total chromium. Electrocoagulation achieved the highest total chromium removal and a substantial reduction in TSS, whereas hydrodynamic cavitation coupled with ozonation exhibited the highest removal of sulfides and BOD. The evaluation using Lactuca sativa demonstrated that physicochemical improvement was not equivalent to a proportional reduction in the residual toxicity of the treated effluents. All treated samples at 100% concentration maintained an acutely phytotoxic character.

Hydrodynamic cavitation coupled with ozonation was the most favorable alternative from an ecotoxicological perspective, whereas electrocoagulation, despite its high efficiency in the removal of chromium and suspended solids, did not produce a significant improvement in toxicity. The residual toxicity of the effluent does not depend exclusively on chromium, but rather on a combination of matrix components, particularly those associated with the remaining organic and sulfur-containing load.

None of the technologies applied individually was able to simultaneously optimize physicochemical contaminant removal and effluent toxicity reduction. Further investigation should experimentally validate the sequential configurations of hybrid treatment systems proposed in the present study.

Chlorides represented a persistent limitation, as none of the technologies evaluated achieved their effective removal. Therefore, a comprehensive treatment scheme would require the incorporation of a specific stage for salt control. The findings confirm the need to complement conventional physicochemical parameters with toxicity bioassays in the evaluation of treated tannery effluents, in order to establish more comprehensively the actual efficiency and environmental safety of the applied technologies.

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