Electrocoagulation for the Pre-Treatment of Table Olive Processing Wastewater: Evaluation of Operational Parameters and Performance

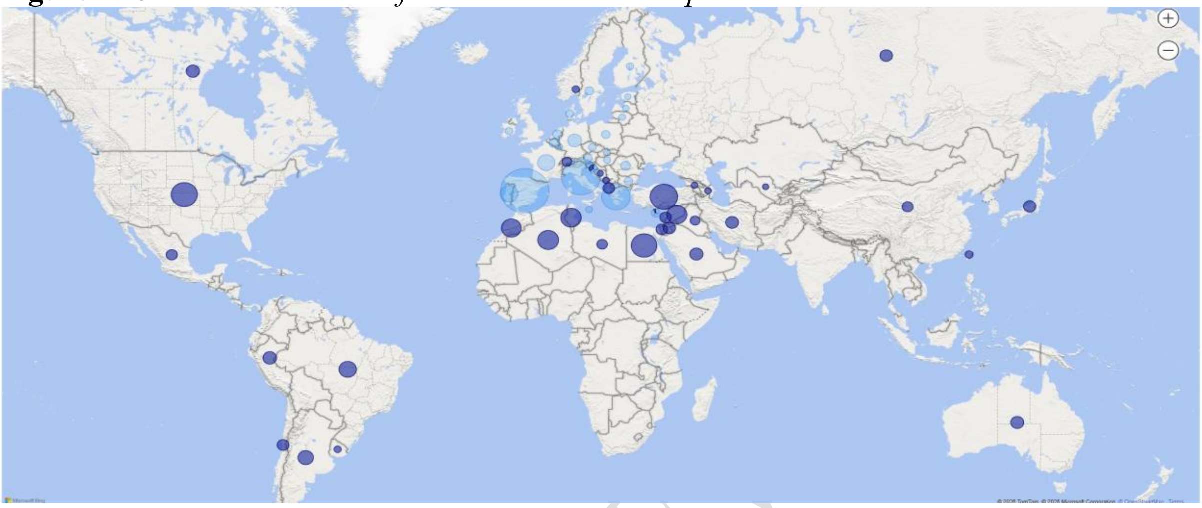
Table olive processing wastewater (TOPW) is a heavily polluted industrial effluent characterized by high salinity, dark color, high organic loads, and phenolic compounds. Because these characteristics can severely inhibit biological treatment, an effective pre-treatment strategy is essential prior to conventional secondary biological treatment. Electrocoagulation (EC), which integrates coagulation, adsorption, and precipitation within a single reactor, without the addition of chemical coagulants, has been extensively recommended as an effective pre-treatment method-particularly for complex, toxic, or high-salinity industrial streams like TOPW. The present study evaluated the application of EC as a pre-treatment alternative for TOPW from a naturally fermented black olive facility in the Akhisar, Türkiye. The raw effluent exhibited a pH of 5.95, a chemical oxygen demand (COD) of 3,160 mg/L, a conductivity of 14760 μS/cm, and a color of 978 Pt-Co units. Batch experiments were conducted in a stainless-steel-electrode-based EC unit, arranged in monopolar parallel configuration with an inter-electrode spacing of 2.5 cm. A Box-Behnken response surface design was employed to assess the impacts of initial pH (3-11), applied voltage (0-5 V), and reaction time (5-60 min), on COD and color removal efficiencies. Under the optimized conditions (pH 11, 5 V, 35 min), the degree of color removal attained 80% (R^2 = 0.9949) and the COD removal reached 34% (R^2 = 0.9244). The high color removal observed under alkaline conditions is attributed to the co-precipitation of colloidal phenolic compounds with aluminum hydroxide flocs. In contrast, the moderate COD reduction indicated that a significant fraction of the dissolved organic matters remained in solution. The results indicate that EC has potential as a pre-treatment stage prior to the subsequent secondary biological treatment of TOPW.

Keywords: *Electrocoagulation; table olive processing wastewater; Box-Behnken design; response surface methodology; COD removal; color removal*

Introduction

Olive cultivation is of great significance in Mediterranean agriculture. Table olives and olive oil represent the primary commercial products derived from olive processing, both of which have experienced a notable increase in global production and consumption in recent years. Based on the International Olive Council (IOC) reports (https://www.internationaloliveoil.org), the size of the global table olives market reached US$ 4.2 billion in 2023 and is expected to reach US$ 5.7 billion by 2032, corresponding to a growth rate of 3.3% during 2024–2032. The global expansion of commercial olive cultivation, which has already exceeded the traditional Mediterranean basin countries is also supported this increased demand. As illustrated in Figure 1, the recent distribution of olive production centers encompasses non-traditional regions exhibiting a Mediterranean microclimate, including Mexico, Peru, Chile, Argentina, and Australia.

Figure 1. *Global distribution of olive cultivation and production centers*



(https://www.internationaloliveoil.org/what-we-do/statistics/)

Olive cultivation is of strategic importance to the development of Türkiye’s agro-industrial sector. The country's favorable geographical location and temperate climate have made Türkiye a significant producer of table olives and olive oil (Ozturk et. al., 2021). The production capacity of Türkiye is comparable to that of other major Mediterranean producers, including Spain, Italy, Greece, Egypt, and Tunisia. In 2024, olive production reached 3,750,000 tons, of which 1,166,000 tons (31%) were table olives (TÜİK, 2025). In 2025, a 35% decrease in total production was observed compared to the previous record year (2,450,000 tons/year). This decline can be attributed to the " off- year" phenomenon in olive trees, together with climatic conditions, particularly drought. However, with changes in dietary habits (Owen et. al, 2000) and increasing demand for healthy food products, olive production is expected to continue increasing in the coming years.

The fruit of the olive tree is a nutrient-rich product, containing oil, amino acids, essential fatty acids, minerals, and phenolic compounds (Huertas-Alonso et al. 2022; Ozturk et. al., 2021). During table olive and olive oil production, these components can leach into the process water, generating a wastewater with high pollution loads in terms of organic compounds, lipids and phenolic substances (Said et al. 2021). Literature indicates that effluents from de-bittering (lye treatment) and brining are characterized by high organic strength and intense color, resulting in low biodegradability and severe operational disruptions in biological systems (Carbonell-Alcaina et. al. 2025; Sanchez-Arevalo et al., 2021; Rincón-Llorente et al. 2018). Thus, effective pre-treatment methods are necessary prior to biological treatment to mitigate phenolic toxicity, reduce the chemical oxygen demand (COD), and remove color. Different treatment approaches have been investigated for the removal of pollutants from wastewater, including physicochemical, biological, and advanced treatment processes (Schattschneider et al., 2024). Process optimization is also essential for achieving effective wastewater treatment while minimizing operational requirements (Balku et al., 2016).

Accordingly, this study evaluates the electrocoagulation process, focusing on the effects of operational parameters, including initial pH, applied voltage, and reaction time, on pollutant removal efficiency. A Box-Behnken response surface design (BBD-RSM) method was used for the experimental design. In this framework, the impacts of initial pH (3-11), applied voltage (0-5 V), and reaction time (5-60 min) on COD and color removal efficiencies were evaluated.

Wastewater Generation & Characterization

The sources of wastewater in table olive processing depend directly on the processing style used (Spanish-style green olives, California-style black olives, Greek-style, etc.). The main characteristics of the wastewater generated by these methods are summarized in Table 1 (Dolgen and Alpaslan, 2020; Huertas-Alonso et. al. 2022; Dolgen and Alpaslan, 2023).

In Spanish-style green olive production, effluent is generated during debittering (tank discharge and washing) and the final discharge of fermentation tanks. Spanish-style green olive processing generates high wastewater volumes, typically ranging from 3.5 to 4.0 L/kg and reaching up to 10-12 L/kg overall. The process generates distinct wastewater streams, including alkaline wastewater from caustic soda debittering and washing, and acidic streams associated with lactic acid fermentation (Rincón-Llorente et. al., 2018). This effluent is heavily polluted, exhibiting high salinity (NaCl), elevated electrical conductivity (EC), extremely high organic loads reaching up to 35,000 mg COD/L, and elevated phenolic concentrations, particularly in the washing fractions due to ongoing phenol hydrolysis (Parinos et. al. 2007).

Table 1. *Wastewater Generation and Characteristics in Table Olive Processing*

Table Olive Production Method	Main Wastewater-Generating Processes	Relative Volume	Main characteristics
Spanish-style green olives	Debittering; Washing; Brine Fermentation	High (3.5–12 L/kg)	High pH (alkalinity); very high salinity/conductivity (NaCl); very high organic load (up to 35,000 mg COD/L); and highest phenolic load
California-style black olives	Debittering; Washing; Discharge of iron gluconate baths	Moderate (~6 L/kg)	High pH (alkalinity); high TDS (includes iron salts); high organic and phenolic loads
Natural fermentation	Fermentation and brining	Low (0.5–1 L/kg)	No alkaline waste; high electrical conductivity (NaCl); high organic and phenolic loads

California-style black olive processing produces wastewater from alkaline debittering and rinsing. Additional wastewater is generated from the discharge of the iron gluconate baths used to stabilize dark coloration. California-style black olive processing yields a moderate output of approximately 6.0 L/kg (Huertas-Alonso et. al., 2022), is characterized by high alkalinity, significant organic and phenolic loads, and high inorganic loads, including elevated total dissolved solids (TDS) and iron residues from color-stabilizing iron gluconate baths.

In contrast, wastewater from naturally fermented olives, including both black and green olives, originates primarily from the fermentation phase and brining stages. Greek-style natural fermentation generates the lowest volume of wastewater (0.5-1.0 L/kg) and and does not generate alkaline effluent due to the absence of lye treatment. However, the brining process still produces wastewater with high electrical conductivity, substantial dissolved organic matter, and significant phenolic concentrations (García-García et al., 2011; Ayed et al., 2017).

Treatment Methods for TOPW

General Overview

The literature proposes various methods for treating wastewater, which can be applied individually or in combination. These include chemical (coagulation–flocculation, electrocoagulation, advanced oxidation), biological (aerobic and anaerobic), and physical (membrane processes and evaporation) techniques (Anagnostopoulos and Tsaltas 2022;). However, selecting an effective treatment scheme for table olive processing effluent is particularly challenging due to its high salt content and elevated phenolic concentrations, both of which severely inhibit direct biological treatment.

Membrane filtration is recently gaining increasing importance in the food industry for wastewater treatment and the recovery of valuable compounds (e.g., yeast and phenolic compounds) (Azadi et. al. 2021; Papadaki and Mantzouridou 2016; Lozada et. al., 2022). Specifically, within the olive industry, membrane filters have significant potential for both wastewater treatment and the concentration of polyphenolic compounds (Cifuentes-Cabezas et al. 2023; Blandin et al. 2020). García-Ivars et al. (2015) reported that modified ultrafiltration (UF) membranes can serve as a primary step for phenolic compound recovery. In particular, implementing two or more UF units operating in series followed by nanofiltration (NF) can achieve high removal efficiencies (Cifuentes-Cabezas et. al., 2022; Cifuentes-Cabezas et. al. 2021; Alcaina et. al., 2025). Sequential systems consisting of ultrafiltration followed by nanofiltration/reverse osmosis (RO) units have been proposed by Tatoulis et al. (2017). In Turkiye, within the scope of the project titled "Research on the Integrated Management of Wastes from Table Olive and Olive Oil Facilities" conducted by the Ministry of Forestry and Water Affairs in the Susurluk Basin, the treatment of brine wastewater was planned using a hybrid process incorporating physical and chemical pre-treatment followed by membrane technology (reverse osmosis) (Dölgen and Alpaslan. 2020).

Evaporation is a thermal separation process based on the concentration of impurities by vaporizing water through heat energy. The evaporation process can occur naturally through solar radiation in evaporation ponds/lagoons or through engineered evaporators (Rincón-Llorente et. al., 2018; Cappelletti et. al., 2011). In natural evaporation, wastewater is retained for extended periods in shallow ponds (25–50 cm deep), where water evaporates under solar radiation. However, natural evaporation presents several drawbacks, including high land requirements, odor emissions, and sensitivity to meteorological conditions (Polonio et al., 2016). In the context of circular economy strategies, solar evaporators may offer a promising solution (Nadal-Bach et al., 2021; Mastoras et. al., 2022). Recently, several experimental studies have investigated solar stills coupled to a Parabolic Trough Collector (PTC) as an additional heat source. However, performances of natural evaporation systems remain relatively low and many of the proposed technologies for improving their performance are still at the demonstration or prototyping stage.

Biological treatment represents as a viable option for table olive processing wastewater (TOPW). Numerous studies in the literature have evaluated both aerobic and anaerobic biological treatment alternatives (Beltran-Heredia et al., 2000; El Moussaoui, T., 2022; Ayed et al. 2017). Depending on operational conditions, aerobic biological processes can achieve chemical oxygen demand (COD) removal efficiencies between 75% and 85% (Garcia et al., 2011). However, higher removal efficiencies are impeded by the presence of polyphenolic compounds, resulting in a dark-colored effluent with residual non-biodegradable COD. Furthermore, as the concentration of complex organic compounds increases, COD removal efficiency drops further. Anaerobic treatment serves as another alternative for TOPW remediation. In cases where neither aerobic nor anaerobic processes alone are sufficiently effective, many researchers propose sequential anaerobic-aerobic treatment schemes (Katsou et al., 2004; Beltran-Heredia et al., 2008). Co-digestion with other substrates with different characteristics would allow to compensate toxicity and nutrient imbalance and to improve synergetic effects between the microorganisms (Rincón-Llorente et. al., 2018). Aerobic treatment alone provides up to 76% COD removal at high hydraulic retention times (HRT), while combined anaerobic-aerobic treatment provides 83.5% COD and 28% total phenol removal while producing significantly less sludge (Ayed et al., 2017).

Chemical treatment processes can be implemented independently or positioned before or after biological treatment to enhance overall removal efficiency (Fleyfel et. al. 2024; Vuppala, et al. 2019). Major chemical treatment methods include conventional coagulation–flocculation, electrocoagulation, advanced oxidation processes (AOPs), such as ozonation, UV radiation, photocatalysis, Fenton reactions, and wet air oxidation), as well as adsorption (Çokay et al., 2024; Shokri and Nasernejad, 2023; Aziz, et al. 2024; Agabo-García et. al. 2023; Fiorentino et al, 2021). Coagulation-flocculation is commonly employed because of its cost-effectiveness. Fleyfel et al. (2024) reported that the application of alum at 800 mg/L resulted in removal efficiencies of 62.89%, 57.16%, and 16.76% for phenols, COD, and total organic carbon (TOC), respectively. In addition to conventional chemical processes, advanced oxidation processes are presented as adequate methods for treating TOPW due to their ability to reduce the organic matter. The prevailing AOP systems employed include ozonation, UV irradiation, photocatalysis, hydrogen peroxide oxidation, Fenton's reaction, electrochemical oxidation and wet air oxidation (Fleyfel et. al. 2024).

While chemical pre-treatment prior to biological processing can mitigate inhibitory effects, it generates substantial volumes of secondary sludge (García et. al. 2011; Salameh et. al., 2015). In this context, electrocoagulation (EC) emerges as a highly promising pre-treatment alternative. It requires no chemical additives and produces significantly less sludge than conventional chemical coagulation while overcoming phenol and salt inhibition. García-García et al. (2011) evaluated electro-coagulation technology as a pretreatment for green table olive processing wastewater. They found that using an aluminum anode and an iron cathode reduced pollution levels faster than other electrode setups. Under optimal conditions-20 to 25 °C, a current density of 25 mA/cm², and a reaction time of 50-min-the process removed 40% of the COD, 78-87% of phenols, and the wastewater color, while adjusting the pH to a range of 6.5 to 7.0.

Electrocoagulation: Mechanism and Operating Parameters

Electrocoagulation (EC) is an electrochemical process in which an applied electrical current drives the anodic dissolution of a metal electrode, releasing coagulating cations directly into the solution. For an aluminum anode, the dissolution reaction can be written as:

$$2Al + 6H_2O + 2OH^- \rightarrow 2Al(OH)_4^- + 3H_2$$

At the cathode, water is reduced and hydrogen gas is produced. The metal hydroxide species formed from the dissolved aluminum remove contaminants through coagulation, adsorption, and precipitation, with the resulting flocs settling out of the water.

EC performance is strongly influenced by operational parameters such as pH, current density (or applied voltage), reaction time, electrode material, and electrode configuration. Among these, pH is critical because it dictates the solubility of the metal hydroxides formed during the process: at strongly acidic or strongly basic pH, hydroxide solubility increases and floc formation declines, thereby reducing system efficiency (Vardar, 2006). Additionally, electrode configuration (monopolar parallel, monopolar series, or bipolar) directly affects current distribution and coagulant generation efficiency.

EC has been applied to a wide range of industrial wastewaters. Eyvaz et al. (2006) investigated COD and turbidity removal from textile effluent using aluminum and iron electrodes in monopolar parallel, monopolar series, and bipolar configurations. Acidic conditions yielded higher COD removal for both electrode materials; aluminum favored an acidic pH for turbidity removal while iron proved more effective under neutral pH conditions. Furthermore, their economic analysis demonstrated that EC was faster and more cost-effective than conventional chemical coagulation.

Arslan et al. (2008) treated a complex effluent containing heavy-metal (nickel and zinc from a plating bath, TOC 173-207 mg/L, Ni 275-291 mg/L, Zn 226-236 mg/L) using stainless steel electrodes arranged with a 2 mm inter-electrode space. Both nickel and zinc concentrations were reduced to below detection limits by using the wastewater's own chloride content as electrolyte, and TOC removal reached 50% at the optimum current density of 22.5 mA/cm^2 and pH 6. Similarly, Akyol (2011) treated paint manufacturing wastewater using iron and aluminum electrodes across a pH range of pH 2-10 and current densities of 5-80 A/m^2. At optimum conditions (35 A/m^2, 15 min, pH 6.95), COD removal reached 93-94% and TOC removal reached 88-89% for both electrode types. However, aluminum electrodes resulted in a lower calculated operating cost (0.129 €/m^3 versus 0.187 €/m^3 for iron).

Regarding olive-related effluents, Salameh et al. (2015) evaluated EC for olive mill wastewater in Jordan using a reactor with three aluminum and three iron electrodes (0.10 × 0.15 × 0.25 m, 200 rpm stirring, 2 cm plate spacing). The feed was characterized by COD of 67.1 g/L, TSS of 31.3 g/L, and a pH of 4.56. At an optimum current density of 45 mA/cm^2, TSS and COD removals was reached 82.5% and 47.5%, respectively; aluminum exhibited higher efficacy for TSS whereas iron was better for COD reduction. Despite these advances, the application of EC specifically to table olive processing wastewater remains much less studied. García-García et al. (2011) applied EC to wastewater from the green table olive packaging industry while Deligiorgis et al. (2007) used electrochemical oxidation with boron-doped diamond electrodes on a similar effluent stream. The present study addresses this research gap by evaluating stainless-steel-electrode-based EC for the treatment of naturally fermented black olive processing effluent.

Material & Methods

Wastewater Source

Wastewater samples were collected from a table olive processing facility located in the Akhisar district (Aegean region, Türkiye). The facility produces naturally fermented black olives. At this facility, all process streams are combined and directed to an equalization tank prior to on-site treatment plant which consists of screen, equalization tank, biological treatment, chemical treatment, and pressurized sand filter units). Samples for the present study were obtained directly from the equalization tank. Upon arrival at the laboratory, the pH, conductivity, and color were measured immediately; the remaining parameters were preserved via acidification and refrigerated until analysis. Table 2 provides a summary of the wastewater characterization and the standard methods used in the analyses (APHA, 1992)

Table 2. *Characterization of table olive processing wastewater*

Parameter	Unit	Value	Analytical Method
pH	-	5.95	Electrometric (SM 4500-H^+ B)
COD	mg/L	3160	Open Reflux Titrimetric (SM 5220 B)
TOC	mg/L	577	High-Temp. Combustion (SM 5310 B)
TSS	mg/L	1528	Gravimetric (SM 2540 D)
TDS	mg/L	11512	Gravimetric (SM 2540 C)
Oil & Grease	mg/L	4614	Gravimetric-Soxhlet (SM 5520 B)
Chloride (Cl^-)	mg/L	4648.5	Argentometric (SM 4500-Cl^- B)
Phosphate (PO_4)	mg/L	32.67	Spectrometric (SM 4500-P D)
Phenol	mg/L	6.5	Chloroform Extraction-Spectrometric (SM 5530 D)
Kjeldahl-N	mg/L	47.6	Macro Kjeldahl (SM 4500 N_{o0r}^{G} B)
Conductivity	µS/cm	14760	Electrode Method (SM 2510 B)
Color	Pt-Co	978.21	Spectrometric (SM 2120 C)

Experimental Setup

EC experiments were conducted in a Plexiglas batch reactor (200 × 200 × 150 mm total volume of approximately 6L. The reactor was equipped with a sampling port and a cooling water circuit to limit temperature rise during extended operational runs. Three stainless steel (SS) anodes and three SS cathodes were arranged in monopolar parallel configuration with a 2.5 cm gap between electrodes, where the anodes and cathodes connected to the positive and negative terminals of a DC power supply, respectively. For each experimental run, 5.25 L of wastewater feed into the reactor, and initial pH adjusted using H_2SO_4 (acidic targets) or a NaOH stock solution (alkaline targets). All experiments carried out at ambient room temperature. After completing the designated reaction time, the treated effluent was transferred to an Imhoff cone and allowed to settle for 60 minutes, after which the supernatant was collected for analysis.

Box-Behnken Design

The experimental design used Box-Behnken response surface methodology (BBD-RSM), a second-order design that avoids extreme multi-factor combinations and requires fewer runs than a full factorial design while still allowing estimation of interaction and quadratic terms. Three independent variables were used. The variables are as follows: A = applied voltage (0-5 V), B = initial pH (3-11), and C = reaction time (5-60 min). The design produced 17 experimental runs, including five center-point replicates. Table 3 presents the design matrix and the measured COD and color removal for each run.

Table 3. *BBD experimental design matrix with measured response values*

Run	A: Voltage (V)	B: pH	C: Time (min)	COD Removal (%)	Color Removal (%)
1	2.5	7	32.5	26.32	65.00
2	2.5	3	60	22.60	61.79
3	2.5	11	60	28.95	77.12
4	5	7	60	21.05	70.00
5	2.5	7	32.5	25.37	64.00
6	2.5	3	5	19.06	50.14
7	5	7	5	28.95	67.72
8	2.5	7	32.5	25.37	65.00
9	0	7	60	13.16	67.84
10	0	3	32.5	22.37	47.61
11	2.5	7	32.5	26.32	62.00
12	5	11	32.5	30.26	79.54
13	2.5	7	32.5	26.37	65.00
14	0	7	5	7.89	60.00
15	2.5	11	5	32.89	67.44
16	5	3	32.5	47.37	83.92
17	0	11	32.5	34.21	64.44

Analytical Methods

The COD was measured by the open reflux titrimetric method (SM 5220 B), color (Pt-Co) spectrometrically (SM 2120 C), and pH electrometrically (SM 4500-H^+ B). The remaining parameters used for wastewater characterization including TOC, TSS, TDS, oil and grease, chloride, phosphate, phenol, Kjeldahl nitrogen, conductivity were measured in accordance with standard methods listed in Table 2.

Results and Discussion

Effect of Initial pH

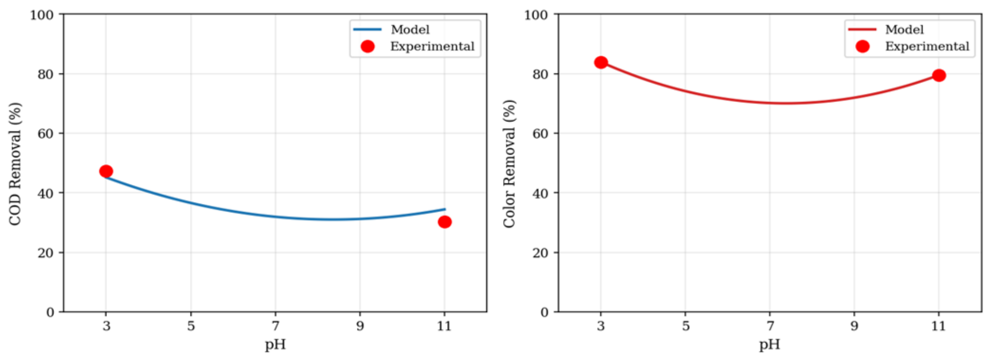
The effect of pH was examined with voltage fixed at 5 V and the reaction time at 32.5 min. The experimental data and Response Surface Methodology (RSM) model curves depicted in Figure 2 demonstrate that the initial wastewater pH plays an important role in determining both COD and color removal efficiencies during electrocoagulation (EC) at fixed operating conditions (V = 5 V; t = 32.5 min).

The results indicate a clear non-linear dependence of both COD and color removal on pH over the investigated range (pH 3-11). Higher removal efficiencies were observed under strongly acidic and strongly alkaline conditions in comparison to neutral pH conditions. The highest overall removal for both parameters was achieved under acidic conditions (47.37% COD removal and 83.92% color removal).

This behavior can be attributed to the presence of soluble iron and aluminum species that undergo hydrolysis at low pH, resulting in the formation of positively charged complexes. These complexes have been observed to promote the charge neutralization of negatively charged organic compounds and phenolic pollutants, thereby enhancing flocculation and precipitation processes. At pH 11, performance reached 30.26% COD removal and 79.54% color removal. Under strongly alkaline conditions, insoluble hydroxide precipitates predominate, driving removal via sweep coagulation and enmeshment. This behavior can be attributed to the predominance of insoluble hydroxide precipitates under strongly alkaline conditions, which enhances pollutant removal through sweep coagulation and charge enmeshment.

Overall, the findings indicate that operating under acidic conditions (pH 3) is optimal for maximizing simultaneous COD and color reduction, while alkaline conditions (pH 11) serve as an effective alternative when color removal is the primary treatment objective.

Figure 2. *Effect of initial pH on COD and color removal (voltage = 5 V, reaction time = 32.5 min)*

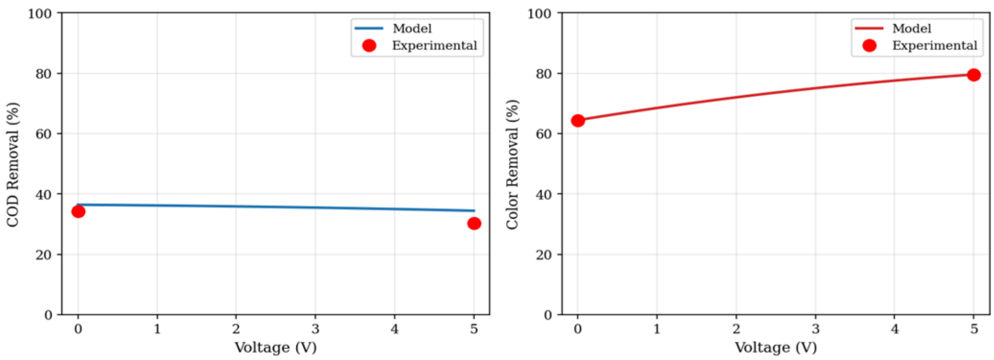


Effect of Applied Voltage

The influence of applied voltage (0-5V) on treatment efficiency was evaluated at alkaline condition (pH 11) and reaction time at 32.5 min. As illustrated in Figure 3, applied voltage had distinctly different impacts on color and COD removals (pH 11, 32.5 min; COD 34.21%, color 64.44%) and run 12 (5 V, pH 11, 32.5 min; COD 30.26%, color 79.54%). The efficiency of color removal increased steadily with applied voltage, rising from 64.44% at 0 V to a maximum of 79.54% at 5 V, with optimal results obtained at 5 V. This enhancement is attributed to the accelerated anodic dissolution rate of the metal electrodes at higher voltage, and improved microflotation resulting from increased electrolytic gas bubble generation.

As shown in Figure 3, color removal efficiency increased steadily with applied voltage, rising from 64.44% at 0 V to a maximum of 79.54% at 5 V. This enhancement is attributed to the accelerated anodic dissolution rate of the metal electrodes at higher voltage, alongside promoted electroflotation caused by heightened gas bubble generation. However, COD removal did not exhibit the same pattern at pH 11, given that COD removal was not high under alkaline conditions to begin with; at neutral pH, by contrast, COD removal did increase with current. However, in contrast to color removal, Figure 3 demonstrates that voltage has an insignificant (or slightly negative) effect on COD removal under these specific conditions (pH 11, 32.5 min). This behavior is attributed to the suppression of sweep flocculation under highly alkaline conditions, caused by the predominant formation of soluble metal hydroxo-complexes.

Figure 3. *Effect of applied voltage on COD and color removal (pH = 11, reaction time = 32.5 min)*



Effect of Reaction Time

The variation of reaction time, ranging from 5 to 60 minutes was examined at a constant applied voltage at 5 V and pH at 11. Figure 4 shows the model curves and the experimental point (32.5 min; COD 30.26%, color 79.54%).

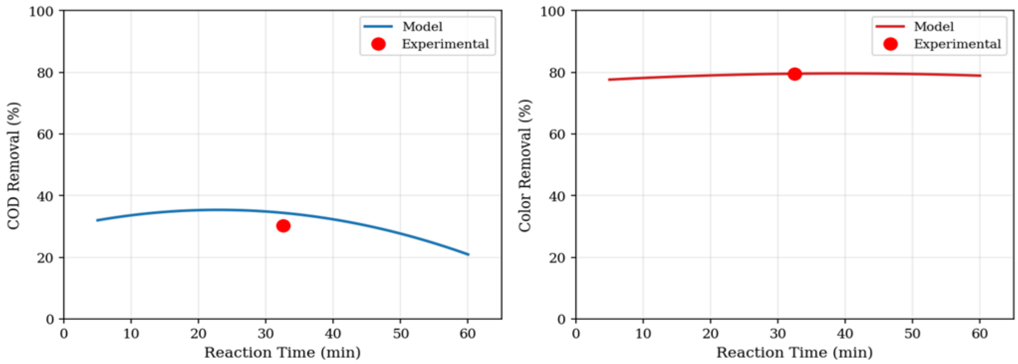
As illustrated in Figure 4, COD removal exhibited a parabolic trend: efficiency increased initially, peaked at approximately 35.30 min, and then declined substantially to nearly 20% by the end of the 60-minute process. For

32.5 min, the experimental COD removal was 30.26%, closely tracking the predicted peak.

Extending the reaction times beyond the optimum did not improve COD removal as expected: by 60-minute reaction time, COD removal efficiency had actually decreased. In high strength organic wastewater, prolonged reaction time can promote the re-solubilization of particulate matter, which likely accounts for this observed drop in removal efficiency. This subsequent drop in COD removal at extended treatment times is attributed to the dissolution or re-solubilization of suspended organic particulate matter back into the aqueous phase under prolonged exposure to alkaline conditions and agitation.

In contrast, Figure 4 demonstrates that color removal was largely insensitive to reaction time within the tested range, maintaining a nearly flat profile around 78-80%. Overall, the model response curves identify an optimal reaction time of approximately 35.30 min, beyond which further electrolysis offers no enhancement in color removal while actively diminishing COD removal efficiency. The high electrical conductivity of the wastewater likely facilitated rapid initial reaction kinetics, enabling this relatively short optimal operational time.

Figure 4. *Effect of reaction time on COD and color removal (voltage = 5 V, pH = 11)*



RSM Model Statistics and ANOVA

The response surface models for COD and color were fitted to the 17-run BBD data using Design Expert software. The ANOVA results are summarized in Table 4.

Table 4. *ANOVA summary for COD and color response models*

Source	Response	df	F-Value	p-Value	Status
Model	COD	9	9.52	0.0036	Significant
A - Voltage	COD	1	24.17	0.0017	-
AB	COD	1	16.20	0.0050	-
B^2	COD	1	20.11	0.0029	-

C^2	COD	1	20.49	0.0027	-
$R^2 = 0.9244$					
Model	Color	12	64.41	0.0005	Significant
A - Voltage	Color	1	14.36	0.0193	-
B - pH	Color	1	156.58	0.0002	-
C - Time	Color	1	66.91	0.0012	-
AB	Color	1	66.16	0.0012	-
$R^2 = 0.9949$					

The color model has an F-value of 64.41 ($p = 0.0005$) and R^2 value of 0.9949, indicating a strong and statistically significant fit. The COD model yielded an overall F-value of 9.52 ($p = 0.0036$) and R^2 value of 0.9244, which is also statistically significant. However, its Lack of Fit F-value is 106.13 ($p = 0.0003$), which is itself significant.

However, the COD model exhibited a significant lack of fit ($F = 106.13$, $p = 0.0003$), indicating that the model does not fully capture all the variability in COD removal across the experimental domain. Therefore, predictions from the COD model should be interpreted with caution.

For the COD model, the statistically significant terms ($p < 0.05$) were A (voltage), the AB interaction, and the quadratic terms B^2 and C^2. For the color model, the significant terms included A, B, C, the AB interaction, and the higher-order terms A^2B, A^2C, and AB^2. Furthermore, the higher F-value for B (pH) in the color model ($F = 156.58$) identifies initial pH as the strongest influential parameter for color removal.

The fitted model equations in coded variables are:

$$COD\ (\%) = 25.95 + 6.25A + 1.86B - 0.38C - 7.24AB - 3.29AC - 1.87BC - 0.26A^2 + 7.86B^2 - 7.93C^2 \quad (R^2 = 0.9244)$$

$$Color\ (\%) = 64.20 + 2.47A + 8.16B + 5.33C - 5.30AB - 1.39AC - 0.49BC + 3.47A^2 + 1.21B^2 - 1.28C^2 \quad (R^2 = 0.9949)$$

where A, B, and C represent the coded values of applied voltage, initial pH, and reaction time, respectively, based on the factor ranges used in the experimental design. The positive coefficient and high F-value of B (pH) in the color equation confirm pH as the strongest individual factor for color removal.

Optimum Conditions and Response Surfaces

Numerical optimization by RSM identified the optimum operating conditions as pH 11, 5 V, and a reaction time of 35.30 min. In these conditions, the model predicted COD removal of 33.8% and color removal of 79.6%, rounded to 34% and 80%. Based on the model equations, the three-dimensional response surfaces plots for color and COD removal as functions of voltage and pH at the optimum reaction time of 35 min, are illustrated in Figures 5 and 6.

Figure 5. *Three-dimensional response surface for color removal (reaction time = 35 min)*

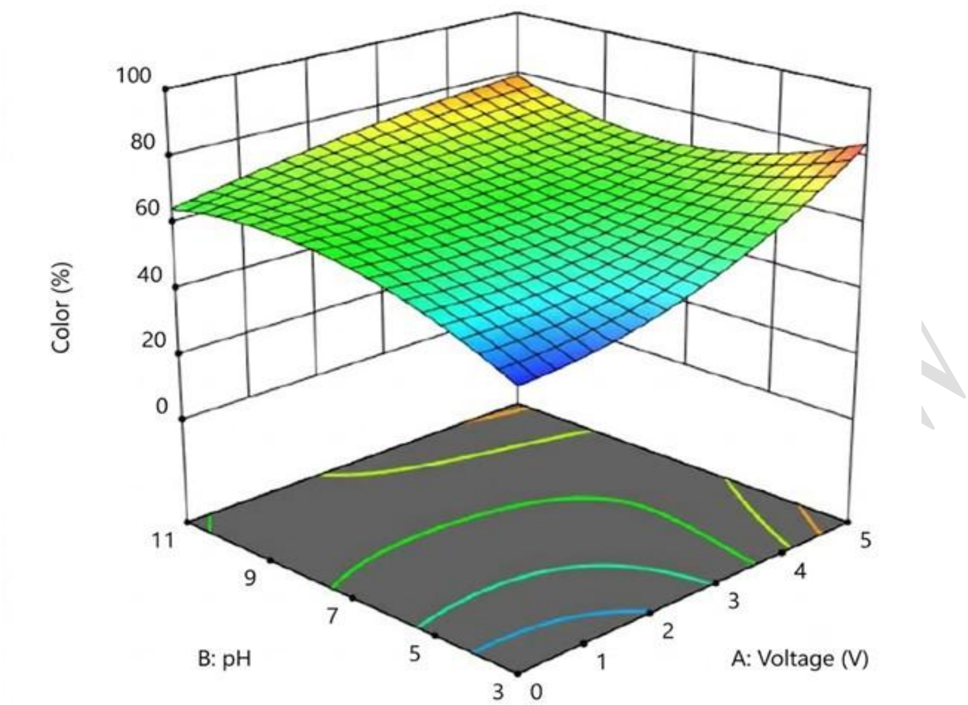
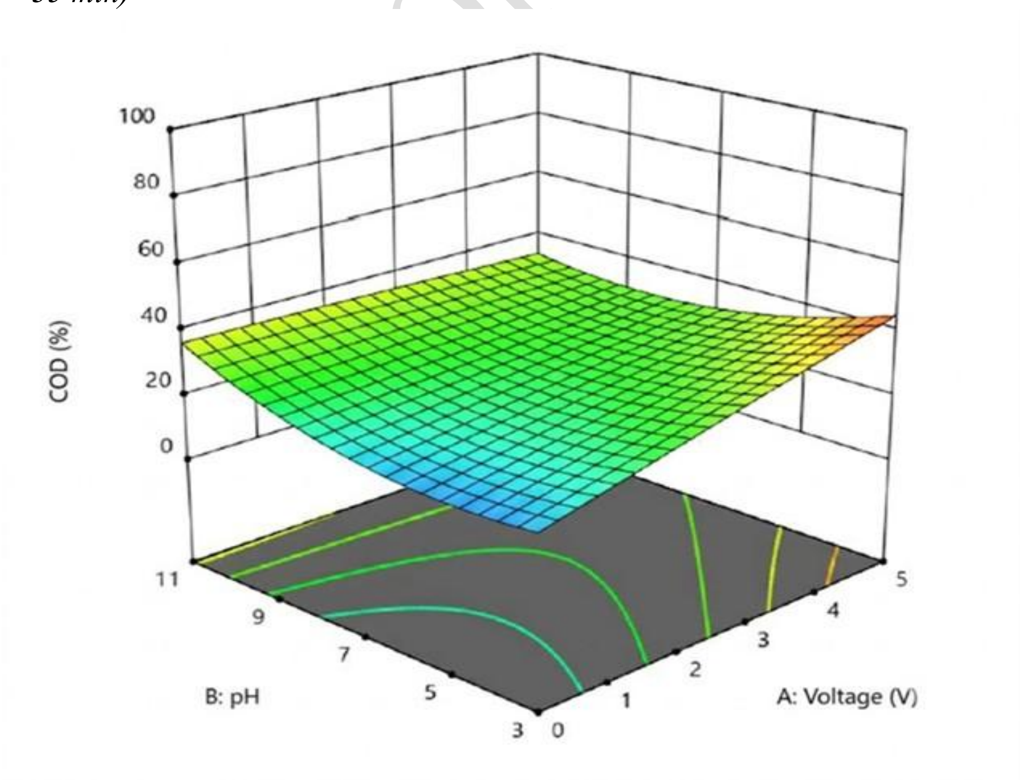


Figure 6. *Three-dimensional response surface for COD removal (reaction time = 35 min)*



The 3D response surface for color removal (Figure 5) demonstrates elevated removal efficiencies in the high-pH, high-voltage region, aligning with the dominant influence of initial pH (B) identified in the ANOVA. In contrast, the COD surface (Figure 6) exhibits more complex topology: the highest predicted COD removal occurs at low pH combined with high voltage, matching run 16 (COD 47.37% at pH 3, 5 V). However, at low voltage, the model instead predicts higher COD removal at high pH. This switch reflects the statistically significant AB (voltage × pH) interaction term in the COD model ($F = 16.20$, $p = 0.0050$).

Even though higher COD removal was achieved at low pH under high-voltage conditions, the numerical optimization selected pH 11 as the overall process optimum due to its superior color removal performance.

The notable discrepancy between color removal (80%) and COD removal (34%) at the optimum conditions reflects that the phenolic compounds responsible for the dark coloration exist partly in colloidal or complexed forms that are readily removed via electrocoagulation. Conversely, a substantial fraction of the overall organic load remains in the soluble phase post-treatment. This behavior underscores the suitability of electrocoagulation as a targeted pre-treatment stage-primarily serving to eliminate color and attenuate phenolic toxicity prior to biological treatment-rather than as a standalone polishing process for high-strength olive processing wastewater.

Conclusions

This study investigated the application of electrocoagulation (EC) with SS electrodes as a pre-treatment method for table olive processing wastewater (TOPW). A Box-Behnken response surface methodology was employed to evaluate the effects of applied voltage, initial pH, and reaction time on COD and color removal.

Under the optimized conditions of pH 11, 5 V, and 35-min reaction time, the EC model achieved 80% color removal and 34% COD removal. The response surface model for color removal exhibited an excellent fit ($R^2 = 0.9949$), identifying initial pH as the dominant factor ($F = 156.58$, $p = 0.0002$), with secondary contributions from voltage and reaction time and their interactions.

The COD model was also statistically significant ($R^2 = 0.9244$), but, its significant lack of fit ($F = 106.13$, $p = 0.0003$) indicates that the second-order polynomial does not fully describe the COD behavior across the investigated design space. Applied voltage was the most influential individual factor for COD removal ($F = 24.17$, $p = 0.0017$). It is noteworthy that the highest COD removal in the whole design (47.37%) was obtained at pH 3, opposed to the overall optimum of pH 11.

The substantial difference between color removal (80%) and COD removal (34%) under the optimum conditions shows that EC predominantly removes the colloidal, color-causing fraction of TOPW rather than fully mineralizing the soluble organic compounds. Consequently, EC appears most effectively as an integrated pre-treatment step for TOPW, particularly for reducing color and potentially attenuating compounds that may inhibit subsequent to biological treatment, rather than as a standalone polishing process.

The relatively high conductivity of the raw wastewater may have supported effective electrochemical operation and contributed to the relatively short treatment time. Further studies should evaluate the performance of EC under continuous-flow conditions and assess its integration with subsequent biological treatment to determine the overall treatment efficiency and operational feasibility.

References

IOC - International Olive Council, Olive sector statistics – December 2025 and forecasts (https://www.internationaloliveoil.org/what-we-do/statistics/) (accessed 28 July 2026).

Ozturk, Munir & Altay, Volkan & Gönenç, Tuba & Turkyilmaz Unal, Bengu & Efe, Recep & Akçiçek, Eren & Bukhari, Andleeb. (2021). An Overview of Olive Cultivation in Turkey: Botanical Features, Eco-Physiology and Phytochemical Aspects. Agronomy. 11. 295. 10.3390/agronomy11020295.

TÜİK, Data Portal, Crop Production Statistics- 2025 https://veriportali.tuik.gov.tr/en/press/53939/metadata (accessed 28 July 2026)

Owen, R.W., Giacosa, A., Hull, W.E., Haubner, R., Würtele, G., Spiegelhalder, B., Bartsch, H., 2000. Olive-oil consumption and halth: The possible role of antioxidants. Lancet Oncol. 1, 107–112. http://dx.doi.org/10.1007/978-3-642-37404-3-4.

Huertas-Alonso, A. J., Gonzalez-Serrano, D. J., Hadidi, M., Salgado-Ramos, M., Orellana-Palacios, J. C., Sánchez-Verdú, M. P., Xia, Q., Simirgiotis, M. J., Barba, F. J., Dar, B. N., & Moreno, A. (2022). Table Olive Wastewater as a Potential Source of Biophenols for Valorization: A Mini Review. Fermentation, 8(5), 215. https://doi.org/10.3390/fermentation8050215.

K.A. Mohamad Said, A.F. Ismail, Z. Abdul Karim, M.S. Abdullah, A. Hafeez A review of technologies for the phenolic compounds recovery and phenol removal from wastewater Process Saf. Environ. Protect. (2021), 10.1016/j.psep.2021.05.015.

Rincón-Llorente, B.; de la Lama-Calvente, D.; Fernández-Rodríguez, M.J.; Borja-Padilla, R. Table Olive Wastewater: Problem, Treatments and Future Strategy. A Review. Front. Microbiol. 2018, 9, 1641–1664.

Sanchez-Arevalo, C.M., Jimeno-Jimenez, A., Carbonell-Alcaina, C., Vincent-Vela, M.C., ´Alvarez-Blanco, S., 2021. Effect of the operating conditions on a nanofiltration process to separate low-molecular-weight phenolic compounds from the sugars present in olive mill wastewaters. Process Saf. Environ. Prot. https://doi.org/ 10.1016/j.psep.2020.10.002.

Carlos Carbonell-Alcaina, Carmen M. Sánchez-Arévalo, Magdalena Cifuentes-Cabezas, Silvia Álvarez-Blanco, María Amparo Bes-Piá, José Antonio Mendoza-Roca, Recovery of phenolic compounds from residual table olive fermentation brines by nanofiltration at different operating conditions, Process Safety and Environmental Protection, Volume 193, 2025, Pages 918-928, ISSN 0957-5820, https://doi.org/10.1016/j.psep.2024.11.110.

Dolgen, D., Alpaslan, M.N. (2020). Characteristics of Wastewater Generated from Table Olive Production and Treatment Methods. Journal of Engineering Sciences and Design. 8(4):1312-23. doi:10.21923/jesd.774689 (In Turkish).

Dolgen, D., Alpaslan, M.N. (2023). Management of Table Olive Wastewater (TOWW) in Turkey, 18th International Conference on Environmental Science and Technology (CEST2023), 30 August-2 September 2023, Athens, Greece.

Balku, Buaisha & Ozalp-Yaman (2016). An Optimum Design for Activated Sludge Systems," Athens Journal of Technology & Engineering.

Schattschneider, C., Piontek, S., Jacobs, H., Böhme, A., Sirena, C., Foitzik, A. (2024), Proof of Principle of Wastewater Treatment using Plasma Discharge to Reduce the Amount of Methylparaben," Athens Journal of Sciences 11(1), 29–38.

Parinos, Constantine & Stalikas, C.D. & Giannopoulos, Th & Pilidis, Georgios. (2007). Chemical and physicochemical profile of wastewaters produced from the different stages of Spanish-style green olives processing. Journal of hazardous materials. 145. 339-43. 10.1016/j.jhazmat.2006.12.061.

Rincón-Llorente B, De la Lama-Calvente D, Fernández-Rodríguez MJ and Borja-Padilla R (2018) Table Olive Wastewater: Problem, Treatments and Future Strategy. A Review. Front. Microbiol. 9:1641. doi: 10.3389/fmicb.2018.01641.

Huertas-Alonso, A.J.; Gavahian, M.; González-serrano, D.J.; Hadidi, M.; Salgado-ramos, M.; Prado Sánchez-Verdú, M.; Simirgiotis, M.J.; Barba, F.J.; Franco, D.; Lorenzo, J.M.; et al. Valorization of Wastewater from Table Olives: NMR Identification of Antioxidant Phenolic Fraction and Microwave Single-Phase Reaction of Sugary Fraction. Antioxidants 2021, 10, 1652.

García-García, P., López-López, A., Moreno-Baquero, J.M., Garrido-Fernández, A., 2011. Treatment of wastewaters from the green table olive packaging industry using electro-coagulation. Chemical Engineering Journal, 170, 59-66.

Ayed, L., Asses, N., Chammem, N., Othman, N.B., Hamdi, M., 2017. Advanced oxidation process and biological treatments for table olive processing wastewaters: constraints and a novel approach to integrated recycling process. Bioresource Technology, 28, 125-138.

Anagnostopoulos DA and Tsaltas D (2022) Current Status, Recent Advances, and Main Challenges on Table Olive Fermentation: The Present Meets the Future. Front. Microbiol. 12:797295. doi: 10.3389/fmicb.2021.797295

Azadi, F., Karimi-Jashni, A., Zerafat, M.M., Saadat, S., 2021. Fabrication, optimization, and performance of a novel double-skinned Al2O3.TiO2 ceramic nanocomposite membrane for forward osmosis application. Environ. Technol. Innov. 22, 101423. http://dx.doi.org/10.1016/j.eti.2021.101423.

Papadaki E, Mantzouridou FT (2016) Current status and future challenges of table olive processing wastewater valorization. Biochem Eng J 112:103–113. https://doi.org/10.1016/j.bej.2016.04.008

Gabriela Soledad Live Lozada, Ana Isabel García López, Antonio Martínez-Férez, Javier M. Ochando-Pulido, On the modeling and optimization of two-phase olive-oil washing wastewater treatment and polyphenols recovery by ceramic tubular microfiltration membranes, Journal of Environmental Management, Volume 316, 2022, 115227, ISSN 0301-4797, https://doi.org/10.1016/j.jenvman.2022.115227.

Magdalena Cifuentes-Cabezas, Alessio Pavani, María Cinta Vincent-Vela, José Antonio Mendoza-Roca, Silvia Álvarez-Blanco, Concentration of phenolic compounds from olive washing wastewater by forward osmosis using table olive fermentation brine as draw solution, Environmental Technology & Innovation, Volume 30, 2023, 103054, ISSN 2352-1864, https://doi.org/10.1016/j.eti.2023.103054.

Blandin, G., Ferrari, F., Lesage, G., Le-Clech, P., Héran, M., Martinez-Lladó, X., 2020. Forward osmosis as concentration process: Review of opportunities and challenges. Membranes 10, 284. http://dx.doi.org/10.3390/membranes10100284.

Cifuentes-Cabezas, M., Vincent-Vela, M.C., Mendoza-Roca, J.A., Álvarez-Blanco, S., 2022. Use of ultrafiltration ceramic membranes as a first step treatment for olive oil washing wastewater. Food Bioprod. Process. 135, 60–73. http://dx.doi.org/10.1016/j.fbp.2022.07.002.

Cifuentes-Cabezas, M., Carbonell-Alcaina, C., Vincent-Vela, M.C., Mendoza-Roca, J.A., Álvarez-Blanco, S., 2021. Comparison of different ultrafiltration membranes as first step for the recovery of phenolic compounds from olive-oil washing wastewater. Process Saf. Environ. Prot. 149, 724–734. http://dx.doi.org/10.1016/j.psep.2021.03.035.

Carlos Carbonell-Alcaina, Carmen M. Sánchez-Arévalo, Magdalena Cifuentes-Cabezas, Silvia Álvarez-Blanco, María Amparo Bes-Piá, José Antonio Mendoza-Roca, Recovery of phenolic compounds from residual table olive fermentation brines by nanofiltration at different operating conditions, Process Safety and Environmental Protection, Volume 193, 2025, Pages 918-928, ISSN 0957-5820, https://doi.org/10.1016/j.psep.2024.11.110.

Tatoulis, T., Stefanakis, A., Frontistis, Z. Christos S. Akratos, Athanasia G. Tekerlekopoulou, Dionissios Mantzavinos & Dimitrios V. Vayenas. Treatment of table olive washing water using trickling filters, constructed wetlands and electrooxidation. Environ Sci Pollut Res 24, 1085–1092 (2017). https://doi.org/10.1007/s11356-016-7058-6.

E. Ferrer-Polonio, J.A. Mendoza-Roca, A. Iborra-Clar, J.L. Alonso-Molina, L. Pastor-Alcañiz, Biological treatment performance of hypersaline wastewaters with high phenols concentration from table olive packaging industry using sequencing batch reactors, Journal of Industrial and Engineering Chemistry, Volume 43, 2016, Pages 44-52, ISSN 1226-086X,

Cappelletti, Giulio & Nicoletti, Giuseppe & Russo, Carlo. (2011). Wastewater from Table Olive Industries. 10.5772/16112.

Petros Mastoras, Stergios Vakalis, Michail S. Fountoulakis, Georgia Gatidou, Panagiota Katsianou, Georgios Koulis, Nikolaos S. Thomaidis, Dias Haralambopoulos, Athanasios S. Stasinakis, Evaluation of the performance of a pilot-scale solar still for olive mill wastewater treatment, Journal of Cleaner Production, Volume 365, 2022, 132695, ISSN 0959-6526, https://doi.org/10.1016/j.jclepro.2022.132695.

J. Nadal-Bach, J.C. Bruno, J. Farnós, M. Rovira Solar stills and evaporators for the treatment of agro-industrial liquid wastes: a review. Renew. Sustain. Energy Rev., 151 (2021), pp. 257-289, 10.1016/j.psep.2021.05.015.

J. Beltran-Heredia, J. Torregrosa, J.R. Dominguez, J. Garcia, Aerobic biological treatment of black table olive washing wastewaters: effect of an ozonation stage, Process Biochem. 35 (2000) 1183–1190, https://doi.org/10.1016/S0032-9592(00)00160-6.

El Moussaoui, T., 2022. Studies on the activated sludge process crucial parameters controlling olive mill wastewater treatment. Sci. Total Environ. 838, 156455. http://dx.doi.org/10.1016/j.scitotenv.2022.156455.

Fleyfel L, Matta J, Sayegh N ...Olive mill wastewater treatment using coagulation/flocculation and filtration processes. Heliyon, 2024; 10.

S. Vuppala, I. Bavasso, M. Stoller, L. Di Palma, G. Vilardi. Olive mill wastewater integrated purification through pre-treatments using coagulants and biological methods: Experimental, modelling and scale-up. J. Clean. Prod., 236 (2019), Article 117622, 10.1016/j.jclepro.2019.117622.

Çokay, E., Eker,S., Taşkın,E. 2024. Treatment of table olive processing wastewater with US/UV processes, Heliyon, 10 (17), https://doi.org/10.1016/j.heliyon.2024.e37484.

Shokri, B. Nasernejad. 2023. Treatment of spent caustic wastewater by electro-Fenton process: kinetics and cost analysis. Process Saf. Environ. Protect., 172 (2023), pp. 836-845, 10.1016/j.psep.2023.02.077.

Aziz, K., Haydari, I., Kaya, S. et al. Phenolic compounds removal in table olive processing wastewater by column adsorption: conditions' optimization. Environ Sci Pollut Res 31, 38835–38845 (2024). https://doi.org/10.1007/s11356-023-26180-5

Cristina Agabo-García, Guillermo Repetto, Mha Albqmi, Gassan Hodaifa, Evaluation of the olive mill wastewater treatment based on advanced oxidation processes (AOPs), flocculation, and filtration, Journal of Environmental Chemical Engineering, Volume 11, Issue 3, 2023, 109789, ISSN 2213-3437, https://doi.org/10.1016/j.jece.2023.109789.

A. Fiorentino, P. Prete, L. Rizzo, R. Cucciniello, A. Proto. Fe3+-IDS as a new green catalyst for water treatment by photo-Fenton-like reactions at natural pH, J. Environ. Chem. Eng. 9 (6) (2021), 106802, https://doi.org/10.1016/j.jece.2021.106802

Salameh, W.K., Ahmad, H., Al-Shannag, M., 2015. Electrocoagulation processes and water treatment of olive mill wastewater by resources management. World Academy of Science, Engineering and Technology.

Eyvaz, M., Bayramoglu, M., Kobya, M., 2006. Tekstil endüstrisi atiksularinin elektrokoagüläsyon ile aritilmasi: Teknik ve ekonomik degerlendrme. itu-dergisi/e, su kirlenmesi kontrolu, 16(1-3), 55-65.

Abdurrahman Akyol, Treatment of paint manufacturing wastewater by electrocoagulation, Desalination, Volume 285, 2012, Pages 91-99, ISSN 0011-9164, https://doi.org/10.1016/j.desal.2011.09.039.

Deligiorgis, A., Xekoukoulotakis, N.P., Diamadopoulos, E., Mantzavinos, D., 2007. Electrochemical oxidation of table olive processing wastewater over boron-doped diamond electrodes: Treatment optimization by factorial design. Water Research, 42, 1229-1237.

APHA (American Public Health Association). Standard Methods for the Examination of Water and Wastewater (19th ed.), APHA, Washington, DC (1992)