ENHANCING POMACE OLIVE OIL WASTEWATER USING PEROXY-ELECTROCOAGULATION

Ramiro Martins[1], Thais Grabowski[2]

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Abstract

The extraction of olive pomace oil is a significant aspect of the Mediterranean edible oil industry; however, the wastewater generated contains pollutants that can harm the environment and public health. In this study, peroxi-electrocoagulation (PEC) with aluminum electrodes was used to treat wastewater and reduce pollutant concentrations. A Box-Behnken Design study was conducted to investigate the relationship between hydrogen peroxide dosage, electric current density, and initial pH in the PEC process, and the removal of chemical oxygen demand (COD) and total phenolic compounds (TPh). The study found that the PEC process could remove an average of 22% of COD and 82% of TPh, with the highest removal obtained with hydrogen peroxide dosages of 30 g L^{-1} and 20 mA cm^{-2}. However, pre-treatment with other processes is necessary to reduce harmful elements in the effluent before undergoing biological treatment.

Keywords: COD removal, industrial wastewater, peroxy-electrocoagulation, pomace olive oil, total phenolic compounds removal.

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1. INTRODUCTION

Olive pomace oil is an edible oil extracted from the residual pulp, pits, and skin of olives after being pressed to extract olive oil [1]. It is a lower-grade oil than extra-virgin olive oil, but it is still widely used in various applications such as cooking, frying, and as a salad dressing because of its mild flavor and relatively high smoke point [1].

The olive pomace oil extraction industry is a significant segment of the edible oil industry, especially in Mediterranean countries, where olives are a staple crop [2]. The production of olive pomace oil involves the use of solvents, such as hexane, to extract the remaining oil from the waste generated in the production of extra-virgin olive oil [3]. The extracted oil was refined, blended, and bottled for distribution.

Wastewater generated by the olive pomace oil extraction industry contains a range of pollutants, including residual solvents, oils, and fats, as well as other chemicals used in the refining process [1]. If not properly managed, wastewater can have a significant impact on the environment and human health.

Wastewater discharge from olive pomace oil extraction poses a risk to both public health and the environment. If not treated properly, the high organic content in wastewater can create hazardous by-products such as volatile organic compounds and toxic sludge. Treatment is crucial to remove pollutants, protect water sources and aquatic life, and prevent contamination of drinking water supplies [4, 5].

The treatment of wastewater from the olive pomace oil extraction industry typically involves a combination of physical, chemical, and biological processes to remove the pollutants. Physical treatments such as sedimentation and filtration are used to remove suspended solids [4]. Chemical treatments such as oxidation and neutralization are used to break down oils and other contaminants [4]. Biological treatments, such as aerobic and anaerobic digestion, are used to degrade the organic matter and remove the residual pollutants [4].

Peroxide-electrocoagulation (PEC) is a hybrid technology that effectively removes pollutants from wastewater generated during olive pomace oil extraction [5]. By applying electrical current to wastewater, PEC generates hydroxyl radicals and hydrogen peroxide, which can effectively degrade and oxidize pollutants, while also producing metal hydroxides that coagulate suspended solids and other contaminants, making them easier to remove [5]. Pre-treatment may be necessary to minimize the presence of harmful elements before biological treatment.

The purpose of this study was to reduce the concentration of pollutants in the effluent by utilizing peroxy-electrocoagulation with aluminum electrodes as a treatment method.

2. MATERIALS AND METHODS

This study used olive pomace oil extraction industry wastewater obtained from a plant located in Mirandela, Portugal. The industrial plant received olive pomace from two-stage olive oil extraction units and the wastewater was sieved and stored at room temperature in the laboratory. The wastewater had a pH of 4.8 and was characterized by a high level of total phenolic compounds (TPh) at 8100 mg L^{-1}, chemical oxygen demand (COD) at 86400 mg L^{-1}, biochemical oxygen demand (CBO5) at 11900 mg L^{-1}, and total solids at 61.7 g L^{-1}.

Peroxy-electrocoagulation process

This study evaluated the effectiveness of the PEC process in treating wastewater from the olive pomace oil extraction industry in a 0.6 L bench-scale reactor. A batch system with magnetic stirring was used to treat 0.3 L of effluent. The electrodes, consisting of two rectangular planar aluminum sheets, were carefully polished and washed with 5% HCl solution and distilled water before each experiment. The electrodes were placed vertically at a constant distance of 0.5 cm and had a constant active surface area of 12 cm². Direct current was applied using a power supply (Topward 6302D), with a reaction time of 30 minutes.

The process included adjusting the pH, adding hydrogen peroxide, reaction period, separating an aliquot, basifying to pH 12, and decanting for 24 hours. Efficacy was evaluated based on the removal of COD and TPh from the supernatant.

Data analysis

The Box-Behnken Design (BBD) is a Response Surface Methodology (RSM) that explores the relationship between a set of independent variables and a dependent variable. The BBD uses a specific range for the independent variables and captures nonlinear relationships to identify the optimal response.

The study utilized BBD was used to analyze the impact of varying hydrogen peroxide dosage ([H_2O_2]) (10, 20, and 30 g L^{-1}), electric current density (CD) (5, 20 and 35 mA cm^{-2}), and initial pH (2.5, 3.5, and 4.5) on the COD and TPh removal efficiencies of the PEC process. ANOVA, in conjunction with RSM, was used to assess the model's response to a second-order polynomial model and determine the significance of variables. This approach helped identify the optimal operating conditions for contaminants removal.

3. RESULTS AND DISCUSSION

Table I shows the COD and TPh removal obtained from the PEC process in the different trials. The results indicated that PEC was more effective in removing TPh than COD. The highest removal rates were achieved with a hydrogen peroxide dosage of 30 g L^{-1} and an electric current density of 20 mA cm^{-2}. At pH 2.5 (trial

5), PEC resulted in a 29% removal of TPh, while at pH 4.5 (trial 15), PEC resulted in an 84% removal of COD.

TABLE I: REMOVAL OF TPH AND COD BY PEC PROCESS

Trial	pH	$[H_2O_2]$ g L^{-1}	CD (mA cm^{-2})	COD (%)	TPh (%)
1	3.5	10	35	21	74
2	3.5	20	20	21	86
3	3.5	10	5	14	74
4	3.5	30	35	23	85
5	2.5	30	20	29	86
6	2.5	10	20	23	71
7	4.5	20	5	18	85
8	4.5	20	35	21	85
9	3.5	20	20	21	82
10	2.5	20	5	20	81
11	3.5	30	5	23	87
12	2.5	20	35	23	78
13	4.5	10	20	15	76
14	3.5	20	20	20	82
15	4.5	30	20	26	88
16	3.5	20	20	28	84

Tables II and III present the ANOVA results for the contaminant removal. For COD removal, only $[H_2O_2]$ was statistically significant ($p<0.05$, Table 2), and for TPh removal, $[H_2O_2]$ and its quadratic term were statistically significant (Table III).

TABLE II: ANOVA OF THE RSM FOR COD REMOVAL BY PEC

	Estimate	t-value	p-value Pr(>|t|)
Intercept	22.9675	25.8998	9.194e-10
x_1: pH	-1.8875	-2.1285	0.062
x_2: $[H_2O_2]$	3.5413	3.9934	3.142e-03
x_3: CD	1.5238	1.7183	0.120
x_1:x_2	1.0150	0.8093	0.439
x_2:x_3	-1.8425	-1.4092	0.176
x_3^2	-2.6813	-2.1380	0.061
R^2	Adjusted R^2		p-value
0.7740	0.6233		0.015

TABLE III: ANOVA OF THE RSM FOR TPH REMOVAL BY PEC

	Estimate	t-value	p-value Pr(>|t|)
Intercept	83.6700	102.7170	5.739e-11
x_1: pH	2.0725	3.5982	0.011
x_2: $[H_2O_2]$	6.3075	10.9508	3.443e-05
x_3: CD	-0.6700	-1.1632	0.289
x_1:x_2	-0.9200	-1.1294	0.302
x_1:x_3	0.6900	0.8471	0.429
x_2:x_3	-0.5800	-0.7120	0.503
x_1^2	-0.5750	-0.7059	0.507
x_2^2	-2.8250	-3.4681	0.013
x_3^2	-0.7850	-0.9637	0.372

R^2	Adjusted R^2	p-value
0.9616	0.9040	1.373e-03

Over 60% of the COD removal results (Table II) were determined by the studied independent variables, despite the low Adjusted R^2 of 0.6233. However, a p-value of 0.034 indicates that the factors were statistically significant for the proposed polynomial equation. As for TPh removal, the model explained 90% of the variability using independent variables, and it was statistically significant with a p-value of less than 5% (Table III).

Fig. 1 and 2 show that the optimal conditions for COD removal using the PEC process with aluminum electrodes were nearly achieved. The efficiency decreased when the current density exceeded 30 mA cm^{-2}, as shown in Fig. 1 and 2 (a, c), which can be attributed to the excessive production of bubbles. Its accumulation on the surface of the electrodes interferes with the attachment of reactive species to contaminants, reducing the process efficiency [6]. Higher [H_2O_2] (>20 g L^{-1}) and lower pH (<3.5) improved COD removal, possibly due to increased solubility of aluminum hydroxide in acidic conditions, enhancing PEC efficiency [4].

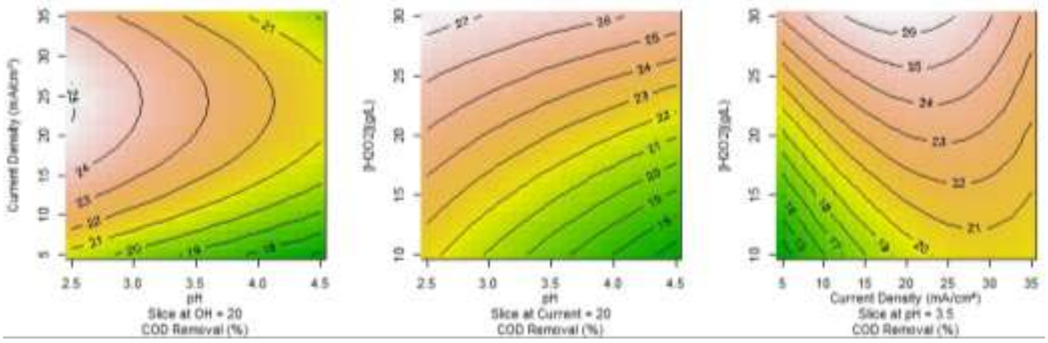

Fig. 1. Contour plots of COD removal by PEC process.

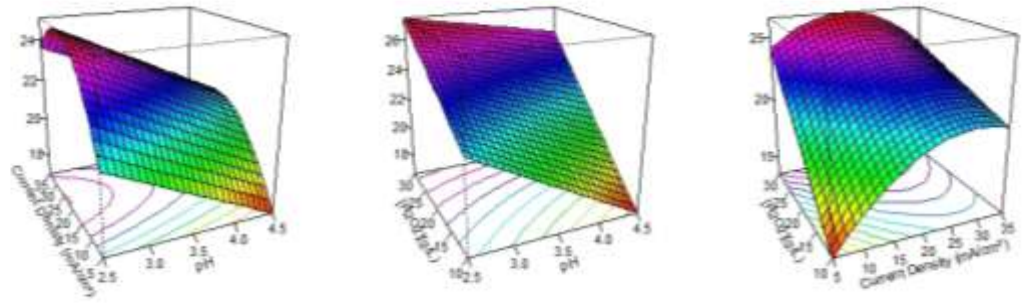

Fig. 2. Surface plots of COD removal by PEC process.

TPh removal using PEC with aluminum electrodes showed that the optimal conditions could be determined by adjusting certain parameters, such as the [H_2O_2] (Fig. 3, 4). Increasing the [H_2O_2] led to a higher removal of TPh (Fig. 3 and 4 – b, c). The range of CD studied did not have a significant effect on the outcome (Fig. 3 and 4 - a, c). However, using CD values above 25 mA cm^{-2} resulted in a decrease in the TPh removal efficiency (Fig. 3, 4). The low efficiency of the process is attributed to the challenge of maintaining a consistent electric current owing to the formation of bubbles [4, 6].

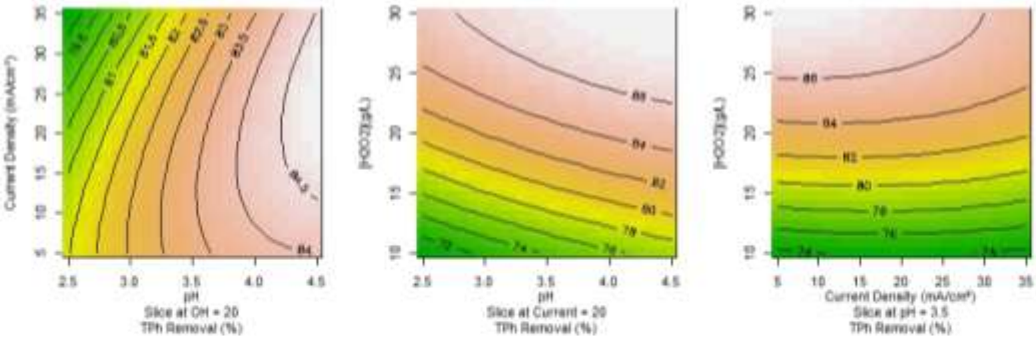

Fig. 3. Contour plots of TPh removal by PEC process.

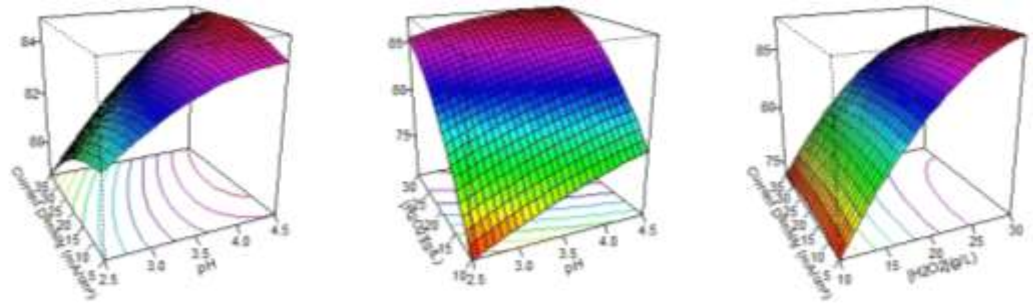

Fig. 4. Surface plots of TPh removal by PEC process

Specifically, the production of excessive oxygen and hydrogen bubbles causes smaller bubbles to merge into larger bubbles, which in turn hinders the coagulation effect. An initial pH above 3 was found to slightly favor the removal of TPh (Fig. 3 and 4 - a, b), but it was not a significant factor in the treatment.

Among the parameters studied, the central point configuration was identified as the optimal operating condition for PEC because of its ability to achieve good TPh and moderate COD removal. Table IV presents the characteristics of the effluent subjected to treatment by the PEC process and the supernatant produced under the central point conditions, which included a pH of 3.5, [H_2O_2] of 20 g L^{-1}, and a current density of 20 mA cm^{-2}. To assess the replicability of the tests conducted on the main pollutants (TPh and COD), standard variation analysis was performed. A standard variation value of less than 5% was deemed acceptable. In this study, the central point configuration yielded standard variations of 1.38% and 3% for TPh and COD, respectively, indicating good consistency in the results.

TABLE IV: CHARACTERIZATION OF WASTEWATER BEFORE AND AFTER PEC PROCESS

Parameter	Unit	Wastewater	PEC
pH	-	4.8	
Conductivity	mS cm^{-1}	17.5	38.7
Total Organic Carbon	mg L^{-1}	35600	33100
Total Carbon	mg L^{-1}	36300	34500
Total Nitrogen	mg N L^{-1}	478	516
Total Phosphorus	mg P L^{-1}	763	366
TPh	mg L^{-1}	8100	800
COD	mg O_2 L^{-1}	86400	69400
BOD_5	mg O_2 L^{-1}	11900	14100
BOD_5/COD		0.14	0.20

Based on the results presented in Table IV, it can be concluded that the PEC process was effective in removing total phosphorus, TPh, and COD from the effluent. However, it should be noted that a proportional removal of total organic carbon was not observed, despite a 20% reduction in COD. Additionally, the PEC process only minimally improved the biodegradability of the effluent, as indicated by the BOD_5/COD ratio.

4. CONCLUSIONS

The PEC process was highly effective and promising for TPh removal, primarily because of the use of hydrogen peroxide as a precursor to hydroxyl radicals. The study findings indicated that the concentration of hydrogen peroxide was one of the most critical factors in the process, with optimal results observed within 30 min. However, while the PEC process proved to be highly efficient in removing pollutants, it was not sufficient to achieve a BOD5/COD ratio that would allow for the successful biological treatment of the effluent. Pretreatment with other techniques is necessary to remove harmful elements from the effluent before initiating biological treatment.

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Ramiro J. Martins was born on February 9, 1967, in Macedo de Cavaleiros, Portugal. He earned his Bachelor's degree in Chemical Engineering from the University of Porto in 1991, a Master's degree in Environment Technology from the University of Braga in 1995, and a PhD in Chemical Engineering from University of Porto in 2004.

Currently, he serves as an Assistant Professor in the Department of Chemical and Biological Technology at the Polytechnic University of Bragança, Portugal. He is also involved in research at the LSRE-LCM Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal and ALICE - Associate Laboratory in Chemical Engineering, FEUP, Porto, Portugal. His research interests revolve around various aspects of environmental engineering. Specifically, he focused on the treatment of heavy-metal-contaminated water through biosorption using low-cost adsorbents. He is also interested in the physicochemical and microbiological characterization of surface waters through biomonitoring as well as the characterization and quality control of various industrial wastewaters. In recent years, he has delved into the energetic valorization of different waste materials, such as glycerol from biodiesel production and agro-industrial by-products through anaerobic digestion. Additionally, he studied the treatment of industrial wastewater such as olive oil and tannery wastewater using Advanced Oxidation Processes (AOP). He also explored the potential for the valorization of water and wastewater treatment plant sludge by using them in the production of ecological bricks and eco-friendly cement mortar.

He is the author of 30 peer-reviewed papers in international indexed journals, 32 books, 13 chapters in books, 95 papers in proceedings of international congresses, and 75 oral/poster presentations at international congresses.

Thais T. Theomaris was born on February 22, 1995, in Curitiba, Paraná, Brazil. Grabowski earned her Bachelor's degree in Chemical Engineering from the Federal Technological University of Paraná in 2021, and a Master's degree in Chemical Engineering from the Polytechnic Institute of Bragança in 2020.

During her graduation, she actively participated in various extracurricular programs, including an academic directory, teaching assistantship, and the Tutorial Education Program (PET). For her thesis, she conducted research on the evaluation of Kraft lignin's potential application as a cosmetic ingredient after completing her coursework. In pursuit of her Master's degree, she took up a summer internship at the Oenology Laboratory, where she conducted research on eco-friendly cement mortar utilizing WWTP sludge for her thesis. Currently, she serves as a first-stage researcher at the Polytechnic University of Bragança, where she conducts research on the treatment and valorization of effluents from the olive pomace oil extraction industry. Her research involves utilizing combined coagulation/flocculation techniques, advanced oxidative processes such as Fenton and electro-oxidation, and aerobic and anaerobic biological processes.

She is the author of 16 oral/poster presentations at national/international congresses.