Treatment for the Olive Pomace Oil Extraction Industry by Appling Peroxy-Electrooxidation

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Abstract

This study aimed to assess the effectiveness of peroxy-electrooxidation (PEO) for treating wastewater from the olive pomace oil extraction industry. The response surface methodology was utilized to optimize the efficiency of the PEO process under varying conditions of electrolysis time, current density, and hydrogen peroxide (H2O2) dosage. Appling graphite/aluminum sheets as cathode/anode in the treatment process showed that the concentration of H2O2 directly affected the efficiency of total phenolic compounds (TPh) removal. It was observed that at an H2O2 concentration of 15 g L-1, the removal efficiency was less than 80%. The removal of chemical oxygen demand (COD) is mainly influenced by the dosage of H2O2 and the reaction time. The experiments conducted on the PEO processes with graphite/iron sheets showed that the highest removal of TPh was achieved with an H2O2 dosage of 30 g L-1 and an intermediate reaction time of 30 minutes. Current density also had an impact on TPh removal. Regarding COD removal, the results showed that the highest removal rates were attained with increased H2O2 concentrations, but reaction time was a positive factor, with better results obtained with 30 and 50 minutes. The PEO is recommended as a pre-treatment for TPh removal but not for COD and other treatment processes should be evaluated.

Keywords: treatment, wastewater, olive pomace oil extraction industry, peroxy-electrooxidation

Introduction

The Mediterranean region is responsible for 98% of the world's olive trees and, consequently, there is a large production of wastewater from olive oil production. Portugal is the fourth largest producer in the European Union, producing 2.29 million hectoliters of olive oil in the 2021/2022 season, generating a turnover of 483.14 million euros in 2019 [1]. With the large production of olive oil, there is also a large volume of olive pomace produced, which is directed to the olive pomace oil extraction industry (OPOEI).

After the oil extraction in the OPOEI, there is a generation of wastewater with a high pollution power, being considered one of the most toxic in the world [2] According to studies, 1m³ of wastewater generated in the OPOEI corresponds to 200 m³ of domestic wastewater [3]. This wastewater is considered challenging for conventional wastewater treatment, requiring the implementation of advanced treatment techniques.

Among the solutions employed to face this challenge, the advanced oxidative processes (AOP) stand out [4]. These methods use technologies to degrade resistant pollutants through the generation of highly reactive free radicals, which decompose the pollutants into molecules less harmful to the environment [5].

The peroxy-electrooxidation (PEO) technique is one of the AOP alternatives that presents a great potential for the efficient removal of organic matter, especially phenolic compounds. The PEO combines electrooxidation, which uses electrochemically generated free radicals, with the addition of hydrogen peroxide (H_2O_2) as a source of oxidizing agent [2].

The main objective of the present study was to evaluate the peroxy-electrocoagulation in the treatment of wastewater from the olive pomace oil extraction industry. In addition, the response surface methodology (RSM) was used to optimize the efficiency of the PEO under different electrolysis times, current densities, and hydrogen peroxide dosage.

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Methods

    The bench-scale PEO process was performed using a 600 ml reactor. 300 ml of effluent was treated in a batch system, with rectangular sheets placed 3 cm apart. During all tests, 10.25 cm² of each electrode plate was submerged in the effluent for the experiments. The electrodes were carefully polished and washed with a 5% HCl solution, followed by distilled water.

    Two rectangular sheets electrodes configurations were tested: aluminum as the anode and graphite as the cathode, and iron as the anode and graphite as the cathode. The PEO process involved the following steps: adding the effluent to be treated, adjusting the pH, adding hydrogen peroxide, starting the reaction time, separating an aliquot at the end of the stipulated time, basifying the aliquot to pH 12, and decanting for 24 hours. The efficacy of the process was evaluated in terms of the chemical oxygen demand (COD) and total phenolic compounds (TPh) removal from the supernatant generated.

    The results were analyzed using the Response Surface Methodology (RSM), a statistical tool that uses a set of experimental tests to determine the optimal response. This includes the Box-Behnken Design (BBD), which evaluates the interaction between the factors and determines the response from the input data, using a smaller number of experimental executions.

    Two BBDs were performed, one for PEO with graphite and aluminum, and the other with graphite and iron as the electrodes. The independent variables were the same in both processes: hydrogen peroxide, electric current density, and reaction time. These values were defined based on preliminary tests.

    After conducting the laboratory analyses and obtaining the results, statistical analysis was performed using Analysis of Variance (ANOVA) with a 95% confidence interval. The ANOVA was employed to evaluate the response of the model to a second-order polynomial model, to determine the optimum conditions.

Results

    Trials performed and the respective COD and TPh removals obtained through the PEO process are arranged in Table 1.

PEO with Graphite/Aluminum Sheets

    Trials performed and the respective TPh and COD removals obtained through the PEO process with aluminum and graphite as the electrode sheets, are arranged in Table 1 (a).

    The concentration of H_2O_2 has a direct impact on the efficiency of TPh removal, as demonstrated by the fact that tests with H_2O_2 15 g L^{-1} show a removal efficiency lower than 80%. On the other hand, COD removal is more dependent on the dose of H_2O_2 and the reaction time.

    Test configuration 2 was defined as the best operational configuration for PEO among the parameters studied. This is because it presents a higher TPh removal rate, lower H_2O_2 concentration, shorter reaction time and significant COD removal. This option was able to achieve TPh removal rates close to those obtained with the maximum concentration of H_2O_2 but using milder operating conditions.

    The statistical significance of the ANOVA was evaluated to fit a second-order polynomial equation ($p<0.05$) and generated the Figure 1-4. Contour and surface plots show COD removal by fixing reaction time (Figure 1. a, Figure 2. a), current density (Figure 1. b, Figure 2. b) and H_2O_2 dose (Figure 1. c, Figure 2. c).

Tab. 1. Removal of TPh and COD using PEO process.

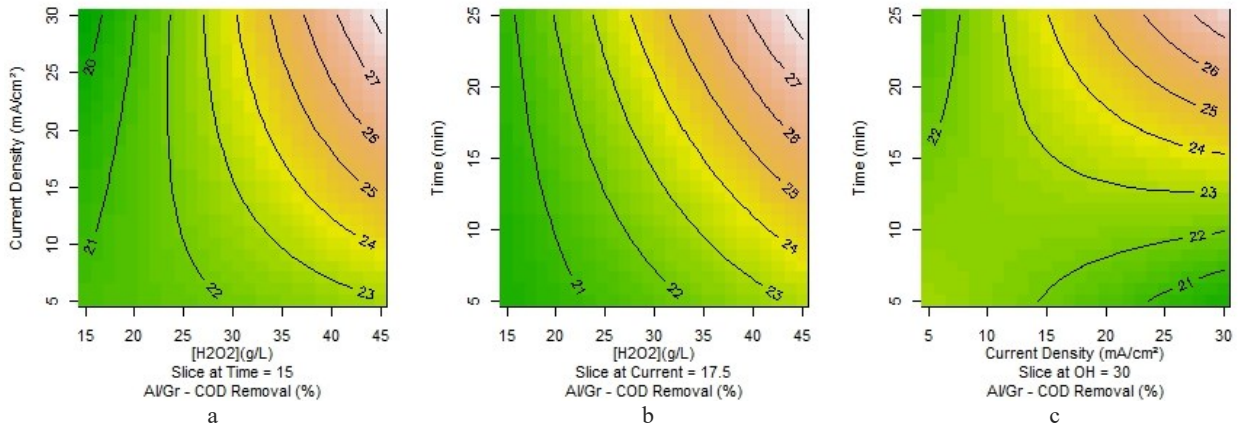| (a) PEO process with graphite/aluminum (cathode/anode) sheets					(b) PEO process with graphite/iron (cathode/anode) sheets				
Trial	H_2O_2 g L^{-1}	Current density (mA cm⁻²)	Time (min)	COD Removal (%)	TPh Removal (%)	Trials	H_2O_2 g L^{-1}	Current density (mA cm⁻²)	Time (min)	COD Removal (%)	TPh Removal (%)
1	15	17.5	5	20	79	1	15	17.5	5	20	79
2	30	17.5	15	23	87	2	30	17.5	15	23	87
3	30	5.0	5	23	85	3	30	5	5	23	85
4	45	5.0	15	25	88	4	45	5	15	25	88
5	15	17.5	25	23	76	5	15	17.5	25	23	76
6	30	30.0	25	26	88.	6	30	30	25	26	88
7	45	17.5	5	22	88	7	45	17.5	5	22	88
8	30	17.5	15	21	85	8	30	17.5	15	21	85
9	15	5.0	15	22	75	9	15	5	15	22	75
10	15	30.0	15	20	75	10	15	30	15	20	75
11	30	5	25	19	84	11	30	5	25	19	84
12	30	30	5	21	86	12	30	30	5	21	86
13	30	17.5	15	24	85	13	30	17.5	15	24	85
14	45	30	15	29	95	14	45	30	15	29	95
15	45	17.5	25	30	88	15	45	17.5	25	30	88

Fig. 1. Contour plots of COD removal from OPOEI effluent after PEO process with aluminum and graphite as the electrode sheets.
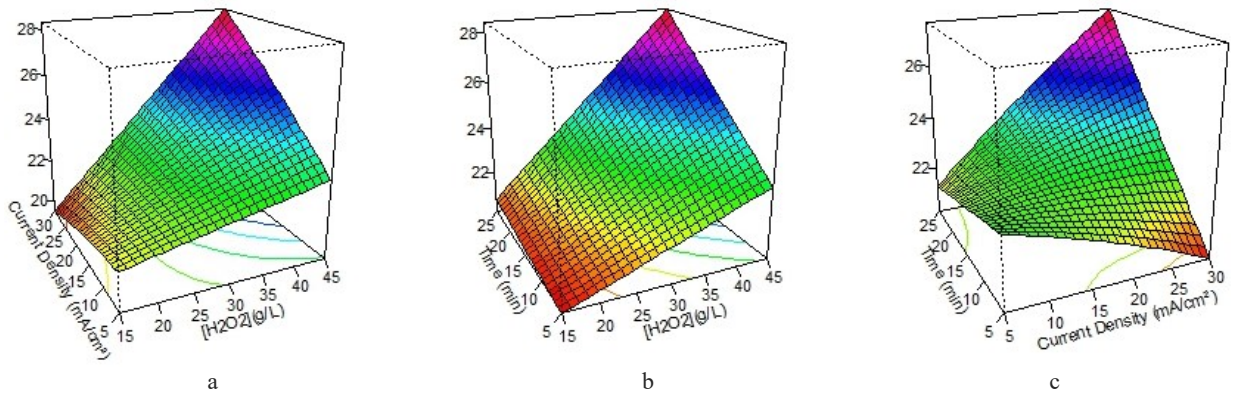

Fig. 2. Surface plots of COD removal from OPOEI effluent after PEO process with aluminum and graphite as the electrode sheets.

After analyzing the contour plots, it was observed that the isoline lines representing time and current density (Figure 1. a, b) exhibit a more linear behavior starting from 30 g L^{-1} of H_2O_2. Additionally, it was found that the maximum removal of COD is achieved by increasing both the time and the current density, indicating that these variables have a positive influence on COD removal.

In the Figure 1 where fixes the H_2O_2 concentration (Figure 1. c), a saddle behavior was identified, suggesting that the limits established in the experiments were not sufficient to determine the best removal condition based on time and current density, and that other factors may be interfering with the removal of COD that were not considered.

The analysis of the surface plots indicates that the H_2O_2 concentration is the factor that most influences the removal of COD, being proportional to this removal. This fact is reinforced by the surface plot with the fixed H_2O_2 concentration (Figure 2. c), which exhibits a slight tendency towards saddle formation, confirming the analysis based on the contour plot of the same variables.

The contour and surface plots of COD removal are depicted in Figure 3. The fixed parameters of reaction time (Figure 3. a, Figure 3. a), current density (Figure 3. b, Figure 4. b), and H_2O_2 concentration (Figure 3. c, Figure 4. c) will be analyzed in detail.
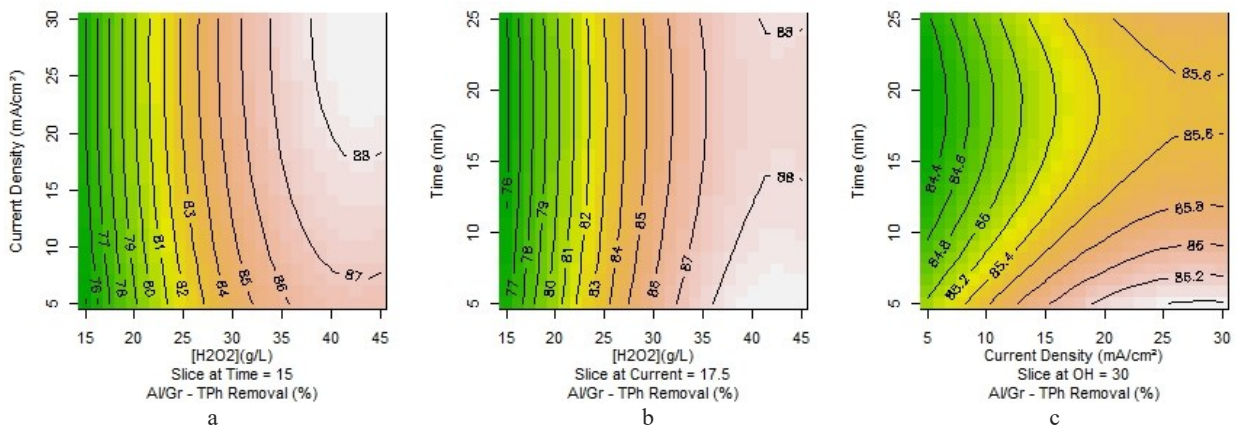

Fig. 3. Contour plots of TPh removal from OPOEI effluent after PEO process with aluminum and graphite as the electrode sheets.
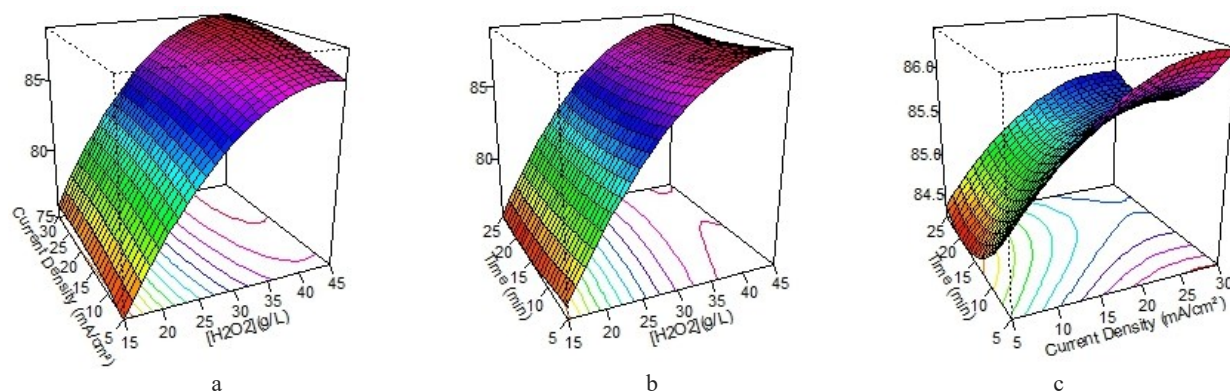
Fig. 4. Surface plots of TPh removal from OPOEI effluent after PEO process with aluminum and graphite as the electrode sheets.

The influence of H_2O_2 concentration on the removal of TPh is direct, as demonstrated by the Figure 3. A, b. These show a close vertical linearity, except for concentrations above 40 g L^{-1}, where the current density begins to have an impact on TPh removal and time no longer interferes. This suggests that the greatest removal of TPh occurs at the beginning of the reaction, with high electric current and TPh oxidation independent of other variables.

After the consumption of H_2O_2, the reaction continues through electrocoagulation, with the release of aluminum ions, or H_2O_2 electro generation at the cathode. At higher current densities, H_2O_2 electro generation may influence TPh removal, but the data is not sufficient to confirm this possibility or define the best conditions.

Without direct influence of H_2O_2, the analysis of time and current density indicates that the higher the current density, the greater the removal of TPh, with the ideal time for removal up to 15 minutes.

Table 2 shows the ANOVA obtained regarding the removal of contaminants. Only the terms where $p < 0.05$ are statically significant, thus for COD and TPh removal only $[H_2O_2]$ is statistically significant. More than 60% of the COD removal results (Table 2) were defined by the independent variables studied. Even with a low Adjusted R^2 (0.613), it was a reasonable outcome. On the other side, the p-value of 0.0396 proved that the factors in question were statistically significant for the proposed polynomial equation. For TPh removal the proposed model had 88% of the variability explained by the independent variables and it was considered statistically significant (p-value lower then 5%).

Tab. 2. ANOVA of the RSM for COD and TPh removal by PEO process, with aluminum and graphite as the electrode sheets, from olive pomace oil extraction industry wastewater.

COD Removal ANOVA data			TPh Removal ANOVA data		
R^2	0.8065		R^2	0.9409	
R^2 - ajustado	0.613		R^2 - ajustado	0.8819	
p-valor	0.0396		p-valor	0.00083	
	Estimate	p-value		Estimate	p-value
Interseção	23.28571	9.275E-09	Interseção	85.66667	2.039E-11
X_1: $[H_2O_2]$	2.625	0.007241	X_1: $[H_2O_2]$	6.875	2.48E-05
X_2: [a]CD	0.875	0.2523	X_2: [a]CD	1.5	0.07025
X_3: time	1.2	0.069795	X_3: time	-0.375	0.61019
X_1: X_2	1.5	0.1742	X_1:X_2	1.75	0.12171
X_1: X_3	1.25	0.24802	X_1^2	-2.8333	0.2898
X_2: X_3	2.25	0.057634	X_2^2	0.41667	0.69917
X_2^2	-0.16071	0.880044	X_3^2	-0.333	0.75672

[a]CD: Current density

PEO with Graphite/Iron Sheets

Trials performed and the respective TPh and COD removals obtained through the PEO process with iron and graphite as the electrode sheets. Are arranged in Table 1 (b).

The results of the experiments indicated that the maximum removal of TPh occurred with a H_2O_2 concentration of 30 g L^{-1} and an intermediate reaction time of 30 minutes. Current density also had an impact on TPh removal. With the highest removals observed at current densities of 5 mA cm^{-2} and 20 mA cm^{-2}. Compared to a density of 35 mA cm^{-2}.

Regarding the removal of COD, the results showed that the highest removals were also achieved with high H_2O_2 concentrations, but reaction time was a positive factor, with better results obtained with 30 and 50 minutes. Test configuration 4 was defined as the best operating configuration for PEO, with iron and graphite sheets, among the parameters studied. This is because it presents the highest removal of TPh, the lowest concentration of H_2O_2, the shortest reaction time. And significant removal of COD. Experiment 4 achieved the best removal of both TPh and COD, even with the lowest current density studied and with an intermediate reaction time.

Contour and surface plots show COD removal by fixing reaction time (Figure 5. a, Figure 6. a), current density (Figure 5. b, Figure 6. b) and H_2O_2 dose (Figure 5. c, Figure 6. c).
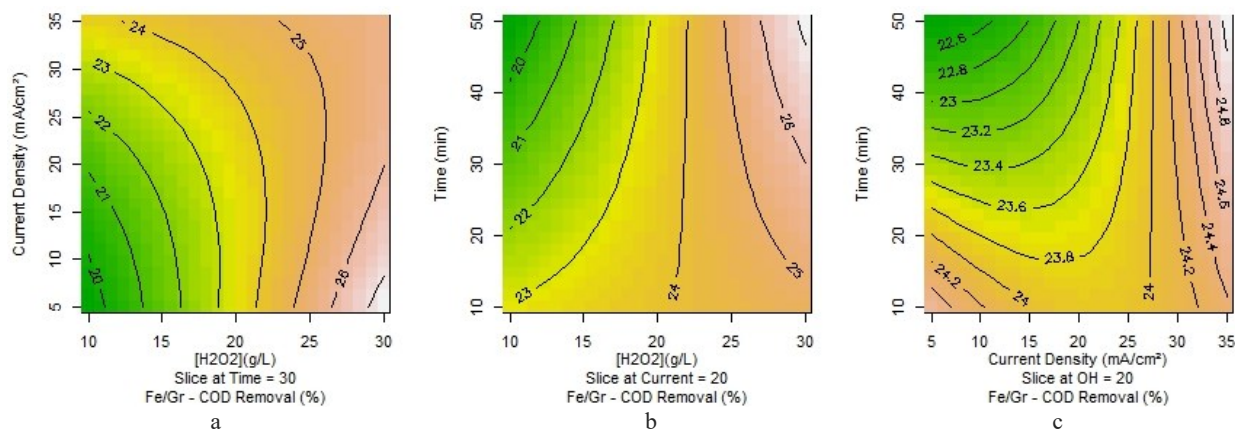
Fig. 5. Contour plots of COD removal from OPOEI effluent after PEO process with iron and graphite as the electrode sheets.
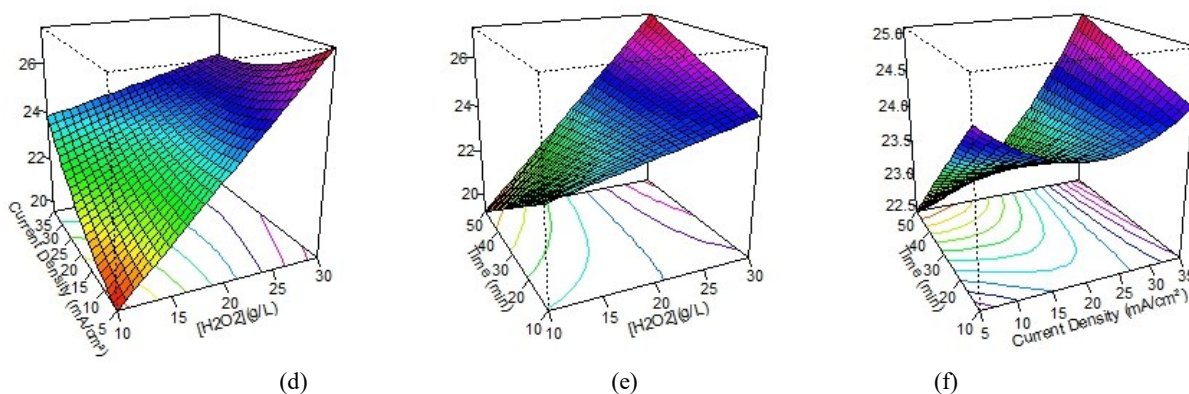

Fig. 6. Surface plots of COD removal from OPOEI effluent after PEO process with iron and graphite as the electrode sheets.

The analysis of the contour graph profiles indicated that, when the current density was fixed (Figure 5. b), the higher the concentration of H_2O_2 and the reaction time, the higher the COD removal. On the other hand. when time was fixed (Figure 5. a), lower current density was more effective in COD removal when associated with high H_2O_2 concentration. The contour graph with H_2O_2 concentration fixed (Figure 5. c) showed a saddle-shaped trend, indicating that low current densities (up to 10 mA cm^{-2}) combined with short reaction times (5 minutes) or high current densities (above 35 mA cm^{-2}) combined with long times (above 40 minutes) result in the highest COD removal.

This behavior suggests the need to expand the study limits and suggests that the H_2O_2 concentration be elevated in the beginning of the process (up to 10 minutes), after which electrocoagulation tends to become more dominant, with its effectiveness increasing with high current densities and long reaction times.

Contour and surface plots show TPh removal by fixing reaction time (Figure 7. a, Figure 8. a), current density (Figure 7. b, Figure 8. b) and H_2O_2 dose (Figure 7. c, Figure 8. c). The influence of H_2O_2 concentration on removal is evident in the Figure 7 that show the variation of H_2O_2 concentration on the abscissa axis (Figure 7. a, b), which have vertical straight-line trends. When we observe the Figure 7 and Figure 8 with the fixed H_2O_2 concentration (Figure 7. c, Figure 8. C), it is possible to verify that a low current density combined with short reaction time (up to 15 minutes) are the most efficient. This behavior is due to the fact that H_2O_2 is consumed in the beginning of the process, similar to what occurs in PEO with aluminum and graphite. This result confirms the choice of test 4 as the most efficient, as, even with a short reaction time and low current density, the TPh removal remains high.
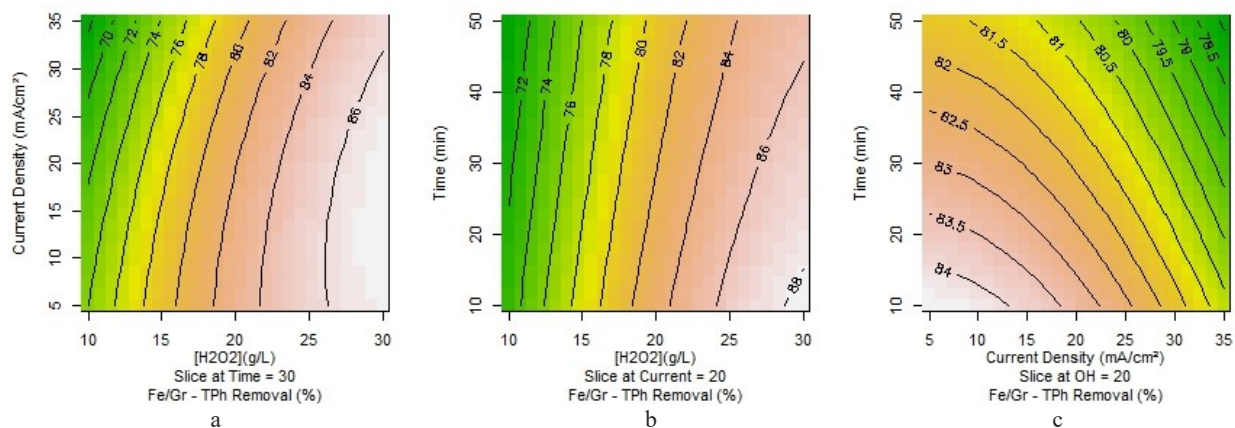

Fig. 7. Contour plots of TPh removal from OPOEI effluent after PEO process with iron and graphite as the electrode sheets.
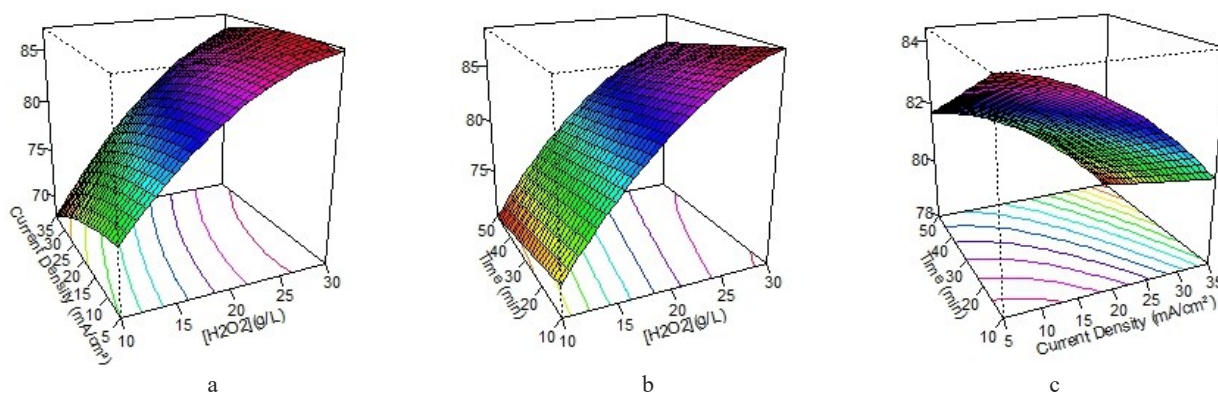
Fig. 8. Surface plots of TPh removal from OPOEI effluent after PEO process with iron and graphite as the electrode sheets.

Table 3 shows the ANOVA obtained regarding the removal of contaminants. For COD removal the concentration of H_2O_2 and the current density are statistically significant and for TPh removal only the concentration of H_2O_2 are statistically significant. More than 60% of the COD removal results (Table 3) were defined by the independent variables studied. Even with a low Adjusted R^2 (0.6174), it was a reasonable outcome, and the p-value of 0.02337 proved that the factors in question were statistically significant for the proposed polynomial equation. For TPh removal the proposed model had 83.3% of the variability explained by the independent variables and it was considered statistically significant.

Tab. 3. ANOVA of the RSM for COD and TPh removal by PEO process, with iron and graphite as the electrode sheets, from olive pomace oil extraction industry wastewater.

COD Removal ANOVA data			TPh Removal ANOVA data		
R^2		0.7814	R^2		0.9165
R^2 - ajustado		0.6174	R^2 - ajustado		0.833
p-valor		0.02337	p-valor		0.002653
	Estimate	**p-value**		**Estimate**	**p-value**
Interseção	23.56075	1.91E-09	Interseção	81.9102	2.217E-10
X_1: $[H_2O_2]$	2.43	0.0035	X_1: $[H_2O_2]$	7.6912	8.20E-05
X_2: [a]CD	0.625	0.0358	X_2: [a]CD	-1.8661	0.08905
X_3: time	-0.362	0.5427	X_3: time	-1.3741	0.18952
X_1: X_2	-1.496	0.1037	X_1:X_2	1.2542	0.37954
X_1: X_3	1.56902	0.0900	X_1^2	-2.6300	0.10076
X_2: X_3	0.70968	0.4040	X_2^2	-0.7690	0.59781
X_2^2	0.53691	0.0537	X_3^2	0.0212	0.98825

[a]CD: Current density

The effluent was treated by the best configurations of PEO process and the supernatant generated from this process, were characterized (Table 4). The best configurations defined were: configuration 2 for PEO graphite/aluminum (H_2O_2 30 g L^{-1}, 17.5 mA cm^{-2}, 15 min); and configuration 4 for PEO graphite/iron (H_2O_2 45 g L^{-1}, 5 mA cm^{-2}, 15 min).

Tab. 4. Characterization of olive pomace oil extraction industry wastewater before and after de PEO processes with graphite/aluminum and graphite/iron sheets.

Parameter	Unit	Wastewater	PEO graphite/aluminum	PEC graphite/iron
pH	-	4.8		
Conductivity	mS cm^{-1}	17.5	43.7	42.3
Total Organic Carbon	mg L^{-1}	35600	26400	26300
Total Carbon	mg L^{-1}	36300	28200	28000
Total Nitrogen	mg N L^{-1}	478	439	435
Total Phosphorus	mg P L^{-1}	763	435	386
TPh	mg L^{-1}	8130	900	1140
COD	mg O_2 L^{-1}	86400	62000	65000
BOD_5	mg O_2 L^{-1}	11900	10200	9700
BOD_5/COD		0.14	0.16	0.15

From Table 4 we can conclude that the PEO process was efficient in removing total organic carbon, total carbon, total phosphorus, TPh and COD. The removal of total organic carbon (graphite/aluminum: 26% and graphite/iron: 26%) and total carbon (graphite/aluminum: 22% and graphite/iron: 23%) was consistent with the removal of COD (graphite/aluminum: 29% and graphite/iron: 25%). The final characterization highlights the efficiency of the aluminum procedure in removing most chemical parameters. The increase in BOD_5/COD ratio is also notable, as aluminum provided greater biodegradability compared to iron.

Despite this improvement, the BOD$_5$/COD ratio of neither treatment reached the level of 0.3 required for biological treatment [3]. The PEO treatment demonstrated a preference for removing non-biodegradable organic matter, despite its low COD removal.

Conclusion

The PEO technique is effective in removing or degrading phenolic compounds. especially when using graphite electrodes as cathode and aluminum as anode. Despite repeated testing. the expected removal efficiency was not achieved. with TPh and COD removal being greater than 85% and 25%. respectively. The degradation of TPh occurred proportionally with H$_2$O$_2$ dosage but removal of COD was influenced by the reaction time and the current density applied. The process was carried out until the consumption of H$_2$O$_2$. with electrocoagulation being the predominant mechanism. The graphite electrode has the potential to electro-generate H$_2$O$_2$. but this was not evaluated in the tests. The PEO is recommended as a pre-treatment for TPh removal but not for COD and other treatment processes should be evaluated.

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