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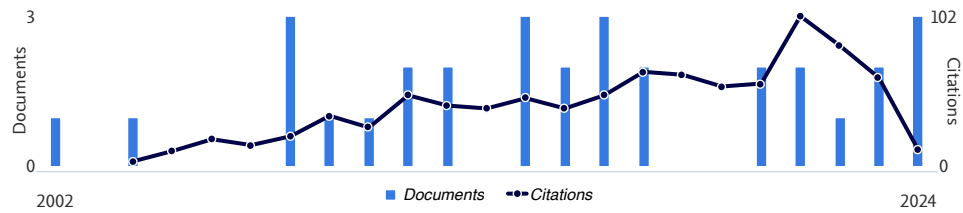
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WASTES: Solutions, Treatments and Opportunities IV contains selected papers presented at the 6th edition of the International Conference Wastes: Solutions, Treatments and Opportunities, that took place on 6-8 September 2023, in Coimbra, Portugal. The Wastes conference, which takes place biennially, is a prime forum for sharing innovations, technological developments and sustainable solutions for waste management and recycling sectors worldwide, with the participation of experts from academia and industry. The papers included in this book cover a wide range of topics, including:

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WASTES: Solutions, Treatments and Opportunities IV

Edited by

Cândida Vilarinho & Fernando Castro

University of Minho, Portugal

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Photo-Fenton treatment of wastewater from olive oil extraction industry

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ABSTRACT: The European industry has a well-established sector in the production of olive oil. The valorization of the olive pomace by extraction highly generates pollutant effluent due to waste leaching and processing in these extractor units (OOEIW). This study aimed to treat OOEIW using the photo-Fenton process. The process efficiency for the removal of organic matter and phenolic compounds was modeled and optimized using response surface methodology with Box-Behnken design. The variables considered were iron catalyst concentration, oxidant concentration, and UV irradiation time. The optimal conditions were determined as $[\text{Fe}^{2+}] = 3 \text{ g L}^{-1}$, $[\text{H}_2\text{O}_2] = 23 \text{ g L}^{-1}$ and time photo reaction 60 min. The process achieved removals of 93% (TPh) and 26% (COD) in the diluted sample (1:10); 90% (TPh) and 39% (COD) in the raw sample.

1 INTRODUCTION

The olive oil industry is a well-established sector in Europe that utilizes various methods for olive oil production, including the two and three-phase continuous methods. These methods generate both liquid and solid waste, including olive oil mill wastewater (OMW) and olive pomace (OP), respectively. These wastes contain toxic phenolic compounds and high organic loads (Domingues et al. 2022, Martins et al. 2022). The treatment of OMW is usually by evaporation in controlled open ponds, which requires vast areas of land and can cause significant environmental issues (Jarboui et al. 2010). The main by-product, the OP, goes to a second extraction, the remaining oil percentage is removed applying an organic solvent. After the process, the exhausted pomace serves as fuel in the industry (Missaoui et al. 2017), and the wastewaters produced, known as olive oil extraction industry wastewater (OOEIW), need to be treated (Domingues et al. 2022).

Advanced Oxidation Processes (AOPs) are recognized for their ability to mineralize various organic compounds in different effluents. Among AOPs, Fenton and photo-Fenton are known for their effectiveness in treating wastewater with high phenolic content (Domingues et al. 2022). The main objective of this study is to optimize the photo-Fenton process for treating wastewater from the olive pomace oil extraction industry. In addition, the response surface

methodology (RSM) was used to optimize the efficiency of the photo-Fenton under different photo-reaction time, and dosages of iron and hydrogen peroxide.

2 MATERIALS AND METHODS

2.1 Effluent's characterization

The effluent was obtained from an olive pomace oil extraction factory located in Northern Portugal. This industrial unit receives olive pomace, mostly from two-phase olive oil extraction units, that are used for refined oil extraction (with hexane) through a sequence of drying and liquid/solid extraction. At the end of the process, the effluents generated go to decanters and then to the stabilization and evaporation ponds, where they remain until eventual disposal in the river near the industrial unit. Samples were collected from the stabilization and evaporation ponds. It was filtered in order to remove suspended solids and stored at room temperature until needed for the experiments.

In Table 1 are present the most important parameters of the effluent, namely the chemical oxygen demand (COD), pH, total phenolic compounds (TPh), total solids (TS) and total volatile solids (TVS).

Table 1. Physic-chemical characterization of olive oil extraction industry wastewater.

Parameter	Value
pH	4.85
COD	85 g O ₂ L ⁻¹
BOD ₅	12 g O ₂ L ⁻¹
Total Volatile Solids (TVS)	37 g L ⁻¹
Total Solids (TS)	62 g L ⁻¹
Total phenolic compounds (TPh)	6.6 g L ⁻¹
Biodegradability (BOD ₅ /COD)	0.14

2.2 Experimental design

The study used the Box-Behnken design (BBD) as a response surface methodology (RSM) to optimize the experimental conditions for the photo-Fenton treatment of OOEIW. The BBD allowed for a reduction in the number of experimental trials without compromising accuracy (Ferreira et al. 2007). The study considered the concentration of H₂O₂, the concentration of Fe²⁺, and the reaction time as independent variables and the removal of TPh and COD as dependent variables. To improve precision, three replicas of the central point were carried out. A second-order polynomial equation was used to fit the data, and ANOVA and regression surface analysis were used to determine the statistical significance of the model factors and responses.

2.3 Treatment procedure

All experiments were carried out in a photoreactor with total capacity equal to 0.7 L (KKS/UV-BRIGHT), the continuous circulation of the solution was achieved by peristaltic pump (Lead Fluid/ YZ15), and the UV-C lamp (nominal power 14 W), that emits radiation with a maximum intensity peak around 254 nm wavelength was set at the center of the reactor. The OOEIW sample was diluted 1:10 and its pH was adjusted to 3.5 adding 2 mol L⁻¹ H₂SO₄. In a typical run, 1 L of the sample solution (Fe²⁺ and H₂O₂ in the predefined quantities in Table 2) were added in the recirculation tank and pumped into the photoreactor, while the UV-Lamp was turned off. The lamp was warmed for 5 min before starting the reaction to ensure constant output. The photo-Fenton was initiated when the reactor was full of sample

solution. The flow was maintained at 20 mL min^{-1} at predetermined times (Table 2). During the experiment, the reactant mixture was continuously stirred magnetically in the recirculation tank. After photoreaction the pH of treated samples was adjusted to 9.5 using 6 mol L^{-1} NaOH. The sample was kept at rest overnight, and the next day the TPh and COD were analyzed. All the experiments were conducted at least twice, and the obtained results were averaged.

2.4 Analytical methods

The BOD₅ determination was made using the standardized respirometry method with the OxiTop equipment (WTW). The procedure was carried out in accordance with section 5210 - B BOD for 5 days (Rice et al. 2012) and with the help of the equipment manual. The COD analysis was performed based on section 5220 - D Closed Reflux Calorimeter Method (Rice et al. 2012). TPh was quantified using the Folin-Coicolteu method and a standard curve was generated with 0 - 100 mg L⁻¹, using phenol as the model compound in adaptation to the method presented by Leouifoudi et al. (2015).

For the analysis of TS, TVS, and TFS were followed the methodology presented in the section 2540 - SOLIDS (Rice et al. 2012). The pH, conductivity and turbidity values were obtained by direct reading using the pHmeter (Model Edge, HANNA), conductivity meter (Model inoLab Level 3, WTW) and turbidimeter (Model TIR 210, VWR), respectively.

3 RESULTS AND DISCUSSION

3.1 Preliminary experiments

Preliminary experiments were carried out to define the variables of photo-Fenton assays. The Fenton process is performed at low pH values (2-4), therefore, the behavior of COD removal from the effluent was studied between this pH range (2.5 - 3.5). In this study, Fenton tests were conducted using 0.1 L of OOEIW in the Jar Test apparatus. Following the addition of H₂O₂, pH correction and addition of Fe²⁺ in that order, each test was continuously stirred at 80 rpm for 20 minutes. To stop the Fenton reaction at the end of the established reaction time, the pH was raised to 10. The tests were then left to settle overnight, and COD in the supernatant was determined.

According to Figure 1, it was found that in the pH range of 2.5 to 3.5, pH has no significant impact on COD removal. In addition, increasing the concentration of the reagents results in a similar COD removal response in the three pH values studied. Within the iron dosage range studied, from 1.5 to 4.5, there are optimal points for COD removal (Figure 1a). Working with H₂O₂ concentrations greater than 20 g L⁻¹ seems to be interesting for COD removal (Figure 1b).

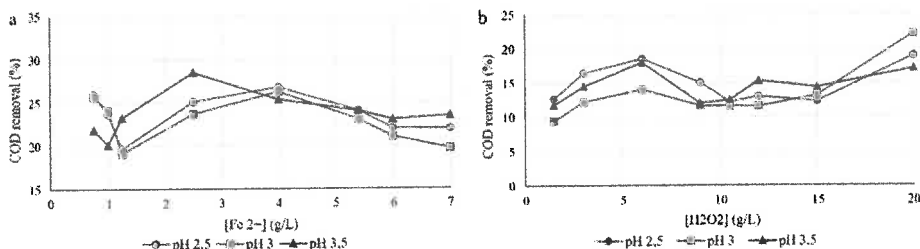


Figure 1. COD removal after Fenton process application in wastewater from the olive oil extraction industry at a pH range of 2.5 to 3.5.

The efficiency of the continuous photo-Fenton process is also influenced by the flow rate of the effluent through the photoreactor. Figure 2 illustrates the COD removal obtained at pH 3.5 using 10 g L^{-1} of H_2O_2 and 3 g L^{-1} of Fe^{2+} at three different flow rates.

According to data presented in Figure 2, intermediate flow rate achieved better removal efficiency after 60 minutes of the experiment compared to low flow rate (2 mL min^{-1}) and high flow rate (200 mL min^{-1}). Therefore, subsequent photo-Fenton experiments were conducted at a constant pH of 3 and flow rate of 20 mL min^{-1} , based on preliminary tests.

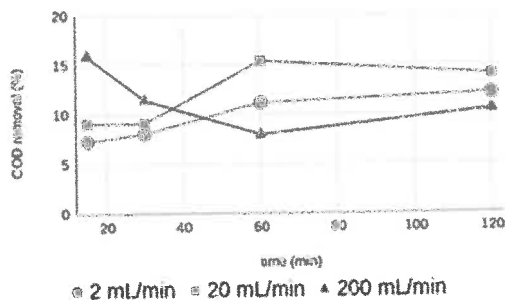


Figure 2. Removal profiles for COD as a function of irradiation time, initial pH 3.5, 10 g L^{-1} H_2O_2 , and 3 g L^{-1} Fe^{2+} obtained from photo-Fenton experiments at flow 2, 20 and 200 mL min^{-1} .

3.2 Photo-Fenton treatment

Box-Behnken design and response surface methodology were employed to illustrate the nature of the response surface in the experimental design and elucidate the optimal conditions of the independent variables. Table 2 shows the results obtained from the present experimental design.

Table 2. Results of TPh and COD removal (%) from olive oil extraction industry wastewater submitted to photo-Fenton (diluted sample 1:10).

Trial	Coded level of variable			Decoded level of variable		Removal (%)		
	X_1	X_2	X_3	$\text{H}_2\text{O}_2^a (\text{g L}^{-1})$	$\text{Fe}^{2+ b} (\text{g L}^{-1})$	t (min)	TPh	COD
1	-1	-1	0	10	1.5	60	53	9.7
2	1	-1	0	30	1.5	60	72	13
3	-1	1	0	10	4.5	60	55	8.7
4	1	1	0	30	4.5	60	81	19
5	-1	0	-1	10	3	30	41	7.7
6	1	0	-1	30	3	30	78	19
7	-1	0	1	10	3	90	60	15
8	1	0	1	30	3	90	89	19
9	0	-1	-1	20	1.5	30	73	11
10	0	1	-1	20	4.5	30	80	22
11	0	-1	1	20	1.5	90	83	14
12	0	1	1	20	4.5	90	60	16
13	0	0	0	20	3	60	77	18
14	0	0	0	20	3	60	77	15
15	0	0	0	20	3	60	77	16

^a g Oxidant L^{-1} Effluent; ^b g catalyst L^{-1} Effluent

Table 2 shows the reduction in TPh ranged from 41 - 89%, while COD showed removals of 7.7 - 22%. From the analyzes performed, it was found that for the removal of TPh, only the variable X_1 [H_2O_2] has statistical significance ($t_{value} > 1.5$) and for the COD reduction, both the X_1 [H_2O_2] and X_2 [Fe^{2+}] variables were significant. It should be noted that positive and negative coefficients in the above equation of the model implies on the desirable and undesirable effects of each variable on the response, respectively. Moreover, the mathematical models only consider factors having a p-value < 0.05 (El Gaayda et al. 2022). It was observed that X_3 (photo reaction time) has no significant influence on the process used to remove TPh and COD, under the proposed conditions of the study. Table 3 shows the ANOVA at a 95% confidence level ($p_{value} < 0.05$) results based on the statistical significance of a second order model for removal of TPh and COD with mathematical interpretation.

Table 3. ANOVA results for response surface methodology.

	Df	Sum sq	Mean sq	F value	p-value
TPh					
FO (X_1, X_3)	2	1600.07	800.03	19.5698	0.000349
TWI (X_2, X_3)	1	223.50	223.50	5.4672	0.041467
PQ (X_1, X_2)	1	325.88	325.88	7.9714	0.018056
Lack of fit	5	304.96	60.99	2.9364	0.131076
COD					
FO (X_1, X_2, X_3)	3	143.387	47.796	10.9141	0.007638
TWI (X_1, X_2)	1	11.560	11.560	2.6397	0.155348
TWI (X_1, X_3)	1	12.602	12.602	2.8778	0.140738
TWI (X_2, X_3)	1	18.923	18.923	4.3209	0.082885
PQ (X_1, X_2)	2	23.301	11.651	2.6604	0.148875
Lack of fit	4	23.109	5.777	3.6488	0.226511

ANOVA analysis indicated that just the FO term in the photo-Fenton process to COD (Table 3) presented p-value below 0.05, being statistically significant. The other terms did not prove to be significant, with p-value higher than 0.05. For TPh removal, in addition to the FO term, two-way interactions and the pure quadratic term showed statically significant. The other criteria for model validation used in previous studies is the lack of fit test (Zainal-Abideen et al. 2012). The lack of fit identifies any deviation between the actual points and those of the fitted surface. For both, TPh and COD, the lack of fit p-value was greater than 0.05 and is considered as significant and interpreted as predicted values by the model that most closely approximates the actual values.

Three-dimensional surface plots were obtained to demonstrate the different relationships among the variables for TPh removal (Figure 3) and COD (Figure 4) from OOEW. Each plot is made with the third independent variable at the BBD center point.

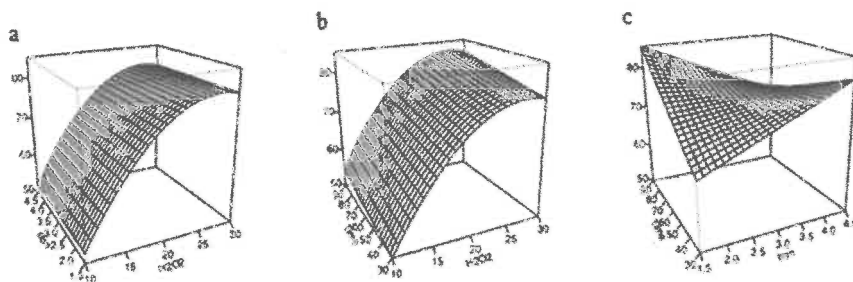


Figure 3. Three-dimension surface and contour plots for TPh removal (a) effect of Fe^{2+} and H_2O_2 at 60 min, (b) effect of time and H_2O_2 at Fe^{2+} 3 g L^{-1} , (c) effect of time and Fe^{2+} at H_2O_2 20 g L^{-1} .

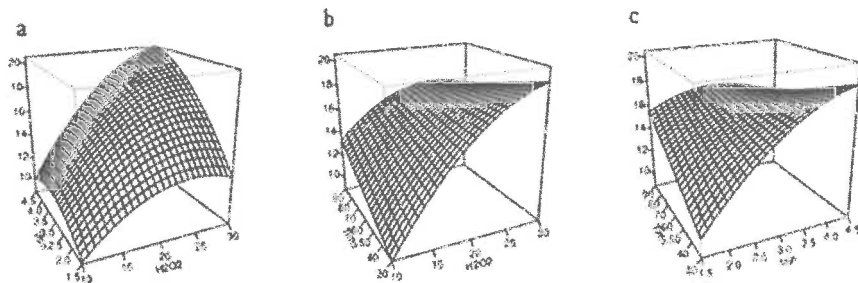


Figure 4. Three-dimension surface and contour plots for COD removal (a) effect of Fe^{2+} and H_2O_2 at 60 min, (b) effect of time and H_2O_2 at Fe^{2+} 3 g L^{-1} , (c) effect of time and Fe^{2+} at H_2O_2 20 g L^{-1} .

The study of iron and hydrogen peroxide dosage is important in the Fenton reaction, which involves the decomposition of hydrogen peroxide into OH radicals in the presence of iron ions to degrade organic matter (Walling, 1975). The amount of hydrogen peroxide required to treat an effluent increase with the organic load, but excessive hydrogen peroxide load can negatively impact organic pollutant degradation by enhancing the scavenging effect of OH radical by H_2O_2 (Ertugay & Acar, 2017). The formation of stable organic Fe^{3+} - complexes can limit the yield of organic pollutant mineralization, but this can be overcome by using UV irradiation to degrade the complexes (Malato et al. 2009). Increasing the amount of H_2O_2 increases TPh and COD removal, while increasing the concentration of Fe^{2+} increases COD removal until reaching an optimal point (Figure 3a, 4a). Excessive iron can make the solution opaque, reducing light penetration, and hindering Fe^{3+} regeneration, decreasing the rate of degradation (Bhatkhande et al. 2004). As the dosage of H_2O_2 increases, there is a significant improvement in the removal efficiency of TPh, while the impact on COD removal is smaller. However, once an optimal concentration of H_2O_2 is achieved, further increases can lead to a decrease in COD removal due to the scavenging effect of H_2O_2 and the formation of HO_2 radicals (Ertugay & Acar, 2017).

The study found that the best operational conditions for the photo-Fenton treatment of OOIEW were 60 min of treatment time, $23 \text{ g H}_2\text{O}_2 \text{ L}^{-1}$ oxidant dosage, and $3 \text{ g Fe}^{2+} \text{ L}^{-1}$ catalyst dosage. Using these conditions, the removal efficiencies of TPh and COD were 93% and 26%, respectively. In a subsequent experiment using the raw sample with these optimal conditions, the removal efficiencies of TPh and COD were 90% and 39%, respectively. The high efficiency of the photo-Fenton process in removing TPh was particularly noteworthy, as TPh is a significant pollutant in OOIEW due to its toxicity (Lanciotti et al. 2005).

4 CONCLUSIONS

This study utilized RSM to optimize the operational parameters of photo-Fenton oxidation process in order to remove COD and TPh from OOIEW. Statistical results showed that H_2O_2 and Fe^{2+} were the most influential factors for COD removal, whereas H_2O_2 was found to be the predominant factor for TPh removal. Through the experiments carried out, considering the best operational parameters applied to the photoreactor, it was possible to verify a high efficiency of the photo-Fenton process applied to the removal of TPh, in real effluent, with a removal of up to 90%. However, for COD removal, only 39% was reached.

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