FENTON-BASED TREATMENT OF WASTEWATER FROM OLIVE POMACE OIL EXTRACTION INDUSTRY

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Abstract

The olive pomace oil extraction industry generates large amounts of wastewater characterized by dark color, high suspended solid content, high turbidity, acidic pH, low biodegradability, high organic matter content, and phenolic compounds. Conventional treatments usually do not have a positive effect on pollutant removal, necessitating the use of different treatment techniques. In this sense, this work used Fenton's Advanced Oxidation Process as a means of treating these effluents, which is capable of removing mainly the organic load (90%) and phenolic compounds (>99%).

Keywords—Advanced oxidative processes, COD removal, fenton, total phenolic compounds.

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1. INTRODUCTION

Worldwide, water security is a fundamental factor for human life; however, with climate change, society's ability to have sufficient quantities of water at its disposal has been affected [1]. Humans depend on water for survival, which has always conditioned society's behavior, enabling the expansion of agriculture, hydroelectric energy production, and industrialization.

However, one of the biggest environmental problems today is the release of untreated or inadequately treated agricultural, domestic, and industrial wastewater into the water systems. This problem is alarming when wastewater sources come from industries with large or small production volumes [2], [3].

The olive pomace oil extraction industry (OPOEI) has demonstrated significant growth with an average of 4% per year, indicating its economic importance in the EU. Countries with the highest potential for olive oil (OO) production are located in the Mediterranean Sea and suffer from severe droughts and water scarcity. This climatic difficulty makes it essential to use techniques and technologies to safeguard this resource, ensure productivity, and minimize its impact on natural resources [1], [4].

The OO extraction process results in large amounts of effluents, and approximately 1 m^3 of effluent is generated per ton of processed olive, corresponding to approximately 5.4 million cubic meter per year worldwide. Spain, Italy, Greece, and Portugal stand out among the countries that produce the most OO and consequently the most significant volumes of wastewater [1], [3], [5], [6].

The wastewater from the OPOEI has variable chemical compositions, such as dark coloration, high organic content, and difficult biodegradability. This composition of wastewater from the OPOEI makes it impossible to incorporate it into conventional biological treatment systems such as aerobic and anaerobic lagoons, indicating the need for pretreatment techniques. It also contains phytotoxic and antibacterial phenolic substances, which make it impossible to dispose of effluents from conventional water and sewage treatment systems [7].

Many pretreatment techniques can modify the characteristics of OPOEI effluents at the entrance of a system, substantially reducing the initial pollutant content or eliminating unwanted substances. Among these techniques, filtration, ultrafiltration, coagulation, flocculation, electrocoagulation, and adsorption have been highlighted [8].

However, such techniques need the help of an advanced posterior treatment to improve their performance. This study aimed to use Fenton's advanced oxidative process (AOP) as an alternative for treating wastewater. This technique uses hydrogen peroxide, activated by a ferrous ion responsible for releasing hydroxyl radicals, which can oxidize organic matter and be used in effluents, such as those presented by the OPOEI industry.

2. MATERIALS AND METHODS

A. Wastewater from OPOEI

The raw effluent used in this study was obtained from a settling pond provided by an OPOEI located in the municipality of Mirandela, in the northern region of Portugal. Initially, effluent was collected from the uppermost part of the pond to avoid suspended solids. Subsequently, the effluent was sieved through a 0.5 mm sieve to remove the maximum amount of insoluble particles from the effluent. Finally, the samples were stored according to methodology *1060-Collection and Preservation of Samples* [9].

B. Fenton Process

Among the AOPs, Fenton is a process that uses the decomposition of hydrogen peroxide (H_2O_2) employing ferrous ions (Fe^{2+}, Fe^{3+}) to produce hydroxyl radicals (HO^o), which are capable of oxidizing organic matter in several industrial effluents, such as OPOEI [1], [10].

This process has the advantages of wastewater treatment, easy operation in existing plants, no energy requirement, use of readily available reagents, and operation under ambient conditions. However, there are also some disadvantages: high costs and risks related to H_2O_2 storage and transport, the need for significant chemical amounts for acidification or neutralization, and the accumulation of sludge containing iron that requires removal at the end of treatment [1], [11].

C. Fenton Procedure

All Fenton's experiments were performed by initially selecting an aliquot of the raw sample, homogenizing it at 700 rpm using a magnetic stirrer, adding the desired volume of iron sulfate (Fe^{2+}), and adjusting the pH between 2 and 4 with NaOH or H_2SO_4 solution. Later, this mixture was subjected to the jar test, where in the first 5 min at 150 rpm, the volume of H_2O_2 was added. This solution was stirred for 35 min at 80 rpm to complete the reaction. The pH of the sample was raised between 9 and 12 to stop the Fenton reaction, after which it was reserved for 24h. This time, the sludge at the bottom and the supernatant were separated, and aliquots were selected for removal analyses.

D. Analytical M FENTON FENTON ethods

The main physicochemical characteristics of the OPOEI wastewater sample were measured with (i) a pH-meter Hanna EDGE for pH, following the Standard Methods [9] obtained, (ii) Chemical Oxygen Demand (COD) from the closed reflux method (5220); (iii) Biochemical Oxygen Demand (BOD_5) from five days method (5210); (iv) Total Solids (TS), Fixed Solids (FS), and Volatile Solids (VS) using 2540-G methodology; (v) Total Phenolic Compounds (TPC) by Folin-Ciocalteu method; (vi) Total Organic Carbon obtained by SHIMADZU TOC-L analyzer; (vii) Total Nitrogen was obtained through a TN module coupled to the TOC analyzer.

E. Response Surface Methodology

Response Surface Methodology (RSM) was used to optimize the experiments in this study. For this purpose, the Box-Behnken Design (BBD) method was selected to investigate and correlate three independent parameters: H_2O_2 (X1), Fe^{2+} (X2), and pH (X3), using 15 experiments, combining the values in three levels, maximum (+1), minima (-1), and three repetitions at the center point (0) (Table I).

The sample used in the BBD assay had an initial COD of 108.5 gL^{-1}. For these H_2O_2 values, the methodology demonstrated by [12] was followed, where, for each 1 g of COD to be removed, 2.125g of H_2O_2 was needed in the solution.

TABLE I: LEVEL OF VARIABLES CHOSEN FOR THE BBD

Factor	Variable	Coded level of variable		
		-1	0	+1
X1	H_2O_2 ($g\ L^{-1}$)	21.7	120	217
X2	Fe^{2+} ($g\ L^{-1}$)	14.3	36.4	58.6
X3	pH	2	3	4

Hydrogen peroxide (37%) and Fe^{2+} (50 $g\ L^{-1}$).

For the volume of Fe^{2+}, it was decided to use the ratio between $H_2O_2:Fe^{2+}$ (gL^{-1}), where the minimum was 0.4:1 and the maximum 15:1; finally, the Fenton reaction occurs at an acidic pH, I opted to use pH values of the solution between 2 and 4. All tests were carried out at ambient temperature and pressure.

The BBD model establishes the relationship between these independent variables using second-order polynomial equation (1):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1} \sum_{i=1}^{k} \beta_{ij} X_i X_j \quad (1)$$

Where X corresponds to the independent variables that affect the response Y, the values of "β" are equivalent to the regression coefficients for the intercept (β_0), linear terms (β_i), quadratic terms (β_{ii}), and interactions (β_{ij}), and "k" corresponds to the number of variables in the system[13].

3. RESULTS AND DISCUSSION

F. Model Evaluation and Statistical Analysis

Fifteen BBD experiments were performed for three individual variables (X1 to X3), and two responses were analyzed for each experiment: COD removal and TPC removal. Table II presents the coded and noncoded variables with the experimental response values.

TABLE II: EXPERIMENTAL DATA FOR COD AND TPC REMOVAL ACCORDING TO BBD

Run	Variable			Removal (%)	
	H_2O_2 (gL^{-1})	Fe^{2+} ($g L^{-1}$)	pH	COD	TPC
1	21.7	14.3	3	30.8	62.7
2	217	14.3	3	80.5	94.5
3	21.7	58.6	3	53.8	89.1
4	217	58.6	3	90.9	> 99
5	21.7	36.4	2	49.3	85.1
6	217	36.4	2	89.0	> 99
7	21.7	36.4	4	45.5	81.4
8	217	36.4	4	88.5	> 99
9	120	14.3	2	71.8	92.4
10	120	58.6	2	80.0	96.7
11	120	14.3	4	69.3	90.0
12	120	58.6	4	82.6	96.7
13	120	36.4	3	77.3	94.7
14	120	36.4	3	77.1	94.6
15	120	36.4	3	77.3	94.8

In this experiment, the highest COD and TPC removal rates occurred when the highest amounts of hydrogen peroxide were added, similar to the experiment performed in [13].

These responses may also be associated with the amount of iron added during testing. Despite this, iron also showed interference; for example, in run 4, it had the highest removal rate for COD and >99% removal rate for TPC; however, compared to run 2, which also used the same amount of H_2O_2, with less Fe^{2+}, the COD removal rate was also lower, at approximately 80%. There was no complete removal of the TPC.

The influence of the pH on the reaction was not related to the best removal rate. For example, runs 4 (pH 3), 6 (pH 2), and 8 (pH 4) achieved approximately 90% COD removal and greater than 99% TPC removal.

The lower removal results were directly linked to the addition of a smaller amount of hydrogen peroxide in runs 1, 3, 5, and 7. Among these values, run 1 was the least efficient for COD and TPC removal, associated with a lower volume of added Fe^{2+} and H_2O_2.

Subsequently, the values presented in Table 2 are used to compute the coefficients in the mathematical models, where each Y response is calculated as a function of the importance of the three operational variables; thus, the reactions, COD removal efficiency (Y1), and TPC removal (Y2) were fitted as quadratic polynomial equations (2) and (3).

$$Y_1 = 77{,}93 + 13.89X_1 + 29.08X_2 - 1.19X_3 + 7.02X_1X_2 - 9.85X_1^2 + 20.83X_2^2 + 1.36X_3^2 \tag{2}$$

$$Y_1 = 93.27 + 11.02X_1 + 2.62X_2 - 0.14X_3 - 1.51X_1X_2 - 7.43X_1^2 - 1.61X_2^2 + 5.74X_3^2 \tag{3}$$

ANOVA was used to assess the reliability of the regression model's reliability [14]. To determine the significance of the results, the "p-value" was set below 0.05. Table III shows that all coefficients of linear effects, quadratic effects, and interaction effects of all factors H_2O_2, Fe^{2+}, and pH, for the two responses, the removal of COD and TPC.

TABLE II: EXPERIMENTAL DATA FOR COD AND TPC REMOVAL ACCORDING TO BBD

Parameter	Unit	Raw Sample	EXP 1		EXP 2	
			value	Removal (%)	Value	Removal (%)
pH		4.42	9.84	-	10.20	-
COD	g L^{-1} O_2	107.7	11.5	90	16.1	85
BOD_5	g L^{-1} O_2	14.7	4.43	70	5.63	62
Biodegradability	BOD_5/COD	0.13	0.38		0.35	
TOC	g L^{-1} C	39.4	7.7	80	9.0	77
OC	g L^{-1} C	39.94	8.02	80	9.23	77
IC	g L^{-1} C	0.555	0.28	50	0.29	59
TS	g L^{-1}	69.7	57.7	17	59.7	14
VS	g L^{-1}	39.8	7.6	81	9.0	77
TN	mg L^{-1} N	470	212	55	217	54
TPC	mg L^{-1}	7986	0	>99%	30	99.6

TABLE III: R-STUDIO'S STATISTICAL AND SENSITIVITY RESPONSES TO THE BBD TEST

COD removal		TPC removal	
R^2	0.9674	R^2	0.9323
R^2 – adjusted	0.9348	R^2 - adjusted	0.8647
p-value	0.0001*	p-value	0.0013*
Individual Variables			
	p-value		p-value
Interception	< 0.0001*	Interception	< 0.0001*
X1	< 0.0001*	X1	< 0.0001*
X2	< 0.0001*	X2	< 0.0001*
X3	0.49159	X3	0.522817
X1:X2	0.02146*	X1:X2	0.012986*
$X1^2$	< 0.0001*	$X1^2$	0.015392*
$X2^2$	0.04324*	$X2^2$	0.122358
$X3^2$	0.24797	$X3^2$	0.234526

* Significant Value

ANOVA analysis for the two responses indicated that the quadratic models successfully fitted the experimental data, with high R^2 regression coefficients (0.9674 for COD removal and 0.9323 for TPC removal). Furthermore, the R^2- adjusted showed values of 0.9348 and 0.8647, showing no inflation effect on R^2 owing to the introduction of insignificant variables; that is, the closer the values of R^2 and R^2-adjusted, the better the reliability of the responses [15]. In addition, by analyzing the variables, the p-value with the lowest value was obtained for H_2O_2, indicating its importance in the reactions.

G. Optimization and validation of the BBD analysis

Response optimization aims to determine the combination of optimal values of the variables that satisfy the objectives defined for the response. Through the R-Studio software, the stationary point can be obtained in the original units, corresponding to each parameter's optimized value, within the interaction calculation between them. Therefore, the targeted response was to obtain the most effective possible removal of COD and total elimination of TPC. About COD removal, the model showed values of 217.17 g L^{-1} [H_2O_2], 54.47 g L^{-1} [Fe^{2+}], and pH 3.43, while for TPC removal, the values obtained were 187.37 g L^{-1} [H_2O_2], 47.22 g L^{-1} [Fe^{2+}] and pH 3.01, wherein both tests, the optimized values are below the maximum initial values.

From these values, the last two tests were performed, EXP 1 using the optimized values for maximum COD removal and EXP 2 using the optimized values for the TPC removal. For both tests, 200 mL of the sample was used at room temperature and pressure in the Jar test for 40 min of total reaction. Subsequently, the final characterization of both samples was performed, as shown in Table IV.

Analyzing the results obtained in EXP 1, the COD removal was 89.3% for the quantities optimized by the software, which was very close to the maximum removal value received by the experimental design. For EXP 2, which used lower amounts of H_2O_2, COD removal (85%) was expected to be lower than that of EXP 1.

BOD_5 removal for EXP 1 was approximately 70%, reaching 4.43 g L^{-1} O_2, whereas in EXP 2, it was 62%. The lower the BOD_5 removal in proportion to the COD, the higher the biodegradability of the sample.

According to Rifi et al. [16], biodegradability refers to whether a particular substance or a set of important substances can be degraded by biological means, such as aerobic or anaerobic digestion. For this, the BOD_5:COD ratio was used; when this ratio was higher than 0.5, the effluent was highly biodegradable. Between 0.5 and 0.3, the effluent has good biodegradability, but pretreatment is recommended before making it available for biological treatment. When the effluent concentration is below 0.3, it is poorly biodegradable and may contain recalcitrant and potentially toxic compounds. Therefore, biological treatments are not recommended.

Therefore, based on the removals established in EXP 1 and EXP 2, the biodegradability index increases from 0.13 to 0.38 and 0.35, respectively, corresponding to possible biological treatment.

The removal percentages of organic matter expressed in the TOC analysis were 80% and 77% in EXP 1 and EXP 2, respectively. Most of the samples contained organic carbon (OC), which is characteristic of the activity from which the matrix originated.

When analyzing the solid group, a slight decrease in total solids was observed, consistent with Fenton's highly oxidative process. For fixed and volatile solids, both experiments showed similar behavior, reflecting a decrease in volatile solids and an increase in fixed solids. This separation process is essential because the sludge formed becomes more consistent, indicating more significant mineralization of the effluent mainly because this effluent can contain not only organic matter but also other complexes of iron and heavy metals, which require specific treatments [11].

The other target pollutant in the experiments was TPC; in EXP 2, the values were optimized for the best TPC removal, and 99.6% removal was obtained. The greater than 99% removal of TPC in EXP 1 shows that the addition of more reagents makes it possible to eliminate this compound from the effluent. The elimination of this pollutant is essential if there is an interest in subsequent biological treatment of the effluent because TPCs can function as antimicrobial agents.

4. CONCLUSION

The Fenton advanced oxidation process can remove and treat wastewater from the Olive

Pomace Oil Extraction Industry. The highest COD and TPC removal efficiencies were approximately 90 and 99%, respectively.

The use of Fenton reagents was determined based on the pollutant concentrations in the sample, mainly the COD, because the studied effluents had diverse characteristics. Among the difficulties in applying this technique is that olive pomace oil production is seasonal, resulting in an effluent formed by specific pollutant loads emitted over time, making the analyses challenging and requiring constant adaptation of the methodology, that is, whenever a new collection is made.

Using BBD, it was possible to establish values for optimal pollutant removal with hydrogen peroxide as the most effective reagent in the sample oxidation process, followed by iron as the activator of this reaction. pH was the least influential parameter for the response because it was only tested under acidic conditions, as reported in the literature.

It was also possible to improve the characteristics of the final effluent compared to the initial effluent, such as the separation of solids to obtain more defined sludges, which is crucial for more effective water treatment systems, and an increase in biodegradability, which is essential for the disposal of this effluent in subsequent treatment processes.

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