



TREATING POMACE OLIVE OIL WASTEWATER BY COAGULATION AND FENTON'S PROCESS

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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. The aim of this study was to suggest a treatment method for a genuine wastewater from an olive oil pomace extraction industry by integrating the Fenton's process with coagulation. $\text{Al}_2(\text{SO}_4)_3$ was applied for effluent coagulation at concentrations of 1000-15000 mg L^{-1} at pH 7. The optimal pH and effect of the flocculants were also investigated. The optimal condition was defined as a dosage of 9000 mg L^{-1} of $\text{Al}_2(\text{SO}_4)_3$ at pH 7, combined with a dosage of 50 mg L^{-1} of Rifloc F45. In the Fenton process, the effect of the iron ions (0.5 to 7 g L^{-1}) and the dosage of H_2O_2 (1.5 to 20 g L^{-1}) were evaluated at three different pH values (2.5, 3, and 3.5). The optimal conditions were defined as H_2O_2 20 g L^{-1} and Fe^{2+} 7 g L^{-1} at pH 3.5, and 44% COD and 82% TPh removal was achieved. Thus, coagulation followed by Fenton's process appears to be a practical solution for treating such effluents and should be considered an attractive option for full-scale OOEIW treatment.

Keywords—COD removal, Fenton process, industrial wastewater, 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 pressing [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 is then refined, blended, and bottled for distribution.

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

Wastewater discharge from olive pomace oil extraction poses a risk to 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 organic matter and remove residual pollutants [4].

Among the various pre-treatment methods, coagulation/flocculation is widely employed owing to its cost-effectiveness and ease of operation [6]. Commonly, coagulating agents consist of inorganic, synthetic organic, or natural organic polymers [7]. Coagulation has become a commonly employed tertiary treatment method in effluent treatment systems due to its ability to effectively eliminate suspended solids, organic matter, and phosphorus.

Compared with conventional treatment methods, advanced oxidation processes (AOPs) offer several advantages, including their versatility in treating a wide range of organic compounds and waste streams [8]. The Fenton process, as an AOPs, is economical and easy-to-apply. Additionally, Fenton's process does not require energy to activate hydrogen peroxide, making it a cost-effective source of hydroxyl radicals

and an easy-to-handle reagent [8]. Another significant advantage of this process is its relatively short reaction time compared to that of other AOPs [8]. Therefore, Fenton's reagent is often preferred in cases where a high reduction in organic matter is required [8].

This study aimed to reduce the concentration of pollutants in the effluent of the olive pomace oil extraction industry by utilizing coagulation/flocculation and Fenton's process as a treatment method.

2. MATERIALS AND METHODS

This study used wastewater from the olive pomace oil extraction industry obtained from a plant located in Mirandela, Portugal. This effluent is referred to as olive oil extraction industry wastewater (OOEIW). 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 5.4 and was characterized by a high level of total phenolic compounds (TPh) at 8100 mg L⁻¹, chemical oxygen demand (COD) at 22870 mg L⁻¹, biochemical oxygen demand (CBO5) at 5300 mg L⁻¹, and total solids at 15.1 g L⁻¹.

Coagulation/flocculation process

Coagulation tests were conducted on a laboratory scale using a Jar Test apparatus. In this study, aluminum sulfate (Al₂(SO₄)₃) was used for effluent coagulation. For each test, 0.1 L of OOEIW was used and the coagulant dosage was added. The pH was adjusted and then followed by rapid stirring (3 min at 150 rpm) and slow stirring (15 min at 20 rpm). The efficiency of the analysis was determined based on the removal of organic matter, as determined by COD, and TPh in the supernatant generated after 2 hours of sedimentation.

In addition, the effect of pH on this process as well as the addition of different types and concentrations of flocculants were evaluated, and the optimal conditions were determined.

Fenton's process

Fenton tests were conducted using 0.1 L of OOEIW after coagulation in the Jar Test apparatus. Following the addition of hydrogen peroxide (H₂O₂), pH correction, and iron, each test was continuously stirred at 80 rpm for 20 min. To stop the Fenton reaction at the end of the established reaction period, the pH was increased to 10. The tests were left to settle overnight, and the COD and TPh in the supernatant were subsequently determined.

3. RESULTS AND DISCUSSION

The coagulant was tested at concentrations of 1000-15000 mg L⁻¹. A pH of 7 was determined based on the optimum coagulant application range [9,10]. Fig. 1

shows the removal obtained in this step.

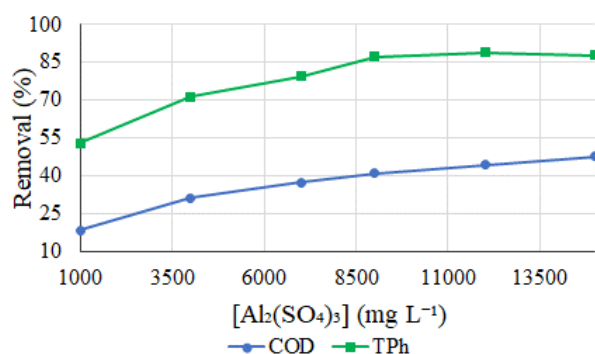


Fig. 1. The effect of the $\text{Al}_2(\text{SO}_4)_3$ coagulant on the removal of COD and TPh from OOEW through coagulation at pH 7.

The interval at which the coagulant was dosed had a noticeable effect on the removal of COD, with removal rates ranging from 19% (at 1000 mg L^{-1}) to a maximum of 48% (at 15000 mg L^{-1}). Removal of TPh was even more significant, with a maximum mean removal rate of 88% (87% for 9000 mg L^{-1} , 89% for 12000 mg L^{-1} , and 88% for 15000 mg L^{-1}).

Yazdanbakhsh et al. (2015) conducted experiments to investigate the impact of increasing $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ dosage (1000 to 6000 mg L^{-1}) at pH 10 (adjusted before coagulant addition) on the coagulation of olive oil mill wastewater (OMW) with high COD (58800 mg L^{-1}) and TPh (444 mg L^{-1}) concentrations [10]. The authors found that the maximum removals of COD and TPh were 88% and 89%, respectively. Azbar et al. (2008) worked with OMW containing 97600 mg L^{-1} of COD and 4023 mg L^{-1} of TPh [11]. At pH 7 and with 6000 mg L^{-1} of $\text{Al}_2(\text{SO}_4)_3$, the authors removed 47% of COD and 27% of TPh. This highlights the significant influence of the effluent matrix on the effectiveness of coagulation with

$\text{Al}_2(\text{SO}_4)_3$ for contaminant removal.

The hydrolysis and polymerization reactions of inorganic coagulants and flocculants such as aluminum salts, iron salts, and inorganic polymers are directly influenced by the pH level. This determines the species of hydrolysis products and their charge density [9]. When the pH is high, the concentration of hydroxide (OH^-) increases the negative charge in oily wastewater systems. This negatively affects the structure of metal iron hydrolysis products, the reaction of continuing polymerization, and ultimately leads to a decline in the coagulation performance [9].

Fig. 2 illustrates the pH effect on the removal of contaminants with $\text{Al}_2(\text{SO}_4)_3$ 9000 mg L^{-1} . The variation in pH had a significant impact on the efficiency of TPh removal, with the maximum removal achieved at pH 8, which was very close to that achieved at pH 7. However, the removal of COD did not significantly change with pH variation, with the highest removal obtained at pH 6 (37%), followed by that at pH 7 (36%).

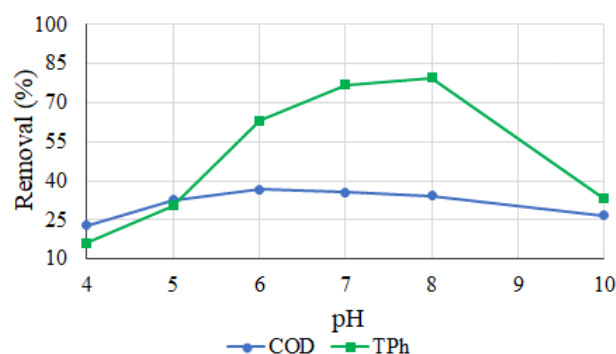


Fig. 2. Effect of pH on the removal of COD and TPh from OOEW through coagulation with $\text{Al}_2(\text{SO}_4)_3$ 9000 mg L^{-1} .

Yazdanbakhsh et al. (2015) study mentioned before investigated the impact of pH on the coagulation of OMW using $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ at a concentration of 2000 mg L^{-1} and found that increasing the pH gradually improved the removal of contaminants [10].

The authors observed a 10% increase in the process efficiency when the pH was increased from 5 to 10, and the maximum removal was achieved at pH 10, where approximately 87% of both COD and TPh were removed, which is different from the results of the

current study. It is important to note that the pH was corrected before adding the coagulant.

To improve the performance of coagulants in removing pollutants from OOEIW, coagulant aids/flocculants, which are high molecular weight polymers with a relatively low charge density, are

commonly used for particle bridging and charge neutralization [6]. In this investigation, two flocculant aids, Zetag 7587 (cationic) and Rifloc F45 (anionic), were chosen to assess coagulation efficiency at pH 6. Fig. 3 illustrates the effect of adding flocculants to the process.

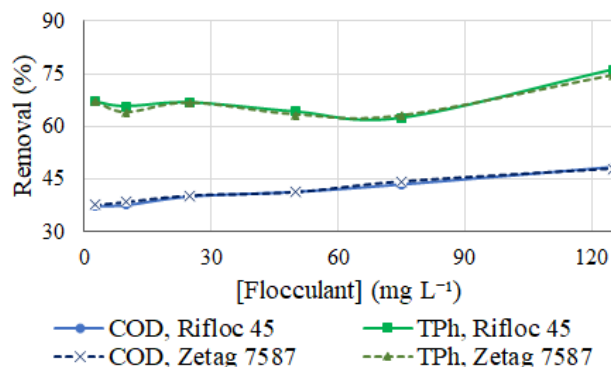


Fig. 3 COD and TPh removals from OOEIW as a function of the flocculants concentration with $\text{Al}_2(\text{SO}_4)_3$ 9000 mg L^{-1} at pH 6.

Interestingly, the type of flocculant used did not affect the removal of contaminants, as both flocculants exhibited identical removal rates. Increasing the concentration of the flocculant did not significantly improve the removal of contaminants (only approximately 10%), and for TPh, the observed removal may have been due to the dilution caused by adding the flocculant. However, the presence of flocculant greatly impacted the appearance of sludge generated during the coagulation process. The sludge changed from a fine sandy appearance to large and well-aggregated flocs. Therefore, adding an intermediate concentration of 50 mg L^{-1} of the flocculant is sufficient to enhance the coagulation process by forming well-aggregated and compacted flocs.

Based on the conducted study, the optimal condition was defined as a dosage of 9000 mg L^{-1} of $\text{Al}_2(\text{SO}_4)_3$ at pH 7, combined with a dosage of 50 mg L^{-1} of Rifloc F45. Under these conditions, the generated supernatant had a final pH of 6.8, a CBO5 of 3900 mg L^{-1} , a COD of 13711 mg L^{-1} , 351 mg L^{-1} of TPh, and total solids of 22 g L^{-1} .

Examination of the iron and H_2O_2 load is crucial in the Fenton reaction, as these parameters play a

significant role in determining the efficiency of the process in breaking down organic matter and the associated costs [8]. Consequently, it is essential to optimize the iron load, ensuring sufficient catalyst to generate hydroxyl radicals, while avoiding excessive use to prevent the formation of a large amount of iron sludge [8].

The selection of the appropriate H_2O_2 dosage is directly linked to the organic charge of the wastewater. As the organic load increases, more H_2O_2 is required for an effective treatment [8]. However, like iron dosage, there is a limit to the amount of H_2O_2 that can be added, as excessive dosages not only increase operational costs, but also reduce the effectiveness of hydroxyl radicals by reacting with H_2O_2 , leading to a decrease in the degradation of organic contaminants [8].

Fig. 4 illustrates the impact of varying Fe^{2+} concentrations at a constant concentration of H_2O_2 20 g L^{-1} at three different pH values on the removal of COD and TPh. Fig. 5 illustrates the impact of varying H_2O_2 concentrations at a constant concentration of Fe^{2+} 0.5 g L^{-1} at three different pH values on the removal of COD and TPh.

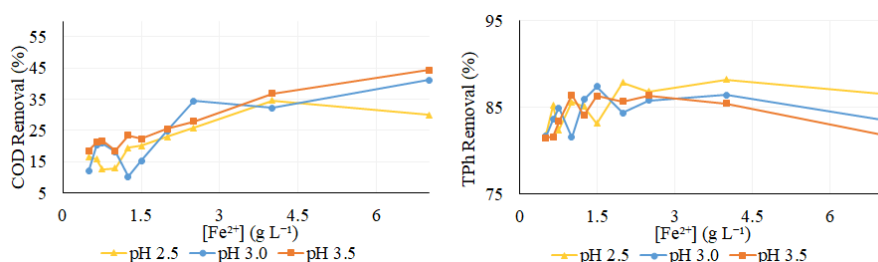


Fig. 4. The iron load effect on Fenton's reaction for OOEIW after coagulation with $[\text{H}_2\text{O}_2]$ 20 g L^{-1} .

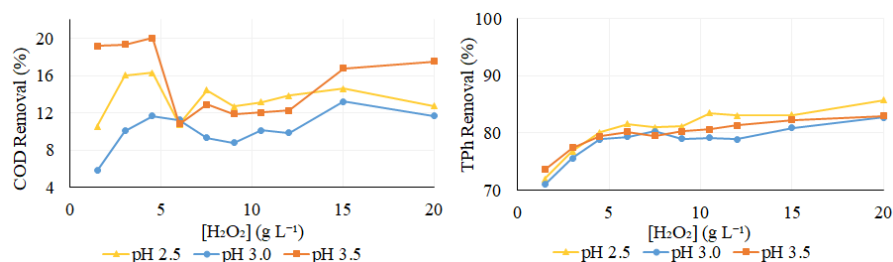


Fig. 5. Hydrogen peroxide load effect on Fenton's reaction for OOEW after coagulation with $[\text{Fe}^{2+}] 0.5 \text{ g L}^{-1}$.

The removal profiles of the contaminants obtained in Fig. 4 and 5 are similar. Fig. 4 shows that increasing the concentration of iron ions led to an increase in COD removal, with the highest COD removal rates of 41% and 44% obtained at pH 3 and 3.5, respectively (with $\text{Fe}^{2+} 7 \text{ g L}^{-1}$). A COD removal of 35% was achieved with $\text{Fe}^{2+} 4 \text{ g L}^{-1}$ and pH 2. TPh removal was more efficient, with an average removal of 85% and a maximum removal of 88% with $\text{Fe}^{2+} 4 \text{ g L}^{-1}$ and pH 2. At these conditions, COD removal was 35%, resulting in a supernatant with 9720 mg L^{-1} of COD and 55.5 mg L^{-1} of remaining TPh.

Domingues et al. (2021) also studied the effect of iron concentration with a constant H_2O_2 concentration of 4 g L^{-1} at pH 3, applying the Fenton reaction to OOEW after coagulation [8]. The authors observed a similar behavior to that observed in this study, with a maximum COD removal of approximately 40% obtained with $\text{Fe}^{2+} 2.5 \text{ g L}^{-1}$.

Regarding COD removal, increasing the H_2O_2 concentration when $\text{Fe}^{2+} 0.5 \text{ g L}^{-1}$ does not necessarily result in an increase in this parameter's removal (Fig. 5). In this test, increasing the $[\text{H}_2\text{O}_2]$ from 1.5 to 20 g L^{-1} at pH 2.5 resulted in a COD removal of 11 to 16%, 6 to 13% at pH 3.0, and 11 to 20% at pH 3.5. The maximum removal was achieved with $\text{H}_2\text{O}_2 4.5 \text{ g L}^{-1}$ at pH 3.5 (20% COD removal with 79% TPh removal). In the case of TPh removal, increasing $[\text{H}_2\text{O}_2]$ led to an increase in the contaminant removal. The average removal was 80%, with a maximum removal of 86% obtained at pH 2.5 with $\text{H}_2\text{O}_2 20 \text{ g L}^{-1}$, removing also 13% of COD and leaving 96.9 mg L^{-1} of TPh and 11910 mg L^{-1} of residual COD. In this pH range, the removal was 72%–86%, with the highest removal observed at $\text{H}_2\text{O}_2 4.5 \text{ g L}^{-1}$ for the subsequent points when increasing the H_2O_2 concentration.

In the study by Domingues et al. (2021), the peroxide dosage effect at pH 3 showed a behavior similar to that observed at pH 3 in this study, but the authors achieved higher removal rates. The best value obtained was the maximum $[\text{H}_2\text{O}_2]$ studied, at 28 g L^{-1} with 53% COD removal and $\text{Fe}^{2+} 2 \text{ g L}^{-1}$ [8].

4. CONCLUSIONS

The treatment of OOEW is crucial for the survival of the industry, as this wastewater is complex, with a high organic load and toxicity. Two technologies were

combined in this study to prepare effluents for biological treatment. Initially, a coagulant was used at a dosage of 9000 mg L^{-1} of $\text{Al}_2(\text{SO}_4)_3$ at pH 7, combined with a dosage of 50 mg L^{-1} of Rifloc F45, resulting in 31% COD and 86% TPh removal. Subsequently, the conditions of the Fenton process were optimized, and with $\text{H}_2\text{O}_2 20 \text{ g L}^{-1}$ and $\text{Fe}^{2+} 7 \text{ g L}^{-1}$ at pH 3.5, 44% COD and 82% TPh removal was achieved.

By combining these two processes, coagulation and Fenton's process, a reduction of approximately 64% COD and 96% TPh was achieved, and the toxicity of the effluent was reduced. Thus, coagulation followed by Fenton's process appears to be a practical solution for treating such effluents and should be considered an attractive option for full-scale OOEW treatment.

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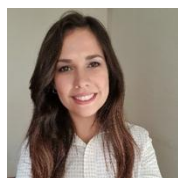
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She is the author of 16 oral/poster presentations at national/international congresses.