Treatment and Valorisation of Pomace Olive Oil Wastewater

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Abstract

Wastewater generated during the production of pomace olive oil is complex and highly variable due to different cultivation and processing characteristics. It has a high toxic organic load, low pH, and high chemical and biological demands. To reduce the concentration of chemical oxygen demand (COD) and total phenolic compounds (TPh) in pomace olive oil wastewater, several treatment processes have been studied. These include: (i) coagulation/flocculation, (ii) electrocoagulation, (iii) peroxy-electrocoagulation, (iv) electrochemical peroxidation, (v) Fenton, (vi) electro-Fenton, (vii) photo-Fenton, and (viii) adsorption. Coagulation/flocculation and electrocoagulation resulted in a maximum COD removal of 16%, while techniques involving the addition of hydrogen peroxide (iii-vii) had an average of 78% TPh removal but only 20% COD removal. Adsorption resulted in a maximum of 29% COD and 75% TPh removal. None of the tested techniques were able to remove more than 50% of COD, indicating the difficulty of removing organic matter in this effluent. However, advanced oxidation techniques were effective in degrading phenolic compounds, although they required relatively high dosages of oxidant.

Keywords: chemical oxygen demand, total phenolic compounds, coagulation, advanced oxidative processes, adsorption

Introduction

Pomace olive oil is produced from the solid residue (pomace) left over after the extraction of olive oil from olive fruits. It is a byproduct of the olive oil industry, and it is obtained through a chemical extraction process that involves the use of solvents such as hexane or petroleum ether to extract the remaining oil from the pomace [1,2].

Pomace olive oil wastewater is the wastewater generated during the production of pomace olive oil. It is a complex and toxic waste with a high organic load, low pH, and high chemical and biological demands [1-3]. It is difficult to treat and has negative impacts on the environment if not properly managed. Therefore, the treatment of pomace olive oil wastewater is important to mitigate its environmental impacts and recover valuable resources such as phenolic compounds and energy [3].

Methods

Different treatment processes have been investigated to reduce the concentration of chemical oxygen demand (COD) and the total phenolic compounds (TPh). The treatments applied individually were: (i) coagulation/ flocculation, (ii) electrocoagulation (EC), (iii) peroxy-electrocoagulation (PEC), (iv) electrochemical peroxidation (PEO), (v) Fenton, (vi) electro-Fenton (EF), (vii) photo-Fenton (PF), and (viii) adsorption. The Response Surface Methodology (RSM) examines the connections between various quantitative factors and one or more outcomes, which can be represented by an equation, being commonly applied for optimizing a given process. In this work the Box-Behnken Design (BBD) was selected to design the experiments that were examined by RMS. The process iii, iv, vi, vii and viii were worked out in this way. In these cases, Analysis of Variance (ANOVA) were used to investigate the model response to a second order polynomial model, it was used to analyze the data and determine the optimum conditions according to the final model.

All the processes were analyzed by the COD and the TPh removal in the supernatant, which was determined after two hours of decantation.

The coagulation/flocculation technique was evaluated in a range of dosage from 200 to 3000 mg L^{-1} of $Al_2(SO_4)_3$ at pH 7. Then, the effect of the best concentration found at pH 6 and 4.5 was checked. With the optimal conditions established, the dosage concentration of flocculant Ambifloc 59001 was determined. All experiments were performed in a coagulation/flocculation apparatus (jar test) with 300 mL of sample. The procedure included adding the sample, correcting the pH, stirring at 150 RPM for 3 minutes, adding the flocculant, stirring at 20 RPM for 15 minutes, and then proceeding to the settling period.

The electrocoagulation (EC) treatments were conducted with a constant electrical current density of 10 mA cm^{-2} for 60 min, with gentle stirring using a magnetic bar. Two rectangular sheets of aluminum and/or iron served as the cathode and anode electrodes in the configurations Al/Al, Al/Fe, Fe/Al, and Fe/Fe (as cathode/anode). The electrodes were placed vertically at 3.5 cm. After a minor pH adjustment to 4, the EC cell was loaded with 400 mL of wastewater.

In the PEC, PEO and EF process, the experiments were conducted in an open, cylindrical glass cell with a capacity of 600 mL. The wastewater was stirred with a magnetic bar. The processes assays were performed with 300 mL of the sample using a pair of plates electrodes, both aluminum for PEC, graphite/aluminum (cathode/anode) for PEO, and both iron for EF. In the PEC and EF process the geometric area of each electrode was 16 cm^2 and the interlectrode gap was 0.5 cm. In the PEC process, the variation in pH from 2.5 to 4.5, the dosage of hydrogen peroxide (H$_2$O$_2$) from 10 to 30 g L^{-1} and the current density from 5 to 35 mA cm^{-2} were evaluated. In the EF process were varied the same parameters, but in different ranges: pH from 2.5 to 4.5, H$_2$O$_2$ dosage from 10 to 25 g L^{-1}, and current density from 20 to 40 mA cm^{-2}. In the PEO process, the geometric area of each electrode was 10.25 cm^2 and the interlectrode gap was 1 cm. In this process, were evaluated the variation of time reaction (5 to 25 minutes), of H$_2$O$_2$ dosage (15 to 45 g L^{-1}) and of current density (5 to 30 mA cm^{-2}).

In the Fenton process, 10 H$_2$O$_2$:Fe^{+2} ratios were evaluated, with the H$_2$O$_2$ dosage ranging from 1.5 to 20 g L^{-1} and Fe^{+2} from 0.55 to 7.3 g L^{-1}, at 3 pH ranges, 2.5, 3.0 and 3.5. The order to add the reagents were evaluated too. Os ensaios foram realizados em um aparelho de coagulação/floculação (jar test) com 100 mL de amostra, agitação de 80 rpm e tempo de reação de 20 minutos.

In the study of PF treatment, experiments were conducted in a photoreactor with a total capacity of 700 mL. A continuous circulation of the solution was achieved using a peristaltic pump, and a 14 W mercury lamp emitting 254 nm light was placed at the center of the reactor. The BBD was also used in these experiments. In these experiments, the dosage of H$_2$O$_2$ was varied from 10 to 30 g L^{-1}, and Fe^{2+} from 1.5 to 4.5 g L^{-1}, while the photoreaction time was also varied. The sample was diluted ten times and its pH was adjusted to 3.5.

For the processes iii-vii at the end of the process, the pH of the samples was raised to 10 to complete the oxidation reaction.

For the adsorption process, tests were carried out with activated carbon with a granulometry of 1 to 2 mm, previously dried at 105°C for 24h. The experimental design was carried out using the BBD, varying the concentration of activated carbon from 60 to 80 g L^{-1}, the stirring speed from 100 to 300 rpm and the adsorption time from 15 to 45 minutes.

Results

Coagulation/flocculation and electrocoagulation techniques achieved similar levels of organic matter removal. In the coagulation/flocculation process, the optimal condition was obtained with a dosage of 1500 mg L^{-1} Al$_2$(SO$_4$)$_3$ and 42 mg L^{-1} Ambifloc 59001 at pH 6, resulting in a removal of about 15.8% of COD and 4.7% of TPh. In electrocoagulation, the Fe/Al configuration (iron as cathode and aluminum as anode) showed the highest COD removal of 16%, while the other configurations had removals of around 4.2%.

In the processes that involve the addition of H$_2$O$_2$, an average of 20% of COD and 78% of TPh was removed. The Fenton process showed the highest COD removal, while PF showed the highest TPh removal. PEO had the best average removal for both contaminants (Table 1).

Tab. 1. Removal of pollutants after advanced oxidation processes.

Process	Av. COD removal (%)	Highest COD removal (%)	Av. TPh removal (%)	Highest TPh removal (%)
PEC	21.6	29.4: pH 2.5; 30 g L^{-1} H$_2$O$_2$; 20 mA cm^{-2}	81.4	87.6: pH 4.5; 30 g L^{-1} H$_2$O$_2$; 20 mA cm^{-2}
PEO	23.0	29.4: 25 min; 45 g L^{-1} H$_2$O$_2$; 17.5 mA cm^{-2}	83.5	88.3: 15 min; 45 g L^{-1} H$_2$O$_2$; 30 mA cm^{-2}
Fenton	18.9	33.9: 40 H$_2$O$_2$:Fe^{+2}; pH 3.5		
EF	20.2	26.8: pH 2.5; 20 g L^{-1} H$_2$O$_2$; 20 mA cm^{-2}	76.4	87.1: pH 4.5; 25 g L^{-1} H$_2$O$_2$; 30 mA cm^{-2}
PF	14.7	21.6: 30 min; 20 g L^{-1} H$_2$O$_2$; 4.5 g L^{-1} Fe^{+2}	70.4	88.6: 90 min; 30 g L^{-1} H$_2$O$_2$; 3 g L^{-1} Fe^{+2}

The statistical significance of the Analysis of Variance (ANOVA) was evaluated to fit a second-order polynomial equation ($p < 0.05$) and generated the following contour plots (Figures 1, 3, and 4). The analysis of the electrolytic processes using aluminum plates showed similar behaviors in the removal of TPh (Figure 1. a, b). In both the PEC and PEO processes, an increase in the concentration of H$_2$O$_2$ led to a greater removal of contaminants. Additionally, the current density had no significant impact on the contaminant removal for a given H$_2$O$_2$ dosage. The processes showed similar efficiencies in removing the TPh. With regards to COD removal, the processes showed distinct behaviors but still achieved similar removal values (Figure 1. c, d).
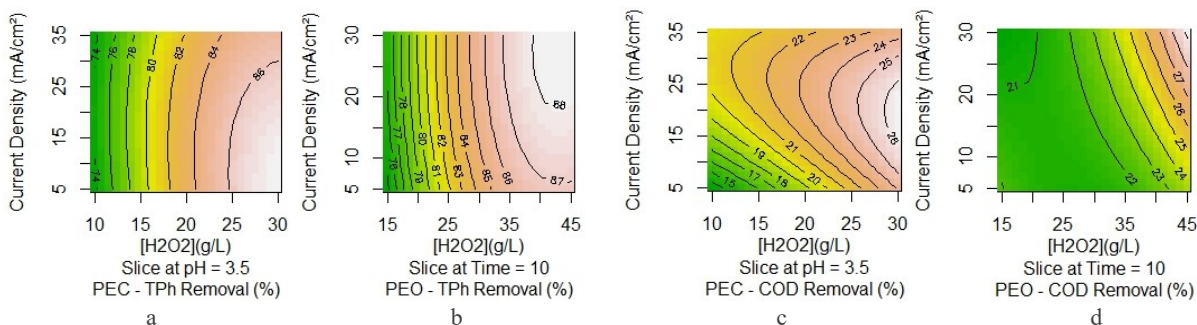

Fig. 1. Removal of COD and TPh from the effluent generated by the olive pomace oil extraction industry by PEC and PEO processes.

Figure 2 displays the behavior of organic matter removal in Fenton process in relation to the concentration H_2O_2 and Fe^{2+}. The experiments conducted yielded an average removal efficiency of 19% (Figure 2), which is similar to the efficiencies observed in other processes examined in this study. The pH values investigated exhibited a comparable removal behavior, suggesting that pH is not a significant factor affecting the process efficiency. In contrast, the concentration of reagents demonstrated more relevance, as lower concentrations of iron (Figure 2. a) resulted in better removal efficiencies. Furthermore, for H_2O_2, intermediate concentrations, such as 5 g L^{-1}, and high concentrations, such as 20 g L^{-1}, also produced satisfactory results (Figure 2. b).
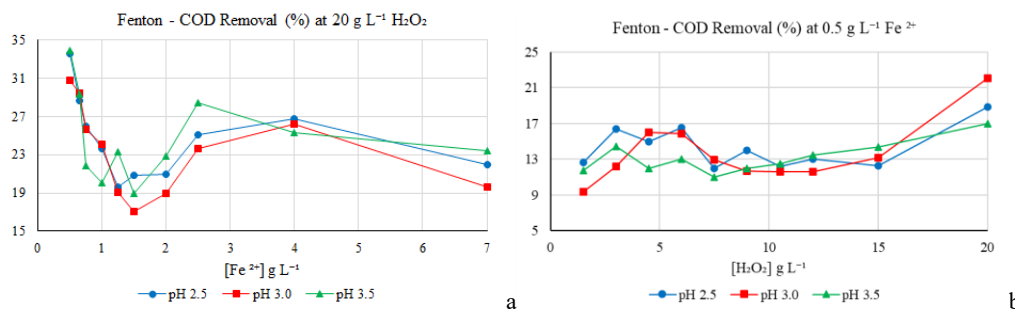

Fig. 2. Removal of COD from the effluent generated by the olive pomace oil extraction industry by Fenton process.

As the current density is responsible for the availability of iron ions in the reactive medium in EF (Figure 3. b, d), this parameter was considered analogous to the iron concentration in Fenton (Figure 2. a) and PF processes (Figure 3. a, c). The EF and PF processes showed opposing behaviors in the removal of COD (Figure 3. a, b), while there is a trend in increasing removal with increasing iron and H_2O_2 concentration in the PF process (Figure 3. a), in EF, decreasing the availability of iron and increasing H_2O_2 dosage results in superior contaminant removal (Figure 3. b). In the removal of TPh, the EF and PF processes displayed very similar contour plots (Figure 3. c, d). The results show that the concentration of iron or current density did not significantly affect the removal of contaminants. However, the efficiency of these processes was greatly improved by increasing the H_2O_2 dose.
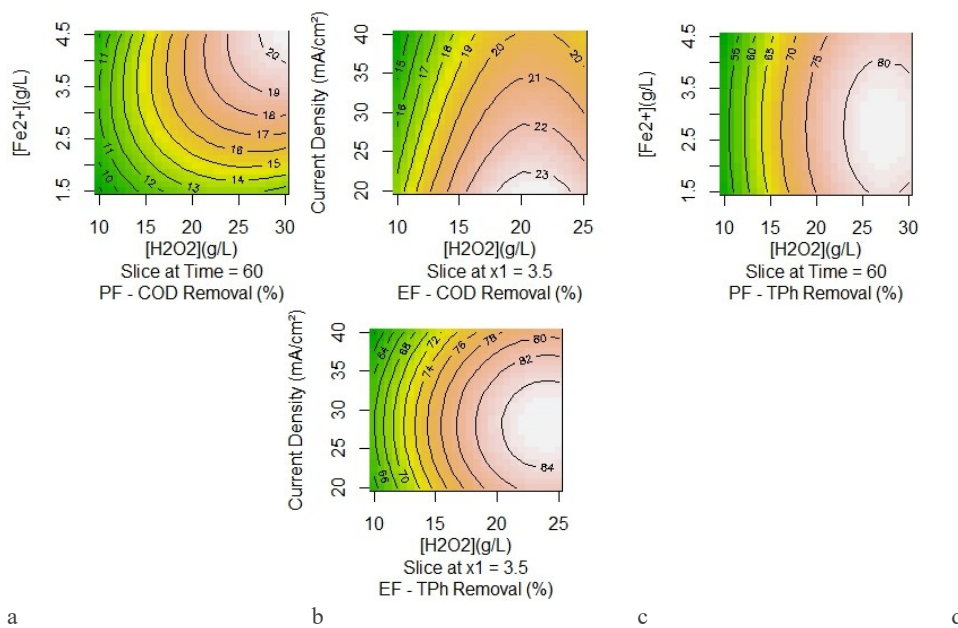

Fig. 3. Removal of COD and TPh from the effluent generated by the olive pomace oil extraction industry by PF and EF processes.

The adsorption technique also showed effectiveness in the removal of pollutants, removing an average of 18.47% of COD and 65.37% of TPh. The condition that achieved the highest removal was one in which 80 g L^{-1} activated carbon was used, agitated at 200 rpm for 45 minutes. Under these conditions, a removal of 29.2% of COD and 75.1% of TPh was achieved.

The results presented in Figure 4 illustrate the contour curves obtained from the adsorption experiments with regard to the parameters studied in the adsorption system. The analysis reveals that the adsorption time and activated carbon concentration exerted similar influences on the removal of the studied contaminants (COD and TPh) (Figure 4. a, b). However, regarding stirring speed, the results showed that, for the same concentration of activated carbon, COD removal was more efficient at lower speed, while removal of the TPh was more efficient at higher speed (Figure 4. c, d). It is important to note, however, that the activated carbon concentration exerted a more significant influence on contaminants removal than stirring speed.

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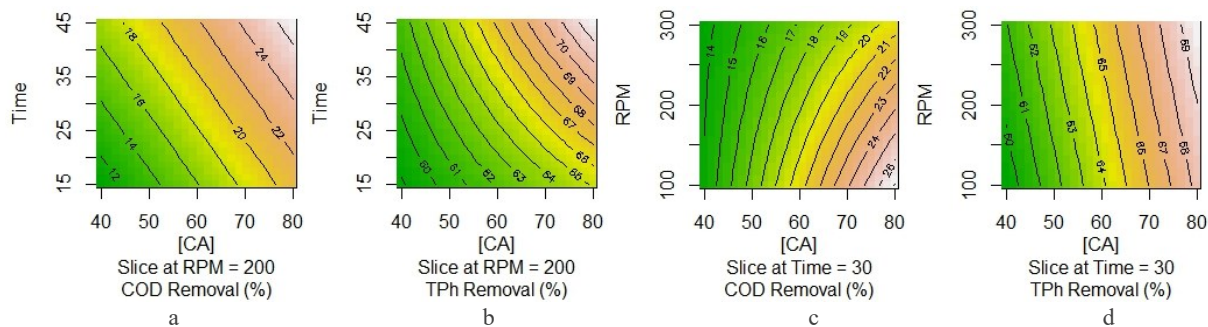
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Fig. 4. Removal of COD and TPh from the effluent generated by the olive pomace oil extraction industry by adsorption process.

The coagulation/flocculation and electrocoagulation processes achieved COD removals of 16%, like the results found in other studies [4], which worked with the same type of effluent and achieved a 12.5% COD removal with 80 mg L^{-1} of PDADMAC at pH 9. Statistical analyses of the processes using experimental planning with the Box-Behnken Design and the addition of hydrogen peroxide showed that the concentration of H_2O_2 was the most relevant factor in increasing the removal of phenolic compounds in all cases. The 34% COD removal in the Fenton process was slightly higher than that found in [4], which obtained a 30% removal with 4 g L^{-1} of H_2O_2 and 2 g L^{-1} of iron in an effluent of the same type.

Although the contaminant removals achieved, the treatments applied individually are not sufficient to make the effluent suitable for discharge into water bodies. Therefore, the application of series processes may be a viable treatment solution for this type of effluent in the future.

Conclusion

The pomace olive oil wastewater has proven difficult to treat, with none of the tested techniques able to remove more than 50% of the COD. Advanced oxidation techniques involving the addition of hydrogen peroxide were effective at removing phenolic compounds but required high dosages of it. The complexity of the wastewater made it challenging to remove COD, while advanced oxidation techniques were effective at degrading phenolic compounds.

Acknowledgments

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