Advancements in treatment and valorisation of pomace olive oil wastewater

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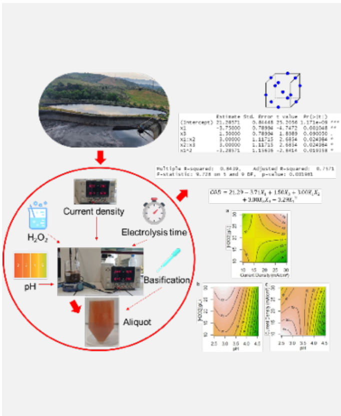

Wastewater from pomace olive oil production is complex and variable due to diverse cultivation and processing characteristics, with a high toxic organic load, low pH, and significant chemical and biological demands. To address this, multiple treatment methods have been studied, such as coagulation/flocculation (i), electrocoagulation (ii), peroxy-electrocoagulation (iii), electrochemical peroxidation (iv), Fenton (v), electro-Fenton (vi), photo-Fenton (vii), and adsorption (viii). Methods (i) and (ii) achieved up to 16% COD removal, while methods involving hydrogen peroxide (iii-vii) averaged 78% TPh removal but only 20% COD removal. Adsorption yielded a maximum of 29% COD and 75% TPh removal. All the methods were within 50% COD removal, highlighting the challenge of organic matter removal. Nonetheless, advanced oxidation techniques effectively degraded phenolic compounds, albeit requiring relatively high oxidant dosages.

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 by-product of the olive oil industry, and it is obtained through a chemical extraction process that involves using solvents such as hexane or petroleum ether to extract the remaining oil from the pomace [1,2].

Pomace olive oil wastewater is generated during the production of pomace olive oil. It is a complex, toxic waste with a high organic load, low pH, and high chemical and biological demands [1-3]. It isn't easy to treat and negatively impacts the environment if not properly managed. Therefore, treating pomace olive oil wastewater is essential to mitigate environmental impacts and recover valuable resources such as phenolic compounds and energy [3].

Material and Methods

Various treatment processes were tested to reduce chemical oxygen demand (COD) and total phenolic compounds (TPh). These included coagulation/flocculation, electrocoagulation (EC), peroxy-electrocoagulation (PEC), electrochemical peroxidation (PEO), Fenton, electro-Fenton (EF), photo-Fenton (PF), and adsorption. Response Surface Methodology (RSM) and Box-Behnken Design (BBD) were employed to optimise the experiments. For coagulation/flocculation, experiments were conducted with $Al_2(SO_4)_3$ dosages ranging from 200 to 3000 mg L^{-1} at pH 7, then at optimal concentrations at pH 6 and 4.5. EC treatments used a constant current density of 10 mA cm^{-2} for 60 min, with Al or Fe electrodes. PEC, PEO, and EF experiments were performed in glass cells with variations in parameters such as pH, hydrogen peroxide (H2O2) dosage, and current density. In the Fenton process, different H_2O_2:Fe^{+2} ratios were tested. PF experiments were conducted in a photoreactor with varying H_2O_2 and Fe^{2+} concentrations. Adsorption tests used activated carbon with varying concentrations, stirring speeds, and adsorption times. After the processes, samples were adjusted to pH 10 to complete oxidation reactions for PEC, PEO, EF, PF, and adsorption.

Results and Discussion

Coagulation/flocculation and electrocoagulation achieved similar organic matter removal. Optimal coagulation/flocculation: 1500 mg L^{-1} $Al_2(SO_4)_3$, 42 mg L^{-1} Ambifloc 59001, pH 6, resulting in 15.8% COD, 4.7% TPh removal. Fe/Al electrocoagulation configuration had the highest COD removal (16%), with others around 4.2%.

In the processes that involve the addition of H_2O_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).

ANOVA was used to fit a second-order polynomial equation ($p < 0.05$), generating contour plots (Figures 1, 3, and 4). Electrolytic processes with aluminium plates showed similar behaviours in TPh removal (Figure 1a, b). Both PEC and PEO processes exhibited increased contaminant removal with higher H_2O_2 concentrations, with current density having no significant impact. Processes had similar efficiencies in TPh removal. For COD removal, processes showed distinct behaviours but achieved identical values (Figure 1c, d).

Table 1. Removal of pollutants after advanced oxidation processes.

Process	COD removal (%)	Highest COD removal (%)	TPh removal (%)	Highest TPh removal (%)
PEC	21.6	29.4: pH 2.5; 30 g L^{-1} H_2O_2; 20 mA cm^{-2}	81.4	87.6: pH 4.5; 30 g L^{-1} H_2O_2; 20 mA cm^{-2}
PEO	23.0	29.4: 25 min; 45 g L^{-1} H_2O_2; 17.5 mA cm^{-2}	83.5	88.3: 15 min; 45 g L^{-1} H_2O_2; 30 mA cm^{-2}
Fenton	18.9	33.9: 40 H_2O_2:Fe^{+2}; pH 3.5		
EF	20.2	26.8: pH 2.5; 20 g L^{-1} H_2O_2; 20 mA cm^{-2}	76.4	87.1: pH 4.5; 25 g L^{-1} H_2O_2; 30 mA cm^{-2}
PF	14.7	21.6: 30 min; 20 g L^{-1} H_2O_2; 4.5 g L^{-1} Fe^{+2}	70.4	88.6: 90 min; 30 g L^{-1} H_2O_2; 3 g L^{-1} Fe^{+2}

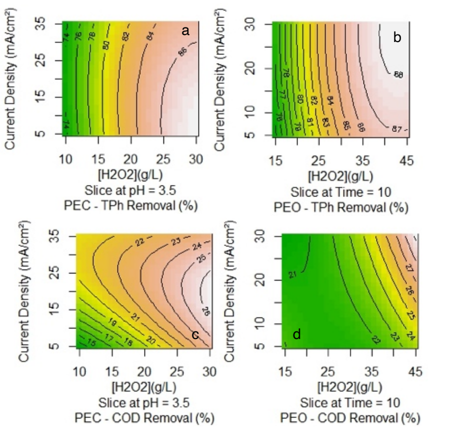

Figure 1. Removal of COD and TPh from the effluent generated by the olive pomace oil extraction industry by PEC and PEO processes.

Figure 2 shows that reagent concentration influences organic matter removal more than pH in the Fenton process. The average removal efficiency was 19%, with lower iron concentrations and intermediate to high H_2O_2 concentrations yielding the best results.

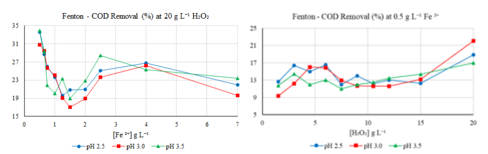

Figure 2. COD removal from olive pomace oil extraction industry effluent using the Fenton process.

In EF (Figure 3b, d), current density influences iron ion availability, analogous to iron concentration in Fenton (Figure 2a) and PF (Figure 3a, c). EF and PF exhibit contrasting COD removal trends (Figure 3a, b). At the same time, PF shows increased removal with higher iron and H2O2 concentrations (Figure 3a), and EF has superior removal with decreased iron availability and increased H2O2 dosage (Figure 3b). For TPh removal, EF and PF show similar contour plots (Figure 3c, d). Results indicate that iron concentration or current density minimally affected contaminant removal, with process efficiency, greatly enhanced by higher H_2O_2 doses.

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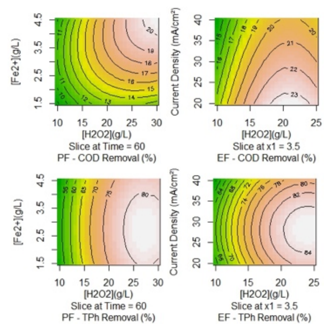

Figure 3. Removal of COD and TPh from olive pomace oil effluent using PF and EF processes.

Conclusions

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. AOP involving the addition of hydrogen peroxide was effective at eliminating phenolic compounds but required high dosages. The complexity of the wastewater made it challenging to remove COD, while advanced oxidation techniques effectively degraded phenolic compounds.

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