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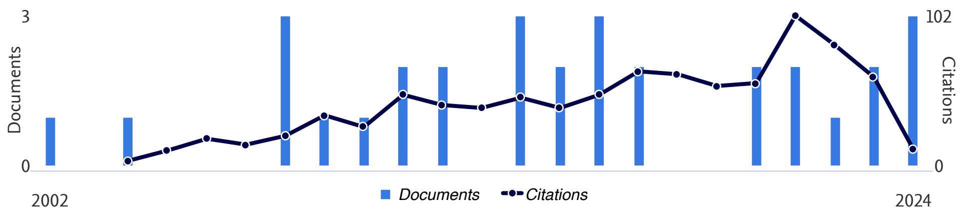

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Edited by

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WASTES: Solutions, Treatments and Opportunities IV – Vilarinho, Castro & Quina (eds)
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Coagulation treatment for olive oil pomace extraction wastewater

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ABSTRACT: The European industry is well-established in the production of olive oil. The valorization of olive pomace by extraction generates pollutant effluent because of waste leaching and processing in these extractor units (OOEIW). The goal of this study was to use the coagulation process to treat OOEIW. The effects of five different coagulants, pH, and flocculant addition were also investigated. $Al_2(SO_4)_3$, $FeCl_3$ and $MgCl_2$ achieved maximum removal of 98% total phenolic compounds (TPh) and 46% chemical oxygen demand (COD). pH had a significant effect on TPh removal with $Al_2(SO_4)_3$. Flocculant addition had little impact on pollutant removal but enhanced sludge appearance. The optimal coagulation conditions were 9 g L^{-1} $Al_2(SO_4)_3$, pH 7, and 50 mg L^{-1} Rifloc F45, resulting in the removal of 40% of COD and 80% of TPh.

1 INTRODUCTION

The olive oil industry is a long-established sector in Europe that employs various techniques for olive oil production, including two- and three-phase continuous methods (Domingues et al. 2022). These techniques generate both liquid and solid wastes, namely, olive oil mill wastewater (OMW) and olive pomace (Domingues et al. 2022). Typically, OMW is treated via evaporation in open ponds, which can lead to significant environmental problems and necessitate large land areas (Missaoui et al. 2017). Olive pomace, which is the primary by-product, is subjected to a second extraction process that removes any remaining oil with an organic solvent (Domingues et al. 2022). The resulting exhaust pomace is utilized as a fuel in the industry (Martins et al. 2022). The wastewater produced during olive oil extraction, known as olive oil extraction industry wastewater (OOEIW), requires treatment, although the optimal treatment method is yet to be determined (Domingues et al. 2021 & 2022, Martins et al. 2022). Several treatment approaches have been explored, including (I) biological processes (aerobic and/or anaerobic operations), (II) physicochemical techniques (coagulation-flocculation), and (III) advanced oxidation processes such as photocatalysis, Fenton/photo-Fenton reactions, ozonation, and electrochemical methods like anodic oxidation and electro-Fenton (Domingues et al. 2021 & 2022, Martins et al. 2022).

Among various pre-treatment methods, coagulation/flocculation is widely employed due to its cost-effectiveness and ease of operation (Khouni et al. 2020). Commonly, coagulating agents consist of inorganic, synthetic organic, or natural organic polymers (Rifi et al. 2022). 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. Coagulation involves destabilizing particles using a coagulant, flocculant, or a combination of both (Rifi et al. 2022). Generally, coagulants are utilized to counteract the negative charges present on oil particles, thereby reducing the electrostatic repulsion from the electrical double layer and

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enhancing particle agglomeration at the interface (Rifi et al. 2022). The main objective of this study is to optimize the coagulation process for treating wastewater from the olive pomace oil extraction industry. To optimize the coagulation process, the efficiency of various coagulants was tested. The effect of pH on this process was evaluated along with the addition of different types and concentrations of flocculants. Finally, optimal conditions were determined and characterized.

2 METHODS

2.1 *Sampling of OOEIW*

To conduct the experiments, effluent was collected on January 3, 2023, from an olive pomace oil extraction plant in Mirandela (northeastern Portugal). This industrial unit receives olive pomace mostly from two-phase olive oil extraction units. The samples were taken from the stabilization and evaporation pond, sieved (0.5 mm) to remove coarse solids, and stored in closed plastic containers at room temperature in the laboratory until coagulation/flocculation tests were performed. The collected OOEIW has a pH of 5.4, a concentration of biochemical oxygen demand (BOD_5) of 5300 mg L^{-1}, an alkalinity of 1992 mg $CaCO_3$ L^{-1}, a chemical oxygen demand (COD) of 22870 mg L^{-1}, a concentration of total phenolic compounds (TPh) of 2426 mg L^{-1}, a total organic carbon (TOC) concentration of 10647 mg L^{-1}, a total carbon (TC) concentration of 10828 mg L^{-1}, a total nitrogen (TN) concentration of 130 mg L^{-1}, a total solids (TS) concentration of 15 g L^{-1}, and a volatile solids (SV) concentration of 9 g L^{-1}.

2.2 *Coagulation process*

Coagulation tests were conducted on a laboratory scale using a Jar-test apparatus. In this investigation, the following salts were tested as coagulants: aluminum sulfate ($Al_2(SO_4)_3$), calcium chloride ($CaCl_2$), iron chloride ($FeCl_3$), iron sulfate ($FeSO_4$), and magnesium chloride ($MgCl_2$). For each test, 0.1 L of OOEIW was used and the coagulant dosage was added. The pH was adjusted followed by rapid stirring (5 min at 150 rpm) and slow stirring (15 min at 20 rpm). The efficiency of the treatment was assessed based on the removal of organic matter, as determined by the COD and TPh in the supernatant generated after 2 h of sedimentation.

In addition to investigating the efficiency of coagulation using different coagulants, 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.

3 RESULTS

3.1 *Screening of various coagulants*

Coagulants were tested at two dosage ranges: low concentrations (100-600 mg L^{-1}) and high concentrations (1000-15000 mg L^{-1}). pH was determined based on the optimal application range of each coagulant. $Al_2(SO_4)_3$ was tested at pH 7 (Zhao et al. 2021, Yazdanbakhsh et al. 2015), $CaCl_2$ at pH 7 (AlMubaddal et al. 2009), $FeCl_3$ at pH 8 (Zhao et al. 2021, Yazdanbakhsh et al. 2015), $FeSO_4$ at pH 8 (Almojjly et al. 2018), and $MgCl_2$ at pH 11 (Xin-Hui Su et al. 2016).

Figure 1a shows the COD removal obtained when dosing low concentrations of coagulants, while Figure 1b shows the TPh removal achieved in this process. Figure 2 shows the removal efficiencies obtained when dosing with high concentrations of coagulants. Figure 2a shows the COD removal in this process, and Figure 2b shows the TPh removal in this process).

Overall, increasing the coagulant concentration resulted in a slight improvement in the COD removal for all coagulants, with the most significant improvements observed for $Al_2(SO_4)_3$, $CaCl_2$, and $MgCl_2$. However, the COD removal efficiency remained low, averaging 16% across all low-dose tests, with a standard deviation of 3%. Regarding the removal efficiency of phenolic compounds, $Al_2(SO_4)_3$, $CaCl_2$, and $FeCl_3$ showed similar performances,

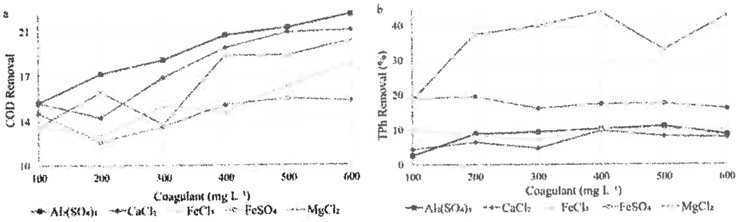

Figure 1. The impact of low-dosage of inorganic coagulants on the removal of COD and TPh from OOEIW through coagulation process. $Al_2(SO_4)_3$ and $CaCl_2$ at pH 7, $FeCl_3$ and $FeSO_4$ at pH 8, $MgCl_2$ at pH 11.

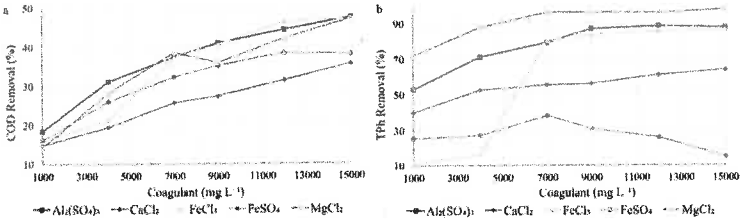

Figure 2. The impact of high-dosage of inorganic coagulants on the removal of COD and TPh from OOEIW through coagulation process. $Al_2(SO_4)_3$ and $CaCl_2$ at pH 7, $FeCl_3$ and $FeSO_4$ at pH 8, $MgCl_2$ at pH 11.

with an average removal of 8% and a standard deviation of 2%. For $FeSO_4$ at low doses, increasing the coagulant concentration did not significantly affect the phenolic compound removal efficiency, with an average of 18% and a standard deviation of 2%. $MgCl_2$ demonstrated considerable TPh removal efficiency, with an average of 40% and a standard deviation of 4% in the range of 200–600 mg L^{-1}. However, increasing the concentration beyond this range did not result in a significant improvement in efficiency.

A higher dose of coagulant was found to have a significant impact on COD removal, with a maximum removal of 47%. Among the coagulants tested, $Al_2(SO_4)_3$, $FeCl_3$, and $MgCl_2$ exhibited more intense COD removal than $FeSO_4$ and $CaCl_2$. The latter showed a weaker response to increasing coagulant concentration, resulting in lower efficiency in removing the contaminant through coagulation. The removal of TPh was even higher, reaching an average maximum removal of 91% using $Al_2(SO_4)_3$, $FeCl_3$, and $MgCl_2$ as coagulants. In this indicator, $CaCl_2$ showed better efficiency than $FeSO_4$, which had a maximum removal of 38% compared to the lowest obtained by $CaCl_2$ of 40% in the high dose range.

Yazdanbakhsh et al. (2015) conducted experiments to investigate the impact of increasing $Al_2(SO_4)_3{\cdot}_{18}H_2O$ dosage (ranging from 1000 to 6000 mg L^{-1}) at pH 10 (adjusted before coagulant addition) on the coagulation of OMW with high COD (58800 mg L^{-1}) and TPh (444 mg L^{-1}) concentrations. The authors found that the maximum removals of COD and TPh were 88% and 89%, respectively. In contrast, $FeCl_3$ at a concentration of 3000 mg L^{-1} showed the highest removal efficiency (92%) for both parameters at pH 6, and the efficiency remained constant thereafter. It should be noted that the pH correction in the study by Yazdanbakhsh et al. was performed before coagulant addition.

Iakovos et al. (2016) investigated the treatment of OMW with COD ranging from 40933 to 82450 mg L^{-1} and TPh from 1980 to 2992 mg L^{-1}. The application of 10000 mg L^{-1} of $FeCl_3$ removed 43% of COD, while the combination of the same coagulant with 400 mg L^{-1} of Floccan 23/20 resulted in a removal of 38%. The authors also applied $CaCl_2$ to treat OMW, achieving a 25% reduction in COD and a 10% reduction in TPh with 10000 m L^{-1} coagulant. When 7000 mg L^{-1} of $MgCl_2$ was applied, 23% of the COD was removed, but only 8% of the TPh was removed.

Azbar et al. (2008) worked with OMW containing 97600 mg L^{-1} of COD and 4023 mg L^{-1} of TPh. At pH 7 and with 6000 mg L^{-1} of coagulant, the authors removed 27% of COD and

19% of TPh with $FeCl_3$, 47% of COD and 27% of TPh with $Al_2(SO_4)_3$, and 30% of COD and 53% of TPh with $FeSO_4$.

Ginos et al. (2006) treated OMW containing 61000 mg L^{-1} of COD and 3500 mg L^{-1} of TPh through coagulation assays. The application of 1000 mg L^{-1} of Mg salts removed less than 10% of the COD and approximately 30% of the TPh. The use of Fe (II) salts resulted in the removal of approximately 15% of COD and 20% of TPh, while the best COD removal was achieved with Fe (III) salts, which removed approximately 50% of COD and 15% of TPh.

3.2 *Effect of pH*

The pH has a direct impact on the hydrolysis and polymerization reaction of inorganic coagulants/flocculants such as aluminum salts, iron salts, and inorganic polymers, which determine the existing species of hydrolysis products and charge density (Zhao et al. 2021). In the case of high pH, the concentration of hydroxide (OH^-) increases the negative charges in oily wastewater systems, which subsequently affects the structure of metal iron hydrolysis products, the reaction of continuing polymerization, and ultimately results in a deterioration of the coagulation performance (Zhao et al. 2021).

Figure 3 illustrates the effect of pH on the removal of contaminants for both $Al_2(SO_4)_3$ and $FeCl_3$ at a constant dose of 9000 mg L^{-1}. The variation in pH had a significant impact on the TPh removal efficiency for $Al_2(SO_4)_3$, with the maximum removal achieved at pH 8, which is 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%). For $FeCl_3$, under the tested conditions, the highest pH reduced the efficiency of TPh and COD removal, with pH values varying from 5 to 8 having little influence on the achieved results.

Yazdanbakhsh et al. (2015) investigated the impact of pH on the coagulation of OMW (with COD and TPh concentrations of 58800 mg L^{-1} and 444 mg L^{-1}, respectively) using $Al_2(SO_4)_3 \cdot 18H_2O$ at a concentration of 2000 mg L^{-1}. The authors found that increasing the pH gradually improved the removal of contaminants, resulting in an approximately 10% increase in process efficiency when the pH was increased from 5 to 10. In their study, the maximum removal was achieved at pH 10, where approximately 87% of both the COD and TPh were removed, which is different from the results of this study. It is important to note that the pH was corrected before adding the coagulant. In another experiment where $FeCl_3$ was used at a concentration of 2000 mg L^{-1}, the maximum removal was achieved at pH 6, which is consistent with the findings of this study, where pH variation did not significantly affect the efficiency of contaminant removal.

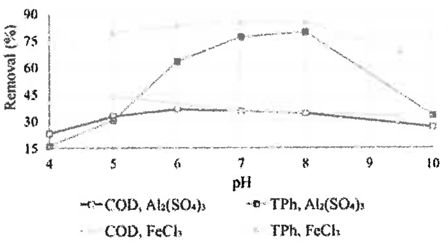

Figure 3. pH effect on the removal of COD and TPh from OOEIW through coagulation process with $Al_2(SO_4)_3$ 9000 mg L^{-1} or $FeCl_3$ 9000 mg L^{-1}.

3.3 *Use of flocculant*

To increase the coagulation efficiency and improve the performance of coagulants in removing pollutants from OOEIW, high-molecular-weight polymers with a relatively low charge density (coagulant aids/flocculants) are commonly used for particle bridging and charge neutralization (Khouni et al. 2020). In the present investigation, two flocculants (coagulant aids) - Zetag 7587

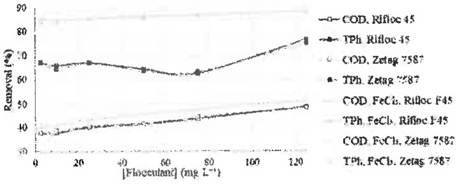

Figure 4. COD and TPh removal from OOIEW as a function of flocculant concentration, with a coagulant concentration of 9 mg L^{-1} and pH 6.

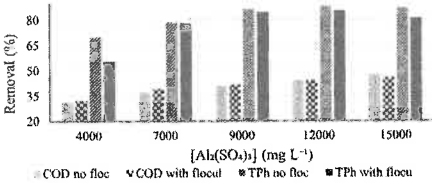

Figure 5. Comparison of the effect of adding Rifloc F45 at a concentration of 50 mg/L on the coagulation process (at pH 6 with $Al_2(SO_4)_3$) for the treatment of OOEIW.

(cationic) and Rifloc F45 (anionic) - were selected to test the coagulation efficiency using both $Al_2(SO_4)_3$ and $FeCl_3$ at a constant dosage of 9 mg L^{-1} and pH 6.

Figure 4 illustrates the effect of adding flocculants to the process. 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 underwent transformation from a fine sandy appearance to large and well-aggregated flocs. Thus, adding an intermediate concentration of flocculant (50 mg L^{-1}) was sufficient to enhance the coagulation process by producing well-aggregated and tightly packed flocs.

Figure 5 compares the removal efficiency achieved with 50 mg L^{-1} Rifloc F45 and without flocculant at different concentrations of $Al_2(SO_4)_3$ at pH 6. Again, it is clear that adding a flocculant to wastewater does not increase contaminant removal. However, it promoted the formation of larger flocs that could be more easily separated from the supernatant during the coagulation stage.

Based on this study, the optimal conditions were defined as a dosage of 9000 mg L^{-1} of $Al_2(SO_4)_3$ 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 BOD_5 of 3900 mg L^{-1}, an alkalinity of 2660 mg $CaCO_3$ L^{-1}, a COD of 13711 mg L^{-1}, 351 mg L^{-1} of TPh, a TOC of 6863 mg L^{-1}, a TC of 7001 mg L^{-1}, a TN of 138 mg L^{-1}, a TS of 22 g L^{-1}, and a VS concentration of 7 g L^{-1}.

4 CONCLUSIONS

The physicochemical coagulation/flocculation process has shown promising outcomes for treating wastewater from the olive pomace oil extraction industry. This method is cost-effective, straightforward, easy to implement, and offers a substitute for uncontrolled discharge into water bodies, contributing to serious environmental concerns. The maximum COD removal was achieved with 9 g L^{-1} of $FeCl_3$ at pH 6, combined with 125 mg L^{-1} of Zetag 7587, resulting in a 52% reduction. A 15 g L^{-1} concentration of $MgCl_2$ at pH 11 led to the highest TPh removal. The ideal condition is a dosage of 9 g L^{-1} of $Al_2(SO_4)_3$ at pH 7, combined with 50 mg L^{-1} of Rifloc F45. Using intermediate concentrations of reagents in comparison to the maximum concentrations used in this study, there was satisfactory removal of contaminants, with an average of 40% for COD with