



# Advanced oxidation processes at ambient conditions for olive oil extraction industry wastewater degradation



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## H I G H L I G H T S

- Refined oil extraction units produce a highly pollutant effluent difficult to treat.
- AOPs alone and combined were evaluated to reduce the oil extraction effluent impact.
- Fenton's process was the most efficient of AOPs used alone to treat the effluent.
- Combination of Fenton's and Ozone reaction achieve the best COD removal.
- Fenton and ozone (pH 9) achieve the best phenolic content and toxicity reduction.

## A R T I C L E I N F O

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## A B S T R A C T

The olive mills are theoretically waste free plants, at the refined oil extraction units, a highly pollutant effluent is generated. In this work the performance of different AOPs in the same multiphase reactor was evaluated to minimize real oil extraction effluent environmental impact. In terms of COD removal, the combination of Fenton and Ozone reaction simultaneously, allows the highest reduction (58.5%) although the combination of Fenton followed by ozone at pH3 lead to a similar removal, about 54%. In what regards mineralization, Fenton peroxidation alone was the most efficient process leading to 53% of TOC removal. Fenton's process presents an interesting role in the effluent treatment. However, if one bears in mind phenolic content removal and toxicity abatement, the best results were obtained by Fenton peroxidation (pH 3) followed by ozonation (pH 9). The treatment processes selection should consider the target results as well as a suitable economic analysis.

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## 1. Introduction

The olive oil production is a well-founded sector of the European industry, especially in the Mediterranean Basin, with countries such as Spain, Greece, Italy and Portugal accounting for more than two-thirds of the worldwide production (IOOC, 2020).

There are different processes used to produce olive oil, being the most common the two and three-phase continuous methods (Messineo et al., 2020). Both methods are intrinsically associated with the formation of liquid effluents, olive mill wastewater (OMW), and solid residues, olive pomace (OP), containing toxic phenolic components and high organic loads. The discharge of these wastes without treatment is a great problem for Mediter-

ranean countries (Pedrero et al., 2020). To increase the overall sustainability of the production, the OP can be further directed to an extraction process where further products are recovered. However, even if olive oil mills are going towards a green path where the wastes are being directed to other industries for valorization, a new environmental problem is raising with the production of a new olive oil extraction industry wastewater (OOEIW). The treatment of these streams is yet not fully investigated (Manzanares et al., 2020). In fact, to the best of our knowledge, there are not much works dealing with this new wastewater coming from the OP extraction units. In comparison, many technologies have been applied for the treatment of the common OMW. Biological processes are vastly explored, such as anaerobic digestion and composting, but the toxic properties of this type of effluents hinders their direct appliance (Aquilanti et al., 2014; Vuppala et al., 2019). Reverse osmosis, nano and ultrafiltration and other filtration methods have shown high efficiencies regarding organic con-

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tent removal but have the shortcoming of membranes fouling and the need of operating with low flow rates (Ioannou-Tofa et al., 2017; Sánchez-Arévalo et al., 2020), moreover, a concentrated stream with high pollutant load is produced. Coagulation and flocculation are also usually applied but mainly as a pre or post-treatment processes (Ai et al., 2020; Vuppala et al., 2019).

Advanced oxidation processes (AOPs) are also the focus of several studies due to their high efficiencies towards the treatment of different effluents (Fernandes et al., 2020). They are associated with the production of highly oxidative radicals ( $\cdot\text{OH}$ ), which can degrade a variety of pollutants (Iboukhoulef et al., 2019; Kilic et al., 2019). Ozonation and Fenton's process are very used treatment methods, occurring generally at room conditions and with simple operation (Salimi et al., 2017). Fenton peroxidation involves the formation of oxidative species through  $\text{H}_2\text{O}_2$  decomposition by an iron source at low pH values (2–4) (Domingues et al., 2019). Ozone is a very effective electron receptor and can easily interact with electron rich molecules, such as phenols, and produce  $\cdot\text{OH}$ ,  $\cdot\text{O}_3^-$  and other radicals (Gomes et al., 2017). This process generally occurs in bubbling reactors with the gas being fed to the liquid bulk through a suitable gas/liquid contactor.

As an alternative to the conventional AOPs, peroxymonosulfate (PMS) or peroxydisulfate (PS) can be used as chemical oxidants. These technologies are usually called sulfate radical based advanced oxidation processes (S-AOP). The highly reactive, short-life sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) are produced in situ by cleavage of the peroxide bond in the persulfate molecule through energy and electron transfer reactions (Genç et al., 2020). Unlike  $\text{H}_2\text{O}_2$ , persulfate can also oxidize some organics directly, without involving radical species (Shaioxiong et al., 2022). S-AOP are processes still little studied in the treatment of olive mill wastewater.

Bearing in mind the new paradigm in olive oils extraction and considering the growth in this sector, it is essential to establish suitable treatment techniques for the new effluents produced in the olive pomace extraction units the olive oil extraction industry wastewater (OOEIW).

Thus, this study aims to further investigate the treatment of the new olive oil extraction industry wastewater, applying Fenton, S-AOPs, ozonation and the combined process for the removal of phenolic compounds and organic matter, and the decrease of the effluent toxicity. To the best of our knowledge this is the first work investigating such technologies for the treatment of this novel wastewater.

## 2. Materials and methods

### 2.1. Effluent collection and characterization

The OOEIW was retrieved from an oil extraction plant in Europe. This unit receives olive mill wastes from several olive mills spread all over the country. Samples were stored in 25 L plastic containers. Prior oxidation treatment, the effluent was coagulated using 40 mg/L of a 0.1 % polydiallyldimethylammonium chloride (PDADMAC) solution, following a typical coagulation procedure described elsewhere, to reduce the organic content and turbidity

**Table 1**  
Physico-chemical parameters of OOEIW post-coagulation.

Parameters	Values ( $\pm$ SD)
COD (g/L)	33.11 $\pm$ 0.33
TOC (g/L)	8.98 $\pm$ 1.27
TPh (g GA L <sup>-1</sup> )	4.11 $\pm$ 0.33
pH	4.83
Luminescence inhibition (%) after 15 min	99.78 $\pm$ 0.05

(Amaral-Silva et al., 2017). The general physico-chemical characteristics of the OOEIW (post-coagulation) are present in Table 1.

### 2.2. Oxidation procedures

The oxidation occurred in a magnetically stirred 2 L glass reactor. In each reaction, 1.5 L of the effluent was used. For the Fenton's process, initially a certain amount of  $\text{FeSO}_4$  was added to the solution corresponding to 2 g/L of  $\text{Fe}^{2+}$  and the pH was altered to 3 using a  $\text{H}_2\text{SO}_4$  solution (0.1 M). The reactions were started by the addition of 4 g/L of  $\text{H}_2\text{O}_2$  and at the end the reaction was stopped increasing pH to 11 with some drops of NaOH solution. These conditions were previously optimized in a work of our group (Domingues et al., 2021).

Ozonation was carried out in the same reactor in a semi-batch way. While the 1.5 L of effluent were added initial to the reactor, the gaseous ozone stream was produced from a pure oxygen stream using an ozone generator (802 N, BMT) and continuously bubbled through a gas diffuser located in the bottom of the reactor. The gas inlet flowrate was kept at 0.2 L min<sup>-1</sup> and both inlet and outlet ozone concentrations were measured using BMT 963 and BMT 964 gas analyzers. Ozone process were generally conducted at pH 3 for comparative reasons. Samples were taken during reaction for further analysis.

The S-AOP experiments took place in a 500 mL spherical reactor made of glass. To this reactor, 250 mL of coagulated OOEIW was added and magnetically stirred at 500 rpm. Then, the catalyst (2 g/L of  $\text{Fe}^{2+}$  from  $\text{FeSO}_4$ ) was added without pH correction. The reaction was then started through the addition of the oxidant agent (PS or PMS). The reaction was stopped, after 120 min, by pouring drops of NaOH and  $\text{H}_2\text{SO}_4$  solution until pH7. Then, the solution was centrifuged in a Nahita centrifuge model 2655 for 5 min at 4000 rpm, and finally was filtered through a 0.45  $\mu\text{m}$  cellulose acetate filter before further analysis.

### 2.3. Analytical techniques

Chemical oxygen demand (COD) was measured following the standard method 5220D (Greenberg et al., 1985). After 2 h of digestion in a HANNA Instruments thermoreactor at 150 °C followed by cooling, the absorbances were measured at 605 nm and compared to a calibration curve with COD values within 0–5000 mg/L prepared using potassium hydrogen phthalate solutions. Total Organic Carbon (TOC) was evaluated using a TOC analyzer (TOC-5000A, Shimadzu, Japan) equipped with an autosampler (ASI-5000A, Shimadzu, Japan). The phenolic content (TPh) was determined spectrophotometrically (PG Instruments T60 spectrophotometer) using the colorimetric Folin-Ciocalteu method (Yilmaz et al., 2015).

The toxicities of the treated solutions after 120 min treatments were tested against *Allivibrio fischeri* bacteria considering their luminescence inhibition. The samples were inoculated in a LUMI-STherm at 15 °C during 15 min and compared to a blank containing a solution of 2 % NaCl. These toxicities were compared with the initial OOEIW result (Table 1).

## 3. Results and discussion

### 3.1. Processes efficiency on COD removal

Different advanced oxidation processes were studied in this work in the treatment of OOEIW, either alone or in combination. The Fenton, Ozonation, Sulfate-AOPs process were studied individually, all reactions were carried out at pH 3.

In the case of the Fenton reaction, the optimal conditions were previously optimized (Domingues et al. 2021)  $[H_2O_2] = 4$  g/L and  $[Fe^{2+}] = 2$  g/L during 120 min. For comparative purposes, S-AOPs were carried out using the same iron catalyst concentration (2 g/L) while using as oxidant PMS or PS at an initial concentration of (4 g/L).

The combination of Fenton's reaction and ozonation was also evaluated, with the Fenton reaction under the conditions indicated above but with a reaction time of 30 min followed by ozonation with a duration of 90 min, being this last process studied at pH 3 (F + O) and pH 9 (F + O pH9). The amount of residual  $H_2O_2$  after Fenton's peroxidation, which later passed to the ozone process was about 1 g/L. Fenton's process and ozonation as a simultaneous process was also evaluated (F and O), in this case the operation pH was 3.

Fig. 1 shows the evolution of COD removal along time for the various processes studied.

The process that allows the highest reduction in COD (~58.5%) is the combination of the Fenton and Ozone reaction simultaneously (F and O), although the combination of Fenton followed by ozone at pH 3 (F + O) lead to a very close removal, about 54%.

The highest COD removal by the combination of Fenton and ozone, both simultaneously and in sequence, can be explained by the presence of different oxidant species in the reaction medium. In the Fenton's process, the decomposition of  $H_2O_2$  due to the oxidation of  $Fe^{2+}$  leads to the formation of  $\cdot OH$ , being this the main actor in the degradation in these reactions. In what regards ozonation, pH is a key parameter, as it determines the extension of hydroxyl radical's formation. In acidic conditions the direct attack of ozone prevails, which is very effective towards electron-rich molecules, while in alkaline medium, ozone tends to decompose forming  $\cdot OH$ , able to degrade a wide range of pollutants (Martins and Quinta-Ferreira, 2014). Thus, the simultaneous existence of molecular ozone and hydroxyl ( $\cdot OH$ ) radicals, that can interact with different types of compounds in the effluent, promotes a higher mineralization level. This is very important due to the complexity of the real water matrix, involving different molecules with different affinities which will require different oxidant moieties to react. Moreover, the presence of the hydroxyl radical and ozone together can be a source of more hydrogen peroxide as can be seen in the

Eqs. (1) and (2) (Mehrjouei et al., 2015) as well as due to the reaction of molecular ozone with unsaturated organic bounds that will also produce  $H_2O_2$ .



On this way, as after Fenton's process iron ( $Fe^{2+}$ ) remains in the reaction medium, the production of extra hydrogen peroxide will be promoting the Fenton's reaction during ozonation. Therefore, this will allow a higher degradation of organic matter.

This may also be an explanation for the lower performance of the Fenton + Ozone at pH 9. The decomposition of ozone into hydroxyl radicals occurs at this pH which will reduce the variety of oxidant moieties and consequent reactions that remove a larger amount organic matter. In fact, at alkaline conditions the decomposition of hydrogen peroxide in water and oxygen can occur as well as the production of hydroxyl radicals via ozone decomposition. The excess of hydroxyl radicals can react with the remaining hydrogen peroxide producing hydroperoxyl radical ( $HO_2\cdot$ ) with lower oxidant power (Domingues et al., 2018). Besides, molecular ozone will not be available for the direct attack to the organic compounds. Although Fenton and ozone simultaneously had a slightly higher efficiency, in 60 min the sequence Fenton's followed by ozonation achieved 57% of COD removal which is similar to the efficiency attained when both processes are ran simultaneously. Besides, the sequential approach represents a lower injected ozone dose and consequently lower operating costs.

The ozonation process (pH 3) alone had a low COD removal (~17%), which is due to the more selective degradation of molecular ozone. In fact, this oxidant can readily oxidize molecules prone to suffer electrophilic attacks but leading to the generation of a high concentration of intermediates (mainly carboxylic acids) that cannot be further oxidized by molecular ozone due to their low electronic density (Cañizares et al., 2007; Martins and Quinta-Ferreira, 2014). Moreover, the oxidative potential of ozone is lower compared to hydroxyl radical. Regarding Fenton's, the higher performance in comparison with ozone can be explained by the already discussed tendency of the hydroxyl radicals to react with a higher variety of molecules.

As far as S-AOPs are concerned, PMS has a better result compared to PS and even ozone alone. However, the percentage of COD removed is much lower than the Fenton process and the integrated/combined processes of Fenton and Ozone. Although the reduction potential of  $SO_4^{\cdot -}$  and  $\cdot OH$  radical species are very similar, 2.5–3.1 and 2.8 V, respectively, very different efficiency results were obtained for the treatment of this real wastewater, with the hydroxyl radical being more effective in the degradation of organic matter. This result can be explained by the fact that the  $SO_4^{\cdot -}$  radical is more selective than the  $\cdot OH$  and therefore does not act with the same intensity on all organic matter (Manos et al., 2020). However, the operating conditions for the OOIEW treatment by S-AOPs were not optimized. In fact, the optimal conditions for the Fenton treatment were used to allow a direct comparison between the two techniques. Thus, before discarding the potential of S-AOPs, a processes optimization for the real effluent of OOIEW treatment is required in the future. All assays were performed in duplicate and never yielded an error greater than 8%.

### 3.2. Effluents mineralization

Since the S-AOPs had not satisfactory results for COD removal, the following study only involved Fenton's process and ozonation.

Fig. 2 shows the degree of mineralization obtained (measured as TOC removal) after 120 min of ozonation, Fenton's process and their combinations.

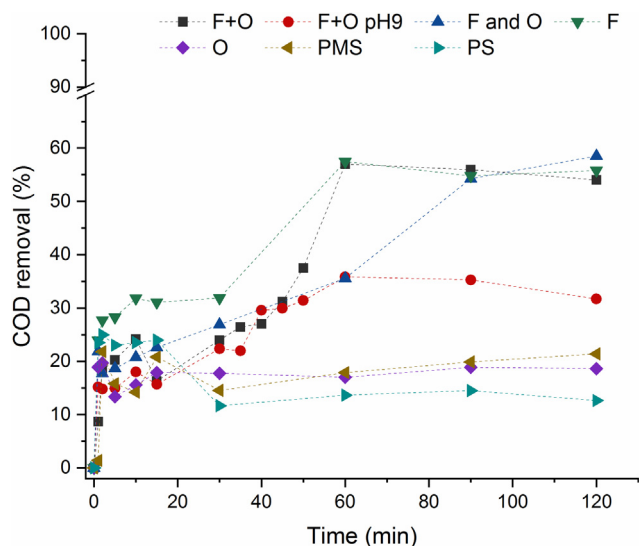
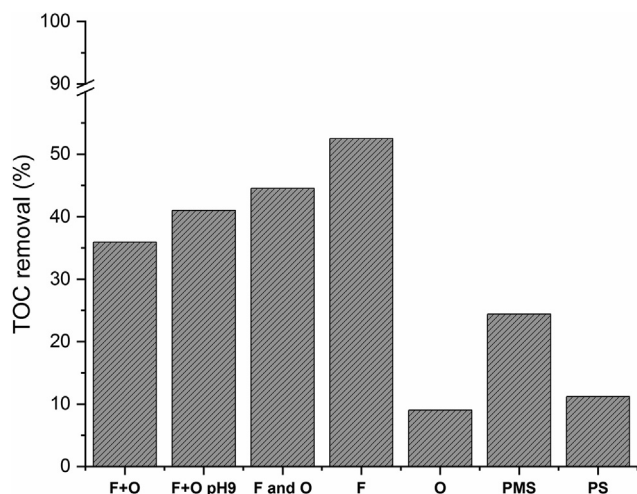


Fig. 1. Chemical oxygen demand (COD) removals during 120 min for different treatments: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).



**Fig. 2.** Total organic carbon (TOC) removals during 120 min for different treatments: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).

Differently from the results of COD removal (Fig. 1), total organic carbon removal for single Fenton's process was the highest achieved among all tested reactions (~55%). To better understand the mineralization efficiency obtained, the partial oxidation yield ( $\mu_{COD_{partox}}$ ) was calculated following Eqs. (3) and (4) (Hellenbrand et al., 1997).

$$COD_{partox} = \left( \frac{COD_0}{TOC_0} - \frac{COD}{TOC} \right) \times TOC \quad (3)$$

$$\mu_{COD_{partox}} = \frac{COD_{partox}}{COD_0 - COD} \quad (4)$$

where  $COD_0$  and  $TOC_0$  represent the initial effluent COD and TOC, respectively. COD and TOC are the treated effluent COD and TOC after 120 min of reaction and  $COD_{partox}$  indicates the COD removed through partial oxidation (i.e not towards the formation of  $CO_2$  and  $H_2O$ ).

The  $\mu_{COD_{partox}}$  may have values between 1, which indicates that the chemical oxygen demand removal is due to partial oxidation route, and 0, representing total mineralization. The calculated parameters are present in Table 2 for all the treatment strategies under evaluation.

Fenton's process had a partial oxidation yield near 0, meaning that all the removed COD is due to total mineralization, leading to the formation of  $CO_2$  and  $H_2O$ . This result corroborates the

**Table 2**

Partial oxidation yield for OOEIW treatment by the different processes: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).

Reaction	$\mu_{COD_{partox}}$
F + O	0.33
F + O (pH = 9)	0.00
F and O	0.22
F	0.00
O	0.54
PS	0.19
PMS	0.11

TOC and COD removals, as the main route of COD removal is due to mineralization, which is accounted as TOC abatement. Contrarily, ozonation is prone to promote partial oxidation without much mineralization occurring ( $\mu_{COD_{partox}} = 0.54$ ). In fact, as referred before, ozone is able to cleave high electronic density organic molecules leading to partial oxidation by-products that are no longer reactive with molecular ozone. Thus, mineralization is not the preferential route. One can observe that the partial oxidation yield is always different of 0 when ozone is present (Table 2) except for the case of Fenton + Ozone (pH = 9). In fact, for pH 9 ozone decomposition into hydroxyl radicals is promoted and these radicals preferably react in a mineralization pathway.

### 3.3. Phenolic content removal and toxicity abatement

Even with high phenolic content in the olive fruit, only a small percentage goes to the oil phase (~2%), meaning that most of these substances are present in the formed OMW (approximately 53%) and OP (approximately 45%) (Rodis et al., 2002; Cardoso et al., 2005). Phenols present a high instability when in storage, easily suffering polymerization during and producing high molecular-weight polymers with higher difficulty to be degraded (Crognale et al., 2006) besides their potential environmental impact. It is therefore essential to find a way to remove these compounds from the treated effluent. This is special important due to the high toxicity associated to these compounds. Table 3 shows the removals of TPh after each process studied.

Regarding the removal of TPh, the best solution is the combination of Fenton followed by Ozone at pH 9 (~76%). Ozone alone achieved a 64% TPh removal. Even with a lower COD removal, Fenton + Ozone at pH 9, had the highest removal of TPh (Table 3). The increase in pH to 9 alone already has a positive effect on the degradation of phenolic acids but this is not reflected in the removal of COD since intermediates are formed that are not read as COD but as COD. PMS and PS were the treatments that removed the least amount of phenolic compounds and once again the selectivity of these processes may be the justification for these results.

Although the phenolic content not being totally representative of the total organic matter present in the OOIEW, they are important pollutants in olive oil industry effluents due to its resulting problems regarding toxicity (Lanciotti et al., 2005).

As said, due to the toxicity of the phenolic compounds, it was also assessed the ecotoxicity of the treated solution towards *Allivibrio fischeri* bacteria (Table 4) and compared to the raw effluent.

The luminescence inhibition results corroborates the previously stated for the reaction at pH 9, that even still being considered toxic as it has a value higher than 30%, it leads to a considerably lower inhibition compared with the remaining solutions (Miralles-Cuevas et al., 2017). Still, it is verified that none of the

**Table 3**

Total phenolic concentration removal (%) after 120 min of different treatments: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).

Reaction	TPh Removal (%) ( $\pm$ SD)
F + O	54.1 $\pm$ 0.9
F + O (pH = 9)	74.9 $\pm$ 0.7
F and O	41.3 $\pm$ 1.3
F	30.0 $\pm$ 1.1
O	56.3 $\pm$ 0.4
PMS	18.5 $\pm$ 0.7
PS	11.7 $\pm$ 0.9

**Table 4**

Luminescence inhibition for the treated OOEIW by the different processes: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).

Reaction	Luminescence inhibition (%) after 15 min (±SD)
Coagulated Effluent	100 ± 0.05
F + O	95.68 ± 1.16
F + Oz (pH = 9)	73.44 ± 3.45
F and O	91.42 ± 0.81
F	94.31 ± 0.14
O	99.80 ± 0.03
PS	99.30 ± 0.21
PMS	99.48 ± 0.07

treatment approaches is able to satisfactorily reduce this cumbersome effluents' toxicity. But one should bear in mind that *A. fischeri* is a very sensitive species. Still further depuration shall be required before the effluents is ready to be discharged into the natural water courses. However, the high reduction on the organic charge specially promoted by the Fenton's process may allow the treated water to be directed to a municipal wastewater treatment plant to be further depurated through biological processes.

### 3.4. Operating costs estimation

In order to have a first glimpse on the treatment processes economic impact, the costs associated to the reactants applied was estimated. It should be bear in mind that the costs associated to pH changed were not considered.

The ozone production is a very important factor due to its associated cost as it involves a great energy consumption. Thus, to evaluate this component it was calculated the injected ozone dose at the end of each ozone step, according to Eq. (5), being the respective values present on Table 5.

$$IOD = \int_0^t \frac{\dot{Q}_G}{V_{Liq}} \times [O_3]_i dt \quad (5)$$

Where  $\dot{Q}_G$  is the gas flowrate (0.2 L min<sup>-1</sup>),  $V_{Liq}$  is volume of liquid used (1.5 L) and  $[O_3]_i$  is the concentration in the inlet stream.

As expected, the sequenced combined reactions (F + O) had a lower IOD as it only accounts for 90 min of ozonation in comparison to 120 min for the remaining tests. Moreover, as previously stated, Fenton + Ozone reactions reached their maximum COD removal (57 %) after only 30 min of ozone, which is related to a IOD of 63.8 mg O<sub>3</sub> L<sup>-1</sup>. This is an interesting lower value than the one obtained for other reactions, reducing the overall cost of the process and making its implementation more feasible. In fact, in this sequence ozone action is aided by hydrogen peroxide and dissolved iron that will enhance the organic matter degradation (as discussed before) not requiring a large amount of IOD.

Single ozone treatment required a considerable higher IOD. Being a very complex effluent and with a diversity of unknown substances, the existence of ozone scavengers is very likely, such as carbonates, sulfates and iodine. These substances quench ozone

**Table 5**

Injected ozone dose (IOD) at the end of the ozone step in different reactions: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9, Fenton and ozone simultaneously (F and O), ozone (O).

Reaction	IOD (mg O <sub>3</sub> L <sup>-1</sup> )
F + O	219.0
F + O (pH = 9)	229.5
F and O	251.8
O	327.2

**Table 6**

Estimated cost for each OOEIW treatment process: 30 min of Fenton followed by 90 min of ozone at pH 3 (F + O) and pH 9 (F + O pH9), Fenton and ozone simultaneously (F and O), Fenton (F), Ozone (O), Sulfate -AOPs with peroxymonosulfate (PMS) and peroxydisulfate (PS).

Process	gCOD rem/L	€/kgCOD rem
F + O	17.8	9.07
F + O pH9	10.2	15.76
F and O	19.3	9.07
F	18.4	8.76
O	6.1	0.096
PMS	7.3	0.039
PS	3.4	0.042

and radicals, producing other radicals with lower oxidative potentials, reducing the process efficiency and increasing ozone demand.

An estimate of the costs of each process was made in order to better compare the methodologies in terms of cost-effectiveness. Each treatment operating cost per gram of COD removed was also estimated considering reactants prices practiced for industries. Table 6 compares the cost of each process per kg of COD removed.

The lowest prices per kg of COD removal shown in Table 6 are for S-AOPs and Ozone. However, this analysis has to be done carefully because, although the processes studied under these particular conditions have a low cost, their efficiency in terms of COD removal is also very low. When considering the cost-benefit of the process, one can verify that the Fenton process that most removes COD per liter of effluent and the one that has a lower cost. It should be noticed that this analysis only contemplates the cost of the reagents but does not take into account the value of the equipment and the maintenance itself, which are considerably higher in processes that include ozone.

## 4. Conclusions

The solid waste produced in two phase decantation olive oil mills is nowadays sent to refined oil extraction units where further oil is extracted through drying and solid/liquid extraction processes.

The effluent produced in these extraction units is an even more concentrated stream than the conventional olive mill wastewater. To the best of our knowledge it this new effluent was never treated by advanced oxidation processes.

In this work, several advanced oxidation processes were analysed in order to identify which is the most efficient in terms of COD, TPh and ecotoxicity:

- The process that allows the greatest reduction in COD (~58.5 %) is the combination of the Fenton and Ozone reaction simultaneously;
- For TOC removal the best result is achieved with Fenton's process alone;
- Fenton plus Ozone at pH 9, had the highest removal of TPh;
- After reaction of Fenton and Ozone at pH 9, even still being considered toxic as it has a value higher than 30 %, the treated OOEIW has a considerably lower inhibition compared with the remaining solutions.

The selection of the best treatment approach must bear in mind the final destination of the effluent and the operating costs associated to each process. Thus, further work is being performed in order to understand the treated wastewater biodegradability and phytotoxicity.

In terms of cost benefit, although the S-AOPs have not been optimized, Fenton appears in this study as the most attractive technology.

## CRedit authorship contribution statement

**Eva Domingues:** Writing – original draft, Data curation, Investigation, Conceptualization, Funding acquisition. **Eryk Fernandes:** Writing – original draft, Data curation, Investigation. **João Gomes:** Writing – original draft, Writing – review & editing, Funding acquisition. **Sérgio Castro-Silva:** Writing – review & editing, Funding acquisition. **Rui C. Martins:** Writing – review & editing, Funding acquisition, Supervision.

## Data availability

No data was used for the research described in the article.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

- Ai, Y., Zhao, C., Sun, L., Wang, X., Liang, L., 2020. Coagulation mechanisms of humic acid in metal ions solution under different pH conditions: A molecular dynamics simulation. *Sci. Total Environ.* 702, 135072.
- Amaral-Silva, N., Martins, R.C., Nunes, P., Castro-Silva, S., Quinta-Ferreira, R.M., 2017. From a lab test to industrial application: scale-up of Fenton process for real olive mill wastewater treatment. *J. Chem. Technol. Biotechnol.* 92 (6), 1336–1344.
- Aquilanti, L., Taccari, M., Bruglieri, D., Osimani, A., Clementi, F., Comitini, F., Ciani, M., 2014. Integrated biological approaches for olive mill wastewater treatment and agricultural exploitation. *Int. Biodeterior. Biodegrad.* 88, 162–168.
- Cañizares, P., Lobato, J., Paz, R., Rodrigo, M.A., Sáez, C., 2007. Advanced oxidation processes for the treatment of olive-oilmills wastewater. *Chemosphere* 67, 832–838.
- Cardoso, S.M., Guyot, S., Marnet, N., Lopes-da-Silva, J.A., Renard, C.M., Coimbra, M.A., 2005. Characterisation of phenolic extracts from olive pulp and olive pomace by electrospray mass spectrometry. *J. Sci. Food Agric.* 85 (1), 21–32.
- Crognale, S., D'Annibale, A., Federici, F., Fenice, M., Quarantino, D., Petruccioli, M., 2006. Olive oil mill wastewater valorisation by fungi. *J. Chem. Technol. Biotechnol.* 81 (9), 1547–1555.
- Domingues, E., Gomes, J., Quina, M.J., Quinta-Ferreira, R., Martins, R.C., 2018. Detoxification of Olive Mill Wastewaters by Fenton's Process. *Catalysts* 8, 662.
- Domingues, E., Assunção, N., Gomes, J., Lopes, D.V., Frade, J.R., Quina, M.J., Quinta-Ferreira, R., Martins, R.C., 2019. Catalytic Efficiency of Red Mud for the Degradation of Olive Mill Wastewater through Heterogeneous Fenton's process. *Water* 11, 1183.
- Domingues, E., Fernandes, E., Gomes, J., Castro-Silva, S., Martins, R.C., 2021. Olive Oil Extraction Industry Wastewater Treatment by Coagulation and Fenton's Process. *J. Water Process Eng.* 39, 101818.

- Fernandes, E., Martins, R.C., Gomes, J., 2020. Photocatalytic ozonation of parabens mixture using 10% N-TiO<sub>2</sub> and the effect of water matrix. *Sci. Total Environ.* 718, 137321.
- Genç, N., Durna, E., Cigun, H.K.K., 2020. Response surface modelling and optimization of microwave-activated persulfate oxidation of olive oil mill wastewater. *Clean: Soil, Air, Water* 48, 1900198.
- Gomes, J.F., Costa, R., Quinta-Ferreira, R.M., Martins, R.C., 2017. Application of ozonation for pharmaceuticals and personal care products removal from water. *Sci. Total Environ.* 586, 265–283.
- Greenberg, A., Clesceri, L., Eaton, A., 1985. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, DC.
- Hellenbrand, R., Mantzavinos, D., Metcalfe, I.S., Livingston, A.G., 1997. Integration of wet oxidation and nanofiltration for treatment of recalcitrant organics in wastewater. *Ind. Eng. Chem. Res.* 36 (12), 5054–5062.
- Iboukhouef, H., Douani, R., Amrane, A., Chaouchi, A., Elias, A., 2019. Heterogeneous Fenton like degradation of olive Mill wastewater using ozone in the presence of BiFeO<sub>3</sub> photocatalyst. *J. Photochem. Photobiol., A* 383, 112012.
- Ioannou-Tfofa, L., Michael-Kordatou, I., Fattas, S.C., Eusebio, A., Ribeiro, B., Rusan, M., Amer, A.R.B., Zuraiqi, S., Waismand, M., Linder, C., Wiesman, Z., Gilron, J., Fatta-Kassinos, D., 2017. Treatment efficiency and economic feasibility of biological oxidation, membrane filtration and separation processes, and advanced oxidation for the purification and valorization of olive mill wastewater. *Water Res.* 114, 1–13.
- IOOC, 2020. IOOC (International Olive Oil Council). Retrieved from <https://www.internationaloliveoil.org/what-we-do/economic-affairs-promotion-unit/>.
- Kilic, M.Y., Abdelraheem, W.H., He, X., Kestioglu, K., Dionysiou, D.D., 2019. Photochemical treatment of tyrosol, a model phenolic compound present in olive mill wastewater, by hydroxyl and sulfate radical-based advanced oxidation processes (AOPs). *J. Hazard. Mater.* 367, 734–742.
- Lanciotti, R., Gianotti, A., Baldi, D., Angrisani, R., Suzzi, G., Mastrocola, D., Guerzoni, M.E., 2005. Use of *Yarrowia lipolytica* strains for the treatment of olive mill wastewater. *Bioresour. Technol.* 96, 317–322.
- Manos, D., Miserli, K., Konstantinou, I., 2020. Perovskite and Spinell Catalysts for Sulfate Radical-Based Advanced Oxidation of Organic Pollutants in Water and Wastewater Systems. *Catalyst* 10, 1299.
- Manzanares, P., Ballesteros, I., Negro, M.J., González, A., Oliva, J.M., Ballesteros, M., 2020. Processing of extracted olive oil pomace residue by hydrothermal or dilute acid pretreatment and enzymatic hydrolysis in a biorefinery context. *Renew. Energy* 145, 1235–1245.
- Martins, R.C., Quinta-Ferreira, R., 2014. A review on the Applications of Ozonation for the Treatment of Real Agro-Industrial Wastewaters. *Sci. Eng. 36*, 3–35.
- Mehrojoui, M., Müller, S., Möller, D., 2015. A review on photocatalytic ozonation used for the treatment of water and wastewater. *Chem. Eng. J.* 263, 209–219.
- Messineo, A., Maniscalco, M.P., Volpe, R., 2020. Biomethane recovery from olive mill residues through anaerobic digestion: A review of the state of the art technology. *Sci. Total Environ.* 703, 135508.
- Miralles-Cuevas, S., Oller, I., Agüera, A., Sánchez Pérez, J.A., Malato, S., 2017. Strategies for reducing cost by using solar photo-Fenton treatment combined with nanofiltration to remove microcontaminants in real municipal. *J. Chem. Eng.* 318, 161–170.
- Pedrero, F., Grattan, S.R., Ben-Gal, A., Vivaldi, G.A., 2020. Opportunities for expanding the use of wastewaters for irrigation of olives. *Agric. Water Manag.* 241, 106333.
- Rodis, P.S., Karathanos, V.T., Mantzavinou, A., 2002. Partitioning of olive oil antioxidants between oil and water phases. *J. Agric. Food. Chem.* 50 (3), 596–601.
- Salimi, M., Esrafilii, A., Gholami, M., Jonidi Jafari, A., Rezaei Kalantary, R., Farzadkia, M., Kermani, M., Sobhi, H.R., 2017. Contaminants of emerging concern: a review of new approach in AOP technologies. *Environ. Monit. Assess.* 189, 414.
- Sánchez-Arévalo, C.M., Jimeno-Jiménez, Á., Carbonell-Alcaina, C., Vincent-Vel, M.C., Álvarez-Blanco, S., 2020. Effect of the operating conditions on a nanofiltration process to separate low-molecular-weight phenolic compounds from the sugars present in olive mill wastewaters. *Process Saf. Environ. Prot.* 148, 428–436.
- Shaoyong, H., Yanxi, C., Xin, L., Lixi, Z., Mingshan, Z., 2022. Heterogeneous Photocatalytic Activation of Persulfate for the Removal of Organic Contaminants in Water: A Critical Review. *ACS ES&T Eng.* 2 (4), 527–546.
- Vuppala, S., Bavasso, I., Stoller, M., Di Palma, L., Vilardi, G., 2019. Olive mill wastewater integrated purification through pre-treatments using coagulants and biological methods: Experimental, modelling and scale-up. *J. Cleaner Prod.* 236, 117622.
- Yilmaz, F.M., Karaaslan, M., Vardin, H., 2015. Optimization of extraction parameters on the isolation of phenolic compounds from sour cherry (*Prunus cerasus* L.) pomace. *J. Food Sci. Technol.* 52 (5), 2851–2859.