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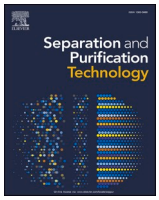

# Photo-Fenton like process as polishing step of biologically co-treated olive mill wastewater for phenols removal

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ABSTRACT

In this study, UVC or sunlight assisted photo-Fenton like process (PFI) using iron(III) iminodisuccinate (Fe-IDS) as catalyst was investigated for the first time as post-treatment method of a Moving Bed Biofilm Reactor (MBBR) for the treatment of olive mill wastewater (OMW). Hydraulic retention time for the MBBR process was 24 h, while the treatment time for the PFI process was 3 h under UVC or solar light irradiation. Before the MBBR treatment, OMW was centrifuged and mixed with synthetic urban wastewater to simulate conditions in a real wastewater treatment plant (WWTP). The MBBR was highly effective in reducing Biological Oxygen Demand ($BOD_5$) and Chemical Oxygen Demand (COD) (97 and 91%, respectively), but less effective (57%) in the removal of total phenols (TPHs). PFI was optimized for TPHs removal through response surface methodology. UVC driven PFI allowed to reach higher TPHs removal than sunlight driven PFI. Fe (III) dosage was set at 2 mg/L while optimum $H_2O_2$ dosage resulted to be 144 mg/L. In these conditions, the UVC driven process allowed to obtain a TPHs removal of 99%, reaching a final TPHs concentration of 0.07 ± 0.01 mg/L.

## 1. Introduction

Nowadays, the majority of the world's olive oil production is concentrated in the Mediterranean basin. Spain, Italy, Greece and Portugal produce about 67% of the world's olive oil [1,2]. A major environmental problem caused by olive oil production is the generation of olive mill wastewater (OMW), a mixture of olive mill residual and olive washing water [3,4]. The estimated production volume of OMW is in the range 7–30 million $m^3$/year, which results in a pollution load equivalent to 22 million people [5,6]. OMW is characterized by a quite acidic pH (3–6), a high content of solids (up to 20 g/L), strong unpleasant smell, high organic pollution (COD values up to roughly 200 g/L) and a $BOD_5$/COD ratio varying from 0.2 to 0.4 [7–9]. Although the interest towards biomass valorisation through the recovery of high value-added compounds from OMW (e.g., polyphenols) is increasing in the scientific community [10,11], such an approach is mainly under study and/or combined with wastewater treatment processes [12–15]. The common approach is the treatment in purposely designed wastewater treatment plants (for large olive mill facilities) or the transportation of OMW (for small olive mill companies) in centralized wastewater treatment plants (WWTPs).

The treatment of OMW is very difficult, firstly because of the high content of recalcitrant compounds (phenolic compounds, lignin, tannins, fatty acids, etc.), secondly because of the seasonal production of olive oil which involves a massive production of effluent in a very short time [16,17]. In addition, phenolic compounds (concentration up to 8 g/L) result in phytotoxicity and toxicity to bacteria, which make them difficult to treat by biological processes [18–20]. Accordingly, phenolic compounds have been enlisted as pollutants of priority concern by the United States Environmental Protection Agency (USEPA) and the European Union (EU) [21].

Due to these characteristics, OMW require a multi-barrier treatment in order to be discharged into the environment safely and in compliance with current regulations. Biological processes are a cheaper solution compared to other methods, but OMW should be chemically pre-treated and eventually mixed to other wastewater to drastically reduce the chemical oxygen demand (COD) and toxicity as well as to improve biodegradability before biological process [22]. Several biological

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processes have been investigated for OMW treatment, among them activated sludge processes, membrane-based processes, anaerobic digestion [23]. One limitation of activated sludge process is related to the growth of filamentous microorganisms or adverse conditions for flocs forming bacteria which result in problems known as bulking, rising and pin point that lead to poor sludge settling capacity [24,25]. Membrane-based processes are strongly limited by high operating costs, membrane fouling and short lifetimes of membranes [26]. Compared to other biological treatment methods, moving bed biofilm reactor (MBBR) has no bulking problem and can operate with a more selected biomass for each treatment step; moreover, no sludge recycling is needed and management is easier [27]. Several studies investigated the treatment of phenolic wastewater by MBBR [28–31] showing its good performances in terms of phenols removal and great stability against hydraulic and toxic shock loads. Advanced oxidation processes (AOPs) are considered highly effective for the treatment of complex wastewater with high COD, five days biochemical oxygen demand ($BOD_5$), and colour. They have been successfully investigated for the degradation of a wide range of refractory or high chemical stability pollutants [32]. The AOP degradation mechanisms rely on the in-situ formation of highly reactive oxidant species, mainly hydroxyl radicals (•OH), which are powerful, non-selective and ubiquitous in nature with a redox potential of 2.8 V [33,34]. In particular, hydroxyl radicals are very effective in the degradation of aromatic rings, adding a hydrogen atom, due to their electrophilic behaviour [35]. Among AOPs, Fenton processes have attracted great interest due to their capacity in the removal of several recalcitrant compounds [36,37]. Fenton process promotes the in-situ generation of •OH radicals by using Fenton reagent, a mixture of $H_2O_2$ as oxidizing agent and iron(II) salts, typically iron(II) sulphate ($FeSO_4$), as a catalyst. UV or solar light enhance Fenton process efficiency due to the higher •OH radical production and the reduction of Fe (III) to Fe(II). This results in a lower iron load required by photo-Fenton compared to Fenton process. Both UV and solar light can be used but a wavelength $<$ 310 nm helps with the production of radicals [38]. Moreover, UV energy input can directly degrade contaminants by breaking some of their chemical bonds [39]. Unfortunately, these processes are effective under acidic pH (optimum al 2.8), which is necessary to reduce iron precipitation as hydroxides and asks for a subsequent neutralization before effluent disposal, leading to sludge formation [40]. To overcome this problem, photo-Fenton like processes, in the presence of iron(II) or iron(III) complexes with aminopolycarboxilic acids (APCAs), such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), ethylenediaminedisuccinic acid (EDDS) [41] and iminodisuccinic acid (IDS) [42] were investigated in the last years at neutral pH. Iron(III)-IDS (Fe-IDS) complex was used for the treatment of both phenol solution and real OMW under both solar and UV-C radiation [42]. Despite the interesting results achieved as well as the potential for the combination of biological and photo Fenton processes in the treatment of OMW, the lack of studies under realistic conditions slows the application of such an approach at full scale.

In this work, IDS supported photo-Fenton (PFI) process, under both UV and solar radiation, was investigated for the first time as polishing step of real OMW treated by MBBR to effectively reduce TPHs before disposal into the environment. PFI operating conditions were optimized using response surface methodology (RSM) varying both oxidant and catalyst concentration. After centrifugation, OMW was mixed to synthetic urban wastewater before MBBR treatment to simulate a co-treatment scenario in a multi-barrier approach of a WWTP. The effect of the process was evaluated in terms of TPHs, COD and $BOD_5$ removals.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Fe-IDS was prepared following a previously reported procedure [42]. Hydrogen peroxide ($H_2O_2$) 30% wt, iron(III) chloride hexaydrate ($FeCl_3.6H_2O$), sodium carbonate ($Na_2CO_3$) and Folin-Ciocalteu reagent were purchased from Sigma Aldrich (Saint Louis, MO, USA) and used without further purification. Iminodisuccinate tetrasodium salt (65% wt, $Na_4C_8H_7NO_8$) (Baypure CX 100®) was purchased from Lanxsess (Cologna, Germany) and used without further purification.

### 2.2. OMW sample

The OMW sample was taken from an olive oil mill located in the province of Salerno (southern Italy), using a 3-phase oil extraction system. The sample was analysed in terms of pH, total suspended solids (TSS), TPHs, COD, $BOD_5$ and $BOD_5$/COD ratio. Before the experiments the sample was centrifuged at 5000 rpm for 30 min to reduce the total solids content. The characteristics of OMW before and after the centrifugation are shown in Table 1.

The centrifuged sample was mixed (0.5%) with synthetic urban wastewater (SWW) before the MBBR step to simulate OMW co-treatment in a WWTP. The SWW was prepared according to the following recipe: saccharose, 200 mg/L; glucose, 200 mg/L; whey protein, 68.33 mg/L; $(NH_4)_2SO_4$, 66.73 mg/L; $NH_4Cl$, 10.91 mg/L; $KH_2PO_4$, 4.43 mg/L; $K_2HPO_4$, 8.99 mg/L; $MgSO_4•7H_2O$, 21 mg/L; $MnSO_4•H2O$, 2.68 mg/L; $NaHCO_3$, 30 mg/L; $CaCl_2•6H_2O$, 19.74 mg/L; $FeCl_3•6H_2O$, 0.14 mg/L [43].

### 2.3. MBBR

The MBBR system consisted in a 2.5 L cylindrical reactor, with a water height as high as 40 cm and an internal diameter of 9 cm (SM1a). The reactor was filled with bio-carriers with a size of 10.5 (Φ) × 8 mm (h). The bio-carriers characteristics are: specific surface area of 950 $m^2/m^3$ (protected surface of 500 $m^2/m^3$), density of 0.15 $g/cm^3$ (SM1b). The bio-carriers were added gradually until reaching the maximum value of filling ratio (35%) allowing a fluid movement inside the reactor. An air pump, equipped with a stone bubble diffuser at the bottom of the system, was used to provide dissolved oxygen for the biological process and keep moving bio-carriers inside the reactor. The reactor was operated in batch mode. The bacterial inoculum, necessary for the start-up phase to promote bacterial growth in the MBBR system, was taken from the recirculation line of an activated sludge process of a real urban WWTP located in the province of Salerno. The sludge was acclimated for one day with the SWW before the inoculation into the MBBR system. The initial biomass concentration in the bioreactor was about 3.0 g/L. After the inoculation step, the MBBR system was fed in batch mode with SWW for two months, until an initial biofilm formation was observed. As biofilm growth started, the suspended sludge was removed to allow a complete growth of the biofilm. As a stable COD removal was observed, the MBBR was fed with the OMW mixed with SWW (OMW (0.5%) and SWW (99.5%)). During the experiment, pH and dissolved oxygen were monitored. The amount of OMW (0.5%) was chosen to obtain an initial COD of the mixed OMW (m-OMW) of about 1 g/L.

The biomass concentration in the reactor was evaluated according to a previously published protocol [44]. In particular, for each analysis, a sample of 10 carriers was dried over night at 105 °C and weighed. Subsequently, the dried biofilm was totally removed by washing the sample in a 1 M NaOH aqueous solution; then the cleaned carriers were

**Table 1**
OMW characteristics before and after centrifugation.

| Parameter | Raw OMW | Centrifuged OMW |
|---|---|---|
| pH | 4.7 | 4.7 |
| TSS (g/L) | 21 | 3 |
| TPHs (g/L) | 7.1 | 5 |
| $BOD_5$ (g/L) | 29.2 | 20 |
| COD (g/L) | 126.9 | 87.1 |
| $BOD_5$/COD | 0.24 | 0.23 |

dried and weighed. The sample's biomass was calculated as the difference in dry weight before and after cleaning. Finally, knowing the total number of carriers (800) and the volume of the MBBR, the biomass concentration was calculated. An equal number of carriers was added to the reactor at each analysis to maintain the total number of carriers constant. $BOD_5$, COD, and TPHs were monitored in the effluent of the MBBR, and the corresponding removal efficiencies were calculated according to the Eq. (1):

$$Z_{RE}(t) = \left(1 - \frac{Z_t}{Z_0}\right) \cdot 100 \quad (1)$$

where:

$Z_{RE}(t)$ = Removal efficiency for Z parameter;
$Z_t$: parameter value after HRT = 24 h;
$Z_0$: initial parameter value

### 2.4. Photo-Fenton process experimental set-up

The PFI tests assisted by UVC light were performed in batch mode. A 1 L cylinder (Φ = 5 cm) was fed with 500 mL of OMW pre-treated by MBBR. The source of UVC radiation (average irradiance 23.2 ± 3.3 W/$m^2$) was a 16 W UVC lamp (emission peak 254 nm, Sankyo Denky GT10T5L), vertically positioned in the cylinder. The temperature was kept constant at 25 ± 1 °C during the entire experiments through a thermostatic bath. Temperature, pH, COD, $BOD_5$, TPHs, iron and residual $H_2O_2$ concentrations were monitored during the tests. Reaction time was set at 180 min. Sunlight-PFI tests were carried in clear sunny days outdoor at the Fisciano campus of University of Salerno (Italy) (40°76′N and 14°79′ W) (average solar irradiance in the range 280–400 nm = 49.8 ± 5.2 W/$m^2$). Reagents were added in the following order: first the OMW and the correct volume of Fe-IDS solution were added and stirred for one minute before to add hydrogen peroxide. Then the UV lamp was switched on (time zero).

Data analysis and kinetics determinations for the optimized process were achieved by OriginLab pro software. All tests were carried out in triplicate. The error is shown as standard deviation (SD) of the mean. Kinetic order and k values were obtained from linear fitting.

Kinetic constant and $t_{1/2}$ were developed according to the Eqs. (2) and (3), respectively:

$$ln\left(\frac{COD_t}{COD_0}\right) = -kt \quad (2)$$

$$t_{\frac{1}{2}} = \frac{ln(2)}{k} \quad (3)$$

### 2.5. Analytical measurements

pH was measured using pH-meter PC 62 DHS (XS Instruments). The residual $H_2O_2$ was removed after PFI treatment to prevent interference in the $BOD_5$ and COD measurements, through the addition of an aqueous solution of concentrated sodium carbonate (20 g/L, 0.19 M), according to a previously proposed method [45]. Total phenolic content was analysed on filtered samples using the Folin-Ciocalteu spectrophotometric method [46]. Specifically, 0.25 mL of Folin-Ciacolteau reagent and 0.75 mL of a saturated sodium carbonate solution (220 g/L, 2.08 M) were added to 5 mL of wastewater sample and left to react for 60 min in dark at 20 °C. Afterwards, the absorbance of the blue solution was measured with a UV–Vis spectrophotometer at a wavelength of 750 nm (Varian Cary R 50 UV–Vis spectrophotometer). COD was analysed according to the CNR-IRSA method 5135, using HACH LCK cuvette, while $BOD_5$ was measured with OXITOP® system according to the OECD 301F. UV-C and sunlight irradiance were measured through an Ocean Optics spectrometer (HR2000, USA). Residual $H_2O_2$ concentration was determined by a colorimetric method based on the use of titanium(IV) oxysulfate, which forms a stable yellow complex with $H_2O_2$ detected spectrophotometrically at 410 nm. The calibration line was obtained by measuring the absorbance of standard aqueous solutions of $H_2O_2$. The absorbance measurement was linearly correlated with $H_2O_2$ concentration in the range of 0.1–100 mg/L [47].

### 2.6. Response surface design and statistical model

In this study, RSM was used for the experimental design of the photo-Fenton process. The dosage of $Fe^{3+}$ ($X_1$) and the dosage of $H_2O_2$ ($X_2$) were selected as numerical factors while the type of radiation ($X_3$) was selected as categorical factor. The experimental design involved 22 runs, based on a two-level central composite factorial design. Each parameter was coded as − 1 (minimum), 0 (medium), +1 (maximum), +α and -α. α is defined as a distance from the centre point which can be either inside the range or outside. It was calculated as:

$$\alpha = \left(2^k\right)^{\frac{1}{4}} \quad (4)$$

where k is the number of numerical factors in the design model ($Fe^{3+}$ and $H_2O_2$ concentration in this work, k = 2).

Therefore, α value was set as 1.414. The ranges and levels are provided in Table 2. RSM design for the three experimental variables in coded units and the corresponding natural values are listed in Table 3. The response taken in consideration for RSM analysis were: TPHs removal (%) and COD removal (%).

Iron(III) dosage interval was chosen to keep the concentration in the effluent as low as possible to avoid a subsequent removal step, while making the effluent in compliance with the Italian regulatory limit for discharge into water bodies (2 mg/L). $H_2O_2$ dosage interval was chosen to investigate a wide range of concentrations both higher and lower than the theoretical stoichiometric amount of $H_2O_2$ to degrade all COD, equal to 2.125 g $H_2O_2$ per gram of COD (about 182 mg/L in this work).

The response was estimated through a second-order polynomial equation according to the Eq. (4):

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i=1}^{n} b_{ij} X_i X_j + \varepsilon \quad (4)$$

where Y is the response of TPHs or COD degradation, $b_0$ is a constant, $b_i$ correspond to linear coefficient of $X_i$, $b_{ii}$ is the second order effect on regression coefficients, $b_{ij}$ is the interaction coefficient and ε is the statistical error.

After the calculation of the optimal process for the removal of TPHs in terms of catalyst and oxidant concentration, three replicates of this process were made and the kinetics of both COD and TPHs removal were calculated.

For the optimization of the process, the following conditions were used:

- Hydrogen peroxide in the range 50–200 mg/L;
- Iron(III) concentration in the range 2–15 mg/L;
- Radiation: UVC or sunlight.

The following goals were selected for the responses:

- COD removal in the range 12.6–64.7, because the MBBR was designed and operated to keep the effluent COD below the Italian

**Table 2**
Ranges and levels of designed factors.

| Variables | Code | Range and levels | | | | |
|---|---|---|---|---|---|---|
| | | −1.414 | −1 | 0 | +1 | +1.414 |
| $Fe^{3+}$ (mg/L) | $X_1$ | 1 | 2 | 8.5 | 15 | 17.7 |
| $H_2O_2$ (mg/L) | $X_2$ | 18.9 | 50 | 125 | 200 | 231.1 |
| Radiation | $X_3$ | – | UVC | – | Sunlight | – |

**Table 3**
RSM design for the three experimental variables in coded units and corresponding natural values.

| Experiment number | Natural variables | | | Coded variables | | |
|---|---|---|---|---|---|---|
| | $Fe^{3+}$ (mg/L) | $H_2O_2$ (mg/L) | Radiation | $X_1$ | $X_2$ | $X_3$ |
| 1 | 8.5 | 18.934 | Sunlight | 0 | −1.414 | +1 |
| 2 | 17.6924 | 125 | UVC | +1.414 | 0 | −1 |
| 3 | 8.5 | 125 | Sunlight | 0 | 0 | +1 |
| 4 | 15 | 200 | UVC | +1 | +1 | −1 |
| 5 | 8.5 | 231.066 | UVC | 0 | +1.414 | −1 |
| 6 | 8.5 | 231.066 | Sunlight | 0 | +1.414 | +1 |
| 7 | 8.5 | 125 | UVC | 0 | 0 | −1 |
| 8 | 1 | 125 | Sunlight | −1.414 | 0 | +1 |
| 9 | 2 | 50 | UVC | −1 | −1 | −1 |
| 10 | 8.5 | 18.934 | UVC | 0 | −1.414 | −1 |
| 11 | 15 | 50 | UVC | +1 | −1 | −1 |
| 12 | 15 | 50 | Sunlight | +1 | −1 | +1 |
| 13 | 1 | 125 | UVC | −1.414 | 0 | −1 |
| 14 | 8.5 | 125 | UVC | 0 | 0 | −1 |
| 15 | 2 | 200 | UVC | −1 | +1 | −1 |
| 16 | 15 | 200 | Sunlight | +1 | +1 | +1 |
| 17 | 17.6924 | 125 | Sunlight | +1.414 | 0 | +1 |
| 18 | 8.5 | 125 | Sunlight | 0 | 0 | +1 |
| 19 | 2 | 200 | Sunlight | −1 | +1 | +1 |
| 20 | 8.5 | 125 | UVC | 0 | 0 | −1 |
| 21 | 2 | 50 | Sunlight | −1 | −1 | +1 |
| 22 | 8.5 | 125 | Sunlight | 0 | 0 | +1 |

regulatory limit for discharge in surface water bodies, so COD final concentration was monitored to control the biodegradability of the final effluent in terms of $BOD_5$/COD ratio, but its minimization was not considered in the process optimization phase;
- TPHs removal >98.9% to reach a final concentration below Italian regulatory limit (0.5 mg/L).

## 3. Results and discussion

### 3.1. MBBR

The MBBR system was fed with SWW (COD = 555.5 ± 2.5 mg/L and $BOD_5$ = 300 ± 20 mg/L) in batch mode for 15 days after its start-up (after the inoculation, sludge was removed, and stable COD removal efficiency was observed). At the end of this phase the biomass concentration was equal to 14 g/L. After this step, the MBBR system was fed by m-OMW (0.5% of OMW and 99.5% of OMW) for a period of 55 days. After mixing, COD, $BOD_5$ and TPHs concentrations were 948.6 ± 25.6 mg/L, 556.0 ± 16.7 mg/L, and 22.6 ± 0.6 mg/L, respectively. During this phase the average biomass concentration was equal to 28.7 ± 4.2 g/L. The higher biomass concentration compared to the SWW phase may be related to the higher inlet COD load. In biological processes the growth rate of biomass is related to the organic load. This result is in agreement with what was observed in a previous study in which two MBBRs were used in series and the biomass concentration was 4 times higher in the first reactor (with higher concentration of COD inlet) than in the second reactor [48]. During SWW phase the $BOD_5$ and COD removal efficiencies were 98.7 ± 0.8% and 96.1 ± 1.7%, respectively. In the m-OMW phase, which was monitored by taking samples every 3 days (a total of 5 samples collected), $BOD_5$, COD and TPHs removal efficiencies reached 97.1 ± 0.3% (final concentration = 16.2 ± 1.9 mg/L), 90.9 ± 1.3% (final concentration = 85.9 ± 14.9 mg/L) and 56.6 ± 6.9% (final concentration = 9.8 ± 1.5 mg/L), respectively (Fig. 1) with a filling ratio of 35%.

The COD removal reached in this work is pretty high if compared to the treatment of similar wastewater. In particular, in a previous work about the treatment of palm oil mill effluent (which is similar to OMW in its composition), with a filling ratio of 50% and HRT of 24 h, the COD removal efficiency was 54% [49]. Moreover, it is noteworthy that MBBR technology allow to reach a higher biomass concentration compared to activated sludge system, which results in a shorter residence time and consequently a smaller reactor volume [24]. Indeed, during m-OMW treatment the $BOD_5$, COD and TPHs removal efficiencies reached 92%, 86% and 42% respectively already after 5 h of treatment time in batch mode (Fig. 1). This make MBBR an attractive solution for industrial wastewater treatment compared to activated sludge. This assumption is also supported by the results obtained in a study on the upgrade of an activated sludge process, transforming it into MBBR for the treatment of a mix of industrial wastewater [50]. In particular, in this work the implementation of the MBBR system allowed to achieve the same COD removal as the activated sludge system after only 6 h of treatment, compared to the 25 h required by the activated sludge process. Furthermore, the absence of suspended biomass in MBBRs further reduces the overall volume of the subsequent solid-liquid separation phase. In our work, both after 24 h and 5 h the MBBR treatment allowed to meet Italian regulatory limits (annex 5, third part, D.Lgs n. 335,152 /2006) for effluent disposal into surface water in terms of COD and $BOD_5$ (COD = 160 mg/L; $BOD_5$ = 40 mg/L) but not for phenolic compounds (0.5 mg/L). The TPHs removal was 56.6 ± 6.9%, leading to a TPHs concentration of about 10 mg/L. The removal of phenolic compounds represents a major challenge in the treatment of OMWs. In particular, studies on the direct treatment of OMW using activated sludge have shown that long treatment times (> 2 d) are required to obtain satisfactory results in terms of COD removal (> 60–70%), but with lower phenols removal (10–40%) which did not allow to meet the corresponding limit for effluent disposal [51,52]. This once again focuses attention on the advantages obtained from the co-treatment which allows to reduce the concentration of phenols entering the biological process and to reduce residence times, as well as the toxic effects given by the phenolic compounds on the biomass. In support of this, a study about the co-treatment of urban wastewater and OMW (1%) in an activated sludge system showed treatment yields even superior to our work. In particular, a COD removal equal to 90% and a TPHs removal equal to 92% was observed. However, this result was achieved only after 100 days of treatment, while after 50 days the removal of phenols was equal to 39%. This suggests the need for long acclimatization times to select the suitable bacterial community [53]. In our study, to obtain a high final effluent quality also in terms of phenolic compounds, PFI process was performed as post-treatment.

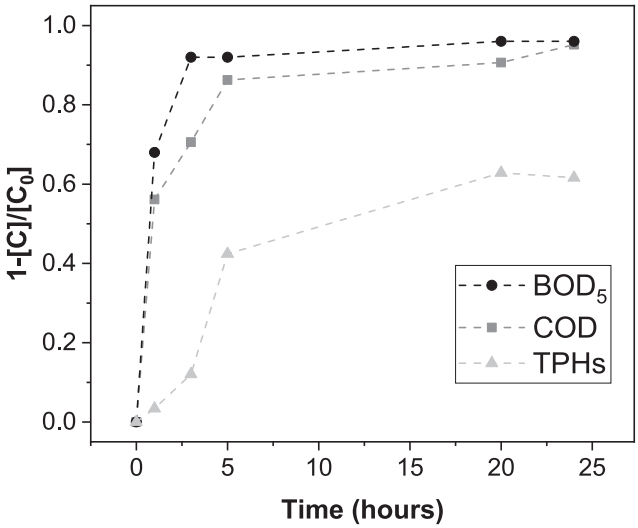


**Fig. 1.** COD, $BOD_5$, TPHs removals during 24 h of treatment with MBBR.

### 3.2. PFI optimization by RSM

Based on the results from the quadratic model in Table SM1 and

Table SM2 of supplementary material file (SM), which shows the actual and predicted values of the two responses (COD removal efficiency and TPHs removal efficiency, respectively), the empirical relationships between the response and the independent variables are the followings (Eq. (5) and the Eq. (6)):

$$Y_{CODrem} = 60.39 + 8.72X_1 + 8.72X_2 + 4.56X_3 - 1.49X_1X_2 + 0.4355X_1X_3 + 1.92X_2X_3 - 6.10{X_1}^2 - 14.77{X_2}^2 \quad (5)$$

$$Y_{TPHrem} = 83.23 - 6.12X_1 + 15.07X_2 - 12.96X_3 - 2.41X_1X_2 - 3.00X_2X_3 + 5.99X_1X_2 - 12.75{X_1}^2 - 11.23{X_2}^2 \quad (6)$$

For COD removal, F-value of the model was 8.86 ($p$-value <0.05 and $R^2$ = 0.8450). The F-value of 8.86 implies the model is significant. $P$-values lower than 0.05 indicate that the model terms are significant as well. In this case $X_1$, $X_2$, $X_3$, $X_2^2$ are significant parameters, a good correlation between the empirical model and the actual values being achieved (Table SM1).

For TPHs removal, instead, F-value was 19.68, p-value <0.05 and $R^2$ = 0.9237. The F-value implies the significance of the model, and the significant parameters were $X_1$, $X_2$, $X_3$, $X_1X_2$, $X_1^2$ and $X_2^2$. Even for TPHs removal, a good correlation between the empirical model and the actual values was observed (Table SM2). In the case of UVC supported PFI, COD removals varied from 14.6 to 64%, increasing as iron(III) concentration increases and $H_2O_2$ concentrations was in a medium range. The lowest COD final value after 180 min was 34 mg/L, using reagent concentrations of 125 mg/L for $H_2O_2$ and 17.7 mg/L for $Fe^{3+}$. Therefore, the optimum dosage of $Fe^{3+}$ should be inferred by response surface (Fig. 2b) and contour plots (Fig. 2a) based on process cost and desired efficiency. Such a trend in the reduction of COD is in agreement with a previous work where palm oil wastewater treatment through classical photo-Fenton process ([$Fe^{2+}$] = 554÷3351 mg/L, [$H_2O_2$] = 1700÷5100 mg/L, initial COD = 2700 mg/L, UV light, pH = 3 and 2 h of treatment) was optimized obtaining COD reductions from 27 to 97% with the medium $H_2O_2$ concentration, as high oxidant concentrations lead to worsening efficiencies [54]. At the best of author's knowledge, no studies are available in the scientific literature on the optimization through RSM of photo-Fenton like processes applied to TPHs removal in a real wastewater matrix. In the present study, TPHs removal obtained with UVC assisted PFI was very high (up to 99.1%). As expected, also TPHs removal efficiency increases with the increase of both $Fe^{3+}$ and $H_2O_2$ concentration. PFI allowed to reach a final TPHs concentration as low as 0.049 mg/L (response surface and contour plots are shown in Fig. 2c and Fig. 2d, respectively).

When UVC radiation is replaced with solar one, the trend for COD

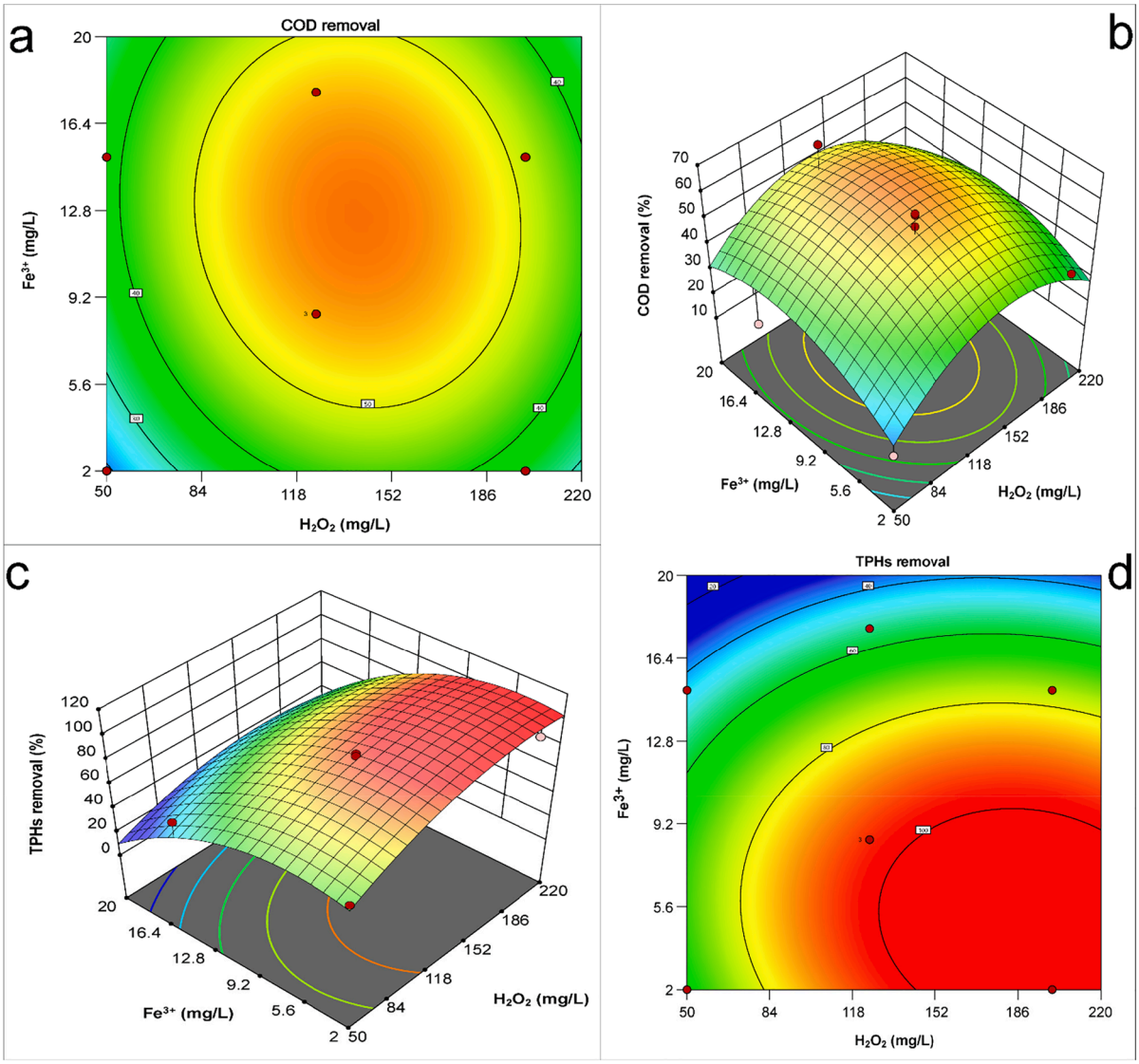


**Fig. 2.** Contour plots (a,d) and response surfaces (b,c) for COD (a,b) and TPHs (c,d) removal with the use of UVC radiation.

and TPHs degradation is the same (removals increases as $Fe^{3+}$ and $H_2O_2$ concentration increase), COD removal efficiency (maximum of 64,7%) being almost the same compared to the UVC assisted process (Fig. 3a and Fig. 3b), but TPHs removal efficiency being lower (maximum 71.2%, final TPHs concentration of 2.4 ± 0.1 mg/L) (Fig. 3c and Fig. 3d). This can be ascribed to the capacity of phenolic compounds to absorb UVC light photons especially when their concentration is high, which plays an important role in phenol degradation through ionization reaction [55].

### 3.3. Process optimization and kinetics

According to RSM analysis, the optimum conditions to operate PFI to effectively remove TPHs are: 2 mg/L of $Fe^{3+}$, 144 mg/L of $H_2O_2$ and UVC radiation. The optimized process allowed to reach an average COD reduction of about 46.7 ± 2.3% (final COD concentration of 40.11 ± 14.9 mg/L) (Fig. 4).

This removal is lower than that of some other conditions tested but, being the final COD concentration already in compliance with the corresponding standard for effluent disposal into the environment, the

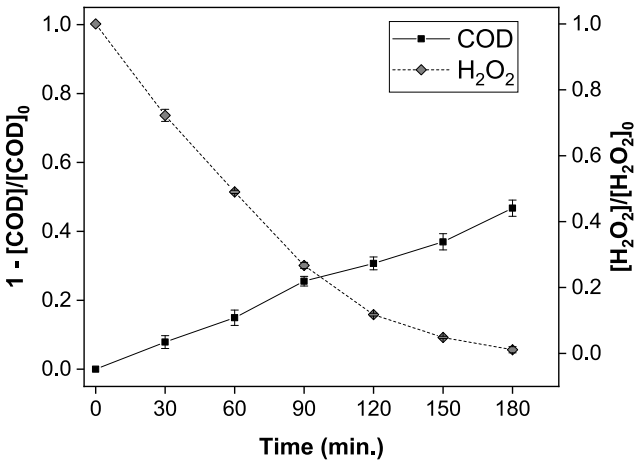


**Fig. 4.** COD removal for optimized process.

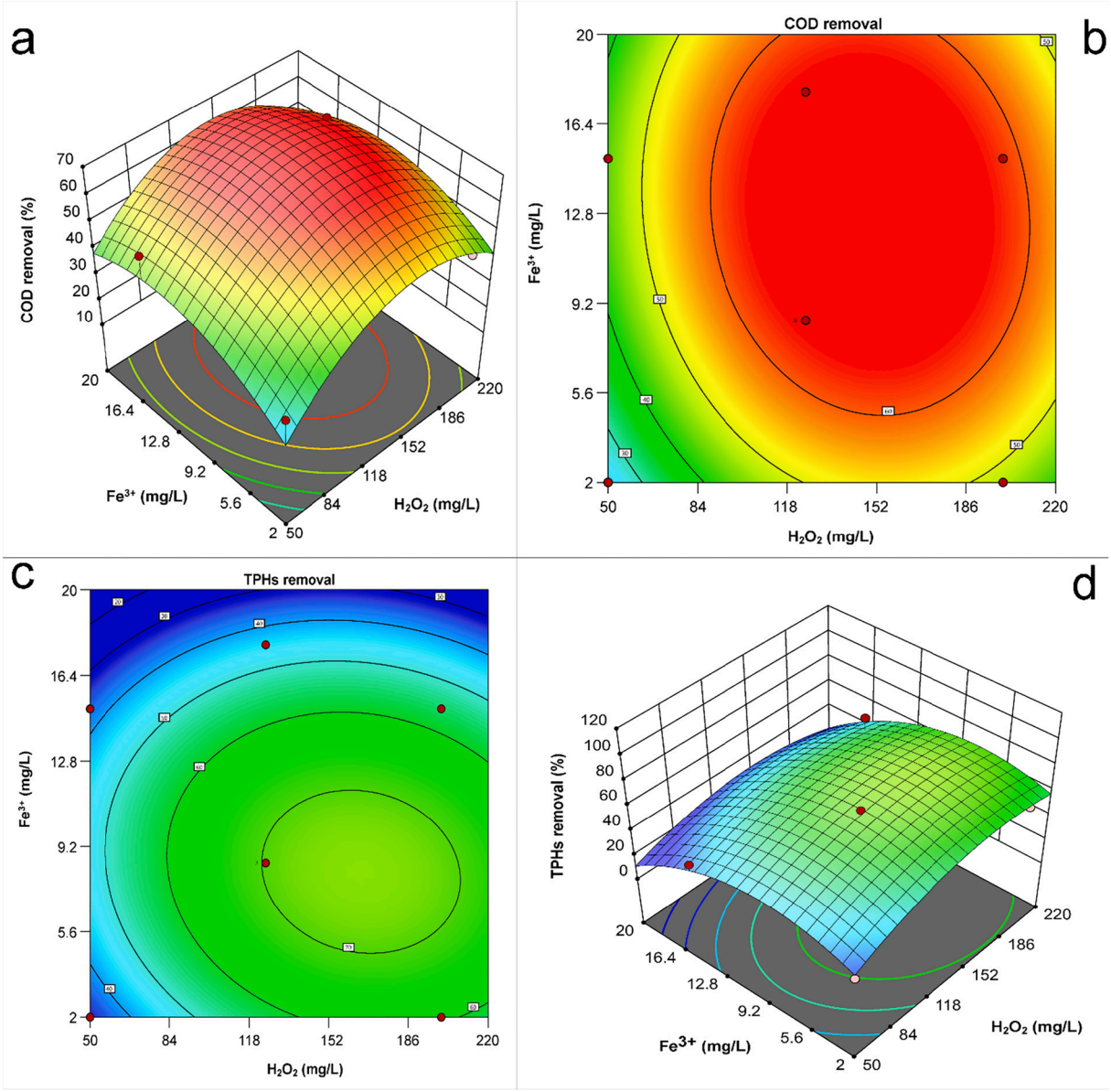


**Fig. 3.** Contour plots (a,d) and response surfaces (b,c) for COD (a,b) and TPHs (b,c) removal with the use of solar radiation.

scope of the polishing step is to achieve a sufficiently low concentration of TPHs, which is the main constrain for effluent disposal. Such conditions allowed to reach an average final concentration of TPHs as low as 0.07 ± 0.01 mg/L (average reduction of 99 ± 1%) within 180 min (Fig. 5) and a final $BOD_5$ concentration of 24.2 ± 0.5 mg/L leading to a $BOD_5$/COD ratio of 0.6 ± 0.1 with a significant increase in wastewater biodegradability. The obtained results can be explained considering that the biological process carried out upstream of the PFI drastically reduced the initial load of recalcitrant pollutants and turbidity, allowing to increase the activity of photo-Fenton process. Moreover, it is known that a wavelength below 320 nm is enough for phenolic compounds degradation by photo Fenton process [56].

To authors' knowledge, the treatment of real OMW (COD = 2.4 g/L) by sunlight assisted PFI process (Fe: 6 mg/L, $H_2O_2$ = 1.7 g/L, pH = 5.2) in terms of COD reduction was investigated only in a previous study where 55% COD removal was observed [42]. The results of our work are also in agreement with those from previous studies where the degradation of TPHs (97% removal after 180 min treatment) in real OMW with UVC assisted photo-Fenton process ($FeCl_3$, $H_2O_2$, UVC radiation, pH = 3) was investigated [57]. Although initial COD and TPHs content was different, the process optimization allowed to achieve phenolic compounds degradation from OMW in milder condition in our work. In particular, the use of IDS as iron ligand allowed to obtain a TPHs reduction of 99.1% within 180 min. at circumneutral pH, with a lower reagent's consumption. The possibility to operate the process at circumneutral pH is very important as it avoids sludge formation at the end of the process and the use of acids to acidify the effluent and bases to neutralize the effluent before disposal, reducing costs and chemicals handling. Lafi et al. studied several combinations of advanced oxidation with ozone ($O_3$), photodegradation by UV radiation, and aerobic biodegradation [58]. In the case of aerobic process as pre-treatment of UV/$O_3$ advanced oxidation, they reached an overall COD reduction of 81.8% (initial COD of 45 g/L). The HRT of aerobic process was much higher than that of this work for MBBR process (4 days Vs 1 day). The optimum time for UV/$O_3$ process resulted to be 3 h, the same which was used in our work for PFI, but the combination of UV radiation and $O_3$ is expensive and energy intensive and $O_3$ toxic by-products should be also monitored and eventually removed [59].

COD and TPHs removal by the optimized PFI process follows a first-order kinetic (Table 4), in agreement with other studies [42,56,57].

For this process the consumption of $H_2O_2$ was higher than 99% and the half-life time resulted to be 214 ± 9 and 26.5 ± 1.9 min for COD and TPHs removal respectively, in agreement with a previous work in which PFI process was applied to real OMW treatment [42].

## 4. Conclusions

The treatment of OMW by conventional methods is really challenging and a multi-barrier approach is necessary to make the effluent in compliance with regulations for disposal into the environment. In this work, UVC and sunlight assisted photo-Fenton like processes using Fe-IDS as catalyst were investigated as post-treatment method of a MBBR for the treatment of OMW. The MBBR, simulating the co-treatment scenario of OMW in a centralized WWTP, resulted to be very efficient for COD removal (91 ± 1%) but less effective for TPHs removal (55 ± 1%). For the first time the photo-Fenton like process was optimized with RSM to maximize the TPHs removal on real OMW matrix. This approach allowed to reach TPHs reduction as high as 99 ± 1% (with a final value of 0.07 ± 0.01 mg/L which is lower than Italian regulatory limit for discharge of treated wastewater in surface water as well as for water reuse) by applying the optimized PFI process ([$Fe^{3+}$] = 2 mg/L, [$H_2O_2$] = 144 mg/L, UVC radiation) as MBBR post-treatment. Moreover, optimized conditions and the use of Fe-IDS complex allowed to perform the photo-Fenton process at circumneutral pH and low reagents loadings, making the process more environmentally and economically sustainable. When PFI was assisted by sunlight, TPHs removals resulted to be lower (71.2%), which makes the application of solar driven PFI feasible as post-treatment only for Countries where the limit is less stringent. In conclusion, the combination of MBBR with UVC-assisted PFI seems to be an attractive option for the co-treatment of OMW in centralized WWTPs.

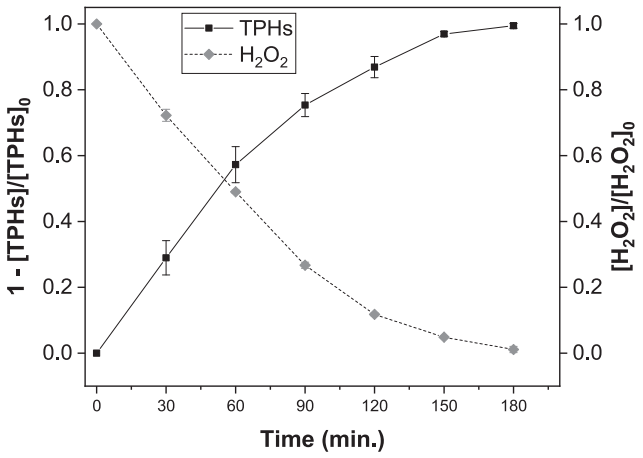


**Fig. 5.** TPHs removal for optimized process.

**Table 4**
Kinetic parameters of optimized process.

| Parameter | Order | \|k\| ($min^{-1}$) | $t_{1/2}$ (min.) |
|---|---|---|---|
| COD | First | $3.24*10^{-3} \pm 9.7*10^{-5}$ | 214 ± 9 |
| TPHs | First | $2.62*10^{-2} \pm 1.3*10^{-3}$ | 26.5 ± 1.9 |

## CRediT authorship contribution statement

**Antonio Faggiano:** Methodology, Investigation, Formal analysis, Writing – original draft. **Marco De Carluccio:** Methodology, Investigation, Formal analysis, Writing – original draft. **Antonino Fiorentino:** Methodology, Supervision, Writing – review & editing. **Maria Ricciardi:** Methodology, Investigation, Writing – original draft. **Raffaele Cucciniello:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Antonio Proto:** Conceptualization, Methodology, Supervision. **Luigi Rizzo:** Conceptualization, Methodology, Supervision, Writing – review & editing, Funding acquisition.

## 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.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2022.122525.

## References


[1] A. Ncube, G. Fiorentino, C. Panfilo, M. De Falco, S. Ulgiati, Circular economy paths in the olive oil industry: a life cycle assessment look into environmental performance and benefits, Int. J. Life Cycle Assess. (2022), https://doi.org/10.1007/s11367-022-02031-2.

[2] S. Hachicha, J. Cegarra, F. Sellami, R. Hachicha, N. Drira, K. Medhioub, E. Ammar, Elimination of polyphenols toxicity from olive mill wastewater sludge by its co-composting with sesame bark, J. Hazard. Mater. 161 (2009) 1131–1139, https://doi.org/10.1016/j.jhazmat.2008.04.066.

[3] A. El-Abbassi, H. Kiai, J. Raiti, A. Hafidi, Application of ultrafiltration for olive processing wastewaters treatment, J. Clean. Prod. 65 (2014) 432–438, https://doi.org/10.1016/j.jclepro.2013.08.016.

[4] B. Zenjari, H. El Hajjouji, G. Ait Baddi, J.-R. Bailly, J.-C. Revel, A. Nejmeddine, M. Hafidi, Eliminating toxic compounds by composting olive mill wastewater–straw mixtures, J. Hazard. Mater. 138 (2006) 433–437, https://doi.org/10.1016/j.jhazmat.2006.05.071.

[5] D. Pham Minh, P. Gallezot, S. Azabou, S. Sayadi, M. Besson, Catalytic wet air oxidation of olive oil mill effluents: 4. Treatment and detoxification of real effluents, Appl. Catal. B Environ. 84 (2008) 749–757, https://doi.org/10.1016/j.apcatb.2008.06.013.

[6] A. Yangui, M. Abderrabba, A. Sayari, Amine-modified mesoporous silica for quantitative adsorption and release of hydroxytyrosol and other phenolic compounds from olive mill wastewater, J. Taiwan Inst. Chem. Eng. 70 (2017) 111–118, https://doi.org/10.1016/j.jtice.2016.10.053.

[7] E. Tsagaraki, H.N. Lazarides, K.B. Petrotos, Olive mill wastewater treatment, in: V. Oreopoulou, W. Russ (Eds.), Util. -Prod. Treat. Waste Food Ind, Springer US, 2007, pp. 133–157, https://doi.org/10.1007/978-0-387-35766-9_8.

[8] S. Vuppala, I. Bavasso, M. Stoller, L. Di Palma, G. Vilardi, Olive mill wastewater integrated purification through pre-treatments using coagulants and biological methods: experimental, modelling and scale-up, J. Clean. Prod. 236 (2019), 117622, https://doi.org/10.1016/j.jclepro.2019.117622.

[9] A. Lissaneddine, M.-N. Pons, F. Aziz, N. Ouazzani, L. Mandi, E. Mousset, Electrosorption of phenolic compounds from olive mill wastewater: mass transport consideration under a transient regime through an alginate-activated carbon fixed-bed electrode, J. Hazard. Mater. 430 (2022), 128480, https://doi.org/10.1016/j.jhazmat.2022.128480.

[10] A. Faggiano, M. Ricciardi, A. Proto, Catalytic routes to produce polyphenolic esters (PEs) from biomass feedstocks, Catalysts. 12 (2022) 447.

[11] A. Serrano, F.G. Fermoso, B. Alonso-Fariñas, G. Rodríguez-Gutierrez, J. Fernandez-Bolaños, R. Borja, Phenols recovery after steam explosion of olive mill solid waste and its influence on a subsequent biomethanization process, Bioresour. Technol. 243 (2017) 169–178, https://doi.org/10.1016/j.biortech.2017.06.093.

[12] Z. Al-Qodah, H. Al-Zoubi, B. Hudaib, W. Omar, M. Soleimani, S. Abu-Romman, Z. Frontistis, Sustainable vs. Conventional Approach for Olive Oil Wastewater Management: A Review of the State of the Art, Water 14, 2022, p. 1695, https://doi.org/10.3390/w14111695.

[13] G. La Scalia, R. Micale, L. Cannizzaro, F.P. Marra, A sustainable phenolic compound extraction system from olive oil mill wastewater, J. Clean. Prod. 142 (2017) 3782–3788, https://doi.org/10.1016/j.jclepro.2016.10.086.

[14] S.M. Niknam, M. Kashaninejad, I. Escudero, M.T. Sanz, S. Beltrán, J.M. Benito, Valorization of olive mill solid residue through ultrasound-assisted extraction and phenolics recovery by adsorption process, J. Clean. Prod. 316 (2021), 128340, https://doi.org/10.1016/j.jclepro.2021.128340.

[15] A.A. Zorpas, C.N. Costa, Combination of Fenton oxidation and composting for the treatment of the olive solid residue and the olive mile wastewater from the olive oil industry in Cyprus, Bioresour. Technol. 101 (2010) 7984–7987, https://doi.org/10.1016/j.biortech.2010.05.030.

[16] P. Paraskeva, E. Diamadopoulos, Technologies for olive mill wastewater (OMW) treatment: a review, J. Chem. Technol. Biotechnol. 81 (2006) 1475–1485, https://doi.org/10.1002/jctb.1553.

[17] L. Rizzo, G. Lofrano, M. Grassi, V. Belgiorno, Pre-treatment of olive mill wastewater by chitosan coagulation and advanced oxidation processes, Sep. Purif. Technol. 63 (2008) 648–653, https://doi.org/10.1016/j.seppur.2008.07.003.

[18] R. Camarillo, J. Rincón, Effect of inhibitory compounds on the anaerobic digestion performance of diluted wastewaters from the alimentary industry, J. Chem. Technol. Biotechnol. 84 (2009) 1615–1623, https://doi.org/10.1002/jctb.2247.

[19] W. Gernjak, M.I. Maldonado, S. Malato, J. Cáceres, T. Krutzler, A. Glaser, R. Bauer, Pilot-plant treatment of olive mill wastewater (OMW) by solar TiO2 photocatalysis and solar photo-Fenton, Sol. Energy 77 (2004) 567–572, https://doi.org/10.1016/j.solener.2004.03.030.

[20] L. Rizzo, G. Lofrano, V. Belgiorno, Olive mill and winery wastewaters pre-treatment by coagulation with chitosan, Sep. Sci. Technol. 45 (2010) 2447–2452, https://doi.org/10.1080/01496395.2010.487845.

[21] European Commission, Directorate-General Joint Research Centre, Institute of Health and Consumer Protection, European Chemicals Bureau, European Union Risk Assessment Report, (2006).

[22] D. Mantzavinos, N. Kalogerakis, Treatment of olive mill effluents: part I. organic matter degradation by chemical and biological processes—an overview, Environ. Int. 31 (2005) 289–295, https://doi.org/10.1016/j.envint.2004.10.005.

[23] Z.S. Lee, S.Y. Chin, J.W. Lim, T. Witoon, C.K. Cheng, Treatment technologies of palm oil mill effluent (POME) and olive mill wastewater (OMW): a brief review, Environ. Technol. Innov. 15 (2019), 100377, https://doi.org/10.1016/j.eti.2019.100377.

[24] Metcalf & Eddy, Metcalf & Eddy - Wastewater Engineering - Treatment and Reuse.pdf, 4th ed., McGraw-Hill, Asia, 2002.

[25] S. Zheng, J. Sun, H. Han, Effect of dissolved oxygen changes on activated sludge fungal bulking during lab-scale treatment of acidic industrial wastewater, Environ. Sci. Technol. 45 (2011) 8928–8934, https://doi.org/10.1021/es2018169.

[26] J.M. Ochando-Pulido, A. Martinez-Ferez, On the recent use of membrane technology for olive mill wastewater purification, Membranes. 5 (2015) 513–531, https://doi.org/10.3390/membranes5040513.

[27] G. Andreottola, P. Foladori, M. Ragazzi, F. Tatàno, Experimental comparison between MBBR and activated sludge system for the treatment of municipal wastewater, Water Sci. Technol. 41 (2000) 375–382, https://doi.org/10.2166/wst.2000.0469.

[28] M. Ahmadi, N. Jaafarzadeh, Z.G. Rahmat, A.A. Babaei, N. Alavi, Z. Baboli, M. V. Niri, Kinetic studies on the removal of phenol by MBBR from saline wastewater, J. Environ. Health Sci. Eng. 15 (2017) 22, https://doi.org/10.1186/s40201-017-0284-0.

[29] S.H. Hosseini, S.M. Borghei, The treatment of phenolic wastewater using a moving bed bio-reactor, Process Biochem. 40 (2005) 1027–1031, https://doi.org/10.1016/j.procbio.2004.05.002.

[30] S.A.A. Nakhli, K. Ahmadizadeh, M. Fereshtehnejad, M.H. Rostami, M. Safari, S. M. Borghei, Biological removal of phenol from saline wastewater using a moving bed biofilm reactor containing acclimated mixed consortia, SpringerPlus. 3 (2014) 112, https://doi.org/10.1186/2193-1801-3-112.

[31] Z.G. Rahmat, N. Jafarzadeh, A. Babaei, N. Alavi, M. Ahmadi, Phenol removal by moving bed biofilm reactor (MBBR) from saline wastewater, Asian J. Microbiol. Biotechnol. Env. Sci. 18 (2016) 833–840.

[32] J. Wang, S. Wang, Toxicity changes of wastewater during various advanced oxidation processes treatment: an overview, J. Clean. Prod. 315 (2021), 128202, https://doi.org/10.1016/j.jclepro.2021.128202.

[33] A. Fiorentino, L. Rizzo, H. Guilloteau, X. Bellanger, C. Merlin, Comparing TiO2 photocatalysis and UV-C radiation for inactivation and mutant formation of Salmonella typhimurium TA102, Environ. Sci. Pollut. Res. 24 (2017) 1871–1879, https://doi.org/10.1007/s11356-016-7981-6.

[34] V. Kumar, M.P. Shah, 1 - advanced oxidation processes for complex wastewater treatment, in: M.P. Shah (Ed.), Adv. Oxid. Process. Effl. Treat. Plants, Elsevier, 2021, pp. 1–31, https://doi.org/10.1016/B978-0-12-821011-6.00001-3.

[35] M.A. Oturan, J.-J. Aaron, Advanced oxidation processes in water/wastewater treatment: principles and applications. A review, Crit. Rev. Environ. Sci. Technol. 44 (2014) 2577–2641, https://doi.org/10.1080/10643389.2013.829765.

[36] A. Fiorentino, B. Esteban, J.A. Garrido-Cardenas, K. Kowalska, L. Rizzo, A. Aguera, J.A.S. Pérez, Effect of solar photo-Fenton process in raceway pond reactors at neutral pH on antibiotic resistance determinants in secondary treated urban wastewater, J. Hazard. Mater. 378 (2019), 120737, https://doi.org/10.1016/j.jhazmat.2019.06.014.

[37] P. Gautam, S. Kumar, S. Lokhandwala, Advanced oxidation processes for treatment of leachate from hazardous waste landfill: a critical review, J. Clean. Prod. 237 (2019), 117639, https://doi.org/10.1016/j.jclepro.2019.117639.

[38] T. Li, C.-Z. Zhang, X. Fan, Y. Li, M. Song, Degradation of oxidized multi-walled carbon nanotubes in water via photo-Fenton method and its degradation mechanism, Chem. Eng. J. 323 (2017) 37–46, https://doi.org/10.1016/j.cej.2017.04.081.

[39] J. Yang, M. Zhu, D.D. Dionysiou, What is the role of light in persulfate-based advanced oxidation for water treatment? Water Res. 189 (2021), 116627 https://doi.org/10.1016/j.watres.2020.116627.

[40] A. Faggiano, M. Ricciardi, A. Fiorentino, R. Cucciniello, O. Motta, L. Rizzo, A. Proto, Combination of foam fractionation and photo-Fenton like processes for greywater treatment, Sep. Purif. Technol. 293 (2022), 121114, https://doi.org/10.1016/j.seppur.2022.121114.

[41] L. Clarizia, D. Russo, I. Di Somma, R. Marotta, R. Andreozzi, Homogeneous photo-Fenton processes at near neutral pH: a review, Appl. Catal. B Environ. 209 (2017) 358–371, https://doi.org/10.1016/j.apcatb.2017.03.011.

[42] A. Fiorentino, P. Prete, L. Rizzo, R. Cucciniello, A. Proto, Fe3+− IDS as a new green catalyst for water treatment by photo-Fenton process at neutral pH, J. Environ. Chem. Eng. 9 (2021), 106802, https://doi.org/10.1016/j.jece.2021.106802.

[43] M. de Carluccio, A. Fiorentino, L. Rizzo, Multi-barrier treatment of mature landfill leachate: effect of Fenton oxidation and air stripping on activated sludge process and cost analysis, J. Environ. Chem. Eng. 8 (2020), 104444, https://doi.org/10.1016/j.jece.2020.104444.

[44] M. Piculell, C. Suarez, C. Li, M. Christensson, F. Persson, M. Wagner, M. Hermansson, K. Jönsson, T. Welander, The inhibitory effects of reject water on nitrifying populations grown at different biofilm thickness, Water Res. 104 (2016) 292–302, https://doi.org/10.1016/j.watres.2016.08.027.

[45] T. Wu, J.D. Englehardt, A new method for removal of hydrogen peroxide interference in the analysis of chemical oxygen demand, Environ. Sci. Technol. 46 (2012) 2291–2298, https://doi.org/10.1021/es204250k.

[46] J.D. Box, Investigation of the Folin-Ciocalteau phenol reagent for the determination of polyphenolic substances in natural waters, Water Res. 17 (1983) 511–525, https://doi.org/10.1016/0043-1354(83)90111-2.

[47] A. Fiorentino, G. Ferro, M.C. Alferez, M.I. Polo-López, P. Fernández-Ibañez, L. Rizzo, Inactivation and regrowth of multidrug resistant bacteria in urban wastewater after disinfection by solar-driven and chlorination processes, J. Photochem. Photobiol. B 148 (2015) 43–50, https://doi.org/10.1016/j.jphotobiol.2015.03.029.
[48] Z. Li, H. Chen, J. Zhang, M. Peng, W. Han, Combined application analysis of MBBR and magnetic coagulation process in a full-scale project, J. Water Process Eng. 49 (2022), 102955, https://doi.org/10.1016/j.jwpe.2022.102955.
[49] S.N.H. Abu Bakar, H. Abu Hasan, A.W. Mohammad, S.R.S. Abdullah, R. Ngteni, K. M.M. Yusof, Performance of a laboratory-scale moving bed biofilm reactor (jMBBR) and its microbial diversity in palm oil mill effluent (POME) treatment, Process. Saf. Environ. Prot. 142 (2020) 325–335, https://doi.org/10.1016/j.psep.2020.05.004.
[50] H. Bachmann Pinto, B. Miguel de Souza, M. Dezotti, Treatment of a pesticide industry wastewater mixture in a moving bed biofilm reactor followed by conventional and membrane processes for water reuse, J. Clean. Prod. 201 (2018) 1061–1070, https://doi.org/10.1016/j.jclepro.2018.08.113.
[51] J.C. Aldana, J.L. Acero, P.M. Álvarez, Membrane filtration, activated sludge and solar photocatalytic technologies for the effective treatment of table olive processing wastewater, J. Environ. Chem. Eng. 9 (2021), 105743, https://doi.org/10.1016/j.jece.2021.105743.
[52] M. Kotsou, A. Kyriacou, K. Lasaridi, G. Pilidis, Integrated aerobic biological treatment and chemical oxidation with Fenton's reagent for the processing of green table olive wastewater, Process Biochem. 39 (2004) 1653–1660, https://doi.org/10.1016/S0032-9592(03)00308-X.
[53] T.E. Elmansour, L. Mandi, A. Hejjaj, N. Ouazzani, Nutrients' behavior and removal in an activated sludge system receiving olive mill wastewater, J. Environ. Manag. 305 (2022), 114254, https://doi.org/10.1016/j.jenvman.2021.114254.
[54] D. Kanakaraju, M.S. Yahya, S.-P. Wong, Removal of chemical oxygen demand from agro effluent by ZnO photocatalysis and photo-Fenton, SN Appl. Sci. 1 (2019) 738, https://doi.org/10.1007/s42452-019-0782-z.
[55] M. Li, D. Wen, Z. Qiang, J. Kiwi, VUV/UV light inducing accelerated phenol degradation with a low electric input, RSC Adv. 7 (2017) 7640–7647, https://doi.org/10.1039/C6RA26043H.
[56] F. He, L.-C. Lei, Degradation kinetics and mechanisms of phenol in photo-Fenton process, J. Zhejiang Univ. (Sci.) 5 (2004) 198–205, https://doi.org/10.1631/jzus.2004.0198.
[57] C.A. García, G. Hodaifa, Real olive oil mill wastewater treatment by photo-Fenton system using artificial ultraviolet light lamps, J. Clean. Prod. 162 (2017) 743–753, https://doi.org/10.1016/j.jclepro.2017.06.088.
[58] W. Lafi, B. Shannak, M. Al-Shannag, Z. Al-Anber, M. Al-Hasan, Treatment of olive mill wastewater by combined advanced oxidation and biodegradation, Sep. Purif. Technol. 70 (2009) 141–146, https://doi.org/10.1016/j.seppur.2009.09.008.
[59] L. Rizzo, S. Malato, D. Antakyali, V.G. Beretsou, M.B. Đolić, W. Gernjak, E. Heath, I. Ivancev-Tumbas, P. Karaolia, A.R. Lado Ribeiro, G. Mascolo, C.S. McArdell, H. Schaar, A.M.T. Silva, D. Fatta-Kassinos, Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater, Sci. Total Environ. 655 (2019) 986–1008, https://doi.org/10.1016/j.scitotenv.2018.11.265.