Various techniques for phenolic removal from olive mill wastewater

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**ABSTRACT**

As the world's population increases, so does the amount of wastewater generated during agricultural activities. Inadequate wastewater management can be the cause of sea and river pollution. However, wastewater can be a potential source of biologically active components that can be obtained via physicochemical, biological, thermochemical or combined treatments. Olive mill wastewater is produced in huge quantities around the world during the production of olive oil. This waste is harmful to the ecological system due to the high content of phenolic components that can be recovered by different methods whereby this waste also gains economic value. This review describes several methods that can be used in phenol removal or isolation from olive mill wastewater.

**Keywords:** olive mill wastewater, phenols, adsorption, photocatalytic degradation, Fenton process

**Introduction**

Olive oil is one of the products consumed all over the world, but large amounts of solid (cake) and fluid (olive mill wastewater, OMW) waste are generated during its production. In the Mediterranean countries, the yearly production of olives reaches 2.4 million tons, which is 95% of overall world production (Solomakou and Goula, 2020). Olive oil can be produced with three extraction processes: discontinuous press process, two-phase or three-phase centrifugal extraction process (Rahmanian et al., 2013). OMW is a dark fluid with high turbidity, intense odour, relatively low pH and high organic content (Solomakou and Goula, 2020). The composition of OMW depends on the olive variety, used extraction equipment and fruit ripeness (Galanakis, 2011). The OMW purification process is very demanding due to its high pollutant load, high concentration of lignins and tannins, fatty acids and phenolic compounds (Vavouraki et al., 2019). Characteristics of OMW are shown in **Table 1**.

More than 30 phenolic compounds are detected in OMW, and their concentration ranges from 0.5 to 24.0 g/L.

**Table 1. Composition of olive mill wastewater (OMW)** (Solomakou and Goula, 2020).

| Characteristic        | OMW     |
|-----------------------|---------|
| pH                    | 2.2 – 5.9 |
| Total carbon (%)      | 2.0 – 3.3 |
| Organic matter (%)    | 57.2 – 62.1 |
| Total nitrogen (%)    | 0.63    |
| Ash (%)               | 1.0     |
| Lipids (%)            | 0.03 – 4.25 |
| Total sugars (%)      | 1.50 – 12.22 |
| Total proteins (%)    | 3.43 – 7.26 |
| Total phenols (%)     | 0.63 – 5.45 |

The concentration of phenols in OMW varies depending on the extraction system used for oil production (Russo, 2007). Flavonoids represent 45 – 65% of the total phenolic amount while the most dominant phenol hydroxytyrosol represents 55 – 70% of total phenolic content (El-Abbassi et al., 2012). Because of the high concentration of phenolic compounds, OMW shows the high chemical and biochemical demand for oxygen values (Barakat and Adib, 2020). Phenolics represent an environmental threat due to their high toxicity which can poison the bacterial activity, aquatic organisms and plants (Lee et al., 2019). Therefore, OMW must be purified and

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treated before being discharged; otherwise, untreated water could cause adverse circumstances in the aquatic system. The foul smell of OMW can also cause problems for the surrounding population (Nuno, 2017). This paper summarizes some of the techniques, which can be used in processes of OMW treatment aiming to reduce phenolic content and make them environmentally friendly, focusing on adsorption, photocatalytic degradation, Fenton process.

**Adsorption**

Adsorption is considered as easy to design and operate technique that is appropriate for phenolic removal from water. The advantage of this method is that no toxic waste is generated and that the sorbent can be used as a fuel source (Aksu and Yener, 2001). In order to conduct a successful adsorption process, the adsorbents need to meet certain properties, such as high hydrophobicity, must be porous with a large surface and be able to selectively accumulate pollutants (Bhatnagar and Minocha, 2006). Table 2 summarizes research dealing with the adsorption of phenols from OMW. Usage of banana peel as biosorbent for removal of phenolics from OMW was reported by Achak et al. (2008). Different parameters of the adsorption process were investigated (pH, contact time and adsorbent dosage). The process was monitored for 1 – 24 h at pH values between 2 and 11. Better adsorption of phenolics from OMW was observed at higher pH values. The process was fast and equilibrium was reached in 3 h of contact. An increase in the sorbent dosage of 10 – 30 g/L led to an increase in adsorption rates of phenolic content from 60 to 88%. The phenols from OMW were also adsorbed with the usage of wheat bran as a biosorbent (Achak et al., 2013). In the adsorption method various pH values, contact time and adsorbent doses were investigated. This research showed that bran wheat as a low-cost biomass is a good alternative for the expensive adsorbent. The adsorption rates of 45 and 67% were achieved at wheat bran concentrations of 10 and 50 g/L, respectively. The process of adsorption was relatively fast and equilibrium was reached after 4 hours of contact. The effectiveness of Azolla and granular activated carbon (GAC) in removing phenolic compounds from OMW has been reported by Ena et al. (2012). Both sorbents showed good adsorption and desorption efficiency. The desorptions of powder were 3.23 and 1.51% from Azolla and GAC matrix, respectively. The GAC powder contained 3.5 times higher content of hydroxytyrosol in comparison with Azolla. Aliakbarian et al. (2015) performed a batch sorption test using various temperatures (10, 25 and 45 °C) and concentrations of activated carbon (10, 20, 40, 60 and 80 g/L) for the removal of phenolic compounds from OMW. The temperature did not affect adsorption rate and the differences in yield were negligible. The sorption capacity of the adsorbent was 36.1 mg/g at 40 °C, 35.4 mg/g at 25 °C and 35.8 mg/g at 10 °C. Yangui and co-workers (2016) used commercial and synthesized adsorbents for the treatment of OMW. For the removal and recovery of phenolic compounds activated carbon and amine-modified (3-trimethoxyisilylpropyl diethylenetriamine (TRI)) SBA-15 and P-10 silica as adsorbents were used. The best removal of phenol components of 87% was accomplished with activated carbon versus 67% and 75% for TRI P-10 and TRI-SBA-15.

Ververi and Goula (2019) used two agricultural wastes (orange juice by-product and pomegranate peel) as adsorbents with the aim to remove phenolics from OMW. The influence of sorbent mass concentration (0.01 – 0.02 g/mL), pH value (4 - 7), temperature (20 – 60 °C) and a sorbent particle size on the adsorption process was studied. The adsorption efficiencies of 89.59 and 93.13% were obtained using orange juice by-product and pomegranate peel, respectively. The best phenolic sorption was achieved at pH 4.75. The by-product of the food industry pomegranate seed was used as an adsorbent for phenols from OMW (Papaioikonomou et al., 2019). Batch experiments were conducted and effects of pH, temperature, sorbent particle size, sorbent mass concentration and initial sorbate concentration were studied. Maximal adsorption rate of 92.8% was achieved after 10 minutes at 30 °C and a pH of 5.0 with a sorbent concentration of 20 g/L and a sorbent particle size of 0.92 mm. Adsorption was very fast and equilibrium was reached after 20 minutes. In order to find optimal adsorbent for phenolic compounds (PC) from Tunisian OMW, Frascari et al. (2019) employed 4 neutral resins (Amberlite XAD16N, FPX66, XAD761 and Optipore SD-2) and one ion-exchange resin (Amberlite IRA958 Cl). The most promising adsorbents for phenolic removal were proven to be Amberlite XAD16N and Amberlite IRA958. Although Amberlite XAD16N showed the highest adsorption capacity (81 mgpc/g dry resin), the Amberlite IRA958 is preferred because of its lower industrial costs. Sahin and co-workers (2020) investigated graphene oxide as a selective adsorbent for the removal of hydroxytyrosol and total phenolic compounds from
OMW. Hydroxytyrosol and total phenolics were adsorbed from OMW in a very good yield of 85 and 67%, respectively. The key parameter in this process was the pH value. The increase of pH from 5.6 to 9.0 led to a higher recovery of hydroxytyrosol from 9.0 to 398.6 mg per g of graphene oxide, respectively. The total phenolic content was also affected by the pH change and the adsorption rate was increased from 62.2 to 1483.9 mg per g of graphene oxide. Turco and Melitesta (2020) used a porous polymeric matrix of polydimethylsiloxane with entrapped oxidized multiwall carbon nanotubes. The study was performed at different pH values and the process was monitored at various times (0.5 – 24 h). Adsorption efficiency was the best at the pH values of 4.8. Further, an increase in pH led to a decrease in the adsorption rate. Phenol removal from OMW was increased with the increase in PDMS/oxMWCNTs amount from 40 to 100 g/L.

### Table 2. Sorbents and conditions applied in the process of adsorption of phenolic compounds from olive mill wastewater (OMW)

| Sorbent | Sorbent concentration [g/L] | pH       | Temperature [°C] | Reference                      |
|---------|-------------------------------|----------|-----------------|--------------------------------|
| Banana peel | 10 – 30                        | 2 - 11   | 30              | Achak et al., 2008            |
| Azolla and granular activated carbon | 12.5 - 200              | -        | 24              | Ena et al. 2012               |
| Wheat bran   | 10 – 60                      | 3 - 11   | 30              | Achak et al., 2013            |
| Activated carbon | 10 – 80              | 4.9      | 10 – 45         | Aliakbarian et al., 2015      |
| Activated carbon | 60            | 4.2      | 22              | Yangui et al., 2016           |
| Orange juice by-product and pomegranate peel | 0.01-0.02       | 4 – 7    | 20 – 60         | Ververi and Goula, 2019       |
| Pomegranate seed | 10 - 50                        | 4 – 8    | 20 – 60         | Papaoikonomou et al., 2019    |
| Amberlite XAD16N    | 10                        | 4.2 – 9.3 | 22              | Frascari et al., 2019         |
| Amberlite FPX66     | 3                          | 3.4; 8.0 | 25 – 27         | Baransi et al., 2012          |
| Amberlite XAD761    | 0.02                        | 2.8 – 2.9; 5.0 | 25      | Michael et al., 2014          |
| Optipore SD-2 Amberlite IRA958 Cl | 1.0                    | 4.3 – 4.5 | 20              | Nogueira et al., 2015         |
| Graphite oxides    | -                          | -        | 25 – 65         | Şahin et al., 2020            |
| Polydimethylsiloxane/oxMWCNTs porous nanocomposite | 40 - 100         | 2 – 10.5 | 25              | Turco and Melitesta, 2020     |

### Table 3. Catalysts and conditions applied in the process of photocatalytic degradation of phenolic compounds from olive mill wastewater (OMW)

| Catalyst                  | Catalyst concentration [g/L] | pH       | Temperature [°C] | Reference                      |
|---------------------------|------------------------------|----------|-----------------|--------------------------------|
| TiO$_2$ supported sepiolite | 0.25 - 1.0                   | 3.0; 5.0; 7.0; 9.0; 11.0 | 25, 35, 45 | Uğurlu and Karaoğlu, 2011     |
| Mixture of activated carbon and TiO$_2$ | 3                        | 3.4; 8.0 | 25 – 27         | Baransi et al., 2012          |
| Fe$^{3+}$                 | 0.02 – 1                     | 2.8 – 2.9; 5.0 | 25      | Michael et al., 2014          |
| nano-TiO$_2$ and nano-Fe$_2$O$_3$ | 1                          | 4.3 – 4.5 | 20              | Nogueira et al., 2015         |
| Glucose doped titanium particles | -                          | -        | 25              | Cuomo et al., 2016            |
| TiO$_2$                   | 0.5 – 1                      | 3.0; 9.0 | -              | Moudden et al., 2020          |
| N-TiO$_2$-SiO$_2$         | 1.0 – 3.0                    | 6.55     | 25, 30, 40, 45 | Vuppala and Stoller, 2020     |
| nano-ZnO–SiO$_2$          | 0.5 – 10                     | 4.0; 7.0; 10.0 | 34 – 37 | Ulusoy and Sponza, 2020       |
| dried olive cake powder and Cu(NO$_3$)$_2$-3H$_2$O | 1.5                        | 6        | 50              | Yuney et al., 2020            |
| CuCr$_2$O$_4$@CaFe–LDO    | 2                           | -        | -              | Oladipo, 2021                 |
Photocatalytic degradation

Photocatalytic degradation is the process often applied for the degradation of pollutants by the usage of metal oxide catalysts. It is considered an effective method for the treatment of wastewaters. The efficiency of the photocatalytic process largely depends on the parameters, such as light intensity, solution pH, exposure time and catalyst amount (Laoufi et al., 2008). Many researchers reported successful phenol degradation with this method in wastewaters from different industries. Various catalysts were used, such as CuO (Feng et al., 2015), TiO$_2$ (Shahrezaei et al., 2012; Al-Kandari et al., 2016), clinoptilolite zeolite and FeO-based nanoparticles (Mirian and Nezamzadeh, 2016), Fe$_2$O$_3$ on carbon nanotubes (Asmaly et al., 2015) and ZnO (Abdollahi et al., 2011). Table 3 shows researches related to photocatalytic degradation of phenol components in OMW.

Uğurlu and Karaoğlu (2011) investigated the removal of phenolic compounds and lignin from OMW under different conditions. In the photocatalytic treatment effects of catalyst dose, pH value, temperature and combination of TiO$_2$ supported sepiolite (TiO$_2$/Sep), H$_2$O$_2$ and UV light were investigated. It has been proven that the efficiency of the photocatalytic process is strongly affected by all investigated parameters. Degradation of phenols and lignin was most efficient at pH 9.0 – 11.0, at catalyst concentrations of 0.25 and 0.5 g/L and temperature of 45 °C. Baransi et al. (2012) performed photocatalytic degradation of two phenolic compounds (cafeic and p-coumaric acid) from OMW. OMW is treated with a mixture of activated carbon and TiO$_2$ at pH values of 3.4 and 8. Photocatalytic degradation was monitored under sunlight and 365 nm UV lamps. Results showed efficient phenolic removal and the best results were obtained in the presence of both TiO$_2$ and powdered activated carbon. For the direct photolysis of caffeic acid, quantum yields of 0.005 and 0.011 were achieved under solar and UV light at 365 nm, respectively. The exposure to 365 nm irradiation contributed to 58 % removal of chemical oxygen demand (COD) and 87 % of phenolic compounds after 24 hours. Nano-TiO$_2$ and nano- Fe$_2$O$_3$ were employed in the treatment of OMW to remove phenolic compounds and decrease chemical oxygen demand (Nogueira et al., 2015). After five days, total phenolic content was decreased by 5.5 and 9.9 % for TiO$_2$/UV and Fe$_2$O$_3$/UV, respectively. Better results were achieved with the addition of H$_2$O$_2$. Usage of catalysts TiO$_2$/ H$_2$O$_2$/UV and Fe$_2$O$_3$/ H$_2$O$_2$/UV obtained reductions in total phenol content were 31.2 and 25.5, respectively. Modified TiO$_2$ particles were used in the photocatalytic process for the degradation of phenolic compounds from OMW in the presence of visible light (Cuomo et al., 2016). The photocatalyst effectiveness was monitored on the system having the various initial amounts of phenols in the presence of different concentrations of glucose-doped titanium particles. With the combination of the mentioned catalyst and visible light, the process of phenol degradation was successfully conducted. Obtained kinetic data indicated that a higher amount of phenolics was degraded within the first 2 hours. Moudden et al. (2020) also employed TiO$_2$ as a catalyst in a photocatalytic technique combined with UV irradiation. In this research degradation rate of vanillic acid in OMW was monitored under different conditions (TiO$_2$ concentration, irradiation time and pH value) and the experimental design methodology was used. The abatement rate of 96.3% was achieved at pH 3, at a TiO$_2$ concentration of 0.5 g/L after 25 minutes. Nanophotocatalyst particles (N-TiO$_2$-SiO$_2$) were used in the process of photocatalitcal degradation of phenolic compounds in OMW and synthetic phenol solution (Vuppala and Stoller, 2020). The addition of catalyst was in the range of 1 – 3 g/L. The process was carried out at temperatures of 25, 35, 40 and 45 °C. An increase in temperature leads to an increased removal of phenols. The best phenol removal (90%) from OMW was achieved at a catalyst concentration of 2 g/L.

Yuney et al. (2020) reported OMW treatment with the photocatalytic technique with the aim of decolourisation and phenol removal. The used catalyst was prepared from the combination of dried olive cake powder, Cu(NO$_3$)$_2$·3H$_2$O and banana extract. The removal efficiency of phenolic compounds achieved with this type of catalyst was 82.7 – 95.0% after 360 minutes. It turned out that the most favourable pH values for this process are in the range of 5 to 11. Complete degradation of seven phenolic compounds found in OMW after 300 min was achieved by catalyst CuCr$_3$O$_4$@CaFe–LDO (Oladipo, 2021). It is proven that 1 g of the mentioned catalyst has the possibility to remove 66% of COD in the dark place without oxygen. Colour and COD removal (~99%) were achieved after 180 min with the combination of CuCr$_3$O$_4$@CaFe–LDO, K$_2$S$_2$O$_8$ and sunlight.

Michael et al. (2014) employed the Fenton solar technique for the purification of OMW. The process was conducted using a pilot-scale photocatalytic reactor in the presence of Fe$^{2+}$ as a catalyst and H$_2$O$_2$ as an oxidant. Prior to photocatalysis, OMW was
subjected to coagulation/flocculation. Applied catalyst and oxidant concentrations were 0.02–0.1 and 0.5–2.0 g/L, respectively. Determined total phenolic content in OMW was 3.1 g/L and it decreased after the photocatalytic process for 99.8% and 99.0% at pH 2.8–2.9 and 5.0, respectively. Ulusoy and Sponza (2020) investigated the removal of three polyphenols (para-coumaric acid, gallic acid, t-para-coumaric acid) and total phenols present in OMW. The process of photocatalysis was conducted under sunlight with nano-ZnO–SiO2. The authors examined the influence of few parameters (doses of nano-ZnO–SiO2 exposure time and pH values) on the removal ability. The best results (phenol yield of 73%) were obtained after 24 hours using 3 g/L nano-ZnO–SiO2. The most favourable pH value for this process was shown to be pH 4. Individual polyphenol components showed maximum yields of 90%, 5% and 5% for gallic acid, t-para-coumaric acid and p-coumaric acid, respectively.

**Fenton process**

In the Fenton process, hydroxyl radicals are formed through the decomposition of H2O2 promoted by iron ions. The process is usually performed at room temperature and pressure (Ochando-Pulido et al., 2017). Many studies deal with the application of Fenton’s techniques in wastewater and water treatment (Burbano et al., 2005; Benzaquen et al., 2015; Amarala-Silva et al., 2016). Despite Fenton’s process disadvantages (sludge formation, operating in acidic conditions, requirement for pH neutralization), industrial interest in Fenton’s techniques is huge because of its ability to treat cumbersome effluents (Dominiques et al., 2018).

The conventional Fenton process was optimized, so three types of Fenton processes can be distinguished: electro-Fenton, photo-Fenton and heterogeneous Fenton process (Zhang et al., 2019). Table 4 summarizes conducted research in which different Fenton’s processes were investigated.

Alver et al. (2015) investigated the organic matter and total phenol removal from OMW with a combination of the coagulation and the Fenton technique. This research studied various operational conditions, such as pH, Fe2+ and H2O2 dosage, as well as [Fe3+]/[H2O2] ratios. With optimal conditions (pH=3, [Fe3+] = 2.5 g/L, [Fe3+]/[H2O2] = 2.5), the best phenolic removal of 81.4% was achieved at 80 minutes. The same conditions were used in photo-Fenton-like process with the presence of artificial radiation. With the application of this technique, 83.8% of phenols were removed. Furthermore, Iboukhoulef et al. (2014) also investigated Fenton-like process using Cu (II) as a catalyst and H2O2 as an oxidant. Research has shown that temperature affects the degradation of phenols in the treated OMW. Removals of 43% and 62% at temperatures 30 °C and 50 °C were achieved, respectively.

Esteves et al. (2018) studied Fenton oxidation treatment of synthetic OMW under continuous and batch mode conditions. Six phenolic acids (caffeic,
vanillic, gallic, *p*-coumaric, 3,4-dihydroxyphenylacetic acid and tyrosol) usually found in OMW were mixed and used for this purpose. Optimization of the process was performed in a batch reactor and optimal conditions (T = 30 °C, initial pH=5, [Fe²⁺]=100 ppm and [H₂O₂]=2 g/L) were applied in a continuous mode. In both, batch and continuous mode degradation of phenolics were high, 99% and 96.9%, respectively. Treatment of OMW by chemical coagulation, acid cracking and Fenton process was reported by Madani et al. (2015). It has been shown that the pH, H₂O₂ and iron-salt dosage affect the efficiencies of the Fenton process. With the acid cracking method at pH 2.5, only 30% of phenols were removed while combinations of the Fenton process, chemical coagulation and Fenton process led to the removal of total phenols of 98.6%. Further, the application of combined biological oxidation, filtration and photo-Fenton process in the treatment of OMW was investigated by García and Hodaifa (2017). These procedures were proven to be very effective in phenol removal which was complete. OMW treatment in a batch reactor by photo-Fenton technique with FeCl₃ as a catalyst was investigated by Garcia and Hodaifa (2017). Various H₂O₂ concentrations (5 – 30 g/L) and four commercial UV lamps were used in this study. Applied process parameters were: temperature 20 °C, pH = 3, catalyst concentration of 3 g/L and direct UV-light. The studied conditions led to the high phenolic removal of 93.6% from OMW. Photo-Fenton reaction was used in the treatment of OMW reported by Hodaifa et al. (2020). In the optimization process, different iron salts as catalysts were used (Fe₂(SO₄)₃, FeCl₃, Fe(ClO₃)₃ and FeSO₄·7H₂O), as well as different H₂O₂ concentrations. The experiments were conducted at 20 °C, pH = 3, with a catalyst/H₂O₂ ratio of 0.03 in the presence of ultraviolet light. The FeCl₃ was proven to be the most effective catalyst with an H₂O₂ concentration of 7.5% (w/v). The phenolic compound removal of 88.4% was achieved at optimal conditions. Catalytic potential of chalcopyrite (CuFeS₂) and mined pyrite (FeS₂) in the photo-Fenton process was studied by Ltaief et al. (2018). These natural low-cost catalysts showed high efficiency in this process by the complete removal of phenolic components (tyrosol, coumaric, vanillic, ferulic and caffeic acid) from treated OMW.

| Process                  | Catalyst | pH   | Temperature [°C] | Reference                      |
|--------------------------|----------|------|------------------|--------------------------------|
| Fenton                   | Fe       | 2 – 4| 25               | Kallel et al., 2009            |
| Fenton                   | FeSO₄·7H₂O| 3    | r.t.             | Alver et al., 2015             |
| Fenton                   | FeSO₄·7H₂O| 3.5  | 20               | Amor et al., 2015              |
| Fenton                   | FeSO₄·7H₂O| 2.5  | 25 – 30          | Madani et al., 2015            |
| Fenton                   | FeSO₄·7H₂O|      |                  |                                |
| Heterogeneous Fenton     | BiFeO₃   | 4.6 -12 | 20 – 60      | Iboukhoulif et al., 2019       |
| Heterogeneous Fenton     | Red mud  | 3    | -                | Domingues et al., 2019         |
| Heterogeneous Fenton-like| Fe-carbon| 3.8  | 25               | Estevés et al., 2020           |
| Fenton-like              | Cu (II)  | 4.7  | 30 – 50          | Iboukhoulif et al., 2014       |
| Fenton-like              | FeCl₃    | 3    | 25               | Estevés et al., 2019           |
| Heterogeneous Fenton     | FeSO₄·7H₂O| 2    | -                | Iboukhoulif et al., 2019       |
| Heterogeneous Fenton     | FeCl₃    | 3    | 20               | Garcia and Hodaifa, 2017       |
| Photo-Fenton             | FeSO₄·7H₂O|      |                  |                                |
| Photo-Fenton             | FeCl₃    | 3    | 20               | Hodaifa et al., 2020           |

Application of the combined electro-Fenton and high-power ultrasound in OMW treatment was reported by Mostafa et al. (2018). Direct and indirect treatment by high-power ultrasound at ultrasound power of 750 W for 90, 60 and 30 minutes. Treatment of the electro-Fenton method has lasted for 4 hours. The combination of these two techniques showed good results and phenol

Table 4. Catalysts and conditions applied in the Fenton process for the removal of phenolic compounds from olive mill wastewater (OMW)
reduction in the range from 58.4 to 80.6%. The highest removal of 80.6% was achieved by direct high-power ultrasound after 90 minutes and 4 hours of the electro-Fenton method.

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