

Various techniques for phenolic removal from olive mill wastewater

Lončarić, Melita; Habuda-Stanić, Mirna; Molnar, Maja

Source / Izvornik: **Croatian journal of food science and technology, 2021, 13, 268 - 276**

Journal article, Published version

Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

<https://doi.org/10.17508/CJFST.2021.13.2.15>

Permanent link / Trajna poveznica: <https://um.nsk.hr/um:nbn:hr:109:258796>

Rights / Prava: [Attribution-NonCommercial-ShareAlike 4.0 International](#)/[Imenovanje-Nekomercijalno-Dijeli pod istim uvjetima 4.0 međunarodna](#)

Download date / Datum preuzimanja: **2024-12-11**



image not found or type unknown

Repository / Repozitorij:

[Repository of the Faculty of Food Technology Osijek](#)



image not found or type unknown



Various techniques for phenolic removal from olive mill wastewater

 Melita Lončarić*, Mirna Habuda-Stanić, Maja Molnar

Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Department of Applied Chemistry and Ecology, Franje Kuhača 18, 31000 Osijek, Croatia

ARTICLE INFO

Article history:

Received: April 19, 2021

Accepted: June 17, 2021

Keywords:

olive mill wastewater

phenols

adsorption

photocatalytical degradation

Fenton process

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.

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

*Corresponding author E-mail: mellita.loncaric@ptfos.hr

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 researches 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 biomaterial 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-trimethoxysilylpropyl 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 (Papaoikonomou 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 mg_{PC}/g_{dry resin}), the Amberlite IRA958 is preferred because of its lower industrial costs.

Şahin 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 Triamine-modified SBA-15 and P-10 silicas	60	4.2	22	Yanguí 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 Amberlite FPX66 Amberlite XAD761 Optipore SD-2 Amberlite IRA958 Cl	10	4.2 – 9.3	22	Frascardi et al., 2019
Graphene oxide	1	3 – 11	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 ²⁺	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), TiO₂ (Shahrezaei et al., 2012; Al-Kandari et al., 2016), clinoptilolite zeolite and FeO-based nanoparticles (Mirian and Nezamzadeh, 2016), Fe₂O₃ 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 TiO₂ supported sepiolite (TiO₂/Sep), H₂O₂ 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 (caffeic and *p*-coumaric acid) from OMW. OMW is treated with a mixture of activated carbon and TiO₂ 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 TiO₂ 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-TiO₂ and nano-Fe₂O₃ 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 TiO₂/UV and Fe₂O₃/UV, respectively. Better results were achieved with the addition of H₂O₂. Usage of catalysts TiO₂/H₂O₂/UV and Fe₂O₃/H₂O₂/UV obtained reductions in total phenol

content were 31.2 and 25.5, respectively. Modified TiO₂ 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 TiO₂ 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 (TiO₂ 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 TiO₂ concentration of 0.5 g/L after 25 minutes. Nanophotocatalyst particles (N-TiO₂-SiO₂) were used in the process of photocatalytic 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 discolourization and phenol removal. The used catalyst was prepared from the combination of dried olive cake powder, Cu(NO₃)₂·3H₂O 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 CuCr₂O₄@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 CuCr₂O₄@CaFe-LDO, K₂S₂O₈ 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 Fe²⁺ as a catalyst and H₂O₂ 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 [Fe²⁺]/[H₂O₂] ratios. With optimal conditions (pH=3, [Fe²⁺]=2.5 g/L, [Fe²⁺]/[H₂O₂]=2.5) applied, 87.2% of total phenols were removed from OMW. Amor et al. (2015) applied the Fenton process in the treatment of OMW combined with anaerobic digestion. Fenton process was conducted at a pH value of 3.5 in the presence

of H₂O₂/Fe²⁺ (molar ration 15:1). This procedure reduced the phenolic content by 82.5%. Iboukhoulef et al. (2019) investigated the removal of phenolic compounds from OMW by combining ozonation and heterogeneous Fenton process using BiFeO₃ as nanocatalyst. Different combinations were used as follows: BiFeO₃ alone, O₃ alone, O₃/H₂O₂, O₃/BiFeO₃, O₃/BiFeO₃/H₂O₂ and O₃/S₂O₈/BiFeO₃. The best phenolic removal of 82.9% was achieved in alkaline conditions by O₃/S₂O₈/BiFeO₃. In the heterogeneous Fenton process, red mud from the alumina industry was used as a source of iron to remove phenol from OMW (Domingues et al., 2019). The process was optimized and 100% phenolic removal was accomplished when 100 mg/L of H₂O₂ and 1 g/L of catalyst were used. Successful removal of phenolics with a heterogeneous Fenton process from OMW was reported by Esteves et al. (2020). In this research, two agro-industrial wastes (olive stones and sawdust) were used as Fe-support catalysts in the Fenton process to oxidize phenolic compounds in OMW. Commercial activated carbon is used as a reference. Usage of catalysts prepared on the biochar supports olive stone and sawdust results in poor adsorption (below 5% of phenolic compounds). OMW pre-treatment by a Fenton method with zero-valent iron and H₂O₂ was investigated in order to improve chemical oxygen demand and degradation of phenolic compounds (Kallel et al., 2009). The procedure was conducted under determined optimal conditions (pH = 2-4, 1M H₂O₂ solution and continuous presence of iron). The degradation of phenols was complete under optimized conditions. Esteves and co-workers (2019) investigated Fenton/Fenton-like processes on OMW. The investigation was performed in batch reactors and the influence of different process parameters was evaluated: effect of pH, type of iron salt, Fe/H₂O₂ mass ratio and reactants addition method. Operating at T=25 °C, pH=3, [Fe³⁺]=1 g/L and [Fe³⁺]/[H₂O₂]=0.04 total phenol removal was 81.4 % after 180 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 ($T = 30\text{ }^{\circ}\text{C}$, initial $\text{pH} = 5$, $[\text{Fe}^{2+}] = 100\text{ ppm}$ and $[\text{H}_2\text{O}_2] = 2\text{ g/L}$) 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 , H_2O_2 and iron-salt dosage affect the efficiencies of the Fenton process. With the acid cracking method at $\text{pH} 2.5$, 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 Ioannou-Ttota et al. (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 FeCl_3 as a catalyst was investigated by García and Hodaifa (2017). Various H_2O_2

concentrations (5 – 30 g/L) and four commercial UV lamps were used in this study. Applied process parameters were: temperature $20\text{ }^{\circ}\text{C}$, $\text{pH} = 3$, 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 ($\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 , $\text{Fe}(\text{ClO}_4)_3$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), as well as different H_2O_2 concentrations. The experiments were conducted at $20\text{ }^{\circ}\text{C}$, $\text{pH} = 3$, with a catalyst/ H_2O_2 ratio of 0.03 in the presence of ultraviolet light. The FeCl_3 was proven to be the most effective catalyst with an H_2O_2 concentration of 7.5% (w/v). The phenolic compound removal of 88.4% was achieved at optimal conditions.

Catalytic potential of chalcopyrite (CuFeS_2) and mined pyrite (FeS_2) in the photo-Fenton process was studied by Ltaïef 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.

Table 4. Catalysts and conditions applied in the Fenton process for the removal of phenolic compounds from olive mill wastewater (OMW)

Process	Catalyst	pH	Temperature [°C]	Reference
Fenton	Fe	2 – 4	25	Kallel et al., 2009
Fenton	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	3	r.t.	Alver et al., 2015
Fenton	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	3.5	20	Amor et al., 2015
Fenton	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	2.5	25 – 30	Madani et al., 2015
Fenton	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ $\text{Fe}(\text{NO}_3)_3$ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	5	30	Esteves et al., 2018
Heterogeneous Fenton	BiFeO_3	4.6 - 12	20 – 60	Iboukhoulef et al., 2019
Heterogeneous Fenton	Red mud	3	-	Domingues et al., 2019
Heterogeneous Fenton-like	Fe-carbon	3.8	25	Esteves et al., 2020
Fenton-like	Cu (II)	4.7	30 – 50	Iboukhoulef et al., 2014
Fenton-like	FeCl_3	3	25	Esteves et al., 2019
Heterogeneous Fenton Photo-Fenton-like	FeS_2 CuFeS_2	2.8	25	Ltaïef et al., 2018
Solar photo-Fenton	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	2	-	Ioannou-Ttota et al., 2017
Photo-Fenton	FeCl_3	3	20	García and Hodaifa, 2017
Photo-Fenton	FeCl_3 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ $\text{Fe}_2(\text{SO}_4)_3$ $\text{Fe}(\text{ClO}_4)_3$	3	20	Hodaifa et al., 2020
Electro-Fenton	FeSO_4	2.5	21	Mostafa et al., 2018

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

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.

Author Contributions: The manuscript was written by Melita Lončarić and corrected by Maja Molnar and Mirna Habuda-Stanić.

Acknowledgments: This research has been supported by the Croatian Science Foundation under the project “Green Technologies in Synthesis of Heterocyclic Compounds” (UIP-2017-05-6593).

References

- Abdollahi, Y., Abdullah, A.H., Zainal, Z., Yusof, N.A. (2011): Photocatalytic degradation of *p*-Cresol by zinc oxide under UV irradiation. *Int. J. Mol. Sci.* 13, 302–315. <https://doi.org/10.3390/ijms13010302>
- Achak, M., Hafidi, A., Mandi, L., Ouazzani, N. (2014): Removal of phenolic compounds from olive mill wastewater by adsorption onto wheat bran. *Desalin. Water Treat.* 52 (13-15), 2875-2885. <https://doi.org/10.1080/19443994.2013.819166>
- Achak, M., Hafidi, A., Ouazzani, N., Sayadi, S., Mandi, L. (2009): Low cost biosorbent “banana peel” for the removal of phenolic compounds from olive mill wastewater: Kinetic and equilibrium studies. *J. Hazard. Mater.* 166 (1), 117-125. <https://doi.org/10.1016/j.jhazmat.2008.11.036>
- Aksu, Z., Yener, J. (2001): A comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents. *Waste Manage.* 21 (8), 695-702. [https://doi.org/10.1016/S0956-053X\(01\)00006-X](https://doi.org/10.1016/S0956-053X(01)00006-X)
- Aliakbarian, B., Casazza, A. A., Perego, P. (2015): Kinetic and isotherm modelling of the adsorption of phenolic compounds from olive mill wastewater onto activated carbon. *Food Technol. Biotech.* 53 (2), 207-214. <https://doi.org/10.17113/ftb.53.02.15.3790>
- Al-Kandari H., Abdullah A., Mohamed A., Al-Kandari S. (2016): Enhanced photocatalytic degradation of a phenolic compounds' mixture using a highly efficient TiO₂/reduced graphene oxide nanocomposite. *J. Mater. Sci.* 114, 1–15. <https://doi.org/10.1007/s10853-016-0074-6>
- Alver, A., Baştürk, E., Kılıç, A., Karataş, M. (2015): Use of advance oxidation process to improve the biodegradability of olive oil mill effluents. *Process Saf. and Environ.* 98, 319-324. <https://doi.org/10.1016/j.psep.2015.09.002>
- Amaral-Silva, N.; Martins, R.C.; Castro-Silva, S.; Quinta Ferreira, R.M. (2016): Fenton's treatment as an effective treatment for elderberry effluents: Economical evaluation. *Environ. Technol.* 37, 1208–1219. <https://doi.org/10.1080/09593330.2015.1107624>
- Amor, C., Lucas, M. S., Garcia, J., Dominguez, J. R., De Heredia, J. B., Peres, J. A. (2015): Combined treatment of olive mill wastewater by Fenton's reagent and anaerobic biological process. *J. Environ. Sci. Heal. A.* 50 (2), 161-168. <https://doi.org/10.1080/10934529.2015.975065>
- Asmaly H.A., Abussaud B., Saleh T.A., Gupta V. K., Atieh M.A. (2015): Ferric oxide nanoparticles decorated carbon nanotubes and carbon nanofibers: From synthesis to enhanced removal of phenol. *J. Saudi Chem. Soc.* 19, 511–520. <https://doi.org/10.1016/j.jscs.2015.06.002>
- Barakat, I., Adib, S.A.A.D. (2020): Toxicity Effect of Olive Mill Wastewater on fish species (common carp) *Cyprinus carpio*. *J. Mater. Environ. Sci.* 11 (9), 1531-1537.
- Baransi, K., Dubowski, Y., Sabbah, I. (2012): Synergetic effect between photocatalytic degradation and adsorption processes on the removal of phenolic compounds from olive mill wastewater. *Water Res.* 46 (3), 789-798. <https://doi.org/10.1016/j.watres.2011.11.049>
- Benzaquén, T.B., Isla, M.A., Alfano, O.M. (2015): Fenton and photo-Fenton processes for the degradation of atrazine: A kinetic study. *J. Chem. Technol. Biotechnol.* 90, 459–467. <https://doi.org/10.1002/jctb.4324>
- Bhatnagar, A., Minocha, A.K. (2006): Conventional and non-conventional adsorbents for removal of pollutants from water—A review. *Indian. J. Chem. Technol.* 13, 203-217.
- Burbano, A.A., Dionysiou, D.D., Suidan, M.T., Richardson, T.L. (2005): Oxidation kinetics and effect of pH on the degradation of MTBE with Fenton reagent. *Water Res.* 39, 107–118. <https://doi.org/10.1016/j.watres.2004.09.008>
- Cuomo, F., Venditti, F., Cinelli, G., Ceglie, A., Lopez, F. (2016): Olive mill wastewater (OMW) phenol compounds degradation by means of a visible light activated titanium dioxide-based photocatalyst. *Z. Phys. Chem.* 230 (9), 1269-1280. <https://doi.org/10.1515/zpch-2015-0725>
- Domingues, E., Assunção, N., Gomes, J., Lopes, D.V., Frade, J.R., Quina, M.J., Martins, R.C. (2019): Catalytic efficiency of red mud for the degradation of olive mill wastewater through heterogeneous Fenton's process. *Water.* 11 (6), 1183. <https://doi.org/10.3390/w11061183>
- Domingues, E., Gomes, J., Quina, M.J., Quinta-Ferreira, R.M., Martins, R.C. (2018): Detoxification of olive mill wastewaters by Fenton's process. *Catalysts.* 8 (12), 662. <https://doi.org/10.3390/catal8120662>
- El Moudden, H., El Yadini, A., El Idrissi, Y., Harhar, H., Tabyaoui, B., Tabyaoui, M., Zarrouk, A. (2020): TiO₂-Photocatalyzed degradation of vanillic acid in olive mill wastewaters. *J. Chem. Technol. Metall.* 55 (5), 1019-1026.
- El-Abbassi, A.; Kiai, H.; Hafidi, A. (2012): Phenolic profile and antioxidant activities of olive mill wastewater. *Food Chem.* 132, 406–412. <https://doi.org/10.1016/j.foodchem.2011.11.013>
- Ena, A., Pintucci, C., Carozzi, P. (2012): The recovery of polyphenols from olive mill waste using two adsorbing vegetable matrices. *J. Biotechnol.* 157 (4), 573-577. <https://doi.org/10.1016/j.jbiotec.2011.06.027>
- Esteves, B.M., Morales-Torres, S., Maldonado-Hódar, F.J., Madeira, L.M. (2020): Fitting Biochars and Activated

- Carbons from Residues of the Olive Oil Industry as Supports of Fe-Catalysts for the Heterogeneous Fenton-Like Treatment of Simulated Olive Mill Wastewater. *Nanomaterials*, 10 (5), 876. <https://doi.org/10.3390/nano10050876>
- Esteves, B.M., Rodrigues, C.S., Madeira, L.M. (2018): Synthetic olive mill wastewater treatment by Fenton's process in batch and continuous reactors operation. *Environ. Sci. Pollut. R.* 25 (35), 34826-34838. <https://doi.org/10.1007/s11356-017-0532-y>
- Esteves, B.M., Rodrigues, C.S., Maldonado-Hódar, F.J., Madeira, L.M. (2019): Treatment of high-strength olive mill wastewater by combined Fenton-like oxidation and coagulation/flocculation. *J. Environ. Chem. Eng.* 7 (4), 103252. <https://doi.org/10.1016/j.jece.2019.103252>
- Feng Y.B., Hong L., Liu A.L., Chen W.D., Li G.W., Chen W., Xia X.H. (2015): High-efficiency catalytic degradation of phenol based on the peroxidase-like activity of cupric oxide nanoparticles. *Int. J. Environ. Sci. Te.* 12, 653–660, 2015. <https://doi.org/10.1007/s13762-013-0442-6>
- Frascardi, D., Rubertelli, G., Arous, F., Ragini, A., Bresciani, L., Arzu, A., Pinelli, D. (2019): Valorisation of olive mill wastewater by phenolic compounds adsorption: development and application of a procedure for adsorbent selection. *Chem. Eng. J.* 360, 124-138. <https://doi.org/10.1016/j.cej.2018.11.188>
- Galanakis, C.M. (2011): Olive fruit dietary fiber: components, recovery and applications. *Trends. Food. Sci. Technol.* 22, 175–184. <https://doi.org/10.1016/j.tifs.2010.12.006>
- García, C.A., Hodaifa, G. (2017): Real olive oil mill wastewater treatment by photo-Fenton system using artificial ultraviolet light lamps. *J. Clean. Prod.* 162, 743-753. <https://doi.org/10.1016/j.jclepro.2017.06.088>
- Hodaifa, G., Agabo García, C., Borja, R. (2020): Study of Catalysts' Influence on Photocatalysis/Photodegradation of Olive Oil Mill Wastewater. Determination of the Optimum Working Conditions. *Catalysts*. 10 (5), 554. <https://doi.org/10.3390/catal10050554>
- Iboukhoulef, H., Amrane, A., Kadi, H. (2016): Removal of phenolic compounds from olive mill wastewater by a Fenton-like system H₂O₂/Cu (II)—thermodynamic and kinetic modeling. *Desalin. Water Treat.* 57 (4), 1874-1879. <https://doi.org/10.1080/19443994.2014.978385>
- Iboukhoulef, H., Douani, R., Amrane, A., Chaouchi, A., Elias, A. (2019): Heterogeneous Fenton like degradation of olive Mill wastewater using ozone in the presence of BiFeO₃ photocatalyst. *J. Photoch. Photobio. A.* 383, 112012. <https://doi.org/10.1016/j.jphotochem.2019.112012>
- Ioannou-Ttofa, L., Michael-Kordatou, I., Fattas, S.C., Eusebio, A., Ribeiro, B., Rusan, M., Fatta-Kassinou, 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. <https://doi.org/10.1016/j.watres.2017.02.020>
- Kallel, M., Belaid, C., Mechichi, T., Ksibi, M., Elleuch, B. (2009): Removal of organic load and phenolic compounds from olive mill wastewater by Fenton oxidation with zero-valent iron. *Chem. Eng. J.* 150 (2-3), 391-395. <https://doi.org/10.1016/j.cej.2009.01.017> Get rights and content
- Laoufi N., Tassalit D., Bentahar F. (2008): The degradation of phenol in water solution by TiO₂ photocatalysis in a helical reactor. *Global NEST J.* 10, 404–418.
- Lee, Z.S., Chin, S.Y., Lim, J.W., Witoon, T., Cheng, C.K. (2019): Treatment technologies of palm oil mill effluent (POME) and olive mill wastewater (OMW): A brief review. *Environ. Technol. Innov.* 15, 100377. <https://doi.org/10.1016/j.eti.2019.100377>
- Ltaïef, A.H., Pastrana-Martínez, L.M., Ammar, S., Gadri, A., Faria, J. L., Silva, A. M. (2018): Mined pyrite and chalcopyrite as catalysts for spontaneous acidic pH adjustment in Fenton and LED photo-Fenton-like processes. *J. Chem. Technol. Biotechnol.* 93 (4), 1137-1146. <https://doi.org/10.1002/jctb.5472>
- Madani, M., Aliabadi, M., Nasernejad, B., Kermanj Abdulrahman, R., Yalili Kilic, M., & Kestioglu, K. (2015). Treatment of olive mill wastewater using physico-chemical and Fenton processes. *Desalin. Water Treat.* 53 (8), 2031-2040. <https://doi.org/10.1080/19443994.2013.860882>
- Michael, I., Panagi, A., Ioannou, L.A., Frontistis, Z., Fatta-Kassinou, D. (2014): Utilizing solar energy for the purification of olive mill wastewater using a pilot-scale photocatalytic reactor after coagulation-flocculation. *Water Res.* 60, 28-40. <https://doi.org/10.1016/j.watres.2014.04.032>
- Mirian Z.A., Nezamzadeh-Ejchieh A. (2016): Removal of phenol content of an industrial wastewater via a heterogeneous photodegradation process using supported FeO onto nanoparticles of Iranian clinoptilolite. *Desalin. Water Treat.* 57, 16483–16494. <https://doi.org/10.1080/19443994.2015.1087881>
- Mostafa, H., Iqdam, B.M., Abuagela, M., Marshall, M.R., Pullammanappallil, P., Goodrich-Schneider, R. (2018): Treatment of olive mill wastewater using High Power Ultrasound (HPU) and Electro-Fenton (EF) method. *Chem. Eng. Proc.-Process Intensification*, 131, 131-136. <https://doi.org/10.1016/j.cep.2018.07.015>
- Nogueira, V., Lopes, I., Freitas, A.C., Rocha-Santos, T.A.P., Gonçalves, F., Duarte, A.C., Pereira, R. (2015): Biological treatment with fungi of olive mill wastewater pre-treated by photocatalytic oxidation with nanomaterials. *Ecotox. Environ. Safe.* 115, 234-242. <https://doi.org/10.1016/j.ecoenv.2015.02.028>
- Nuno, A.S., Rui, C.M., Paulo, N., Sérgio, C.S., Rosa, M.Q.F. (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. <https://doi.org/10.1002/jctb.5128>
- Ochando-Pulido, J.M., Pimentel-Moral, S., Verardo, V., Martínez-Ferez, A. (2017): A focus on advanced physico-chemical processes for olive mill wastewater treatment. *Sep. Purif. Technol.* 179, 161-174. <https://doi.org/10.1016/j.seppur.2017.02.004>
- Oladipo, A.A. (2021): CuCr₂O₄@ CaFe-LDO photocatalyst for remarkable removal of COD from high-strength olive mill wastewater. *J. Colloid. Interf. Sci.* 591, 193-202.

- Papaoikonomou, L., Labanaris, K., Kaderides, K., Goula, A.M. (2019): Adsorption-desorption of phenolic compounds from olive mill wastewater using a novel low-cost biosorbent. *Environ. Sci. Pollut. Res.* 1-15. <https://doi.org/10.1007/s11356-019-07277-2>
- Russo, C. (2007): A new membrane process for the selective fractionation and total recovery of polyphenols, water and organic substances from vegetation waters (VW). *J. Membr. Sci.* 288, 239–246 <https://doi.org/10.1016/j.memsci.2006.11.020>
- Şahin, S., Cığeroğlu, Z., Özdemir, O.K., Elhoussein, E., Gülmez, Ö. (2020): Investigation of graphene oxide as highly selective adsorbent in recovery of hydroxytyrosol from olive mill wastewater. *Int. J. Environ. Sci. Technol.* 17 (12), 4803-4814. <https://doi.org/10.1007/s13762-020-02813-x>
- Shahrezaei F., Akhbari A., Rostami A. (2012): Photodegradation and removal of phenol and phenolic derivatives from petroleum refinery wastewater using nanoparticles of TiO₂. *Int. J. Energ. Environ.* 3, 267–274.
- Solomakou, N., Goula, A.M. (2020): Novel Low-Cost Biosorbents of Phenolic Compounds from Olive Mill Wastewaters. In *Multidisciplinary Digital Publishing Institute Proceedings*. 67 (1), 1.
- Turco, A., Malitesta, C. (2020): Removal of Phenolic Compounds from Olive Mill Wastewater by a Polydimethylsiloxane/oxMWCNTs Porous Nanocomposite. *Water*, 12 (12), 3471. <https://doi.org/10.3390/w12123471>
- Uğurlu, M., Karaoğlu, M.H. (2011): TiO₂ supported on sepiolite: preparation, structural and thermal characterization and catalytic behaviour in photocatalytic treatment of phenol and lignin from olive mill wastewater. *Chem. Eng. J.* 166 (3), 859-867. <https://doi.org/10.1016/j.cej.2010.11.056>
- Ulusoy, Ç., Sponza, D.T. (2020): Removal of Polyphenolic Compounds from Olive Mill Wastewater with Sunlight Irradiation Using Nano-Zno-Sio₂ Composite. In *Environmentally-Benign Energy Solutions*. 345-361. Springer, Cham. https://doi.org/10.1007/978-3-030-20637-6_19
- Vavouraki, A.I., Zakoura, M.V., Dareioti, M.A., Kornaros, M. (2019): Biodegradation of Polyphenolic Compounds from Olive Mill Wastewaters (OMW) during Two-stage anaerobic Co-digestion of Agro-industrial mixtures. *Waste Biomass Valori.* 11, 5783-5791. <https://doi.org/10.1007/s12649-019-00887-4>
- Ververi, M., Goula, A. M. (2019): Pomegranate peel and orange juice by-product as new biosorbents of phenolic compounds from olive mill wastewaters. *Chem. Eng. Proc.-Process Intensification*, 138, 86-96. <https://doi.org/10.1016/j.cep.2019.03.010>
- Vuppala, S., Stoller, M. (2020): Nanocomposites Photocatalysis Application for the Purification of Phenols and Real Olive Mill Wastewater through a Sequential Process. *Appl. Sci.* 10 (20), 7329. <https://doi.org/10.3390/app10207329>
- Yangui, A., Abderrabba, M., Sayari, A. (2017): Amine-modified mesoporous silica for quantitative adsorption and release of hydroxytyrosol and other phenolic compounds from olive mill wastewater. *J. Taiwan Inst. Chem. E.* 70, 111-118. <https://doi.org/10.1016/j.jtice.2016.10.053>
- Yuney, K., Oladipo, A.A., Gazi, M., Younis, D.Z. (2020): CuO coated olive cake nanocomposites for rapid phenol removal and effective discoloration of high strength olive mill wastewater. *Chemosphere.* 253, 126703. <https://doi.org/10.1016/j.chemosphere.2020.126703>
- Zhang, M.H., Dong, H., Zhao, L., Wang, D. X., Meng, D. (2019): A review on Fenton process for organic wastewater treatment based on optimization perspective. *Sci. Total Environ.* 670, 110-121. <https://doi.org/10.1016/j.scitotenv.2019.03.180>