Olive Mill Wastewater Treatment: A Recent Review

Linda Al-Hmoud1), Basel Al-Saida2), Arwa Sandouqa1)

1) Chemical Engineering Department, School of Engineering, The University of Jordan, Amman 11942, Jordan
2) Department of Chemistry, Faculty of Science, Al-Balqa Applied University, Salt 19117, Jordan

Olive oil-producing countries in the Mediterranean region generate a considerable amount of olive mill wastewater (OMW), contributing to a severe environmental polluting issue due to its high pollution load. This effluent is exceptionally toxic to the whole soil-air-water ecosystem, and the living organisms inhabiting it (i.e., plants, animals, aquatic organisms, microorganisms, *etc.*). Many researchers have assessed the efficiencies of different treatment techniques to find an environmentally friendly and economically viable solution to be generally adopted. In light of that, the present review article summarizes the state-of-the-art concerning the OMW treatment options, with their pros and cons when possible.

Keywords: olive mill wastewater (OMW); physical treatment, chemical treatment, integrated treatment

Introduction

In the Mediterranean countries, olive oil production is an important economic activity among agro-industrial production. Simultaneously, the discharge of Olive Mill Wastewater (OMW) is a severe problem in these regions. In Jordan, olive oil production is one of the major agricultural industries, with 21 thousand tons produced yearly. In 2018, the process of olive oil extraction generated more than 120,000 m3 of olive mill wastewater (OMW), also known as *Zebar*, along with 33 thousand tons of olive cake (Department of Statistics, 2018, Ministry of Agriculture 2019). OMW's composition depends on several factors, such as the climate, cultivation, and grinding method used to produce olive oil. Several processes are used to produce olive oil, such as traditional pressing and two-phase and three-phase decanting processes. A brief presentation of the two major continuous oil extraction systems is shown in **Figure 1** (Tsagaraki *et al.,* 2007).

In general, OMW is characterized by its strong odor, acidity, dark color, and high organic load (COD, BOD), total dissolved solids (TDS), and high concentration of phenols (Al Bawab *et al.*, 2018a, Azzam 2018, Domingues *et al.*, 2018). In terms of pollution effect, 1m3 of OMW is equivalent to 100-200 m3 of domestic sewage. Its uncontrolled water reservoir disposal leads to severe problems for the natural water bodies (groundwater reservoirs, aquatic surface reservoirs, seashores, and sea) and ecosystems. (Tsagaraki *et al.*, 2007). **Table 1** shows that in Jordan, OMW contains high phenolic contents, high COD, high total suspended solids (TSS), high total dissolved solids (TDS), high concentrations of cations and anions, and low pH value. The high organic load (chemical and biochemical oxygen demand may reach up to 100 to 200 g/L) of OMW makes it hard to manage and difficult to meet the legal thresholds for their discharge to the environment. The presence of toxic compounds in their constitution makes the common biological treatments inefficient.

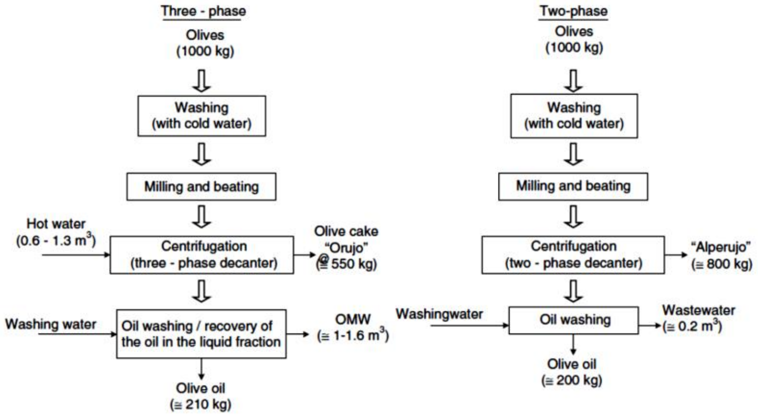

Fig. 1 Three- and two-phase centrifugation systems for olive oil extraction (Tsagaraki *et al.,* 2007)

Consequently, several methods have been proposed and developed to reduce the environmental impact of OMW. These methods can be classified into physical, chemical, and biological processes. There are also integrated methods, where more than one treatment method is used in series to achieve the required elimination goal. This review aims to present different ways proposed and investigated recently to eliminate and reduce OMW pollutants to make them suitable to be discharged to the environment.

Received on November 17, 2020; accepted on November 28, 2020, correspondence concerning this article should be addressed to L. Al-Hmoud (E-email address: l.alhmoud@ju.edu.jo). ORCiD ID for Linda al-Hmoud https://orcid.org/0000-0002-5560-1060

1 OMW Treatment Methods

Various methods have been tested to find an efficient and cost-effective treatment process/system for olive mill wastewater (OMW). These methods are based on chemical, biological, and physical scientific aspects and have often used more than one form. Some methods tried to recover and recycle some valuable components from OMW. Accordingly, the numerous treatment processes that have been recently proposed and investigated are presented here under three categories: physical, chemical, and integrated treatments.

Table 1 Characteristics of OMW in Jordan (Azzam *et al.*, 2015, Al Bsoul *et al.*, 2019, Al-Essa. 2018, Al-Shaweesh *et al.*, 2018)

Property	pH	Phenols	COD	TSS	TDS	Ca	Cu	K	Mg	Na	Zn
Unit	-	mg/L	g/L	g/L	g/L	mg/L	mg/L	g/L	mg/L	mg/L	μg/L
Value	4.6-5.9	300-3000	10-50	5-21	2-35	2.1	0.9	0.2-8	1.9	0.7	33

1.1 Physical treatment

OMW physical treatment methods presented here include liquid extraction, filtration/non-filtration, flotation, adsorption, flocculation, coagulation, used alone or in combination with one or the other. **Table 2** summarizes the reviewed physical treatment methods, their targets/aims, and main results and findings. Abu-Lafi *et al.*, (2017) investigated the enrichment of phenolic compounds from OMW by liquid-liquid extraction. Ethyl acetate was found to be an excellent solvent for the extraction and enrichment process. Ethyl acetate was found to be an excellent solvent for the extraction and enrichment process. Results showed that the extract contains mainly hydroxytyrosol and tyrosol among OMW's main three phenolic compounds, but no oleuropein. Further, OMW extract has strong potential to act as a natural antioxidant and preservative for olive oil. Its addition to olive oil samples positively influenced olive oil's stability as reflected by its acid value, peroxide value, and total phenolic content. The extract's antimicrobial activity was also investigated and showed positive activities as antibacterial and antifungal and activities against yeast. Liquid extraction was also used to isolate phenolic compound content from OMW, before passing it through a membrane filtration system (Sygouni *et al.*, 2019). OMW was collected from olive mills using two-phase extraction systems. The liquid extraction with water and ethanol mixture was optimized by testing extraction parameters such as solvents' mixture, duration, and temperature) at laboratory scale. The maximum total phenolic content (TPC) recovery was attained when a mixture of 50% ethanol and 50% distilled water (50% E-50%W) was used as a solvent. Then extracted solution was fed to a pilot membrane filtration system consisting of ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes in series. UF removed all fats, lipids, and solids while the phenolic and all remaining organic compounds were concentrated in the NF and/or RO retentates. The final effluent in the permeate stream after the RO membrane was found almost clean from polyphenols (10 mg/L), whereas the low concentration of carbohydrates (146 mg/L) and low COD (~284 mg/L) values were detected. This COD value is much lower than the feed stream (>32,000 mg/L) value, giving evidence that it is possible to clean the two-phase OMW with simultaneous recovery of high amounts of phenolic substances. Gikas *et al.*, (2018) found that hybrid natural systems can be used efficiently and economically in treating OMW. The set-up consisted of two hybrid pilot-scale natural systems. The first system comprised two open tanks, one vertical flow constructed wetland and the one free water surface flow, while the second one comprised two open tanks, with calcium hydroxide added to one of them, and one free water surface flow. The results showed that both natural systems are effective in pollutants removals such as TSS (~94%), COD (~65%), and PHE (~64%) in the liquid phase. Calcium hydroxide addition had no significant effect on system efficiency. Moreover, the final pollutant effluent concentrations remained high for disposal in water bodies or used for irrigation. Ait-hmane *et al.*, (2018) examined raw OMW treatment by multi-soil-layering (MSL) ecotechnology. The system comprises soil mixture blocks (soil-sandy texture, sawdust, metal iron, and charcoal) arranged in a brick-like pattern and surrounded by permeable gravel layers to avoid clogging. OMW was diluted by urban wastewater and fed to the system at a continuous hydraulic loading rate (HLR) of 100 L/(m^2.day). Results showed that increasing OMW concentration in the feed to MSL from 10% to 50% induced a pH alkalizing (from 7.9 to 8.5) of treated water and enhanced the system efficiency. Increasing OMW concentration improved TSS (from 95.7% to 99.1%), COD (from 85.0% to 91.8%), BOD (from 54.4% to 82.6%), total phosphorus (from 55.5% to 90.1%), NH_4^+ (from 69.2% to 98.6%) and phenolic compounds (from 91.5% to 100%) reduction. However, when the percentage of OMW percentage in the system feed exceeded 50%, the system efficiency decreased for all parameters. A clogging starting sign (acidic pH, deficient residual oxygen in the outlet) appeared. At 50% OMW concentration, the maximum superficial organic load of 1.4 kg COD/(m^2.day) and 0.516 kg BOD_5/(m^2.day) were obtained, assuring MSL to be an efficient, low-cost treatment method.

Table 2 Summary of Reviewed Physical Treatment Methods, Target, and main Results and Findings.

Process Target/Aim	Process	Result	Reference
Removal of pollutants	Hybrid pilot-scale natural systems	Both natural systems are effective in pollutants removal, such as TSS (~94%), COD (~65%), and polyphenols (~64%).	Gikas *et al.*, 2018
	Multi-soil-layering (MSL) ecotechnology	Efficient, low-cost treatment method	Ait-hmane *et al.*, 2018
	Non-oxidized and oxidized Granular Activated Carbons (GAC, GAC-OX) particles impregnated with surface-active materials (nonionic surfactants (Span 20, Span 80, and Brij 93)	Economical process for OMW remediation	Al Bawab *et al.*, 2018
Isolation of phenolic compounds	Liquid-liquid extraction with ethyl acetate	Ethyl acetate is found to be an excellent solvent for phenolic compound extraction and enrichment from OMW. OMW extract has strong potential to act as a natural antioxidant and preservative for olive oil	Abu-Lafi *et al.*, 2017
	Liquid extraction followed by membrane filtration	Efficient lowering of phenols concentration to (10 mg/L), carbohydrates to (146 mg/L), and COD to (~284 mg/L).	Sygouni *et al.*, 2019
	Surfactant enhanced aquifer remediation (SEAR). Modified surfactants were used: sodium polypropylene oxides sulfate (L167–4S), combined with cationic hydrotropes TBAB	The recovery of phenols using a mixture of 4% L167–4S and TBAB (1:2 molar ratio) was 99.5-99.8%, while by using a combination of 4% L167-4S: TBAB (1:2 molar ratios) the recovery was 95%	Al Bawab *et al.*, 2017
Removal of TSS and oil and grease	Filtration by tubular honeycomb silicon carbide membranes	Efficient to remove TSS and oil and grease.	Fraga *et al.*, 2017
Removal of TSS, TOC, and oil and grease	Nanofiltration	High rejections were obtained for total suspended solids (83 to >99 %), total organic carbon (64 to 99%), chemical oxygen demand (53 to 77%), and oil and grease (67 to >82%).	Sanches *et al.*, 2017
Removal of TSS, FM, TPh, and COD	Combined process (filtration, coagulation, flocculation)	Filters lead to high TSS (~82.5%) and fatty matter (~73.8%) removal, with only 11.3% total phenolic compounds (TPh) and 23.2% COD depletion. Coagulation/flocculation operating at pH = 5 with 250 mg/L ferric chloride coagulant and 5 mg/L of polyelectrolyte flocculant can remove ~10.8% of TPh and 31.3% of COD.	Enaime *et al.*, 2019
Removal of TSS, TPh, and COD	Combined coagulation-flocculation process	Combination of the lime and the ferric chloride allows the removal of 87% of TSS, 58% of COD, and 75% of phenolic compounds	Alaoui *et al.*, 2016
Removal of phenolic compounds	Adsorption by activated carbon prepared from waste "peach stones" carbonized at 900 °C	Reduction of phenols by 91% at the optimal conditions (acidic media: pH = 2, T = 20°C, 2 g of activated carbon/100 ml of OMW, and 1 hour of contact time).	Ziati *et al.*, 2017
	Adsorption by resins (Amberlite™ XAD 4, XAD 16, and FPX 66 resins)	Reduction of 75% of soluble phenolic content was observed when 20% of FPX 66 was applied compared to 65% reduction of phenolics with 20% of XAD 4 and XAD 16.	Vavouraki *et al.*, 2020
	Adsorption by resins (Amberlite™ FPX 66 resins)	A reduction of 68% polyphenols and 60% carbohydrates content. Both Langmuir and Freundlich models fitted the equilibrium data, and kinetic data followed a pseudo-second-order model.	Vavouraki. 2020
	Adsorption by natural Clay (ghassoul)	The quantity of adsorbed polyphenols was 161 mg/g at 25°C. Both Langmuir and Freundlich model models are favorable to describe the adsorption phenomena, and kinetic data were realized at the pseudo-second-order model. Adsorption of polyphenols was exothermic in nature; $\Delta H^0 < 0$, ordered; $\Delta S^0 < 0$, and spontaneous; $\Delta G^0 < 0$.	Allaoui *et al.*, 2020

	Adsorption by natural Clay, volcanic tuff (VT), and charcoal	Reductions in both COD (40%) and phenols (80%) were observed when activated charcoal was employed, without any reasonable reductions when treated natural Clay and treated natural volcanic tuff (VT) were used alone. When all three materials were employed in combinations, results were strongly dependent on the used charcoal level.	Azzam. 2018
Removal of phenolic compounds and heavy metal	Adsorption by Jordanian bentonite activated by hydrochloric acid at 25 °C	Optimum adsorbent concentration is found to be 1 g of activated bentonite/10 mL of OMW. The percentage uptakes exceeded 99% for Zn, Fe, and Mn ions. It reached 65.2% for K^+ and 61.5% for Na^+ ions. Phenolic compounds removal reached 66% at the optimum adsorbent concentration.	Al-Essa. 2018
Removal of organic content	Adsorption by titanium dioxide (TiO_2) nanoparticles	The three examined TiO_2 nanoparticle concentrations (1.0, 1.5, 2.0 g/L), 1.5 g/L of TiO_2 caused the maximum COD uptake, in which it dropped from 1000 ppm to about 100 ppm in 120 min. Adsorption equilibrium data can be fitted to Freundlich isotherm, and the adsorption kinetics follow a pseudo-second-order reaction. The adsorption process was spontaneous and exothermic.	Al Bsoul *et al.,* 2019
	Adsorption by hybrid materials by batch and continuous column methods Montmorillonite (Mt) mineral clay functionalized with the biosurfactant Quillaja saponins (SPN)	Both batch and column methods were influential in OMW's decontamination, where 60-78% organic content reduction was attained.	Sciascia *et al.,* 2019
Removal of polyphehenols and organic content	Treatment by activated sludge (AS)	COD and polyphenols were highly eliminated (90%, 92%, respectively)	Elmansour *et al.,* 2020
	A continuous pilot system of activated sludge (AS)	The continuous pilot system effectively removed 95% of COD and 93% of the phenolic compounds.	El Moussaoui *et al.*, 2018
Removal of TSS, TPh, and COD	Combined coagulation-flocculation process	Combination of the lime and the ferric chloride allows the removal of 87% of TSS, 58% of COD, and 75% of phenolic compounds	Alaoui *et al.*, 2016
Removal of polyphenols, COD, and BOD	Combined coagulation-flocculation by an integrated system comprising of 0.1 g of γ-Fe_2O_3 nanoparticles (particle size less than 10 nm) and 1 kg sand	Removed 99% of total phenols, 97.2% of COD, and 95.3% of BOD_5	Al-Shaweesh *et al.,* 2018
	Coagulation and flocculation by aluminum sulfate (Alum), and chitosan	found that alum performance is better than chitosan, at pH values ≥ 4.0. The use of 800 mg/L of alum led to reductions of about 17%, 57%, and 63% in TOC, COD, and phenols, respectively.	Vuppala *et al.*, 2019

The isolation of phenolic compounds from wastes faces many challenges. Because they do not need expensive equipment and organic solvents, and their energy consumption is relatively low, surfactants have been used for phenolic compounds separation from wastes. Surfactant enhanced aquifer remediation (SEAR) technology was evaluated (Al Bawab *et al.*, 2017) for separating phenolic compounds from OMW. They proposed a new modified surfactant, sodium polypropylene oxides sulfate (L167–4S), combined with cationic hydrotropes tetra butyl ammonium bromide (TBAB) in 1:1 and 1:2 molar ratios. Phenol was used as a model sample of the phenolic compounds in the OMW to evaluate phenolic compounds' recovery efficiency from OMW. The amount of the needed surfactant to extract the phenol was determined using the three-dimensional phase behavior of the phenol, water, and the proposed surfactants. Their study results show that the recovery of phenols using a mixture of 4% L167–4S and TBAB (1:2 molar ratio) was 99.5-99.8% and that COD recovery was 99.5-99.8%. When the mixture of 4% L167-4S: TBAB (1:2 molar ratios) was introduced into the real OMW sample, 95% of organic content was removed from the aqueous phase. On a different aspect, surfactants were used to enhance OMW's remediation by cost-effective media of two granular activated carbon (Al Bawab *et al.,* 2018b). Non-oxidized Granular Activated Carbons (GAC) and oxidized Granular Activated Carbons (GAC-OX), particles impregnated with surface-active materials (nonionic surfactants (Span 20, Span 80, and Brij 93) at three different concentrations (10, 30, 55 mM) were investigated for OMW treatment. Experimental results showed that 10 mM nonionic surfactant concentration was the optimum concentration used in media preparation. Increasing the surfactant concentration to 30 and 55 mM causes a considerable reduction in the phenolic compounds removal percentage. Also, using the oxidized version of 10 mM impregnated GAC media enhanced the percent phenol removal. For both GAC-OX and GAC adsorbent media, the percent removal increases within 15 days during soaking with media without mixing. After 15 days, the percent removal was relatively reduced, which may be due to phenolic compounds desorption. The used adsorbent media is claimed to provide an economical way for OMW remediation.

Activated carbon on its own was also used for the adsorption of phenolic compounds from OMW. Activated carbon prepared from waste "peach stones" was studied by Ziati *et al.,* (2017). The peach stones were cleaned, dried, crushed, and finally carbonized at 900°C. They showed that using this adsorbent for polyphenols concentration reduction resulted in 91% removal at the optimal conditions (acidic media: pH=2, ambient temperature: T=20°C, 2g of activated carbon/100 ml of OMW, and 1 hour of contact time). Furthermore, the adsorption kinetics was rapid, adequately described by the Freundlich model, and pseudo-second-order type.

The adsorption process is believed to be an efficient technique in removing contaminants from OMW. Recently, along with activated carbon, polymeric resins, titanium dioxide, and other adsorbent extracted from a natural source was investigated in adsorbing phenolic compounds from OMW. Amberlite™ XAD 4, XAD 16, and FPX 66 resins were examined in different mass ratios (10, 15, 20%) for phenolic removal from diluted 50% OMW (Vavouraki *et al.,* 2020). A reduction of 75% of the soluble phenolic content was observed when 20% of FPX 66 was applied compared to 65% reduction of phenolics with 20% of XAD 4 and XAD 16. During batch anaerobic digestion experiments of resin pre-treated OMW at mesophilic conditions (37°C), methane production was elevated for FPX-pretreated OMW. Polyphenols in OMW were proved to inhibit OMW fermentation and, thus, methane production. More detailed adsorption experiments were conducted to examine FPX 66, a cross-linked styrene-divinylbenzene polymer, as a sorbent (Vavouraki, 2020). It was used to remove polyphenols and carbohydrates derivatives from OMW. The results showed a 68 and 60% reduction of polyphenols and carbohydrates contents, respectively, within the first one hour, at a pH of 5.24. Moreover, polyphenol removal increased by increasing polyphenol concentration but decreased from 77% to 40% by increasing OMW pH value from 7.5 to 9. Both Langmuir and Freundlich models fitted the equilibrium data, and kinetic data showed that adsorption of polyphenols derived from OMW on FPX 66 resin followed the pseudo-second-order model. A 70% polyphenols recovery and 60% carbohydrates recovery were achieved upon adsorbent resin regeneration with ethanol/isopropanol mixture (in a 50 to 50%) ratio at pH=4.

Natural Clay (ghassoul) was used as an adsorbent in the removal of polyphenols from OMW after being analyzed using XRD, SEM/EDX, FTIR, surface area (BET method), thermal analysis (TGA/ DTA), and X-ray fluorescence (XRF) (Allaoui *et al.,* 2020). The results showed that the adsorbed polyphenols' quantity was 161 mg/g at 25°C, and decreased with increasing temperature. Both Langmuir and Freundlich model models are favorable to describe the adsorption phenomena of polyphenols onto ghassoul clay. However, the Freundlich model is more suitable, and kinetic data was realized at the pseudo-second-order model. Furthermore, the thermodynamic data indicates that the adsorption of polyphenols was exothermic in nature; $\Delta H^0 < 0$, ordered; $\Delta S^0 < 0$, and spontaneous; $\Delta G^0 < 0$.

Other simple natural local materials, natural Clay, volcanic tuff (VT), and charcoal, were also investigated as possible adsorbents employed to decrease the high levels of phenols and organic matter of OMW (Azzam 2018). When used alone, treated natural Clay and treated natural volcanic tuff (VT) did not generally produce reasonable reductions in COD levels nor phenols concentrations present in OMW. However, when activated charcoal was employed, significant reductions in OMW's COD and phenols concentrations were observed, 40% and 80%, respectively. When all three materials were employed in combinations, the results showed a strong dependency on the levels of charcoal used.

Fast, simple, green, non-toxic, and the economical method was used for OMW treatment (Al-Essa. 2018). Activated Jordanian bentonite activated by hydrochloric acid at 25 °C was used as an adsorbent and applied in batch and column techniques. After studying several parameters that affected the adsorption capacity, it was found that maximum removal of total phenolic compounds and heavy metal ions (Zn, Fe, and Mn) was achieved at pH 6 and that the adsorption capacity of phenolic compounds was enhanced with an increase in the solution temperature and with the adsorbent dose. The optimum adsorbent concentration is found to be 1 g of activated bentonite/10 ml of OMW. The percentage uptakes exceeded 99% for Zn, Fe, and Mn ions, while it reached 65.2 and 61.5 for K^+ and Na^+ ions, respectively. The efficiency of phenolic compounds removal increases with an increase in solution temperature and adsorbent dose, with 66% removal achieved at the optimum adsorbent concentration.

Similar findings were observed when titanium dioxide (TiO_2) was investigated as an adsorbent in OMW treatment (Al Bsoul *et al.,* 2019). COD removal efficiency, adsorbent amount, temperature, and pH value were studied. Isotherm studies revealed that the adsorption equilibrium data could be fitted to Freundlich isotherm, and the kinetic study indicated that adsorption did follow a pseudo-second-order reaction. The results also showed that the adsorption process was spontaneous and exothermic. Also, among the three examined TiO_2 nanoparticle concentrations (1.0, 1.5, 2.0 g/L), 1.5 g/L of TiO_2 caused the maximum COD uptake, in which it dropped from 1000 ppm to about 100 ppm in 120 min. COD uptake was inversely proportional to temperature and salts' addition (e.g., sodium chloride, NaCl and potassium chloride, KCl). Finally, COD uptake was found to increase as the pH increases to a particular value (4.9), then fall again; thus, an optimum pH value was found. Sciascia *et al.,* (2019) used hybrid materials based on montmorillonite (Mt) mineral clay functionalized with the biosurfactant Quillaja saponins (SPN), to accomplish the simultaneous decontamination and valorization of OMW. SPN/Mt hybrids were synthesized by varying pH and surfactant/clay ratio and characterized by constructing the adsorption isotherms. The performances of these materials were evaluated in the removal of organic content. SPN/Mt hybrids treated real OMW samples using two different protocols; batch and column. In the batch strategy, OMW batch samples were treated by adding dry SPN/Mt hybrids under continuous stirring. Alternatively, the organoclays were packed in a chromatography column filled with multiple alternate layers of sand and organoclay. Both batch and column methods were useful in the decontamination of OMW, where 60-78% organic content reduction was attained. Regardless of the employed protocol, the clay surface's organophilic modification enhances adsorption capability toward the potentially toxic organic molecules present in the OMW. Comparing the two methods, batch treatments can treat a sizeable OMW volume, but further treatments are needed to separate the adsorbed organic compounds for industrial purposes.

The preparation of the columns is both time and products consuming, and the treated OMW volumes are smaller than in batch treatments, but the column treatments present the advantage of already having a packed organoclay from which the chromatographic separation of the different organic compound could be more comfortable. Elmansour *et al.,* (2020) investigated the possibility of treating OMW by activated sludge (AS) pilot, which was highly diluted (1%) by urban wastewater (UWW). Successful biomass growth of 7.12 g_{MLVSS}/L and activity were obtained despite the high polyphenols' concentration (up to 128 mg/L). High eliminations of COD (90%) and polyphenols (92%) were attained. Similar aspects have been conducted by El Moussaoui *et al.,* (2018) but in a continuous mode. Their results also showed successful growth of the biomass, and the continuous pilot system was capable of effectively removing 95% of COD and 93% of the phenolic compounds. Fraga *et al.,* (2017) filtered OMW using new tubular honeycomb silicon carbide membranes (**Figure 2**) and attained high removals of total suspended solids and oil and grease. They used these new membranes at a pilot scale to treat OMW collected after the sedimentation process at a real wastewater treatment plant. They evaluated the filtration conditions and found that back pulses combined with backwashes help maintain the permeate flux and avoid high transmembrane pressure increase. Results also show that, under total recirculation of the retentate that causes an increased concentration of pollutants in the feed stream, the permeate quality is maintained over time. They suggested using silicon carbide membrane filtration as an alternative to dissolved air flotation and efficiently removing total suspended solids and oil and grease from OMW.

In a study performed by Sanches *et al.,* (2017), real OMW pre-treated by dissolved air flotation was used to assess nanofiltration treatment's feasibility. Four pilot nanofiltration assays were conducted at different volume reduction factors (VRF), the volume ratio between the initial feed of and the retentate: 29, 45, 58, and 81. Data attained demonstrated that nanofiltration can be operated at considerably high VRF values and still effectively remove several components from real OMW pre-treated by dissolved air flotation. A significant flux decline (~50%) was observed at the highest VRF, and the increase in osmotic pressure is believed to be the main reason. Considerably high TSS (83 to >99 %), TOC (64 to 99%), COD (53 to 77%), and oil and grease (67 to >82%) removals were obtained across all experiments. The permeate total phenol concentration could not comply with European legislation for discharge into water bodies. The concentration of total phenols determined in the permeate and volatile compounds contributed to COD being above the legal limits. The recovery of phenolic compounds was found to be economically not feasible. Accordingly, the use of advanced oxidation processes (AOPs) to further reduce COD was suggested to comply with legislation regarding these components.

A combined process comprising two consecutive olive stone (OS) filters followed by a coagulation-flocculation process was developed to perform an efficient pre-treatment of raw OMW (Enaime *et al.,* 2019). The study results showed that using OS filters leads to high total TSS (~82.5%) and fatty matter (FM, ~73.8%) removal from raw OMW, where total phenolic compounds (TPCs) and COD depletion reached 11.3 and 23.2%, respectively. Different parameters affecting the coagulation-flocculation process were studied: pH, coagulant type and concentration, and flocculant type and concentration. The results showed that operating the process at pH = 5 with ferric chloride coagulant at a concentration of 250 mg/L and 5 mg/L of polyelectrolyte flocculant can remove about 10.8% of the TP and 31.3% of the COD.

The combined coagulation-flocculation system attracted many researchers because of its encouraging results toward the treatment of OMW. Alaoui *et al.,* (2016) evaluated the coagulation treatment process's effectiveness with lime and ferric chloride in removing OMW pollutants. Raw OMW was collected from a three-phase olive mill. Their study showed that combining the lime and the ferric chloride allows removing 87% of TSS, 58% of COD, and 75% of phenolic compounds. OMW treatment by this combined coagulation-flocculation system allowed a destabilization of colloidal particles and transformed the phenolic compounds, which facilitated the agglomeration of the hydroxide floc by simple decantation. They suggested adding a chlorination step to reuse treated OMW as wash water or for irrigation of green spaces. After chlorination, the percentages of COD removal and decolorization reach 65% and 71%, respectively.

Al-Shaweesh *et al.,* (2018) used ferric oxide nanoparticles to reduced total phenols concentration in olive mill wastewater (OMW). When γ-Fe_2O_3 nanoparticles (particle size less than 10 nm) were used as a coagulant, its coagulation-flocculation separation efficiency into two phases was noticed to be weak. However, the removal percentage of total phenols reached 87%. They prepared an integrated system comprising of 0.1 g of γ-Fe_2O_3 nanoparticles (particle size less than 10 nm) and 1 kg sand. When this

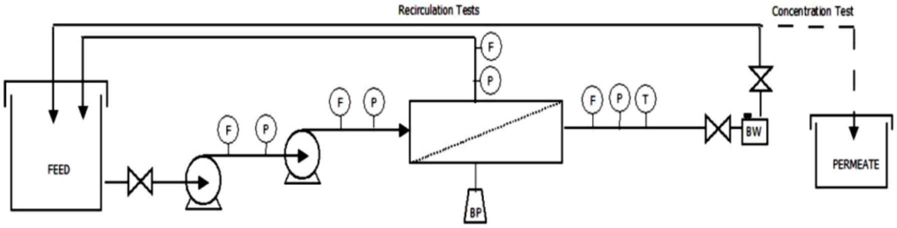

Fig. 2 Schematic diagram of the pilot filtration unit with cleaning devices (BP—Backpulse and BW—Backwash) used to treat the real OMW in different operation modes (Fraga *et al*., 2017)

mixture was used as filter media with diluted real OMW, it removed 99% of total phenols, 97.2% of COD, and 95.3% of BOD_5. Interestingly, Fe_2O_3/sand mixture has shown an excellent capacity to remove some OMW minerals, namely Cr^{+3}, Cu^{+3}, K^+, Ca^{+2}, and Na^+. This might indicate that Fe_2O_3 nanoparticles have multi-adsorption sites that can accommodate different contaminants, enhancing multilayer adsorption.

Vuppala *et al.*, (2019) worked on optimizing coagulation and flocculation conditions for real OMW treatment, focusing on the effect of different pH and coagulant dosage values. System efficiency was checked at three various pH levels (4.5, 4.0, and 3.0), at a fixed dosage of two coagulants – 400 mg/L of aluminum sulfate (Alum), and 100 mg/L of chitosan. The top-performing pH = 4.5 was selected and kept constant for the optimization study of the coagulant dosage, alum, and chitosan, ranging from 400 to 1,200 mg/L of and 300 to 700 mg/L, respectively. It was shown that 1 hour of sedimentation was enough to reach a 99% reduction of turbidity for both chitosan and alum. Among the tested coagulants, the study found that alum performance is better than chitosan, provided the process is operated at pH values ≥ 4.0. The use of 800 mg/L of alum led to reductions of about 17%, 57%, and 63% in TOC, COD, and phenols. A further decrease of 82% in COD, 72% in TOC, and 99% in phenols levels were achieved after the clarified water's biological oxidation treatment.

1.2 Chemical treatment

Researchers focused on electrohydrolysis and electrocoagulation, photocatalytic membrane reactor utilization, Fenton and Fenton-like processes, and hydrothermal carbonization among different available chemical treatment methods. **Table 3** summarizes the reviewed chemical treatment methods, their targets/aims, and main results and findings. Hydrothermal carbonization (HTC) represents an efficient and valuable pre-treatment technology for wastes conversion into highly dense carbonaceous materials for various energetic, environmental, and agricultural applications. The use of the HTC process for the treatment of OMW has been recently investigated (Volpe *et al.*, 2018; Azzaz *et al.*, 2020). Olive waste stream mixture, coming from a three phase-continuous centrifugation olive oil mill, was subjected to HTC at 180, 220, and 250 °C for 3-h residence time in stainless steel electrically heated batch reactor (Volpe *et al.*, 2018). Raw OMW and corresponding hydrochars were characterized. As HTC temperature increases, the hydrochars samples carbonization and energy densification ratio increase, with the latter reaching a maximum value of 142% at 250 °C. The obtained hydrochars were pelletized using a lab-scale pelletizer without the addition of binders or densifying agents, and the one produced at 250 °C showed the best characteristics for palletization. Upon energy characterization (HHV, TGA), ATR-FTIR analysis, fouling index evaluation, and pelletization results, it was suggested that olive mill waste hydrochars could be used as energy-dense and mechanically stable biofuels. Characterization of HTC liquid fractions in terms of nutrients and polyphenolic compounds enabled us to evaluate their potential use as liquid fertilizers. Results showed that HTC could represent a greener alternative for the valorization of olive mill industry waste streams.

Similarly, HTC of OMW generated by three-phase mills was carried out using a high-pressure laboratory autoclave at three different temperatures 180, 200, and 220°C for 24-h residence time (Azzaz *et al.*, 2020). Both solid and liquid produced from thermal conversion were analyzed. Results showed that solid (hydrochars) yield decreased from 57% to 25% when processing temperature was increased from 180 °C and 220 °C, while the fixed carbon percentage increased, accompanied by a decrease in ash and volatile matter percentages, suggesting that decarboxylation is the main reaction driving the HTC process. The O/C ratio decreased, allowing for an increase in the high heating value (HHV) by 32% for hydrochar prepared at 220 °C. On the other hand, organic contents, acids, alcohols, phenols, and sugar derivatives of process liquid were analyzed and high in concentrations and varied with carbonization temperatures. Upon considering the generated HTC products' physicochemical properties, they suggested using hydro chars in energy-related applications, while the liquid fraction could be beneficial in the agricultural field.

Ultra-pure hydrogen production via co-valorization of OMW and bioethanol in Pd-membrane reactors was presented by Alique *et al.*, (2020). Fresh OMW was initially conditioned by filtration and distillation processes. The effect of pressure (1–5 bar), oxidizing conditions (N_2 or air as carrier gas), gas hourly space velocity (150–1500 h^{-1}), and alcohol concentration on the co-reforming process (5–10% v/v) were studied. At the optimum conditions (T=450°C, P=5.0 bar, feed: 15 g/h mixture OMW–EtOH and 15 ml/min N_2, 10% v/v EtOH concentration), 30 Nml/min of ultra-pure hydrogen was obtained.

Table 3 Summary of Reviewed Chemical Treatment Methods, their Target, and main Results and Findings

Process Target/Aim	Process	Results and Findings	Reference
Removal of pollutants	Photocatalytic degradation by nano-ZnO-Magnetite composite	Optimum conditions: nano-ZnO-Magnetite concentration of 3 g/L, the irradiation time of 30 minutes, and the pH value of 4. At these conditions, COD, total phenol, TS, total nitrogen, and total phosphorus removal efficiencies were 80%,	Sponza and Balaban. 2018

Removal of pollutants and hydrogen production		75%, 70%, 97%, and 85%, respectively.	
	Electrocoagulation (EC)	Using response surface methodology (RSM), optimum conditions were reached at current density of 21.1 mA/ cm^2 and 58.9 min of EC time. The highest removal efficiency for TPh, approximately 83%, was obtained. This prediction agreed with the laboratory result (83.5%).	Niazmand *et al.*, 2020
	Electrocoagulation (EC) using aluminum and iron electrodes in the laboratory- and pilot-scale reactors	Aluminum electrodes were found to be more efficient than iron electrodes In the pilot-scale reactor, optimum results were attained at a current density of 5.65 mA/cm^2, with 42.5% COD and 85.3% color removal from biologically pre-treated TOPW.	Benekos *et al.*, 2019
	Electrocoagulation (EC) using aluminum electrode reactor s in the laboratory- and pilot-scale reactors	Under the optimum conditions of 2 h electrolysis time, 41.6 mA/cm^2 current density, and 2 g/L of added salt, the discoloration of OMW diluted ten times is around 91%, and the reduction of the COD is 50%.	Yassine *et al.*, 2018
	Electrocoagulation (EC) powered by the photovoltaic solar system using two aluminum electrodes	Removal of ~79% COD, 95% polyphenols, and 98% dark color within 40 min of treatment at 32.14 mA/cm^2 CD, 5.6 initial pH, and electrodes positioned 35 cm from the bottom of the riser compartment.	Elkacmi *et al.*, 2020
	Fenton process and ozone/Fenton combined process	With Fenton only process, high color (51.6 %), CODs (58%), DOC (27.9%) and phenol (93.9%) removals were achieved with 10 H_2O_2/Fe^{2+} molar ratio. The combined ozone/Fenton process at the same optimum conditions enhanced treatment performance by 21%, 49%, and 22% in color, DOC, and CODs removals.	Kirmaci *et al.*, 2018
	Electrohydrolysis (EH) using two parallel aluminum electrodes	After 24 hours of EH treated OMW settling, 75% COD, 56% soluble COD, 93% turbidity, 61% total solids (TS), 94% TSS, and 92% color removal efficiencies were determined. After 6 h of EH, 1500±50 ml gas was produced, and 88% hydrogen content of gas was obtained.	Erdem *et al.*, 2016
	Electrohydrolysis (EH) using aluminum electrodes,	After 8 h reaction time at an electric potential gradient of 8 V, 73% total COD, 84% suspended solids, 91% color, and 75% phenol removal efficiencies were attained. At the end of the operating period of 8 h, 1037 ml of hydrogen gas was obtained.	Ayman Oz & Eker. 2019
Valorization of olive mill industry waste streams	Hydrothermal carbonization (HTC)	Hydrochars with high carbonization and energy densification ratio. HTC liquid fractions, rich in nutrients and polyphenolic compounds, can be used as liquid fertilizers.	Volpe *et al.*, 2018
	Hydrothermal carbonization (HTC)	The hydrochars high heating value (HHV) increases with increasing process temperature, while its solid yield decreases. Liquid Physico-chemical properties suggest using it in the agricultural field	Azzaz *et al.*, 2020
	Pd-membrane reactors	At the optimum conditions (T = 450°C, P = 5.0 bar, feed: 15 g/h mixture OMW–EtOH and 15 ml/min N_2, 10% v/v EtOH concentration), 30 Nml/min of ultra-pure hydrogen was obtained.	Alique *et al.*, 2020
	Plasma technology	COD and BOD of olive mill wastewater are decreased by 94.4% and 95.4%, respectively. Dissolved oxygen amount increased from 0.36 to 6.97 mg/L. Plasma gas with high H_2 content (60-75% H_2, 4-10% CO_2, 1-2% CO, and 14-18% O_2) was obtained.	Ibrahimoglu *et al.*, 2018
Removal of organic content	Photocatalytic membrane reactor: Silicon carbide membranes with their surfaces being modified with TiO_2	high removals of COD (89%), TOC (87%), and phenolic compounds (95%) at 20 min of operation.	Fraga *et al.*, 2019
Removal of phenolic	Photochemical degradation of tyrosol (TSL) by UV-254 nm	Sulfate and hydroxyl radicals were responsible for TSL	Kilic *et al.*, 2019

compounds	irradiated common oxidants	degradation. Degradation of TSL followed pseudo-first-order kinetics The highest TOC removal (~35%) was achieved by UV/ persulfate treatment.	
OMW pre-treatment	Acid flocculation followed by photocatalytic membrane	Acid flocculation fully satisfies the requirements and can be adopted as a stand-alone pre-treatment process Photocatalysis increases the plant productivity by 18% - 59%, but it is unreasonable economically, as it doubles the cost.	Stoller *et al.,* 2017

Another valorization technique produced plasma gas with high H_2 content (Ibrahimoglu *et al.*, 2018). Plasma technology was used to reduce pollution parameters in OMW and draw water to discharge limits. COD and BOD of olive mill wastewater are decreased by 94.4% and 95.4%, respectively. The dissolved oxygen amount increased from 0.36 to 6.97mg/L. Besides the disposal, plasma gas with high H_2 content (60-75% H_2, 4-10% CO_2, 1-2% CO, and 14-18% O_2) was obtained. The treated water was tested and found that it can be used in agricultural areas for irrigation, as its SAR (Sodium Adsorption Ratio) value was found to be 1.14.

Membrane processes appear to be suitable to purify OMW from organic matter and other pollutants but suffer severe fouling. Stoller *et al.,* (2017) discussed the technical and economic benefits of using photocatalysis as a pre-treatment step for OMW treatment process by membranes. They treated 2-phase and 3-phase OMW through HNO_3 acid flocculation by (AF), and photocatalysis using titania nanoparticles (PC). They found that photocatalysis as an additional pre-treatment process appears to be beneficial from a technical point of view, as it increased the plant productivity by 18%-59%. On the other hand, photocatalysis as an additional pre-treatment process is not economically reasonable since costs are doubled. Acid flocculation appears to satisfy the requirements fully and should be adopted as a stand-alone pre-treatment process for this kind of wastewater.

OMW photocatalytic degradation was also investigated by Sponza and Balaban (2018). They treated raw OMW taken from the olive mill industry by nano-ZnO-Magnetite composite via adsorption and photocatalytic degradation. They found that for photocatalytic degradation under UV, the optimum conditions were nano-ZnO-Magnetite concentration of 3 g/L, the irradiation time of 30 minutes, and pH value of 4. At these conditions, COD, total phenol, TS, total nitrogen, and total phosphorus removal efficiencies were 80%, 75%, 70%, 97%, and 85%, respectively.

Fraga *et al.,* (2019) developed a new design of a photocatalytic membrane reactor and tested it for treating real OMW and enhancing its organic compounds' degradation. The reactor has a cuboid shape with a squared base and is made of polyethylene. Commercial high flux flat sheet silicon carbide membranes are used, and their surfaces were modified with TiO_2 obtained by the sol-gel process, using Degussa P25 and silicon carbide nanoparticles. Results proved the photocatalytic activity of the membrane, achieving high removals of chemical oxygen demand (89%), total organic carbon (87%), and phenolic compounds (95%) with this system at 20 min of operation. The high particulates concentration in OMW causes cake formation on the membrane surface that prevents light from reaching the membrane's photocatalytic layer, leading to a reduction of the produced permeate quality. They suggested solving this problem in a pilot/full-scale system through effective pre-treatment and applying previously proven strategies to minimize fouling, such as backwashing and back pulsing, Fraga *et al.,* (2017).

Kirmaci *et al.,* (2018) investigated the Fenton process, and ozone/Fenton combined process applicability to remove color, soluble CODs, phenol, and dissolved organic carbon (DOC) from real OMW. Two H_2O_2/Fe^{2+} molar ratios (10 and 20) with 0.5 mM H_2O_2 concentration were used to optimize the Fenton process. High color (51.6 %), CODs (58%), DOC (27.9%) and phenol (93.9%) removals were achieved with the 10 H_2O_2/Fe^{2+} molar ratio. Compared to the only-Fenton process, when combined ozone/Fenton process (**Figure 3**) was employed at these optimum conditions, OMW's enhanced treatment performance by 21%, 49%, and 22% in terms of color, DOC, and CODs removals, respectively, was observed. The treatment performance was significantly affected by ozonation time, and the optimum reaction

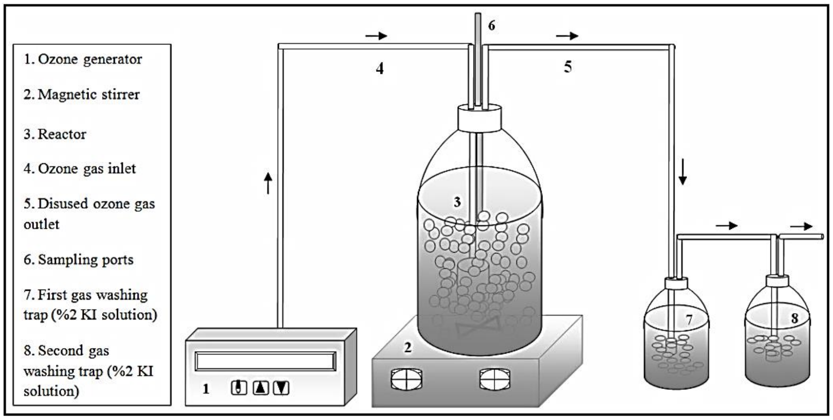

Fig. 3 Schematic diagram of lab-scale combined ozone/Fenton process (Kirmaci *et al.,* 2018)

time was determined to be 90 minutes. Ozonation combined with bio-treatment can convert the nonbiodegradable and hard-to-biodegrade compounds into readily biodegradable compounds for the bio-treatment, resulting in a safer effluent disposal environment.

Kilic *et al.,* (2019) studied the photochemical degradation and mineralization of tyrosol (TSL), a model phenolic compound present in OMW, by UV-254 nm irradiated common oxidants: peroxymonosulfate (PMS), hydrogen peroxide (H_2O_2), and persulfate (PS). The photogenerated radicals in the degradation systems were quantified by using probe methods. Results revealed that sulfate and hydroxyl radicals were responsible for TSL degradation and mineralization, with $SO_4^{\bullet-}$ being the dominant species in UV/PS and UV/PMS systems. Under all experimental conditions examined in the study, degradation of TSL followed pseudo-first-order kinetics, with the efficiencies following the order of UV/PS > UV/H_2O_2 > UV/PMS. The better removal of TSL by UV/PS AOP compared to other systems was correlated with its high quantum yield and the higher concentration of sulfate radicals in the system. The effects of phosphate buffer concentrations and the presence of inorganic anions (i.e., Cl−, SO42− and NO3−) were also investigated and found to have a limited impact on all degradation systems tested. On the other hand, inorganic ions decreased the TOC removal for both UV/PMS and UV/H2O2 processes significantly. Among the three processes, UV/PS was the least affected by inorganic ions and achieved the highest TOC removal (~35%). For all degradation systems, the removal efficiency of TSL was slightly higher in an acidic medium (pH=4.0). Overall, UV/PS system showed faster degradation kinetics than UV/H_2O_2 and UV/PMS for the degradation and mineralization of TSL. Investigation of degradation byproducts and the treated water's biotoxicity is needed for a more comprehensive estimation of the treatment efficiency. In recent years, electrohydrolysis (EH) and electrocoagulation (EC) processes have attracted increasing interest as promising methods because of their simple equipment, easy operation, environmental compatibility, low capital cost, and capacity to remove a wide variety of pollutants present in wastewaters and reduction in sludge amount. Electrohydrolysis (EH) has an added advantage as it produces hydrogen energy from different waste/wastewaters with high organic content.

Erdem *et al.,* (2016) assessed the effectiveness of OMW electrohydrolysis using a lab-scale 1 L glass reactor in removing pollutants and producing hydrogen. Electrohydrolysis process was performed with 600 ml raw OMW sample volume, using two parallel aluminum electrodes and 10 V DC power supply for six hours. After 24 hours of settling, 75% COD, 56% soluble COD, 93% turbidity, 61% total solids (TS), 94% TSS, and 92% color removal efficiencies were determined in the supernatant. At the end of the electrohydrolysis period of 6 h, 1500±50 ml gas was produced, and 88% hydrogen content was obtained.

Ayman Oz and Eker (2019) investigated the electrohydrolysis (EH) process, using aluminum electrodes, to remove organic compounds, detoxification, and discoloration of OMW, with simultaneous energy production in the hydrogen gas form. Overall results showed that the process is beneficial for color and turbidity parameters. The most effective conditions for removing pollutants were determined as 8 h reaction time and electric potential gradient of 8 V. Under these conditions, 73% total COD, 84% suspended solids, 91% color, and 75% phenol removal efficiencies were attained. Also, at the end of the operating period of 8 h, 1037ml of hydrogen gas was obtained. The process is claimed to be a suitable alternative for hydrogen production from wastewater streams and existing treatment options or an additional pre-treatment step in managing the effluents from the olive mill industry. Process performance can be upgraded, and discharge standards can be met by improving the reactor design or by combining the process with other treatment processes. Niazmand *et al.,* (2020) investigated the optimization of electrocoagulation (EC) conditions for the olive debittering wastewater (ODW) purification by response surface methodology (RSM). To optimize the process, a central composite design (CCD) was applied with variables including EC time (10.0–60.0 min) and current density (3.0–30.0 mA/cm^2). The results indicated a noticeable effect of current density and EC time on the efficiency of total phenolic compounds (TPCs) and COD removal. They reached optimum conditions at a current density of 21.1 mA/ cm^2 and 58.9 min of EC time, at which the highest removal efficiency for TPCs, approximately 83%, were obtained. **Figure 4** shows the laboratory set-up used to verify the theoretical finding, in which 83.5% TPCs removal was attained.

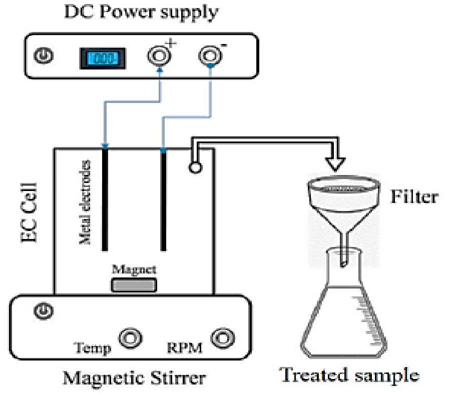

Fig. 4 The electrocoagulation–filtration set-up used in the laboratory analysis. (Niazmand *et al.,* 2020)

Experimentally, Benekos *et al.,* (2019) investigated electrocoagulation (EC) for table olive processing wastewater (TOPW) treatment using different current densities and initial COD concentrations. Using aluminum and iron electrodes, experiments were performed in both laboratory- and pilot-scale reactors to determine the EC efficiency as a single treatment process or as a post-treatment step, respectively. In both laboratory and pilot-scale experiments, aluminum electrodes were found to be more efficient in reducing COD and color than iron electrodes, as well as in metal and energy consumptions. In the pilot-scale reactor, optimum results were attained at a current density of 5.65 mA/cm^2, with 42.5% COD and 85.3% color removal from biologically pre-treated TOPW.

Electrocoagulation is an aluminum electrode reactor is also used to treat OMW collected from a traditional oil mill (Yassine *et al.*, 2018). It was found that increasing electrolysis time and current intensity significantly enhance the treatment performance but also increase electrode metal and energy consumptions. Study results showed that under the optimum conditions of 2 h electrolysis time, the current density of 41.6 mA/cm^2, and added salt of 2 g/L, the discoloration of the OMW diluted ten times is around 91%, and the reduction of the COD is 50% leading to decrease of OMW pollutant power.

Elkacmi *et al.,* (2020) investigated the detoxification of OMW in an external loop airlift reactor (ALR) by electrocoagulation (EC) powered by a photovoltaic solar system as a renewable and sustainable energy source. A continuous flow with two aluminum electrodes was used to study the effect of operating parameters such as initial pH, electrolysis time, current density (CD), and the electrode's axial position. The results showed removal of about 79% of COD, 95% of polyphenols, and 98% of dark color within 40 min of treatment at 32.14 mA/cm^2 CD, 5.6 initial pH, and electrodes positioned 35 cm from the bottom of the riser compartment. Electrical energy consumption and electrode consumption were found to be 9.86 kWh/m^3 and 0.1118 kg/m^3, respectively. Consequently, these obtained results under optimal conditions revealed that coupling the electrocoagulation process with a photovoltaic solar system in a continuous airlift reactor offers a low operation cost compared to other treatment processes.

1.3 Integrated treatments

To achieve acceptable wastewaters that can be readily discharged to the environmental water bodies, many researchers investigated integrated systems, in which more than one treatment method is used in series. **Table 4** summarizes the reviewed integrated treatment methods, their targets/aims, and main results and findings. Amaral-Silva *et al.*, (2016) applied integrated coagulation/flocculation and Fenton processes to OMW treatment. They showed that coupling the coagulation stage with flocculation promotes greater removal efficiency than single coagulation for higher organic matter removal by gravitational settling. The highest COD removal was attained when 0.1 g/L of 2045-SH flocculant was applied to wastewater previously treated with 1 g/L of P19 coagulant, leading to 82% elimination and 84% abatement of total polyphenolic content (TPh). A further combination with the Fenton process revealed that it is possible to reach larger COD and TPh content abatement (90% and 92%) and a biodegradability enhancement to 0.52 compared to the 0.05 of the raw OMW. They studied the main parameters that can affect this system: operating pH, Fe^{2+} and H_2O_2 concentrations, and the ratio between them. An improvement in the pollutants' degradation is observed with higher H_2O_2 levels and higher H_2O_2/Fe^{2+} ratio until a plateau is reached. Also, increasing iron load, up to a certain level, permits a better COD removal, after which higher iron concentration promotes an adverse effect on the performance rate, possibly due to the Fe^{2+}-induced radical scavenging. The treated stream TSSs and TDSs decreased by 95% and 69%, respectively.

Interestingly, they observed that a higher amount of hydrogen peroxide for the same iron dose promotes less biodegradable treated wastewater; lower BOD_5/COD ratio. They also noticed that adding hydrogen peroxide to the Fenton reactor intermittently reduces the H2O2 scavenger effect toward hydroxyl radicals. Its concentration is maintained at a low level reducing the oxidant waste during the treatment and promoting a higher oxidation rate and efficiency. They also showed that the pre-adjustment of pH and its maintenance within the selected range (3.0 ± 0.1) enhanced the COD and TPh removal rates by Fenton oxidation. The integrated coagulation-oxidation system presents a process in which 92.6% COD and 98.3%. TPh removals are attained. Besides, BOD_5/COD ratio was improved from 0.05 to 0.39.

On a similar aspect, Esteves *et al.,* (2019) treated undiluted highly-loaded OMW (TOC_0 = 8.5 g/L and COD_0 = 24.4 g/L, both after sedimentation), coming from the operation of a three-phase olive mill, using. For the Fenton-like system (Fe^{3+}/H_2O_2), they found that the gradual addition of H_2O_2 along with pH readjustments during the process leads to better COD and TPh reduction and enhanced TOC degradation rate, especially in earlier stages of the reaction. On the other hand, the reagents addition method does not affect the overall extent of TOC removal. When operating at initial conditions of pH = 3.0, T = 25°C, $[Fe^{3+}] = 1.0\ g\cdot L^{-1}$ and $Fe/H_2O_2 = 0.04$, removal of 34.9% TOC, 55.7% COD and 81.4% TPh were attained after 180 min. Radiation filtration by OMW dark color and high turbidity hindered significant improvements in photo-Fenton-like process efficiency (41.8% of TOC, 63.2% of COD, and 83.8% of TPh removals under the same conditions).

In comparison with the classic Fenton process (Fe^{2+}/H_2O_2), they found that the extent of TOC removal is greater with Fenton-like oxidation (Fe^{3+}/H_2O_2). At the same time, the degradation rate is higher for the classic process. Ferric chloride acted in the Fenton-like process both as catalyst and coagulant/flocculant. After the oxidation process, one hour of sedimentation allowed for 76.7% COD and 96.4% TPh global reductions in the investigated system. Moreover, this combined process improved the effluent's biodegradability (BOD_5:COD ratio) from the initial value of 0.11 to 0.33, and decreased toxicity against the bioluminescent Vibrio fischeri bacteria from 53% to 4%.

Table 4 Summary of Reviewed Integrated Treatment Methods, Target, and main Results and Findings.

Process Target/Aim	Process	Results and Findings	Reference
Removal of pollutants, reduce organic load and improve the biodegradability	Integrated coagulation/flocculation and Fenton processes	The highest COD removal (82%) was attained when 0.1 g/L of 2045-SH flocculant was applied to wastewater previously treated with 1 g/L of P19 coagulant, leading to 84% abatement of TPh content. A further combination with the Fenton process allowed reaching larger COD and TPh content abatement (90% and 92%) and a biodegradability enhancement to 0.52 compared to the 0.05 of the raw OMW. The integrated coagulation-oxidation system allows attaining 92.6% COD and 98.3% TPh removals.	Amaral-Silva *et al.*, 2016
	Fenton-like oxidation (Fe^{3+}/H_2O_2), followed by coagulation/flocculation	For the Fenton-like, the gradual addition of H_2O_2 and pH readjustments during the process lead to better COD and TPh reduction and TOC degradation rate. Ferric chloride acted in the Fenton-like process both as catalyst and coagulant/flocculant. One hour of sedimentation after the oxidation process allowed for 76.7% COD and 96.4% TPh global reductions in the investigated system and improved the effluent's biodegradability from the initial value of 0.11 to 0.33.	Esteves *et al.*, 2019
	The combination of electrocoagulation (using Fe electrodes), catalytic ozonation, and biodegradation	Optimal conditions for the electrocoagulation process are at 5 mA⁄cm^2 CD for 45 min reaction time. The combined system's overall efficiency in removing COD and TOC was 98.4% and 97.2%, respectively.	Khani *et al.*, 2020
	Coagulation/flocculation with electrolytes and polyelectrolytes	Among the screened electrolytes, $FeCl_3$ was the most effective one in terms of COD reduction (43%), and PDA DMAC was the most effective polyelectrolytes (46% COD reduction). The best results were obtained when 20 g/L of $Ca(OH)_2$ as an electrolyte was combined with PDADMAC polyelectrolyte at 1.25 g/L: reductions of 43% in TS, 27% in TSS, 56% in COD, and 76% in phenols.	Iakovides *et al.*, 2016
	Flocculation, photolysis and microfiltration, integrated with microalgal growth stages	Physico-chemical treatments allowed for a significant reduction of OMW organic load. The final treated water is claimed to be suitable for irrigation use, discharge to receiving waters, or reuse in the process itself, allowing it to close the process water cycle.	Malvis *et al.*, 2019
	Integrated two-stage process	First stage: pre-ozonation, primary sediment separation, electrocoagulation and lime suspension treatment. In the first stage, 59% of COD, 86% of total phenols, 70% of color and 91% of TS reduction was attained. Second stage: pre-ozonation reactor, oxidation process using ((Fe_2O_3+CuO)/Clay) catalytic system, followed by adsorption on charcoal. In the second stage, 96% of COD, 100% of total phenols and color and TSS reduction was attained.	Jomaa and Hourieh. 2020

Khani *et al.*, (2020) studied the combination of electrocoagulation, catalytic ozonation, and biodegradation to reduce organic load and improve OMW's biodegradability. Electrocoagulation was performed using Fe electrodes at a current density of 7.3, 5, and 0.5 mA⁄cm^2. The electrocoagulation process's optimal conditions are found to be at 5 mA⁄cm^2 CD for 45 min reaction time. The treated wastewater under these optimal conditions was then fed to a catalytic ozonation process (COP) reactor (**Figure 5**). In the COP, 44% TOC and 56% COD removals were achieved after 90 min. Eventually, the COP reactor effluent was introduced into the biological reactor. The combined system's overall efficiency in removing COD and TOC was 98.4% and 97.2%, respectively.

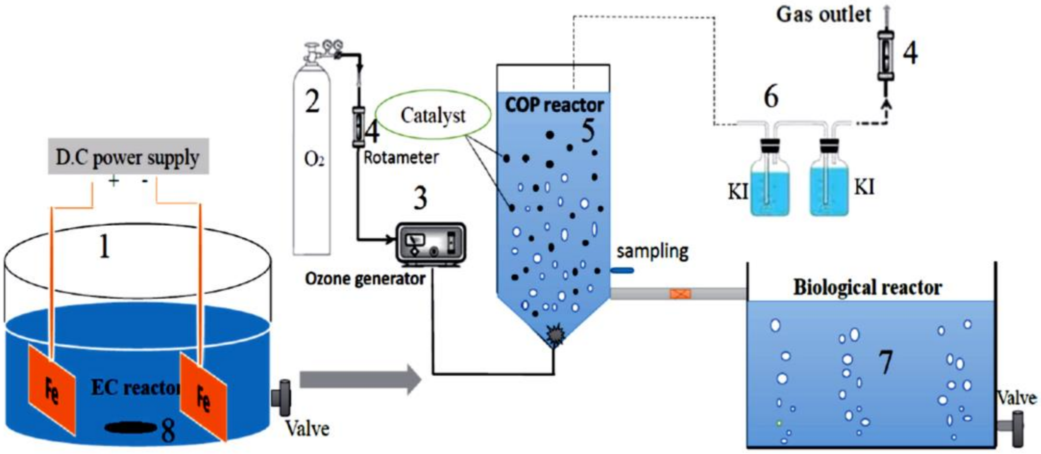

Fig. 5 Schematic diagram of olive oil wastewater treatment processes; 1. Electrocoagulation cell, 2. Oxygen capsule, 3. Ozone generator, 4. Rotameter, 5.COP reactor, 6. Gas trapper, 7. Biological reactor, 8. Magnetic mixer (Khani *et al.*, 2020)

Iakovides *et al.*, (2016) presented experiments of coagulation/flocculation with electrolytes [$FeCl_3$, $Ca(OH)_2$, CaO, $CaCl_2$] and polyelectrolytes (PDADMAC, PAH, PAA, PEI, Floccan 22-23) as a physicochemical method for the OMW treatment. They focused on decreasing the suspended particles' electrical charge by monitoring the changes in the zeta potential of the particles. Among the screened electrolytes, $FeCl_3$ was the most effective in terms of COD reduction (43%). On the other hand, PDADMAC was the most effective polyelectrolytes (46% COD reduction). Moreover, they identified the isoelectric point through zeta potential measurement, and it coincided with the coagulant concentration that caused optimum organic load reduction percentages. The best results were obtained when 20 g/L of $Ca(OH)_2$ as an electrolyte was combined with PDADMAC polyelectrolyte at 1.25 g/L, where reductions of 43% in TS, 27% in TSS, 56% in COD, and 76% in phenols were observed.

Malvis *et al.*, (2019) proposed an integral process based on Physico-chemical (flocculation, photolysis, and microfiltration) and microalgal growth stages for the treatment of real OMW obtained from an olive oil extraction plant. The primary treatment (flocculation-sedimentation, photolysis and microfiltration) allowed for significant reduction of OMW organic load (96.2% of COD, 80.3% of TOC and 96.6% of total phenolic compounds (TPCs)). Secondary treatment eliminated the rest of OMW organic load. In the secondary treatment, they conducted different experiments using the microalgae Chlorella pyrenoidosa on a laboratory scale in stirred batch tank reactors at different OMW concentrations in the culture medium: 5%, 10%, 25%, 50%, 75%, and 100% (v/v). The 50% (v/v) was found to be the optimum OMW concentration at which the highest maximum specific growth rate ($\mu_m = 0.07\ h^{-1}$) and volumetric biomass production ($P_b = 1.25$ mg/(L.h)) were achieved. They claimed the final treated water to be suitable for irrigation use, discharge to receiving waters, or reuse in the process itself, allowing them to close the process water cycle.

Jomaa and Hourieh (2020) used an integrated two-stage process to treat OMW under atmospheric pressure and room temperature. They reduced 59% of COD, 86% of total phenols, 70% of color, and 91% of TS in the first stage, including pre-ozonation of raw OMW, primary sediment separation, followed by electrocoagulation, and lime suspension treatment. In the second stage, treated OMW was driven to a pre-ozonation reactor followed by an oxidation process using ((Fe_2O_3+CuO)/Clay) catalytic system at 25 min residence time by adsorption on charcoal. This stage reduced 96% of COD, 100% of total phenols, and color and TSS.

Conclusions

From the literature reviewed herein, it can be concluded that there is no ideal olive mill wastewater (OMW) treatment solution. Several environmentally friendly and economically viable solutions are presented and proposed, including physical, chemical, and integrated treatment methods. No one method is suitable for all types of OMWs, as they differ from one region to another in their chemical and physical properties and characteristics. Although OMWs is currently considered waste, it can become a valuable energy source and high value-added natural products. Future research should explore various treatment methods and combine different approaches to utilize the most appropriate and economically feasible process.

Nomenclature

AOP =advanced oxidation process
ATR-FTIR: =Attenuated total reflectance-Fourier transform infrared spectroscopy
BET =Brunauer–Emmett–Teller

BOD =biochemical oxygen demand
CD =current density
COD =Chemical Oxygen Demand
DOC =dissolved organic carbon
EC =electrocoagulation
EDX =energy-dispersive X-ray
EH =electrohydrolysis
FTIR =Fourier transform infrared spectroscopy
GAC =Granular Activated Carbons
GAC-OX =oxidized Granular Activated Carbons
HHV =high heating value
HTC =Hydrothermal carbonization
MSL =multi-soil-layering
Mt =montmorillonite
NF =nanofiltration
OMW =Olive Mill Wastewater
PMS =peroxymonosulfate
RO =reverse osmosis
SEM =scanning electron microscope
SPN =Quillaja saponins
TBAB =tetra butyl ammonium bromide
TDS =total dissolved solids
TGA/DTA =thermal gas analysis
TOPW =table olive processing wastewater
TPCs =total phenolic compounds
TPh =total phenolic content
TS =total solids
TSL =tyrosol
TSS =total suspended solids
UF =ultrafiltration
XRD =X-ray Diffraction
XRF =X-ray fluorescence

References

Abu-Lafi, S., Al-Natsheh, M. S., Yaghmoor, R., and Al-Rimawi F. “Enrichment of Phenolic Compounds from Olive Mill Wastewater and In Vitro Evaluation of Their Antimicrobial Activities”, *Evidence-Based Complementary and Alternative Medicine*, **2017**, 1-9 (2017).

Ait-hmane, A., Ouazzani, N., Latrach, L., Hejjaj, A., Assabbane, A., Belkouadssi, M., and Mandi L. “Feasibility of Olive Mill Wastewater treatment by Multi-Soil-Layering Ecotechnology”, *J. Mater. Environ. Sci.*, **9**, 1223-1233 (2018).

Al Bawab, A., Alshawawreh, F., Abu-Dalo, M., Al-Rawashdeh, M., and Bozeya A. “Separation of soluble phenolic compounds from olive mill wastewater (OMW) using modified surfactants”, *Fresenius Environ. Bull.*, **26**, 1949-1958 (2017).

Al Bawab, A., Ghannam, N., Abu-Mallouh, S., Bozeya, A., and Abu-Zurayk R. “Olive mill wastewater treatment in Jordan: A Review”, *Proceedings of IOP Conf. Ser.: Mater. Sci. Eng.*, **305**, 012002 (2018a).

Al Bawab, A., Ghannam, N., Abu-Zurayk, R., Odeh, F., Bozeya, A., Abu Mallouh, S., Al-Rawashdeh, N., and Abu-Dalo M. “Olive Mill Wastewater Remediation with Granular Activated Carbon Impregnated with Active Materials”, *Fresenius Enviro. Bull.*, **24**, 2118-2126 (2018b).

Al Bsoul, A., Hailat, M., Abdelhay, A., Tawalbehc, M., Jum'h I., and Bani-Melhem K. “Treatment of olive mill effluent by adsorption on titanium oxide nanoparticles”, *Sci. of the Total Environ.*, **688**, 1327–1334 (2019).

Alaoui, N.S., El Laghdach, A., Stitou, M., and Bakkali A. “Treatment and valorization of olive mill wastewaters”, *Mediterranean J. of Chemistry*, **5**, 458-464 (2016).

Al-Essa, K. “Activation of Jordanian Bentonite by Hydrochloric Acid and Its Potential for Olive Mill Wastewater Enhanced Treatment”, *J. of Chemistry*, **2018**, 1-10 (2018).

Alique, D., Bruni, G., Sanz, R., Calles, J. A., and Tosti S. “Ultra-Pure Hydrogen via Co-Valorization of Olive Mill Wastewater and Bioethanol in Pd-Membrane Reactors”, *Processes*, **8**, 1-16, (2020).

Allaoui, S., Bennani, M. N., Ziyat, H., Qabaqous, O., Tijani, N., and Ittobane N. “Kinetic Study of the Adsorption of Polyphenols from Olive Mill Wastewater onto Natural Clay: Ghassoul”, *J. of Chemistry*, **2020**, 1-11 (2020).

Al-Shaweesh, M., Matouq, M., Al-Kabariti D., Khamash D., Al-Zawaidah S., Hindiyeh M., and Omar W. “Olive mill wastewater (OMW) treatment by using ferric oxide dephenolization and chemical oxygen demand removal”, *Global NEST Journal*, **20**, 558–563 (2018).

Amaral-Silva, N., Martins, R. C., Castro-Silva, S., and Quinta-Ferreira R. “Integration of traditional systems and advanced oxidation process technologies for the industrial treatment of olive mill wastewaters”, *Environmental Technology*, **37**, 2524-2535 (2016).

Ayman Oz, N., and Cagla Uzun Eker A. “Simultaneous hydrogen production and pollutant removal from olive mill wastewaters using electrohydrolysis process”, *Chemosphere*, **232**, 296-303 (2019).

Azzam, M. O. “Olive mills wastewater treatment using mixed adsorbents of volcanic tuff, natural clay, and charcoal”, *J. of Environ. Chem. Eng.*, **6**, 2126-2136 (2018).

Azzam, M. O., Al-Gharabli, S. I., and Al-Harahsheh M. “Olive mills wastewater treatment using local natural Jordanian clay”, *Desalination and Water Treatment*, **53**(3), 627-636 (2015).

Azzaz, A. A., Jeguirim, M., Kinigopoulou, V., Doulgeris, C., Goddard, M.-L., Jellali, S., and Ghimbeu C. “Olive mill wastewater: From a pollutant to green fuels, agricultural and water source and bio-fertilizer – Hydrothermal carbonization”, *Sci. of the Total Environ.*, **733**, 1-12 (2020).

Benekos, A. K., Zampeta, C., Argyriou, R., Economou, C. N., Triantaphyllidou I. E., Tatoulis T. I., Tekerlekopoulou, A. G., and Vayenas D. V. “Treatment of table olive processing wastewaters using electrocoagulation in laboratory and pilot-scale reactors”, *Proc. Safety and Environ. Prot.*, **131**, 38-47 (2019).

Department of Statistics, “Agricultural Statistics Bulletin (National Strategy for Agricult ural Development Surveys)”, The Hashemite Kingdom of Jordan (2018).

Department of Strategic Planning and Institutional Development, Ministry of Agriculture “Annual Report”, The Hashemite Kingdom of Jordan (2019).

Domingues, E., Gomes, J., Quina, M. J., Quinta-Ferreira, R. M., and Martins R. C. “Detoxification of Olive Mill Wastewaters by Fenton’s Process”, *Catalysts*, **8**, 1-17 (2018).

El Moussaoui, T., Jaouad, Y., Mandi, L., Marrot, B., and Ouazzani N. “Biomass behaviour in a conventional activated sludge system treating olive mill wastewater”, *Environ. Tech.*, **39**, 190-202 (2018).

Elkacmi, R., Boudouch, O., Hasib, A., Bouzaid, M., and Bennajah M. “Photovoltaic electrocoagulation treatment of olive mill wastewater using an external-loop airlift reactor”, *Sustain. Chem. and Pharmacy*, **17**, 100274 (2020).

Elmansour, T., Mandi, L., Ahmali, A., Elghadraoui, A., Aziz, F., Hejjaj, A., Delbuba, M., and Ouazzani N. “Effect of polyphenols on activated sludge biomass during the treatment of highly diluted olive mill wastewaters: biomass dynamics and purifying performances”, *Water Sci. and Tech.*, **82**, 1416-29 (2020).

Enaime, G., Baçaoui, A., Yaacoubi, A., Wichern, M., and Lübken M. “Olive mill wastewater pretreatment by combination of filtration on olive stone filters and coagulation–flocculation”, *Environ. Tech.*, **40**, 2135-2146 (2019).

Erdem, S., Bag, H., Can Yarimtepe, C., Ince, O., and Ayman N.“Hydrogen gas production and pollutant removal from olive mill wastewater by electrohydrolysis”, *WIT Trans. on Ecology and the Environ.*, **205**, 271-277 (2016).

Esteves, B. M., Rodrigues, C. S., Maldonado-Hódar, F. J., and Madeira L. “Treatment of high-strength olive mill wastewater by combined Fenton-like oxidation and coagulation/flocculation”, *J. of Environ. Chem. Eng.*, **7**, 1-12 (2019).

Fraga, M. C., Sanches, S., Crespo, J. G., and Pereira V. “Assessment of a New Silicon Carbide Tubular Honeycomb Membrane for Treatment of Olive Mill Wastewaters”, *Membranes*, **7**, 1-16 (2017).

Fraga, M. C., Huertas, R. M., Crespo, J.G., and Pereira V. J. “Novel Submerged Photocatalytic Membrane Reactor for Treatment of Olive Mill Wastewaters”, *Catalysts*, **9**, 1-16 (2019).

Gikas, G. D., Tsakmakis, I. D., and Tsihrintzis, V. “Hybrid Natural Systems for Treatment of Olive mill Wastewater”, *J. Chem. Technol. Biotech.*, **93**, 800-809 (2018).

Iakovides, I. C., Pantziaros, A. G., Zagklis, D. P., and. Paraskeva C. “Effect of electrolytes/polyelectrolytes on the removal of solids and organics from olive mill wastewater”, *J. Chem. Technol. Biotec.*, **91**, 204-211 (2016).

Ibrahimoglu, B., and Yilmazoglu M. “Disposal of olive mill wastewater with DC arc plasma method”, *J. of Environ. Manag.*, **217**, 727-734 (2018).

Jomaa, N., and Hourieh Y. “Integrated Process for the Treatment of Olive Oil Mill Waste Water (OMW)”, *Chemistry Res. J.*, **5**, 121-129 (2020).

Khani, M. R., Mahdizadeh, H., Kannan, K., Kalankesh, L. R., Kamarehei, B., Baneshi, M. M., and Shahamat Y. “Olive Mill Wastewater (OMW) Treatment by Hybrid Processes of Electrocoagulation/Catalytic Ozonation and Biodegradation”, *Environ. Eng. & Manag. J.*, **19**, 1401-1410 (2020).

Kilic, M. Y., Abdelraheem, W. H., He, X., Kestioglu, K., and Dionysiou D. “Photochemical treatment of tyrosol, a model phenolic compound present in olive mill wastewater, by hydroxyl and sulfate radical-based advanced oxidation processes (AOPs)”, *J. of Haza. Mater.*, **367**, 734-742 (2019).

Kirmaci. A., Duyar A., Akgul V., Akman D., and Cirik K. “Optimization of combined ozone/Fenton process on olive mill wastewater treatment” *Aksaray University J. of Sci. and Eng.*, **2**, 52-62 (2018).

Malvis, A., Hodaifa, G., Halioui, M., Seyedsalehi, M., and Sánchez S. “Integrated process for olive oil mill wastewater treatment and its revalorization through the generation of high added value algal biomass”, *Water Res.*, **151**, 332-342 (2019).

Niazmand, R., Jahani, M., Sabbagh, F., and Rezania S. “Optimization of Electrocoagulation Conditions for the Purification of Table Olive Debittering Wastewater Using Response Surface Methodology”, *Water*, **12**, 1-18 (2020).

Sanches, S., Fraga, M. C., Silva, N. A., Nunes, P., Crespo, J. G., and Pereira V. “Pilot scale nanofiltration treatment of olive mill wastewater: a technical and economical evaluation”, *Environ. Sci. Pollut. Res.*, **24**,3506-3518 (2017).

Sciascia, L. Casella, S., Cavallaro, G., Lazzara, G., Milioto, S., Princivalle, F., and Parisi F. “Olive mill wastewaters decontamination based on organo-nano-clay composites”, *Ceramics Int.*, **45**, 2751-2759 (2019).

Sponza D.T., and Balaban M. “Treatment of Olive Mill Effluent by Nano-Zinc Oxide-Magnetite”, *American J. of Nanotech. & Nanomedicine*, **1**, 028-042 (2018).

Stoller, M., Ochando-Pulidob, J.M., Vilardia, G., Vuppalaa, S., Bravia, M., Verdonea, N., and Di Palmaa L. “Technical and Economic Impact of Photocatalysis as a Pretreatment Process Step in Olive Mill Wastewater Treatment by Membranes”, *Chem. Eng.Trans.*, **57**, 1171-1176 (2017).

Sygouni, V., Pantziaros, A. G., Iakovides, I.C., Sfetsa, E., Bogdou, P. I., Christoforou, E. A., and Paraskeva C. “Treatment of Two-Phase Olive Mill Wastewater and Recovery of Phenolic Compounds Using Membrane Technology”, *Membranes*, **9**, 1-16 (2019).

Tsagaraki, E., Lazarides, H. N., and Petrotos K. B. “Olive Mill Wastewater Treatment” In: Oreopoulou V., Russ W. editors. Utilization of By-Products and Treatment of Waste in the Food Industry. Boston, MA.: Springer, 2007.

Vavouraki, A. I. “Removal of Polyphenols from Olive Mill Wastewater by FPX 66 Resin: Part II. Adsorption Kinetics and Equilibrium Studies”, *Int. J. Waste Resour.*, **10**, 1-7 (2020).

Vavouraki, A. I., Dareioti, M. A., and Kornaros M. “Olive Mill Wastewater (OMW) Polyphenols Adsorption onto Polymeric Resins: Part I—Batch Anaerobic Digestion of OMW”, *Waste Biomass Valor*, (2020).

Volpe, M., Wüst, D., Merzari, F., Lucian, M., Andreottola, G., Kruse, A., and Fiori L. “One stage olive mill waste streams valorisation via hydrothermal carbonization”, *Waste Manag.*, **80**, 224-234 (2018).

Vuppala, S., Bavasso, I., Stoller, M., Di Palma, L., and G. Vilardi "Olive mill wastewater integrated purification through pre-treatments using coagulants and biological methods: experimental, modelling and scale-up', *J. of Cleaner Prod.*, **236**, 1-11 (2019).

Yassine, W., Akazdam, S., Zyade, S., and Gourich B. "Treatment of Olive Mill Wastewater Using Electrocoagulation Process", *J. of Appl. Surfaces and Interfaces*, **4**, 24-30 (2018).

Ziati, M., Khemmari, F., Cherifi, O., and Didouche F.Y. "Removal of Polyphenols from Olive Mill Wastewater by Adsorption on Activated Carbon Prepared from Peach Stones", *Rev. Roum. Chim.*, **62**, 865-874 (2017).