Advanced oxidation technologies for the treatment and detoxification of olive mill wastewater: a general review
Reda Elkacmi and Mounir Bennajah

ABSTRACT

Olive oil production has an economic importance for Mediterranean countries, ensuring employment opportunities and export earnings. The crushing units produce two types of residues, one solid (pomace) and the other liquid, called olive mill wastewater (OMW). This by-product has adverse effects on the olive oil sector and particularly on the quality of waters into which they are discharged. Hence, there is a critical need to orient the scientific research toward the treatment of this hazardous waste. Several techniques have been proposed and developed for OMW management. However, the advanced oxidation processes (AOP) remain the most advantageous with high treatment efficiencies. This trend allowed achieving a significant detoxification of OMW. A considerable amount of effort has been expanded to provide detailed and critical reviews on the use of this alternative technology in the treatment of water and wastewaters. Regrettably most, if not all, of these review papers were not focused mainly on OMW application. This paper aims to highlight the ancient and recent progress of various types of oxidation techniques for OMW treatment. Moreover, principles, advantages, limitations, and efficiencies of each method are presented, to gain a more scientific understanding of the most feasible approach regarding the treatment of this harmful residue.

Key words | advanced oxidation processes, chemical, electrochemical, olive mill wastewater, photochemical, sonochemical

INTRODUCTION

Currently, there is a lack of common international laws regulating the discharge of olive mill wastewater (OMW), resulting in an increasing environmental hazard. The hazard of OMW is mostly due to its high acidity (pH between 3 and 6), its high organic load (COD over 80–200 g/L), (BOD₅ over 12–60 g/L) and its high content of microbial growth-inhibiting compounds, such as phenolic compounds and tannins (Cebeci et al. 2016; Azzam 2018; Bampalioutas et al. 2019).

The estimated annual volume of OMW generated by the Mediterranean region is approximately 30 million m³ and this huge amount is creating a serious ecological and environmental issue resulting in severe consequences for the soil and water quality (Gudiña et al. 2016).

The extraction of olive oil is achieved through traditional methods of discontinuous pressing in the traditional mills or ‘mâasra’, as named locally in Morocco, and produced 0.5 m³ of OMW from 1,000 kg of processed olive, while the continuous method (two-phase and three-phase systems) releases about 1.5 m³ per 1,000 kg of olive (Elkacmi et al. 2016a). A disadvantage of this last method is that it uses more water to extract the oil compared with the other techniques and consequently generates larger quantities of OMW. Water is used in some of these stages to extract most of the olive oil. Once the olives are crushed mechanically, the resulting paste is mixed and kneaded to increase the yield of recovery and help small
oil droplets to coalesce and agglomerate, thus facilitating the separation of the oil and water phases. Less water is required for the discontinuous process (about 40%) compared to the continuous system, which varies from 70 to 110% (Bouknana et al. 2014), therefore traditional techniques contribute to preserving water resources.

For the above-mentioned traditional press system, the extraction is carried out without significant addition of water, which affects the organic loading rate and suspended solids. Indeed, the OMW of traditional units are more loaded and more concentrated than those of modern units. Some authors have reported that the COD of OMW from the continuous olive oil extraction process varies over the range of approximately 20–200 g/L, compared to 100–390 g/L for the press processes (Sassi et al. 2006).

OMWs have a cloudy appearance, reddish-brown to black in color and this color is a function of the state of degradation of the phenolic compounds and the olives from which they derive, it has a smell reminiscent of olive oil, but when fermented it assumes a fetid smell.

As is widely known, the composition of this type of aqueous waste depends on several factors, such as climatic and soil conditions, harvesting and carriage systems, olive cultivars, degree of fruit maturation, storage time, irrigation management and processing technology (Kipcak & Akgun 2018). Table 1 summarizes the overall composition of OMW given by several authors from the top 10 olive oil producing countries according to the International Olive Council (IOC) in 2016 (IOC 2016).

In Morocco, as in other olive oil producing countries, in most cases OMW is still discharged into water or land without any treatment, either directly or through the public sewer system. These effluents are responsible for serious problems of pollution, creating a major nuisance and disturbance to the receiving environment. Several studies have proven the negative effects of these wastes on soil properties and plants (Buchmann et al. 2013), on aquatic ecosystems (Leris et al. 2019) as well as in air medium (Casanovas et al. 2013). For all these reasons, much attention has been paid to the fight against pollution posed by this harmful waste. In the last decade, various management methods have been applied for the prevention of pollution caused by OMW, which can be categorized into physical, biological, chemical and electrochemical.

OMW evaporation ponds (lagooning) remains one of the most popular physical techniques, especially in developing countries like Morocco due to its ease and lower cost (González-González & Cuadros 2013), but due to the need for large surfaces, the release of bad odors, and the very low degradation, it was replaced by more efficient and costly evaporation panels to maximize the elimination of the liquid fraction of the effluent (De Ursinos & Padilla 1992).

Membrane filtration is another common investigated OMW treatment method and this novel process can remove 88% of the dark color, 95% of COD and 70% of phenolic compounds (El-Abbassi et al. 2011). However, it must always be preceded by a pre-treatment, with a

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Table 1: Main characteristics of raw OMW from the top 10 olive oil producing countries

<table>
<thead>
<tr>
<th>Countries</th>
<th>Production (ton)</th>
<th>pH</th>
<th>EC ms/cm</th>
<th>COD g/L</th>
<th>BODs g/L</th>
<th>TSS g/L</th>
<th>Total phenols g/L</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spain</td>
<td>1,401,600</td>
<td>4.7</td>
<td>–</td>
<td>82</td>
<td>–</td>
<td>15</td>
<td>1.2</td>
<td>Garcia et al. (2000)</td>
</tr>
<tr>
<td>Italy</td>
<td>474,600</td>
<td>5.0</td>
<td>–</td>
<td>28.4</td>
<td>–</td>
<td>29</td>
<td>1.409</td>
<td>Cassano et al. (2015)</td>
</tr>
<tr>
<td>Greece</td>
<td>320,000</td>
<td>4.6</td>
<td>17–47</td>
<td>24.9</td>
<td>11.6</td>
<td>50.3</td>
<td>8.1</td>
<td>Chatzisymeon et al. (2009b)</td>
</tr>
<tr>
<td>Turkey</td>
<td>143,000</td>
<td>4.28–4.85</td>
<td>10.04–12.01</td>
<td>55.73–91.55</td>
<td>29.93–38.60</td>
<td>14.08–33.50</td>
<td>2.439–4.509</td>
<td>Değermenci et al. (2016)</td>
</tr>
<tr>
<td>Tunisia</td>
<td>140,000</td>
<td>4.8</td>
<td>8.8</td>
<td>58.5</td>
<td>17</td>
<td>41.7</td>
<td>9.1</td>
<td>Mekki et al. (2008)</td>
</tr>
<tr>
<td>Morocco</td>
<td>130,000</td>
<td>3.12</td>
<td>11.25</td>
<td>24.49</td>
<td>11.64</td>
<td>3.59</td>
<td>3.15</td>
<td>Elkacmi et al. (207b)</td>
</tr>
<tr>
<td>Portugal</td>
<td>109,100</td>
<td>5.1–5.8</td>
<td>–</td>
<td>7.45–68.48</td>
<td>0.5–9.50</td>
<td>3.13–30.22</td>
<td>0.027–1.051</td>
<td>Amaral et al. (2008)</td>
</tr>
<tr>
<td>Algeria</td>
<td>83,500</td>
<td>4.7</td>
<td>–</td>
<td>74.5</td>
<td>–</td>
<td>–</td>
<td>16.5</td>
<td>Iboukhoulef et al. (2013)</td>
</tr>
<tr>
<td>Jordan</td>
<td>29,500</td>
<td>4.91</td>
<td>7.64</td>
<td>58.614</td>
<td>36.329</td>
<td>–</td>
<td>2.269</td>
<td>Ayoub et al. (2014)</td>
</tr>
</tbody>
</table>
high-energy demand and permanent renewal of the membranes, hence the high cost of the process.

Biological treatment of OMW has been the subject of several studies, which have shown the possibility of treating OMW microbiologically. Aerobic and anaerobic biological degradation were effective in removing organic matter from OMW. The major disadvantage of aerobic biological degradation is the consumption of oxygen, while anaerobic biological degradation requires an aerobic pre-treatment to reduce the rate of aromatic compounds (González-González & Cuadros 2015; Bampalioutas et al. 2019).

Other investigators employed physicochemical methods, such as adsorption, to promote the biodegradability of organic compounds by using several adsorbents: activated carbon (Azzam et al. 2016), zeolite (Aly et al. 2018), sawdust (Jeguirim et al. 2012), bentonite (Al-Essa 2018), natural clays (Azzam et al. 2015) and different adsorbent matrices such as Azolla, granular active carbon, resin, and zeolite (Padovani et al. 2013; Vereri & Goula 2019). Due to the high organic load of OMW, these chemical processes generally require the addition of large amounts of reagents, which raises the problem of the production of putrescible sludge and the high cost of used products.

Another alternative for OMW treatment is the coagulation-flocculation process based on the addition of chemical substances (aluminium sulphate ($\text{Al}_2$($\text{SO}_4$)$\text{O}_3$) and ferric sulphate ($\text{Fe}_2$($\text{SO}_4$)$\text{O}_3$) causing coagulation, precipitation, or destruction of organic load (Esteves et al. 2019). This type of treatment remains the most global and the least expensive compared to the mass of materials eliminated, but the presence of residual aluminum and iron can cause significant problems for ecosystems and human health, such as Alzheimer’s and other diseases (Xu et al. 2018a).

Other techniques were also investigated for the conversion of OMW to high value added products. For example, the possibility of utilizing these effluents as fertilizer or compost and examining the effect of these techniques on soil properties and plant growth (Paredes et al. 2002; Belaqziz et al. 2016; Galliou et al. 2018), use as animal feed, biogas production (Salgado et al. 2015; Maragkaki et al. 2018), polyphenols recovery (Cassano et al. 2016; Víctor-Ortega et al. 2016) and other natural products such as volatile fatty acids (VFAs) (Scoma et al. 2016), dietary fiber suspensions (Galanakis et al. 2010), oleic, linoleic acid and glycerol (Elkacmi et al. 2016b, 2017a).

In recent years, research studies in the field of water and wastewater treatment have proved that electrochemical techniques can effectively remove or reduce a wide range of soluble or colloidal pollutants such as wastewater containing heavy metals, suspensions, oil and oil-in-water emulsion.

The first document reporting the use of electricity in water treatment was published in the UK nearly 40 years ago (Strokach 1975), this innovative method has been shown to be effective in water purification using anodic dissolution of iron metal. Similarly, Pan et al. (2016) and Hashim et al. (2017) confirmed that the electrocoagulation process was capable of reducing contaminants from drinking water. In addition, the use of various combinations of oxidants, radiation and catalyst has been studied for the degradation of organic pollutants from drinking water (Krystynik et al. 2015; Wang et al. 2016; Sillanpää et al. 2018).

Due to the lack of water resources in many countries, it is a truism nowadays to guide research towards novel and efficient technologies in order to reduce the organic loads from various types of industrial effluents. Advanced oxidation processes (AOP) have proved very successful in treating wastewaters including tannery wastewaters (Vilardi et al. 2018), textile wastewaters (Pourgholi et al. 2018), municipal wastewaters (Serna-Galvis et al. 2019), oil refinery wastewaters (Bustillo-Lecompte et al. 2018), pulp and paper wastewaters (Klidi et al. 2018), dairy wastewaters (Markou et al. 2017), pharmaceutical wastewaters (Yang et al. 2018), surfactant wastewater (Arslan et al. 2018) and mine wastewaters (Meng et al. 2019). It has also been used to remove heavy metals (Li et al. 2019), landfill leachate (Joshi & Gogate 2019), phenol (Niu et al. 2018) and many other components (Huang et al. 2018; Sable et al. 2018; Tuwabini & Makkawi 2018; Rubio-Clemente et al. 2019).

The application of AOP to OMW has attracted considerable attention due to its high efficiency, ease of operation, short reaction time, low sludge production, safety and environmental compatibility. Numerous studies have been carried out for reducing the pollutant load including COD, polyphenols, suspended solids, turbidity and coloration by different advanced oxidation techniques.

Based on the Scopus database and from the first review study conducted by Rege et al. (1991), more than 3,500
review papers dealing with the applications of AOP for water and wastewater treatment have been published. Figure 1 presents a summary of review articles undertaken on water and wastewater treatment by AOP over the past 30 years.

With the notable exception of Ochando-Pulido et al. (2017), conversely, until now, a review study summarizing all research results of these attractive techniques in OMW treatment has, to our knowledge, not been reported elsewhere. Their review article presented the application of these AOP processes for the removal of different toxic pollutants from OMW, including total organic carbon (TOC), COD, BOD₅, color, and phenolic compounds with emphasis on the parameters assessed, removal effectiveness, and the degradation mechanisms of pollutants. However, the authors only elaborated on a few physicochemical techniques while disregarding many of the key related articles that are available in open literature. The main missing item is the combination section, being the most efficient and widely studied technique in the last decades for OMW treatment. Moreover, many AOPs are either not mentioned or not classified in most articles. Classification in that sense would be performed based on the nature and the mode of production of hydroxyl radicals (chemical, photochemical, sonochemical and electrochemical).

For all these reasons, the objective of this paper is to overview and discuss the applications of AOP proposed to date for the detoxification of OMW, to give greater insight and details on the AOP technologies comprising chemical, photochemical, sonochemical, and electrochemical applications, as well as their combination with biological techniques and other technologies. The influence of operating parameters that affect these processes and the comparison of results with those obtained from other investigations are discussed. Over 351 publications are presented with 314 cited and analysed that can serve as a basis to help inform researchers and professionals concerning the application of AOP for OMW purification and decontamination.

**ADVANCED OXIDATION PROCESSES (AOP)**

**Principle of (AOP)**

AOP was described in the USA in 1987 by Glaze et al. (1987) as 'water treatment processes at ambient temperature and pressure'. These methods were based on the intermediacy of hydroxyl and other radicals and remain among the most efficient and environmentally friendly technologies that contribute to a high degree of recalcitrant organic compounds oxidation (Yang et al. 2016).

With the advent of AOP, it has been known that the common principle is the 'in situ' generation of highly potent and reactive oxidizing species called free radicals such as hydroxyl radical (OH⁻), superoxide ion (O²⁻), ozonide anion (O₃⁻), hydrogen peroxide (H₂O₂⁻), HO₂⁻ and HO₃⁻ radicals, and their oxidation potentials (vs. SHE) are given in the following order: OH⁻ (E₀ = 2.80 V) > O₃⁻ (E₀ = 2.07 V) > H₂O₂ (E₀ = 1.77 V) > HO₂⁻ (E₀ = 1.70 V) > O₂ (E₀ = 1.23 V). Once the hydroxyl radicals are formed, the organic pollutants are oxidized producing biodegradable intermediates, and are then mineralized to water, carbon dioxide and inorganic salts.

Many advantages of AOP have been reported: (i) Significant reduction of inorganic and organic compounds (Miklos et al. 2018); (ii) complete mineralization of organic contaminants to carbon dioxide, water and mineral salts (Leal et al. 2018); (iii) generating non-toxic by-products without release of secondary pollutants (Bustillo-Lecompte et al. 2018); (iv) high reactivity and non-selectivity of hydroxyl radicals towards pollutants (Yang et al. 2019); (v) uses as treatment or pretreatment of wastewater (Ramteke & Gogate 2015).

It should be noted that the AOP can be classified according to the nature of the phases (homogeneous or heterogeneous) or depending on the mode of production...
of hydroxyl radicals: Chemical, photochemical, sonochemical, and electrochemical. Moreover, they can also be coupled with other techniques, such as AOP, physicochemical or biological processes. Tables 2–6 provide a summary of all AOPs applied to several kinds of wastewater.

The efficiency of all these processes depends on several parameters such as pH, temperature, type of pollutant, oxidant concentration, UV light intensity and parasite reactions consuming hydroxyl radicals.

OMW is one of the most polluting among all industrial wastes. The number of studies proving its risk to humans, natural resources and the environment is very important, therefore, the search for solutions of this problem has become a public concern and an absolute necessity.

**Table 2** | Summary of main chemical advanced oxidation processes for water and wastewaters treatment

<table>
<thead>
<tr>
<th>Advanced oxidation process</th>
<th>Description</th>
<th>Wastewater/organic matter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Fenton’s reagent (Fe$^{2+}$/H$_2$O$_2$)</td>
<td>Tannery wastewater</td>
<td>Vilardi et al. (2018)</td>
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<td></td>
<td>Mine wastewater</td>
<td>Meng et al. (2019)</td>
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<td></td>
<td>Heavy metals</td>
<td>Li et al. (2019)</td>
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<td></td>
<td>Textile wastewater</td>
<td>Babaei et al. (2017)</td>
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<tr>
<td></td>
<td>Paper wastewater</td>
<td>Xu et al. (2019)</td>
<td></td>
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<tr>
<td></td>
<td>Petroleum refinery effluent</td>
<td>Diya’uddeen et al. (2015)</td>
<td></td>
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<tr>
<td></td>
<td>Phenols</td>
<td>Gümüş &amp; Akbal (2016)</td>
<td></td>
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<tr>
<td></td>
<td>P-hydroxyl benzoic acid</td>
<td>Rivas et al. (2009a)</td>
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<tr>
<td></td>
<td>Landfill leachate wastewater</td>
<td>Iskander et al. (2019)</td>
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<td></td>
<td>Winery wastewater</td>
<td>Ferreira et al. (2018)</td>
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<td></td>
<td>Olive mill wastewater</td>
<td>Esteses et al. (2017)</td>
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<tr>
<td></td>
<td>Petroleum refinery effluent</td>
<td>Aziz &amp; Daud (2012)</td>
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<tr>
<td></td>
<td>Textile wastewater</td>
<td>Khataee et al. (2019)</td>
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<td></td>
<td>Formaline wastewater</td>
<td>Kajitvichyanukul et al. (2006)</td>
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<td></td>
<td>Pesticides</td>
<td>Cheng et al. (2016)</td>
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<tr>
<td></td>
<td>Antibiotics</td>
<td>Mackulak et al. (2015)</td>
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<td></td>
<td>Olive mill wastewater</td>
<td>Kallel et al. (2009a)</td>
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<tr>
<td></td>
<td>2,4-xylidine</td>
<td>Rios-Enriquez et al. (2004)</td>
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<tr>
<td></td>
<td>Phenols</td>
<td>Ovejero et al. (2001)</td>
<td></td>
</tr>
<tr>
<td>Fenton-like reaction (Fe$^{3+}$/H$_2$O$_2$)</td>
<td>1,1-dimethylhydrazine</td>
<td>Makhotkina et al. (2006)</td>
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<td></td>
<td>Olive mill wastewater</td>
<td>Iboukhoulef et al. (2016)</td>
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<td></td>
<td>Drinking water</td>
<td>Yu et al. (2016)</td>
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<tr>
<td></td>
<td>Landfill leachate wastewater</td>
<td>Amr et al. (2016)</td>
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<td></td>
<td>Pharmaceutical wastewater</td>
<td>Ebrahim et al. (2018)</td>
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<td></td>
<td>Paper wastewater</td>
<td>Wu et al. (2018)</td>
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<td></td>
<td>Textile wastewater</td>
<td>Malik et al. (2017)</td>
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<td></td>
<td>Tannery wastewater</td>
<td>Schrank et al. (2017)</td>
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<td></td>
<td>Olive mill wastewater</td>
<td>Benitez et al. (1999a)</td>
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<td></td>
<td>Drinking water</td>
<td>Čehovín et al. (2017)</td>
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<td></td>
<td>Pharmaceutical wastewater</td>
<td>Yang et al. (2018)</td>
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<td></td>
<td>Textile wastewater</td>
<td>Bilińska et al. (2017)</td>
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<td></td>
<td>Landfill leachate wastewater</td>
<td>Chen et al. (2019)</td>
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<td></td>
<td>Olive mill wastewater</td>
<td>Beltrán et al. (1999)</td>
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<td></td>
<td>Ezono</td>
<td>Minière et al. (2018)</td>
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<tr>
<td></td>
<td>Paper wastewater</td>
<td>Kumar &amp; Sharma (2017)</td>
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<tr>
<td></td>
<td>Nitrogen-containing compounds</td>
<td>Oliviero et al. (2003)</td>
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<tr>
<td></td>
<td>Olive mill wastewater</td>
<td>García García et al. (1990)</td>
<td></td>
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<tr>
<td></td>
<td>Phenols, carboxylic acids, and nitrogen-containing</td>
<td>Kumari &amp; Saroha (2018)</td>
<td></td>
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<tr>
<td></td>
<td>Olive mill wastewater</td>
<td>Rivas et al. (2001e)</td>
<td></td>
</tr>
</tbody>
</table>

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Coloring matter, COD, polyphenols and organic compounds are the major contaminants in the OMW and have to be removed before discharging the effluent into the aquatic ecosystem. Considering the above points, AOP has consistently proved to be the most concrete solution to remove excessive pollutants from OMW. As presented in the tables, the generation of hydroxyl radicals achieved...
Table 5 | Summary of main electrochemical advanced oxidation processes for water and wastewaters treatment

<table>
<thead>
<tr>
<th>Advanced oxidation processes</th>
<th>Description</th>
<th>Wastewater/organic matter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical</td>
<td>Anodic oxidation (AO)</td>
<td>Drinking water</td>
<td>Trellu et al. (2016)</td>
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<td></td>
<td>Textile wastewater</td>
<td>Bassyouni et al. (2017)</td>
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<td>Paper wastewater</td>
<td>Kliki et al. (2018)</td>
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<td>Landfill leachate wastewater</td>
<td>Ukundimana et al. (2018)</td>
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<td></td>
<td>Tannery wastewater</td>
<td>Körbahti &amp; Turan (2016)</td>
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<td></td>
<td>Petroleum refinery effluent</td>
<td>Mohanakrishna et al. (2018)</td>
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<td></td>
<td>Pharmaceuticals wastewater</td>
<td>Garcia-Segura et al. (2015)</td>
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<td></td>
<td>Pesticides</td>
<td>Millán et al. (2019)</td>
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<td></td>
<td>Phenols</td>
<td>Pillai &amp; Gupta (2016)</td>
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<td>Olive mill wastewater</td>
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<td></td>
<td>Electro-Fenton (EF)</td>
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<td>Zhao et al. (2012)</td>
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<td></td>
<td>Phenols</td>
<td>Gülmuş &amp; Akbal (2016)</td>
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<tr>
<td></td>
<td>Olive mill wastewater</td>
<td>Bellakhal et al. (2006)</td>
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</table>

Table 6 | Summary of main combinations of advanced oxidation processes for water and wastewaters treatment

<table>
<thead>
<tr>
<th>Advanced oxidation processes</th>
<th>Description</th>
<th>Wastewater/organic matter</th>
<th>References</th>
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<td>Olive mill wastewater</td>
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through different AOP allow maximum removal efficiency of the organic load.

In this review paper, the five categories of AOP for treatment of OMW are summarized below.

**Chemical advanced oxidation processes**

**Fenton and Fenton-like reagent** ($\text{Fe}^{2+}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$)

Fenton processes have been classified as a simple way of producing (OH') radicals, not only for their simplicity and short reaction time, but also because of their flexibility allowing easy manipulation (run and control), as well as requiring less equipment and the inexpensive chemicals required (Nidheesh et al. 2013; Babuponnusami & Muthukumar 2014; Xu et al. 2018a, 2018b). There are a number of important factors that affect the treatment efficiency outstandingly including pH, temperature, reagents ($\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2$) concentrations, and the initial concentration of pollutants.

The oxidation reaction with $\text{H}_2\text{O}_2$ is not powerful enough to completely degrade organic contaminants. However, when mixed with a catalyst iron (II) ($\text{Fe}^{2+}$) to form the Fenton reagent, the oxidation potential of ($\text{H}_2\text{O}_2$) increases. A mixture of ($\text{Fe}^{2+}$) salts and ($\text{H}_2\text{O}_2$) is added directly to the wastewater, according to the following reaction:

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^* \quad (1)$$

The hydroxyl radicals ($\text{OH}^*$) produced during the decomposition of hydrogen peroxide in the presence of ferrous iron are highly reactive and a non-specific oxidant, able to reduce a wide range of organic pollutants in water and wastewater. Four main stages of Fenton process have been identified: pH adjustment to a range of 2.5–3.5 to avoid precipitation and formation of iron hydroxides, thus inducing low catalytic activity, followed by oxidation reaction, neutralization/coagulation and precipitation in a solid–liquid separation tank (Gopu et al. 2018).

For OMW, as for many other industrial wastewaters, this chemical process showed highly significant efficiency. For example, Rivas et al. (2001d) studied the reduction of the COD of a 500 mL OMW sample diluted with synthetic urban wastewater (initial COD concentration = 14.65 g/L), by using initial reagents concentrations varying between 0.2 and 1.0 M for $\text{H}_2\text{O}_2$ and 0.01–0.1 M for $\text{Fe}^{2+}$, acidic pH (2.5–3) and temperature (0–50 °C). This work reported that 80–90% of COD was removed after 8 h with 0.01 M of $\text{Fe}^{2+}$ and 1 M of $\text{H}_2\text{O}_2$ at a temperature of 54 °C. Furthermore, a kinetic study of the process was carried out to describe the $\text{H}_2\text{O}_2$ decomposition and the reaction between $\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2$.

Vlyssides et al. (2004) were able to ensure complete elimination of phenolic compounds, 60% of DCO and 40% of DBO5 within 2 h, by the addition of 2–3 g/l of ($\text{FeSO}_4$, 7$\text{H}_2\text{O}$) and 3 mL of $\text{H}_2\text{O}_2$ ratio of 60%. Similar findings were reported by Nasr et al. (2004) who used 5 mol of $\text{H}_2\text{O}_2$ and 0.4 mol of $\text{Fe}^{2+}$ in a 250 mL capacity reactor containing 100 mL of OMW sample to achieve removal of 86% of COD per liter of crude OMW.

Lucas & Peres (2009a) concluded that using ($\text{H}_2\text{O}_2$: $\text{Fe}^{2+}$) with a 15 molar ratio, treatment of 500 mL of Portuguese OMW by Fenton’s reagent removed 70% COD under 30 °C of temperature and initial pH of 3.5. A modified pseudo-first-order equation was developed to simulate the kinetics of the COD removal to describe the process for future industrialization.

Esteves et al. (2017) recently studied the treatment of synthetic OMW by Fenton’s process in a batch and continuous stirred-tank reactor (CSTR). The effect of the different influential parameters mentioned above was determined and the OMW sample was prepared by mixing the six most abundant phenolic acids. The treatment achieved up to 63% total organic carbon (TOC) reduction and maximum degradation of total phenol (TPh) up to 99% in a batch reactor (250 mL of OMW). Under the same operating conditions ($\text{Fe}^{2+} = 100$ ppm, $\text{H}_2\text{O}_2 = 2.0$ g/L, $T = 30$ °C) and in a continuous stirred-tank reactor (2 and 26 mL/min$^{-1}$ flow rates), they obtained 47.5% of TOC and 96.9% of TPh removal efficiencies as well as 75% of COD and 70% of BOD$_5$ abatements have been registered in both reactors.

Despite all these positive results, the Fenton reaction has a number of disadvantages: the slow regeneration rate of $\text{Fe}^{2+}$, the need to operate in an acid medium, the use of high doses of reagents, the need for separation of the
dissolved iron and the high accumulation of iron sludge which requires additional treatment to treat this secondary pollution. The replacement of iron by other catalyst metals, the photo Fenton process and the combination with other techniques were suggested as an alternative to overcome these limitations (Oturan & Aaron 2014).

Kallel et al. (2009a) demonstrated that Fenton process zero-valent iron (Fe\(^0\)) and H\(_2\)O\(_2\) permit high degradation efficiency of organic pollutants. The effect of H\(_2\)O\(_2\) and Fe\(^0\) concentration, pH and initial COD concentration were elucidated. The results obtained after the reaction time of 3 h showed complete decolorization of OMW samples and 50\% of COD removal under optimal conditions (2.0–4.0 of pH, 9.5 M of H\(_2\)O\(_2\) and 20 g/L of Fe\(^0\)). The same author confirmed that at acidic pH, COD removal increased with H\(_2\)O\(_2\) initial concentration and reached the maximum value of COD removal of around 92\% by using 1 M as the optimal dose of H\(_2\)O\(_2\). In addition, phenolic compounds were identified using gas chromatography coupled to mass spectrometry (GC–MS), it can be concluded that zero-valent Fe/H\(_2\)O\(_2\) has the potential to completely degrade these organic compounds present in OMW (Kallel et al. 2009b).

Nieto et al. (2009, 2010, 2011) first proposed the oxidation of OMW using FeCl\(_3\) as catalyst, with this homogeneous Fenton-like system (Fe\(^{3+}\)/H\(_2\)O\(_2\)), and they reported the possibility of treating these effluents from laboratory scale to industrial applications. Over 92.6\% of COD and 99.8\% of TPh were removed at pH 3.0, H\(_2\)O\(_2\) = 100 g/L, FeCl\(_3\)/H\(_2\)O\(_2\) ratio = 0.04, and temperature of 8–12 °C. The kinetic study was carried out using a two-step first order model. The kinetic parameters at room temperature and pH of 3 were determined. In the temperature range 5–40 °C, the results showed that maximum efficiency was achieved at 30 °C (Nieto et al. 2011). The optimization of the operating parameters using a continuous stirred tank reactor (CSTR) at pilot scale was investigated by Hodaifa et al. (2013). Experimental results showed that the optimum FeCl\(_3\)/H\(_2\)O\(_2\) ratio was in the range of 0.026–0.058, Fe\(^{3+}\) = 0.34–0.40 g/L to give a removal efficiency of 97\% of COD and 99\% of phenolic compounds with reaction times not longer than 3 h.

A Cu\(^{2+}\)/H\(_2\)O\(_2\) Fenton-like process was reported to significantly enhance the removal of phenolic compounds from OMW (Iboukhoulef et al. 2016). Results indicated that the use of copper Cu (II) as a catalyst is capable of achieving an average purity level ranging from 43 to 62\% degradation at 30 and 50 °C, respectively in 65 min of treatment.

**Peroxonation (O\(_3\)/H\(_2\)O\(_2\))**

As an alternative approach, ozonation has been widely used in water and wastewater management, and ozone (O\(_3\)) is typically utilized as a powerful oxidizing agent (E\(_0\) = 2.07 V) for removing organic and inorganic pollutants from aqueous solutions.

The detoxification of OMW by this application has been extensively investigated, especially in combination with other techniques. Oxidation by H\(_2\)O\(_2\) and O\(_3\) separately is not effective for high concentrations of pollutants, as stated by Benitez and his research group (Benitez et al. 1997a). From a diluted OMW sample (10–50\%), over 6 and 22\% COD, 40 and 70\% aromatic compounds and 90\% TPh removal were achieved, at a temperature of 20 °C and 10 mbar of ozone pressure. Benitez et al. (1999a) concluded that by using O\(_3\) alone, 17–28\% of COD, 100\% of polyphenols and 76\% of aromatic compounds were removed after 2 h at a temperature of 40 °C and pressure of 17.7 mbar. Canizares et al. (2009) were capable of removing 77.2\% of COD and 67.8\% of TOC. Chedeville et al. (2009) chose to use a suitable gas/liquid contactor allowing the application of ozonation for OMW treatment. At pH = 5, temperature of 20 °C, liquid flow rate of 0.9 L/h, gas flow rate of 0.5 Nm\(^3\)/h and ozone concentration of 25 g/Nm\(^3\), the degradation of phenolic compounds was up to 80 and 48\% of COD removal with 95\% of ozone mass transfer.

The combination between O\(_3\) and H\(_2\)O\(_2\), called peroxonation process, was reported as more efficient than ozonation alone because hydrogen peroxide is intended to accelerate the decomposition of ozone in water and thus produce more hydroxyl radicals according to the reaction below:

\[
O_3 + H \rightarrow O_2 + HO_2 + OH^* \tag{2}
\]

Previous results have shown the efficacy of the oxidation system by O\(_3\)/H\(_2\)O\(_2\) for drinking water and wastewater treatment (Shokri et al. 2016; Bourgin et al. 2017;
Malvestiti *et al.* 2018; Wang *et al.* 2018). Unfortunately, few studies have been found in the literature regarding the detoxification of OMW by this combination. Beltrán *et al.* (1999) found that using $10^{-3}$ M of H$_2$O$_2$ combined with 3–4 g of ozone, allowed a total disappearance of aromatic content and coloration, 90% COD and 60% total carbon (TC) removal, and a remarkable increase in the biodegradability (BOD/COD) from 0.16 to 0.8. It has been found that this system suffers from the low solubility of O$_3$ in aqueous solutions on the one hand and high cost of reagent on the other.

**Wet air oxidation and catalytic wet air oxidation**

Numerous studies have been reported in the literature regarding the treatment of water and wastewater by using wet air oxidation (WAO) and catalytic wet air oxidation (CWAO). The aim of these processes is to oxidize organic and inorganic pollutants in aqueous media at high pressure up to 200 bar and temperature ranging from 125 to 320 °C (Liu *et al.* 2017; Barge & Vaidya 2018). The principle of the techniques is based on promoting contact between oxygen and the aqueous solution to ensure the conversion of organic compounds to carbon dioxide, water and harmless products (Yousefifar *et al.* 2017). García García *et al.* (1990) presented the use of pure oxygen under 250 °C and 35 bars partial pressure for removing 99% of phenolic compounds. Rivas *et al.* (2000) investigated the efficiency of supercritical wet air oxidation by using hydrogen peroxide as the oxygen source. They were able to reduce COD by 79% and phenol by 98% at 250 bar of total pressure and 500 °C of temperature from OMW samples diluted 50 times.

Catalytic Wet Air Oxidation (CWAO) can be considered as a more efficient alternative for OMW treatment. Many heterogeneous catalysts were used such as metal oxides, noble metals, etc. Rivas *et al.* (2000b) described the use of CuO/C and Pt/Al$_2$O$_3$ for the oxidation of OMW diluted 10 times with synthetic urban wastewater, 50 and 80% of COD and phenolic compounds have been removed, respectively, under relatively mild conditions of temperature and pressure (180 °C and 70 bar total pressure). Pham Minh *et al.* (2006, 2007a, 2007b, 2008) investigated the application of platinum and ruthenium catalysts supported on titanium (TiO$_2$) and zirconium (ZrO$_2$) oxides for the degradation of two phenolic compounds (p-hydroxybenzoic and p-hydroxyphenylacetic acids) present in OMW at 140 °C and 50 bar total pressure. Their results suggested that approximately 97% of TOC and a total reduction of phenolic compounds were achieved in a stirred batch autoclave and in a fixed bed reactor. Gomes *et al.* (2007) published data on organic matter and color reduction using Pt/C and Ir/C as catalysts. The results revealed that the maximum COD and color removal efficiency was recorded at 200 °C and 6.9 bar of oxygen partial pressure after 8 h of reaction time.

Wet hydrogen peroxide catalytic oxidation (WHPCO) is another form of advanced oxidation technology based on hydroxyl (OH$^-$) and perhydroxyl (HO$_2^-$) radicals generation using solid catalysts. Najjar *et al.* (2009) proposed the use of Fe–BEA zeolite as catalysts at moderate temperature ($T = 28$ °C) and atmospheric pressure. It was concluded that the WHPCO could be successfully used in the elimination of 59% of color, 40% of TPh, 30% of COD and 28% of TOC after 12 h of treatment. Giordano *et al.* (2007) studied the degradation of phenolic compounds using copper supported on zeolite and pillared clay, a removal efficiency of more than 90% was registered in 3 h at 80 °C.

It is important to indicate that WHPCO is still more advantageous than CWAO because the first technique operates under mild conditions, whereas the second one requires specific conditions and materials which make it more expensive and less widely employed.

**Photochemical advanced oxidation processes**

**Photolysis of H$_2$O$_2$ (H$_2$O$_2$/UV)**

The use of UV radiation has received considerable attention for the abatement of organic pollutants from water and wastewater. The combination of H$_2$O$_2$ and UV radiation allows increasing OH$^-$ formation, which will react with H$_2$O$_2$ by secondary reactions:

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{OH}^* \quad (3)$$

$$\text{H}_2\text{O}_2 + \text{OH}^* \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \quad (4)$$

Given its ability to produce more radicals, OH$^-$ and HO$_2^-$ were the first to be more reactive as a highly highly active...
oxidizing agent, and only a few studies in the literature have focused on the use of photolysis of H₂O₂ for the treatment of OMW. Ugurlu & Kula (2007) suggested using this photochemical advanced oxidation process. The first results of this study showed that 90% of color, 90% of phenol and 30% of lignin were removed after 7 days. The second part of the study also showed that the removal rate was increased to 99, 100 and 40% of color, phenol and lignin, respectively, after the treatment of OMW with lime.

As a single H₂O₂/UV application does not appear to be efficient for OMW treatment, it is discussed to combine it with other techniques, which will be exemplified later in this paper.

Hodaifa et al. (2015) were capable of obtaining removal percentages of 40–48% for COD, 39.4–51.9% for TC, 33–48% for TOC, and 66.8–93.4% for turbidity under operation conditions: pH = 3, temperature of 293.15 K and agitation rate of 150 rpm.

Photolysis of O₃ (O₃/UV)

The photolysis of O₃ (O₃/UV) involves the irradiation of ozone molecules by UV radiation, promoting the formation of OH radicals according to the main reactions (5) and (6):

\[
\text{O}_3 + \text{H}_2\text{O}_2 + \text{hu} \rightarrow \text{O}_2 + 2\text{OH}^* \quad (5) \\
2\text{OH}^* \rightarrow \text{H}_2\text{O}_2 \quad (6)
\]

It is well known that many papers demonstrated that the O₃/UV system could be an effective tool for the treatment of wastewaters resulting from textile, pharmaceutical, winery, paper and petroleum industries (Benitez et al. 1997b; Lucas et al. 2010; Souza et al. 2016; Bonfante de Carvalho et al. 2018; García-Ballesteros et al. 2019; Paucar et al. 2019). In the case of OMW, it should be noted that the only study focused on its management by this combination is the research described by Benitez et al. (1997b). In this paper, the effect of the UV radiation alone on the degradation of COD, TPh and aromatic compounds of the OMW was reported. In addition, a comparative study with ozone plus UV radiation was established. They reported an increase on the removal efficiencies of the pollutants by the combined system (O₃/UV) instead of using UV alone, the abatement rates of COD, TPh and aromatic compounds removals ranged between 5.2–10.3, 0–58.1 and 73.1–97.5%, respectively.

As explained before, the use of ozone alone or combined with hydrogen peroxide or UV radiation is often insufficient to meet wastewater treatment objectives due to the selectivity of molecular ozone, while their combination with other techniques becomes a major necessity.

Photo-Fenton (H₂O₂/Fe²⁺ (Fe³⁺)/UV)

Aiming to produce a relative high concentration of Fenton catalyst, the use of a photo-Fenton system as a method for the treatment of various types of wastewater has been technically developed. The method is based on the Fenton reaction between H₂O₂ and Fe²⁺ or Fe³⁺ coupled with UV radiations.

In the case of OMW, under optimum conditions, Badawy et al. (2009) investigated the effectiveness of this photochemical oxidation in removing 84, 87, 97.44 and 98.31% of TOC, COD, TPh and total suspended solids (TSS), respectively. In another research paper, Justino et al. (2010) were able to achieve complete elimination of phenolic compounds from supplemented diluted OMW or buffer with phenols. They concluded that the photo-Fenton technique is more efficient than biological or enzymatic treatments. This finding is similar to the results of Gernjak et al. (2005), who reported a total degradation of six abundant phenolic compounds from agro-industrial wastewaters.

Gernjak et al. (2004) studied the treatment of OMW by solar photo-Fenton in a falling film photoreactor. Results showed that 85% of COD and total dephenolization were achieved for 19 L of pre-treated OMW by using Fe²⁺ = 5 mM and H₂O₂ = 5 g/L.

In another recent study conducted by García & Hodaifa (2017), the treatment of local OMW by photo-Fenton using artificial UV light lamps was investigated in a batch reactor. Over 90% of COD, TC, TOC, TPh and turbidity were removed efficiently at a pH of 3, FeCl₃ = 3.0 g/L, H₂O₂ > 8 g/L within 30 min of reaction time.

Photo-peroxanation (H₂O₂/O₃/UV)

Ozone combined with hydrogen peroxide and UV radiation was considered an effective method for the treatment of
hazardous organic compounds in drinking water and wastewaters. H2O2 and UV light are used to activate ozone in neutral aqueous solutions. In this combined system, O3 absorbs UV radiation and produces hydrogen peroxide, which forms hydroxyl radicals by photolysis of H2O2.

In another part of their article, Beltrán et al. (1999) found that the same elimination rates quoted in the paragraph above relate to the peroxonation (O3/H2O2) by using ozone combined with hydrogen peroxide and/or 254 nm UV radiation.

Given that the phenolic compounds are responsible for the toxicity of OMW, Kusic et al. (2006) also used photo-peroxonation process for the degradation of these natural constituents. A complete phenol removal and a reduction in the TOC by 58% of the aqueous solution was achieved. Nevertheless, this technique has limitations, such as the low solubility of O3.

Homogeneous photocatalysis (Fe3+/UV)

This AOP process involves the excitation of Fe3+ with UV radiation, without addition of other chemical components such as H2O2. This homogeneous photocatalysis system consists of the photo-reduction reaction of iron (III) in aqueous solution to produce iron (II) and OH radicals.

On the other hand, as has also been stated in the paragraph above, the polyphenols are one of the most abundant elements in the OMW. Mazellier & Bolte (1997) studied the effectiveness of the Fe3+/UV system in the treatment of phenolic compounds. They concluded that 80–85% of 2,6 dimethylphenol (DMP) was removed.

Heterogeneous photocatalysis

Proven by the large number of publications devoted to this technique since its discovery and development (Fujishima & Honda 1972; Frank & Bard 1977), the use of heterogeneous photocatalytic processes was found to be one of the most efficient ways of generating hydroxyl radicals. The addition of semiconductor materials stimulate the reduction of a wide variety of organic and inorganic compounds in drinking water and wastewater (Liu et al. 2010; Hassan et al. 2016; Palaniandy et al. 2016; Zhao et al. 2017; Rasheed et al. 2018; Singh et al. 2019a, 2019b).

Several photocatalysts, such as ZrO2, MoO3, Fe2O3, ZnO, CeO2, Al2O3, Bi2O3, CdO, CdS, HgO, PbO, Sb2O3 and TiO2, have been tested (Karunakaran & Anilkumar 2007). Experiments showed impressive results of treatments using titanium dioxide (TiO2). When the latter was subjected to ultraviolet spectrum, hydroxyl radicals were generated on the surface of the semiconductor and oxidize organic pollutants. TiO2 proved to be effective in reducing the organic load of OMW relative to other photocatalysts due to its many potential advantages including: (i) high stability, good performance and low cost, (ii) operation under ambient conditions with the possibility of using solar irradiation, (iii) the absence of significant mass transfer limitations when fine particles are used as photocatalysts.

El Hajjouji et al. (2008) reported heterogeneous photocatalysis for treatment and detoxification of diluted OMW (1/100). After 24 h of experiment, removal efficiencies for COD, coloration and TPh were 22.2, 57 and 94.3%, respectively. In this study, the authors confirmed that the difference between the three abatement results were caused by the presence of three phases, which correspond to the presence of three categories of organic molecules and the presence of pectin compounds, differing in their sensitivity to oxidation by the UV/TiO2 system.

Chatzisymeon et al. (2009c) achieved complete decolorization (>90%) and 50% of mineralization. They also concluded that treatment efficiency was increased with decreasing initial COD and increasing contact time and catalyst concentration. Badawy et al. (2009) investigated the effect of catalyst type, pH, catalyst dose and irradiation time for the treatment of three-phase OMW. They were able to remove 68.8, 67.3, 40.19 and 48.9% of COD, TOC, TPh and TSS, respectively, after 60 min irradiation time.

Baransi et al. (2012) proposed the addition of powdered activated carbon (PAC) to TiO2 for the photocatalytic degradation of caffeic acid and p-coumaric acid, which are considered among the most abundant phenolic compounds. The authors found out that the combined TiO2-PAC sorbent yielded a significant removal rate in comparison to removal by TiO2 and PAC alone, 87% of the total polyphenols were degraded and only 57.9% of COD was reduced within 24 h of 365 nm UV irradiation.

Ruzmanova et al. (2015) examined the performance of prepared catalyst Magnetic Core Titanium Dioxide
Nanoparticles (Fe$_3$O$_4$/SiO$_2$/TiO$_2$) for the treatment of OMW. After 2 h of experiment, 50% of the COD was removed by using 1.5 g/L of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ nanoparticles.

A major drawback of using (TiO$_2$/UV) system for the treatment of OMW, making it difficult for use on an industrial scale, is the colloidal nature of the fine particles of the semiconductor. Therefore, the recovery of the catalyst becomes more difficult due to the slow sedimentation rate of the fine particles. Additionally, the UV irradiation efficiency and life of UV lamps were reduced by the formation of dark catalytic sludge (Oturan & Aaron 2014).

**Sonochemical advanced oxidation processes**

A new technology developed by several researchers has been shown to be an attractive alternative in destroying a wide range of organic contaminants. The sonochemical process is a boon to water and wastewater treatment because it has the capability of reducing the polluting load by ultrasonic radiation.

This technique is based on the use of ultrasonic irradiation to activate the chemical reactions, the hydroxyl radicals are produced in water by applying sound wave frequencies of 20 kHz and 1 MHz:

\[
\text{H}_2\text{O} + \text{irradiation (20kHz–1 MHz)} \rightarrow \text{OH}^* + \text{H}^* \quad (7)
\]

High-power ultrasound produces strong microbubble cavitation in aqueous solution which generates shock waves and reactive free radicals as very powerful oxidants that can degrade a wide range of organic compounds. Due to its simplicity and no production of toxic by-products, this technique has great applying perspectives in drinking water and wastewater treatment (Atanassova et al. 2005; Xiao et al. 2014; Yehia et al. 2015; Almasi et al. 2016; Zhou et al. 2018).

It is of great interest to highlight that a considerable amount of effort has been expended in the use of ultrasonic irradiation for OMW treatment as well as the reduction of phenolic compounds. It has been shown that the sonochemical degradation of OMW depends on several operating parameters. Figure 2 generalizes the parameters related to the technique, the parameters related to the reaction medium, and the parameters related to pollutants.

Significant numbers of studies have focused on the applicability of this method for the degradation of phenolic compounds. Some extensive and detailed articles, which focus mainly on the degradation of these constituents in aqueous medium, are summarized in Table 7.

To the best of our knowledge, there have been a few publications that focused on the application of the sonochemical advanced oxidation processes alone for the treatment of OMW, this is due to the fact that the amount of generated OH$^*$ radicals remains low and insufficient, as well as the high cost of the process. For this reason, several researchers have studied the combination of sound irradiation with other oxidants such as H$_2$O$_2$ and O$_3$ or combined with other technologies, in order to increase the efficiency of the decomposition of pollutants and to reduce the treatment time.

Atanassova et al. (2005) documented a reduction of the antioxidant activity and total phenolic content of diluted OMW samples collected from olive extraction units that use a continuous process (two- and three-phase systems). The authors reported that under optimal values of process parameters (80 kHz ultrasonic frequency, 150 W applied power, 240 min irradiation time and 25 °C), the removal performance of TPh were reduced by about 14 and 24% for the sonicated two-phase and three-phase samples, respectively. They also reported that in the presence of 5 and 10% NaCl, the removal rate of TPh was 19 and 15%, respectively for the two-phase samples with 31 and 28%, respectively, for the three-phase samples.
<table>
<thead>
<tr>
<th>Phenols</th>
<th>Experimental conditions</th>
<th>Main results</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-nitrophenol</td>
<td>Power = 84 W, frequency = 20 kHz, T = 30 °C, pH = 5</td>
<td>The p-nitrophenol reduction fit the first order kinetics model with current-dependent parameters. The reaction products are: NO2-, NO3-, benzoquinone, hydroquinone, 4-nitrocatechol, formate, and oxalate.</td>
<td>Kotronarou et al. (1991)</td>
</tr>
<tr>
<td>Phenol</td>
<td>Power = 30 W, frequency = 20, 487 kHz, T = 25 °C</td>
<td>After 300 min sonication, the degradation rate of phenolic pollutants is higher at 487 kHz than at 20 kHz.</td>
<td>Petrier et al. (1994)</td>
</tr>
<tr>
<td>p-nitrophenol</td>
<td>Frequency = 321 kHz, T = 25 °C, pH 4–10, Water-absorbed power = 170 W/kg</td>
<td>A detailed study on the sonolysis of 4-nitrophenol in argon-saturated solution. The reaction products are: NO2-, NO3-, 4-Nitrocatechol, hydroquinone, benzoquinone, 4-aminophenol.</td>
<td>Tauber et al. (2000)</td>
</tr>
<tr>
<td>2-, 3- and 4-chlorophenol and pentachlorophenol</td>
<td>Power = 200 W, Frequency = 200 kHz, Under air and argon atmosphere</td>
<td>A total degradation rate under argon and 80–90% after one-hour of sonolysis.</td>
<td>Nagata et al. (2000)</td>
</tr>
<tr>
<td>p-chlorophenol</td>
<td>Three different ultrasonic devices used: Probe and cup-horn system: Power = 475 W, frequency = 20 kHz, T = 35–39 °C, atmospheric pressure</td>
<td>After 20 min sonication, over 2, 25 and 50% degradation was achieved in cup-horn, beaker and probe respectively. The degradation of intermediate products follow a first-order kinetic rate. The reaction products are: hydroquinone, 1, 4-benzoquinone, 4-chlorocatechol, 4-chlororesorcinol.</td>
<td>Teo et al. (2001)</td>
</tr>
<tr>
<td>p-coumaric and p-hydroxybenzaldehyde</td>
<td>Power = 150 W, Frequency = 80 kHz, T = 25–70 °C</td>
<td>After 150 min sonication, 56 and 60% of COD and polyphenols have been removed.</td>
<td>Vassilakis et al. (2004)</td>
</tr>
<tr>
<td>Phenol, 4-chlorophenol (4-CP), 2,6-dichlorophenol (2,6-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), and pentachlorophenol (PCP)</td>
<td>Power = 200 W, Frequency = 580 kHz, T = 20 °C</td>
<td>After 40 min sonication, the degradation rate of chlorinated phenolic pollutants followed the order: 580 kHz (91–93%) &gt; 1,000 kHz (84–86%) &gt; 28 kHz (17–34%). The degradation rate followed the order: PCP &gt; 2,5,4,6-TeCP &gt; 2,4,6-TCP &gt; 2,6- DCP &gt; 4-CP &gt; phenol at various frequencies.</td>
<td>Park et al. (2011)</td>
</tr>
</tbody>
</table>
Electrochemical advanced oxidation processes

It is worth mentioning that one of the most studied treatments is the use of an electrochemical advanced oxidation process for toxic pollutant degradation. The main objective of this technique is to minimize the amount of chemical reagents by producing the oxidants directly in the medium by electrochemistry (Burgos-Castillo et al. 2018). It has been proven that the electrochemical process offers simplicity, efficiency, environmental compatibility, safety and selectivity, with a low cost particularly when compared to biological treatment (Li et al. 2018). Among the existing electrochemical treatments, there are two major forms of free radical production: Direct (anodic oxidation process) and indirect (electro-Fenton process).

Anodic oxidation (AO)

The main interest of the direct action lies in its effectiveness in eliminating a specific compound in solution. This technique allows an electron transfer of the pollutant to the surface of a working electrode (Hamad et al. 2018).

The mechanism can be represented as shown below:

\[ M + H_2O \rightarrow M(OH^+) + H^+ + e^- \] (8)

where M represents the material of the anode and M (OH\(^+\)) the hydroxyl radical adsorbed on the surface of the anode. The latter is a very powerful oxidant capable of completely oxidizing organic substances.

Several insoluble electrodes with high oxygen overvoltage (BDD, Pt, Ti/IrO\(_2\), Ti/RuO\(_2\), Ti/SnO\(_2\), PbO\(_2\), Gr, etc.) are commonly used. The choice of electrode material as well as the electrolysis conditions have great importance in the liquid effluent treatment (Penteado et al. 2017; Tran et al. 2017).

Concerning OMW, a considerable number of reported studies have demonstrated that the removal of organic compounds from these hazardous wastes by AO is very simple and highly efficient. Israilides et al. (1997) described an electrolysis cell containing a Ti/Pt as anode and stainless steel 304 as cathode in the presence of sodium chloride (NaCl) 4% as electrolyte, after 10 h of treatment, 80% TOC, 95% COD, 99.5% TPh and 99% TSS removal have been registered with an energy consumption of 2.3 kW h/kg COD removed. Longhi et al. (2001) applied AO with PbO\(_2\) at current densities ranging from 500 to 2,000 A/m\(^2\). They concluded that the removal efficiency of TPh was increased at a level that allows complementary biological treatments without significantly decreasing the total organic content of the effluent.

Another group of researchers have also been working on the electrochemical oxidation of OMW by the use of a Ti/Ta/Pt/Ir as anode. After 120 min of treatment, the main results of this study are a complete degradation of phenols and decolorization with 55% COD reduction (Gotsi et al. 2005). Similarly, Giannis et al. (2007) obtained 70.8% COD reduction, complete odor, color and TSS removal after 8 h of electrolysis by using the same electrode materials and NaCl 3% as electrolyte.

Belaid et al. (2006) adopted a modified Grignard reactor divided into two cylindrical compartments separated by a cation-exchange membrane using platinized expanded titanium electrodes. As a result, 90% color efficiency, 85% removal of phenols, 40% COD and 45% TOC reduction were achieved from undiluted OMW after 5 h of treatment at 9.8 A current intensity. Panizza & Cerisola (2006) have also shown that the AO over Ti/TiRuO\(_2\) was able to completely remove the COD, the aromatics and coloring matters, after 30 h at 5 A and in the presence of 5 g/L NaCl. Un et al. (2008) determined that 99.6% DCO, 99.85% turbidity, 99.54% oil-grease and 100% TPh could be removed by the use of Ti/RuO\(_2\) anode with a specific energy consumption (SEC) and energy cost of around 5.35–27.02 kWh/kg COD and 0.88 €/kg COD, respectively. Optimum conditions included 7 h treatment time, 135 mA/cm\(^2\) current density, 2 M NaCl concentration, 7.9 cm\(^3\)/s recirculation rate of OMW and 40 °C temperature.

Kotta et al. (2007) investigated the electrochemical oxidation of OMW with Ti/Pt anodes. They determined that the presence of unfiltered solids had virtually no impact on TPh removal (95% after 180 min of treatment at 20 A). In addition, it was observed that the dissolved solids content in OMW samples affects the electrochemical treatment efficiency, since it increases the color and the COD value of samples. In a similar way, Kul et al. (2015) also used Ti/Pt as anode and Ti mesh plates as cathode. The effects of the different operational parameters were investigated.
The results showed that AO could remove 100% of COD, 78% of TOC and 100% of TPh after 5 h of treatment without any pH adjustment using NaCl concentration of 0.25 M at current density of 7.69 mA/cm² and temperature of 10 °C. The SEC was 451.25 kWh/m³ and the running cost was determined as 6.02 €/kg COD.

It is worth highlighting that several articles authored by Canizares et al. (2002, 2003a, 2003b, 2004a, 2004b, 2004c, 2004d, 2004e, 2005, 2007b, 2009) were interested in the use of a new electrochemical technique based on the introduction of a new type of electrode material, namely boron-doped diamond (BDD), for the degradation of organic pollutants present in wastewaters including OMW. The results revealed that AO with conductive diamond electrochemical oxidation (CDEO) was considered as one of the most effective methods for the total mineralization of aromatic compounds in the OMW with very high efficiency. Up to 98.4% of COD abatement and 99% of TOC removal could be ensured with a SEC of 110 kWh/m³ and operation cost ranged between 2.4 and 4 €/kg equivalent O₂ (Canizares et al. 2006).

The BDD has also been proposed to be a good candidate for the oxidation of table olive processing wastewater (TOPW) (Deligiorgis et al. 2008). In the best conditions (30 A for 14 h), it was possible to achieve 73% COD removal with 16.3 g COD/(m³Ah) energy efficiency. Similarly, Chatzisymeon et al. (2009b), Bouhssine et al. (2013) and Jum‘h et al. (2017) confirmed that this type of electrode material promotes a remarkable depuration of OMW. Based on the first, the effect of initial COD load, treatment time, current intensity, initial pH and H₂O₂ dose were investigated. Under 20 A current intensity and 15 h electrolysis time, the results were a 19% reduction in COD and a 56% decrease in phenols with a SEC of 96 kWh/kg COD removed. Moreover, the kinetic study determined that the COD removal obeyed the zero-order model (Chatzisymeon et al. 2009b). Bouhssine et al. (2013) also tested the BDD anode system performance in OMW treatment. The best results were obtained using a current density of 1.29 A/cm² after 30 min of electrolysis, achieving 43, 60 and 63% for dark color, COD and TPh removal, respectively. Jum‘h et al. (2017) were capable of removing 85% COD with no supporting electrolytes and over 90% COD removal efficiency can be achieved by adding Na₂SO₄ and NaCl after 7 h of treatment for COD loads of 72.9 and 33.8 g/L, and after 2 h for a COD load of 0.18 g/L. In addition, the results showed minimal values of turbidity ranging between 0.98 and 8 NTU and a complete discoloration for the three different raw OMW samples (Jum‘h et al. 2017).

Chatzisymeon et al. (2009a) also evaluated the efficiency of Ti/IrO₂ anode in the electrochemical treatment of model solutions containing various aromatic compounds and an OMW sample. The results revealed that it was possible to achieve 100% color, 100% TPh and 30% COD removal at 43 Ah/L charge passed, 80 °C temperature, 50 A/cm² current density and 5 mM NaCl concentration.

Using a Ti/RuO₂ anode, Papastefanakis et al. (2010) compared their results with those of Ti/IrO₂ (Chatzisymeon et al. 2009a). The OMW oxidation over Ti/RuO₂ was more effective in the degradation of 52% COD than the Ti/IrO₂ anode (30%) with color reduction of 86%, 38% of TOC and 84% of TPh at 50 mA/cm² and 28 Ah/L charge passed. In addition, they concluded that decolorization of OMW using a Ti/RuO₂ anode was also less sensitive to changes in salt concentrations.

More recently, Fajardo et al. (2017) obtained good results in the treatment of OMW by the same anode materials. In the first part, they reported that 100% of COD and TPh were removed from synthetic mixture of six phenolic compounds at pH of 3.4, 10 g/L of NaCl and 119 mA/cm² of current density. While the second part discusses the detoxification of an undiluted OMW, after 180 min of treatment with the same optimised parameters, 17.2 and 100% of COD and TPh removal, respectively, were achieved with SEC of 162 kWh/m³.

Unfortunately, the main drawback of this process lies in its high operating cost due to the high energy consumption (Liu et al. 2017a, 2017b). In addition, the conductivity of the effluent must be sufficient to allow the passage of the current without excessive electricity consumption. When the conductivity of the OMW is too low, an addition of sodium chloride is generally necessary. In addition, the presence of a solid deposit on the cathode surface increases the electrolytic cell’s resistance (Khaled et al. 2015; Markou et al. 2017).

**Electro-Fenton (EF)**

Several studies emphasize that the electro-Fenton process (EF) is a powerful technique for the treatment of water

This indirect electrochemical method has emerged as a novel treatment technology for the reduction of a wide range of toxic organic compounds. As is the case in the AO, the EF process involves the in situ generation of the reagents necessary for the production of hydroxyl radicals by applying electrical energy. According to Fenton’s mechanism cited above under ‘Fenton and Fenton-like reagent (Fe²⁺/Fe³⁺/H₂O₂)’, this method represents a Fenton’s reaction assisted by electrochemistry, it is based on the fact that Fe²⁺ ions react with H₂O₂ to electrochemically release (OH⁻) radicals. As reviewed by Babuponnusami & Muthukumar (2014), the EF process can take multiple configurations depending on the addition or the formation of Fenton’s reagent and hydrogen peroxide during electrolysis. Also, it should be noted that the efficiency of this system is influenced by various parameters such as pH of the medium, temperature, current intensity, type of electrode and catalyst concentration.

It is worth noting that, in early reports, the EF process was widely applied to remove recalcitrant phenolic compounds from synthetic mixtures (Gümüş & Akbal 2016; Khatri et al. 2018), which gives a clear idea about the feasibility of this technique towards OMW composed predominantly of these organic matters.

However, a limited number of studies have focused on the field of OMW treatment by EF alone which leads to modest treatment efficiencies. Khoufi et al. (2004) indicated that EF oxidation could be an important stage for a complete detoxification of OMW, which yielded a dephenolization of around 78%. Afterwards, Bellakhal et al. (2006) confirmed that EF with a Pt/carbon-felt cell proved to be effective with a dose of 0.5 mM of Fe²⁺, low-intensity electrical current of 200 mA at pH = 3 leading to a complete mineralization in 9 h and a total decolorization after 7 h.

The EF process comes with the added benefit and advantage of overcoming some drawbacks of the Fenton reagent, but at the same time it still suffers from major limitations such as the need for acidic medium activity, separation of the dissolved iron, the management of the resulting iron sludge and the excessive concentration of iron cations at the end of the treatment (Roth et al. 2016). Last but not least, note that, in conjunction with other conventional technologies, this kind of AOP becomes more efficient and more useful, especially with the biological methods, which will be discussed at the end of this review article.

**Electrocoagulation (EC)**

With regard to the technique of electrocoagulation (EC), also listed under electrochemical oxidation, over the years, several studies have been developed on EC treatment processes for difficult and recalcitrant wastewaters like OMW, mainly owing to its simplicity, low energy consumption, effectiveness, low sludge formation and low dissolved solids (Elkacmi et al. 2017c).

The main basic steps of electrocoagulation process are presented in Figure 3. Both iron and aluminum can create active coagulant species to remove the organic load and phenolic compounds. Significant effort has been made to adopt this technique for the treatment of OMW.

Inan et al. (2004) investigated the treatment of OMW by electrocoagulation. Over 52% of COD for the aluminum anode against 42% COD for the iron anode were removed efficiently at a pH of 6.2, current density of 20 mA/cm² and a residence time of 30 min.

Adhoum & Monser (2004) proposed the use of aluminum electrodes to remove 76% of COD, 91% of polyphenols and 95% of dark color after 25 min of electrolysis with low electrode consumption (2.11 kg/m³ of treated OMW). Ün et al. (2006) studied the treatment of fresh OMW using either iron or aluminum as sacrificial electrodes in the presence of H₂O₂ and polialuminum chloride (PAC). Under optimal conditions (2.3% H₂O₂ + 0.5 g/L PAC), the removal efficiency of COD was in the range of 62–86% whereas oil-grease and turbidity removal was 100%. Moreover, they found that the energy cost was in the range of 0.18–6.75 €/kg COD removed. Khoufi et al. (2007) obtained higher COD and TPh removal efficiencies (over 43% removal for COD and 90% for TPh) when utilizing both electrocoagulation and sedimentation combinations. Hanafi et al. (2010) were able to remove more than 70% of COD, PP and coloration from an OMW sample diluted five times after 15 min with initial pH of 4.2, 2 g/L of NaCl, and current density of 250 A/m².
Esfandyari et al. (2015) reported that 96% COD, 93.6% BOD₅, 94.4% TPh, 91.4% color, 88.7% turbidity, 97% TSS and 97.1% oil and grease were removed from the OMW diluted four times by using bipolar aluminum electrodes under optimized conditions (\([\text{H}_2\text{O}_2]\) = 1,000 mg/L, \(\text{NaCl} = 1\ g/\text{L},\ \text{pH} = 4,\ \text{current density} = 40\ mA/cm²,\ \text{and reaction time} = 30\ min\)).

Table 8 summarizes the advantages and disadvantages of each technique. Some processes such as O₃/H₂O₂, O₃/UV and TiO₂/UV are limited by the mass transfer phenomena, while the low cost, efficiency and environmental benefits are an added advantage of some other techniques such as Fenton and sonochemical oxidation processes.

Fenton’s reagent remains the most reliable and widely used method for detoxification of OMW. Iron and H₂O₂ are cheap and non-toxic elements, there are no mass transfer limitations due to the homogenous catalytic nature, no energy involved as catalyst, as well as a considerable flexibility and ease of construction of industrial installations, but in view of the limitation of sludge reduction, the electrochemical processes have been shown to be effective in treating OMW. Encouraging results were yielded either by direct anodic oxidation or by indirect electro-Fenton methods. A comparative of the removal efficiencies and operating costs of the main AOP applied for OMW treatment is reported in Table 9. Despite its high energy consumption compared to other techniques, the electrooxidation can be considered as a suitable alternative to achieve an effective and total detoxification of OMW.

**Combination of AOP with other treatment processes**

A considerable number of studies have also been undertaken on the combination of different AOP for a complete treatment and fractionation of OMW. As presented in Table 6, among combined treatments applied to OMW we can find three forms: coupling with (AOP), coupling with biological treatments, as well as coupling with physico-chemical processes.

**Combination with AOP**

In some cases, AOP are used as a pre-treatment whenever the aim is to improve the degradation of organic compounds and reduce the toxicity of OMW, sometimes being followed by another AOP making the combined overall process more efficient. Garcia & Beltran-Heredia (2008) published the results of a combined Fenton’s reagent and ozonation process. The first process leads to about 33 and 90% COD and TPh removal, respectively. While the latter process leads to 26% of COD and 62% of TPh removal efficiencies. Also, they have concluded that 73–84% COD abatement can be reached with the combination of the two AOPs. Martins et al. (2010) ran a Fenton process pretreatment before ozonation under different operational conditions in order to reduce the COD level. They observed a COD removal rate of around 73–84%.

Canizares et al. (2007a) studied the treatment of OMW with three AOPs: conductive diamond electrooxidation
(CDEO), ozonation and Fenton oxidation. The study found that both ozonation at alkaline pH and Fenton oxidation are not able to achieve a complete mineralization compared to CDEO, due to the presence of carboxylic acids as intermediate products which can no longer be oxidized by hydroxyl radicals. They also concluded that combined Fenton oxidation and CDEO increased the COD removal performance.

Kaplan et al. (2011) described the removal efficiency of three toxic phenolic compounds in OMW (vanillic acid, o-coumaric acid and protocatechuic acid) under UV light irradiation during the electro-Fenton process. The experimental results reveal that 90% mineralization was achieved after consumption of 0.27 mAh over 3 h of treatment using carbon felt working electrodes. Recently, a similar approach was adopted by Flores et al. (2017). There

<table>
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<tr>
<th>Techniques</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺/Fe³⁺/H₂O₂</td>
<td>Simple, low cost materials, production of strong oxidant, high efficiency, easy implementation in the industrial scale</td>
<td>Low regeneration rate of Fe²⁺, low pH requirement, high doses of reagents, sludge generation, parasitic reactions, difficulty in storage and transport of H₂O₂</td>
</tr>
<tr>
<td>O₃/H₂O₂</td>
<td>Simple free radical production, high bactericide activity, less time consuming, high removal efficiencies</td>
<td>Low solubility of O₃ in aqueous solutions, limited mass transfer, high cost of reagent, ineffectiveness at high pollutants concentrations, high energy consumption, short lifetime of UV lamps</td>
</tr>
<tr>
<td>WAO and CWAO</td>
<td>Mild operating conditions, small plant for operations, higher mineralization of pollutants, adapted with flow rates and effluent compositions, no production of secondary pollution</td>
<td>High capital cost, high energy consumption</td>
</tr>
<tr>
<td>H₂O₂/UV</td>
<td>Simple, cheap and sure source of radicals, high decomposition yield of H₂O₂, oxidation of a wide range of organic compounds, no sludge production</td>
<td>Difficulty in storage and transport of H₂O₂, short lifetime of UV lamps, low absorption coefficient of H₂O₂, lack of reactor design for UV illumination, generation of by-products</td>
</tr>
<tr>
<td>O₃/UV</td>
<td>Easy handling, relatively short reaction times, production of strong oxidant</td>
<td>Selectivity of molecular ozone, high operating cost, limited mass transfer, incomplete treatment of effluents, short lifetime of UV lamps, generation of by-products</td>
</tr>
<tr>
<td>H₂O₂/Fe²⁺ (Fe³⁺)/UV</td>
<td>High efficiency, equipment simplicity, no sludge production, an additional generation of radicals, possibility of coupling with solar energy</td>
<td>High operating cost, high energy consumption, short lifetime of UV lamps</td>
</tr>
<tr>
<td>H₂O₂/O₃/UV</td>
<td>High hydroxyl radicals production, combines O₃/H₂O₂ and UV/O₃ systems, high removal efficiencies</td>
<td>High cost of reagent, high energy consumption, short lifetime of UV lamps</td>
</tr>
<tr>
<td>Fe³⁺/UV</td>
<td>High efficiency, no need for hydrogen peroxide addition, less expensive method in comparison with H₂O₂/Fe²⁺ (Fe³⁺)/UV and H₂O₂/UV processes, no mass transfer limitation</td>
<td>Low pH requirement, high energy consumption, short lifetime and limited efficiency of UV lamps</td>
</tr>
<tr>
<td>TiO₂/UV</td>
<td>Simple, available and low cost materials, operation at ambient conditions, wide pH range, oxidation of a wide range of organic compounds, possibility of coupling with solar energy</td>
<td>Formation of dark catalytic sludge, limited mass transfer, short lifetime and limited efficiency of UV lamps, difficulty in the recovery of the catalyst after treatment, difficulty of use on industrial scale</td>
</tr>
<tr>
<td>Sonochemical</td>
<td>Simple, environment friendly, ambient operating conditions, no production of toxic by-products</td>
<td>High capital cost, low OH⁻ radical production, incomplete treatment of effluents</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>Rapid, strong oxidation ability, lower temperature and pressure requirements, treatment of large volumes, no need for chemical reagents or large amounts of catalyst, low sludge production</td>
<td>High energy consumption, high operating cost, need for maintenance, need for high conductivity effluent</td>
</tr>
<tr>
<td>References</td>
<td>Technique</td>
<td>OMW source</td>
</tr>
<tr>
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</tr>
<tr>
<td>Canizares et al. (2009)</td>
<td>Fe²⁺/Fe³⁺/H₂O₂</td>
<td>Not identified</td>
</tr>
<tr>
<td>Mert et al. (2010)</td>
<td>Fe²⁺/H₂O₂ Fe³⁺/H₂O₂</td>
<td>Not identified</td>
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<tr>
<td>Canizares et al. (2009)</td>
<td>O₃/H₂O₂</td>
<td>Not identified</td>
</tr>
<tr>
<td>Michael et al. (2014)</td>
<td>H₂O₂/Fe²⁺ (Fe³⁺)/UV Three-phase</td>
<td>COD = 15,000 mg/L</td>
</tr>
<tr>
<td>Ahmed et al. (2011)</td>
<td>H₂O₂/Fe²⁺ (Fe³⁺)/UV Three-phase</td>
<td>COD = 2000–7000 mg/L TOC = 180–300 mg/L</td>
</tr>
<tr>
<td>Yalılıklı et al. (2013)</td>
<td>Acide cracking + coagulation + ultrafiltration + O₃/H₂O₂/UV</td>
<td>Not identified</td>
</tr>
<tr>
<td>Chatzisymeon et al. (2009c)</td>
<td>TiO₂/UV Three-phase</td>
<td>COD = 5100 mg/L</td>
</tr>
<tr>
<td>Canizares et al. (2009)</td>
<td>CDEO</td>
<td>Not identified</td>
</tr>
<tr>
<td>Chatzisymeon et al. (2009b)</td>
<td>BDD anodic</td>
<td>Three-phase</td>
</tr>
<tr>
<td>Hanafi et al. (2010)</td>
<td>Electrocoagulation</td>
<td>Classic process</td>
</tr>
<tr>
<td>Israilides et al. (1997)</td>
<td>Electrooxidation</td>
<td>Not identified</td>
</tr>
<tr>
<td>Un et al. (2008)</td>
<td>Electrooxidation</td>
<td>Three-phase</td>
</tr>
</tbody>
</table>

(continued)
was a comparative study involving three AOPs for 4-hydroxyphenylacetic acid degradation spiked in OMW. The three processes compared are anodic oxidation (AO), electro-Fenton (EF) and photoelectro-Fenton (PEF). The results showed that PEF gives the highest removal efficiencies due to the large photolytic action of UV radiation on photosensitive by-products. A reduction of 80% of TOC and improvement in biodegradability were observed.

Ghanbari et al. (2015) proposed a new combination system between electro-Fenton-like and anodic oxidation processes. At pH 3–3.5 and 300 mA electrical current, the research group observed a significant improvement in the COD removal of up to 65% by this system in comparison with the separate application of electro-Fenton-like and electro-generation of H₂O₂ along with anodic oxidation using PbO₂ and copper anodes.

**Combination with biological treatments**

It has been confirmed in a large number of studies that biological processes are relatively simple techniques that can be successfully employed in the OMW treatment field. However, the presence of high concentrations of aromatic and phenolic compounds inhibits the activity of the microorganisms, which leads to rather poor results of removal efficiencies making this kind of treatment inappropriate for OMW detoxification, thus increasing the interest in combined systems for improved performances.

A compilation of relevant published data with respect to biological process, AOP and the main results under various process conditions is presented in Table 10.

The Fenton process is an effective conventional method for the removal of organic pollutants, which can be used as a pretreatment for OMW purification. Amor et al. (2015) studied the pretreatment of OMW by Fenton reagent. The obtained results revealed that 63.6–88% COD removal efficiency could be achieved in the combination of Fenton’s reagent with the anaerobic biological treatment. Lucas et al. (2013) indicated that aerobic biodegradation alone cannot ensure a complete treatment. In this regard, the use of Fenton’s reagent pretreatment becomes a major necessity to improve the removal yields (80.7% COD and 93.7% TPh). Using the same combined system for green TOPW, the removal of organic load in terms of COD and

<table>
<thead>
<tr>
<th>References</th>
<th>Technique</th>
<th>OMW source</th>
<th>Initial pollutant concentration</th>
<th>Removal efficiency</th>
<th>Mode</th>
<th>Operating cost</th>
<th>Specific energy consumed</th>
<th>Operating cost</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amaral-Silva et al. (2011)</td>
<td>Fenton-coagulation-biological</td>
<td>Not identified</td>
<td>COD = 6450 mg/L, TSS = 3190 mg/L, TPh = 21 mg/L</td>
<td>%COD = 89%</td>
<td>Batch</td>
<td></td>
<td>2.96 kWh/m³</td>
<td>1.4 €/kg COD removed</td>
<td>2.7 €/m³</td>
</tr>
<tr>
<td>Lab scale</td>
<td>Coagulation: pH = 3.4, [Fe²⁺SO₄] = 3000 mg/L, [Fe²⁺] = 1500 mg/L, [H₂O₂] = 15,000 mg/L</td>
<td>Industrial scale</td>
<td>Flow rate: 1.5 m³/h, V = 450 m³, T = 22 ± 2°C</td>
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<tr>
<td></td>
<td>Biological</td>
<td>Treatment time: 60 days</td>
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<thead>
<tr>
<th>References</th>
<th>Technique</th>
<th>OMW source</th>
<th>Initial pollutant concentration</th>
<th>Removal efficiency</th>
<th>Mode</th>
<th>Operating cost</th>
<th>Specific energy consumed</th>
<th>Operating cost</th>
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<tbody>
<tr>
<td>Ghanbari et al. (2016)</td>
<td>Fenton-reagent</td>
<td>Not identified</td>
<td>COD = 6450 mg/L, TSS = 3190 mg/L, TPh = 21 mg/L</td>
<td>%COD = 89%</td>
<td>Continuous</td>
<td></td>
<td>2.96 kWh/m³</td>
<td>1.4 €/m³</td>
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<tr>
<td>Lab scale</td>
<td>Coagulation: pH = 3.4, [Fe²⁺SO₄] = 3000 mg/L, [Fe²⁺] = 1500 mg/L, [H₂O₂] = 15,000 mg/L</td>
<td>Industrial scale</td>
<td>Flow rate: 1.5 m³/h, V = 450 m³, T = 22 ± 2°C</td>
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<tr>
<td></td>
<td>Biological</td>
<td>Treatment time: 60 days</td>
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TPh can reach 79–94.77 and 36.66–73.33% removal efficiencies, respectively (Kotsou et al. 2004). Beltran-Heredia et al. (2001) used two chemical oxidation processes (Fenton’s reagent and ozonation) followed by anaerobic digestion and up to 72.5% of COD and 94.8% of TPh were removed under optimal conditions.

Always in combination with anaerobic treatment, WHPCO allowed achieving around 75, 78 and 61% of COD, BOD5 and TOC removals, respectively (El-Gohary et al. 2009). In addition, Azabou et al. (2010) reported 70% reduction of the inhibition of the marine photobacteria Vibrio fischeri luminescence with a remarkable reduction of the COD, colour and TPh by using two different catalytic systems: ((Al–Fe) pillared inter layer clay (PILC/H2O2/ultraviolet radiations) at 25 °C and ((Al–Fe)PILC/H2O2) at 50 °C. Rivas et al. (2000) carried out a study concerning the treatment of TOMW by an integrated WAO-aerobic biodegradation process. This study illustrated the ability to remove 77.1, 48.4 and 87% of COD, TC and TOC removal, respectively. Another study by Minh et al. (2008) showed that over 97% TOC and 100% TPh removal were obtained after coupling CWAO and an anaerobic digestion treatment.

An electrochemical process coupled with a biological system is also a promising treatment technology that significantly reduces COD, TPh and color. For example, the results attained by Kyriacou et al. (2005) and Gonçalves et al. (2012) reveal the potential of combined systems (anaerobic/aerobic process/electrochemical process) for OMW depollution. The use of RuO2 DSAs-type as an anode for anaerobically digested OMW gives a complete removal of 99, 100 and 100% of COD, TPh and color, respectively (Gonçalves et al. 2012). Furthermore, Kyriacou et al. (2005) applied an electrochemical process to TOPW after aerobic microbial degradation using a selected strain of Asperillus niger, the percentage of COD and TPh removal were around 96%. Khoufi et al. (2006) showed that a combined process EF and anaerobic digestion provides a total depuration of OMW compared to EF alone.

Benitez et al. (2001a) proposed a treatment process comprising H2O2/UV, Fenton’s reagent and photo-Fenton, followed by an anaerobic process. The combined system yielded 63–78% of COD abatement, and they found that 277–282 mL CH4/g COD was removed for the methane yield coefficient.

Costa & Alves (2013) suggested applying heterogeneous photocatalysis (TiO2/UV) after anaerobic digestion. Under the best conditions, a 90.8 ± 2.7% destruction of TPh was obtained, with a 79.5 ± 1.9 and 50.3 ± 6.3% reduction of color and COD respectively. Oz & Uzun (2015) studied the combination of ultrasound oxidation and anaerobic degradation of fresh and diluted OMW. The main results revealed that methane production increased up to 20% for ultrasound pretreated diluted OMW compared with the untreated one.

Oxidation oxidation coupled with biological treatment has raised much attention in OMW treatment during the past decades. Andreozzi et al. (1998) reported that the use of a combined ozone-anaerobic process improved the unsaturated lipids and TPh reduction by 50%, while the COD abatement remained unchanged.

Benitez et al. (1999a) tested the combination of two successives steps: an ozonation followed by an aerobic degradation, and an aerobic degradation followed by an ozonation. In the first combined process, 84.6% of COD was removed at pH = 7, T = 20 °C and PO3 = 1.73 kPa. In the second combined system, the total conversion obtained was 81.8% at PO3 = 1.69 kPa and the same pH and temperature. Two years later, Benitez confirmed that ozonation followed by aerobic degradation led to 85 and 88% of COD and TPh reduction, respectively (Benitez et al. 2001b). In a similar way, the same authors’ group found that a single ozonation process led to 82–92% of COD reduction, an O3/UV system led to 88–96% of COD reduction, and aerobic degradation of the OMW previously oxidized by an ozonation treatment provided 96–97% of COD reduction, which is similar to the combined ozonation plus UV radiation (Benitez et al. 2002). Also, in another study on black olive wastewater, Benitez et al. (1999b) found a reduction of 85% of COD and 88% of TPh by using a coupled ozonation and aerobic degradation process (Benitez et al. 1999b).

Beltran-Heredia et al. (2000a, 2000b) demonstrated that the application of ozone to aerobically pretreated OWM has been found to result in significant removal efficiencies (Beltran-Heredia et al. 2000a), in comparison to the results of ozonation followed by aerobic degradation (Beltran-Heredia et al. 2000b). Over 98.57% of COD, 97.6% of polyphenols and 95.82% of aromatic compounds were removed efficiently.
<table>
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<th>Advanced oxidation processes</th>
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<tbody>
<tr>
<td>Fenton’s process</td>
<td>Anaerobic process</td>
<td>pH: 3.5</td>
<td>(i) Fenton’s reagent leads to a 17.6 and 82.5% of COD and TPh reduction, respectively</td>
<td>Amor et al. (2015)</td>
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<tr>
<td></td>
<td></td>
<td>Temperature: 20 °C</td>
<td>(ii) Anaerobic process leads to COD conversion between 52.6 and 74.0%</td>
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<tr>
<td></td>
<td></td>
<td>H₂O₂/Fe²⁺ ratio: 15:1</td>
<td>(iii) Combined Fenton reagent/anaerobic digestion treatment leads to COD conversion between 63.6 and 88.0%</td>
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<tr>
<td></td>
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<td>H₂O₂/COD ratio: 0.2</td>
<td>(iv) Methane production ranged between 281 and 322 mL of CH₄/g COD removed</td>
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<tr>
<td>Fenton’s process and ozonation</td>
<td>Aerobic process</td>
<td>pH: 4.84</td>
<td>(i) Fenton’s reagent leads to 32.7 and 94% of COD and TPh reduction, respectively</td>
<td>Beltran-Heredia et al. (2001)</td>
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<tr>
<td></td>
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<td>Temperature: 10, 20, 30 and 40 °C</td>
<td>(ii) Ozonation process leads to 26.6 and 43.7% of COD and TPh reduction, respectively</td>
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<td>Fe²⁺/H₂O₂ ratio: 1:10, 1:15 and 1:20</td>
<td>(iii) Combined Fenton reagent/anaerobic digestion treatment leads to a 84.2 and 81.3% of COD and TPh reduction, respectively</td>
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<tr>
<td></td>
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<td>Ozonation times: 1.8–8.7 h</td>
<td>(iv) Combined ozonation/anaerobic digestion treatment leads to a 72.5 and 94.8% of COD and TPh reduction, respectively</td>
<td></td>
</tr>
<tr>
<td>Fenton’s process</td>
<td>Aerobic process</td>
<td>pH: 3.5</td>
<td>(i) Aerobic biodegradation alone leads to 83 and 61% of COD and TPh removal, respectively</td>
<td>Lucas et al. (2015)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O₂/COD ratio: 0.20</td>
<td>(ii) The combined process leads to 80.7 and 93.7% of COD and TPh removal, respectively</td>
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<tr>
<td></td>
<td></td>
<td>H₂O₂/Fe²⁺ molar ratio: 15</td>
<td>The combined process leads to 79–94.77% and 36.66–73.33% of COD and TPh reduction, respectively</td>
<td>Kotsou et al. (2004)</td>
</tr>
<tr>
<td>Wet hydrogen peroxide catalytic oxidation (WHPCO)</td>
<td>Anaerobic process</td>
<td>pH: 2–5</td>
<td>COD, BOD₅ and TOC removal rates of 75, 78 and 61%, respectively</td>
<td>El-Gohary et al. (2009)</td>
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<tr>
<td></td>
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<td>Fe²⁺/H₂O₂ ratio: 1:10, 1:25 and 1:50</td>
<td>Reduction of the inhibition of the marine photobacteria <em>Vibrio fischeri</em> luminescence by 70%</td>
<td>Azabou et al. (2010)</td>
</tr>
<tr>
<td>Wet hydrogen peroxide catalytic oxidation (WHPCO)</td>
<td>Anaerobic process</td>
<td>pH: 5.2</td>
<td>Aerobic biodegradation of wet air oxidized TOPW leads to 77.1, 48.4 and 87% of COD, TC and TOC removal, respectively</td>
<td>Rivas et al. (2000)</td>
</tr>
<tr>
<td>Wet air oxidation (WAO)</td>
<td>Aerobic process</td>
<td>pH: 7</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>Temperature: 20 °C</td>
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<td></td>
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<td>Treatment time: 10 h</td>
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<tr>
<th>Advanced oxidation processes</th>
<th>Biological processes</th>
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<tbody>
<tr>
<td>Catalytic wet air oxidation</td>
<td>Anaerobic process</td>
<td>pH: 4.7–5.4</td>
<td>Removal efficiencies of 97 and 100% were obtained for TOC and TPh, respectively</td>
<td>Minh et al. (2008)</td>
</tr>
<tr>
<td>(CWAO)</td>
<td></td>
<td>Temperature: 140 and 190 °C. Total air pressure: 70 bar</td>
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<td></td>
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<td>(i) By using IrO2 anode, 14, 91 and 85% removal rates of COD, TPh and color, respectively</td>
<td>Gonçalves et al. (2012)</td>
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<tr>
<td></td>
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<td>(ii) By using RuO2 DSAs-type as anode, 99, 100 and 100% removal rates of COD, TPh and color, respectively</td>
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<td>(iii) In the combined process, total depuration of OMW has been achieved</td>
<td>Khoufi et al. (2006)</td>
</tr>
<tr>
<td>Electrochemical process</td>
<td>Anaerobic process</td>
<td>pH: 4.7–8.9</td>
<td>(i) EF process leads to 65.8 and 33.1% of TPh and toxicity reduction, respectively</td>
<td>Kyriacou et al. (2005)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature: 20 ± 2 °C.</td>
<td>(ii) Aerobic biodegradation alone leads to 66–86 and 65% of COD and TPh removal, respectively</td>
<td></td>
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<tr>
<td></td>
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<td>Electrolysis charge: 10.4×10^4 CL^{-1}</td>
<td>(iii) The combined process leads to 96% of COD and TPh reduction</td>
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<tr>
<td></td>
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<td>Supporting electrolyte KNO3 concentrations: 0.1 M</td>
<td>(iv) The single UV radiation leads to 35 and 20% of COD and aromatic compounds removal, respectively</td>
<td>Benitez et al. (2001a)</td>
</tr>
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<td>(v) The H2O2/UV system gives 41–76% of COD and 52% of aromatic compounds removal</td>
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<td>(vi) The combined process leads to 63–78% of COD reduction, and 277–282 mL CH4/g COD removed for the methane yield coefficient</td>
<td></td>
</tr>
<tr>
<td>H2O2/UV Fenton’s reagent</td>
<td>Anaerobic process</td>
<td>pH: 12.6</td>
<td>Over 90.8 ± 2.7%, 79.3 ± 1.9% and 50.3 ± 6.3% removal efficiencies of TPh, color and COD respectively</td>
<td>Costa &amp; Alves (2015)</td>
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<tr>
<td>Photo-Fenton</td>
<td></td>
<td>Temperature: 20–35 °C.</td>
<td></td>
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<td></td>
<td></td>
<td>[Fe^{2+}]: 2.4×10^{-3} and 4.8×10^{-3} M</td>
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<td>[H2O2]: 0.035–0.11 M</td>
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<tr>
<td>Heterogeneous photocatalysis</td>
<td>Anaerobic process</td>
<td>pH: 4.8–7.5</td>
<td>(i) The application of ultrasound alone increased soluble chemical oxygen demand/total chemical oxygen demand SCOD/TCOD ratio from 0.59 to 0.79</td>
<td>Oz &amp; Uzun (2015)</td>
</tr>
<tr>
<td>(TiO2/UV)</td>
<td></td>
<td>Temperature: 37 °C.</td>
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<td></td>
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<td>Treatment time: 8–24 h</td>
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<tr>
<td>Ultrasound</td>
<td>Anaerobic process</td>
<td>pH: 5.14</td>
<td>(ii) An increase in methane production of 20% for ultrasound pretreated diluted OMW compared with the untreated one</td>
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<td>Temperature: 35 ± 2 °C.</td>
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<td>Power: 50–100 W</td>
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<td></td>
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<td>Frequency: 20 kHz</td>
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<td></td>
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<td>Power densities: 0.2 and 0.4 W/mL</td>
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<tr>
<td>Method</td>
<td>Process</td>
<td>pH</td>
<td>Temperature</td>
<td>Ozone Pressure</td>
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<tr>
<td>Ozonation</td>
<td>Anaerobic process</td>
<td>5.09–8</td>
<td>35 °C</td>
<td>1.69 and 1.73 kPa</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Aerobic process</td>
<td>7</td>
<td>20 °C</td>
<td>1.69 and 1.73 kPa</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Aerobic process</td>
<td>13.5</td>
<td>28 ± 0.2 °C</td>
<td>0.82 and 1.22 kPa</td>
</tr>
<tr>
<td>Ozonation, O₃/UV</td>
<td>Aerobic process</td>
<td>9.07–13.05</td>
<td>20 °C</td>
<td>4.70 kPa</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Aerobic process</td>
<td>13.5</td>
<td>28 ± 0.2 °C</td>
<td>0.82 and 1.22 kPa</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Aerobic process</td>
<td>7–13.6</td>
<td>10, 20 and 30 °C</td>
<td>5.093 and 5.601 kPa</td>
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<tr>
<td>Ozonation</td>
<td>Aerobic process</td>
<td>4–9</td>
<td>10–30 °C</td>
<td>4.36 and 4.48 kPa</td>
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<tr>
<td>Ozonation</td>
<td>Aerobic process</td>
<td>pH: 4–10</td>
<td>(i) For TOPW, 87.4% of COD and 97.3% of TPh were removed&lt;br&gt;(ii) For OMW, 99% of COD and 90% of TPh were removed</td>
<td>Rivas et al. (2001c)</td>
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<td></td>
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<td>Flow-rate: 20 L/h</td>
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<td>Acidic timing (min): 0–20, 155–165&lt;br&gt;Alkaline timing (min): 20–155, 165–180</td>
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<tr>
<td>Ozonation, O$_3$/UV</td>
<td>Aerobic process</td>
<td>pH: 3</td>
<td>(i) Ozonation followed by aerobic degradation leads to 87% of COD reduction&lt;br&gt;(ii) Aerobic degradation followed by ozonation process leads to 80% of COD reduction&lt;br&gt;(iii) O$_3$/UV followed by aerobic degradation leads to 90.7% of COD reduction&lt;br&gt;(iv) Aerobic degradation followed by O$_3$/UV leads to 81.8% of COD reduction</td>
<td>Lafi et al. (2009)</td>
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<td></td>
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<td>Temperature: 25 °C</td>
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<td>Treatment time: 4–6 h</td>
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<td>Flow-rate: 35 L/h</td>
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<tr>
<td>Ozonation</td>
<td>Anaerobic process</td>
<td>pH: 7.5</td>
<td>(i) Anaerobic digestion resulted 81, 95, 95% and 295 L CH$_4$/kg COD of COD, BOD$_5$, TPh removal and methane yield coefficient, respectively&lt;br&gt;(ii) Ozonation post treatment leads to 16–52% of COD and 68–89% of TPh reduction</td>
<td>Beltran de Heredia &amp; Garcia (2005)</td>
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<td></td>
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<td>Temperature: 35 °C</td>
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<td>Biological treatment time: 55 days&lt;br&gt;Ozonation time: 30–240 min&lt;br&gt;Ozone pressure: 1–4.9 kPa&lt;br&gt;Flow-rate: 90 L/h</td>
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<tr>
<td>Ozonation</td>
<td>Encapsulated biomass</td>
<td>pH: 7–8.5</td>
<td>(i) Ozonation alone leads to 20% COD and 61% TPh removal&lt;br&gt;(ii) The combined process leads to 36% COD and 61% TPh removal</td>
<td>Oz et al. (2018)</td>
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<td></td>
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<td>Temperature: 20–25 °C</td>
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<td></td>
<td>Treatment time: 1 h O$_3$ – 48 h&lt;br&gt;biotreatment&lt;br&gt;Flow-rate: 1 L/min</td>
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Rivas et al. (2000) studied the treatment of TOPW and OMW by combined ozonation and aerobic biodegradation. For the first effluent, 87.4% of COD and 97.3% of TPh were removed, and for the second one 99 and 90% of COD and TPh removal, respectively, were reached. With a procedure similar to that developed above, Lafi et al. (2009) concluded that COD removal was 87% when using ozonation followed by aerobic digestion, and 90.7% of COD after O₃/UV followed by an aerobic process.

Beltran de Heredia & Garcia (2005) ran a continuous anaerobic digestion before the ozonation process in order to follow the evolution of COD, BOD₅, TPh concentration and methane production. The results achieved under the stable conditions during 55 days in the bioreactor proves that anaerobic biodegradation can be successfully used to remove 81% of COD, 95% of BOD₅ and TPh, with a gas production rate of 295 L CH₄/kg COD. When ozonation was implemented after anaerobic process, 16–52% of COD and 68–89% of TPh degradation was achieved after 4 h of treatment.

Recently, Oz et al. (2018) proposed a new combined system of ozonation process and encapsulated biomass. Their experimental results showed that up to 36% of COD and 61% of TPh were removed, through ozone pretreatment of OMWW followed by addition of Delftia EROSY capsules to OMW for 48 h incubation, which was greater than that obtained by the individual ozonation under the same operating conditions.

**Combination with physico-chemical treatments**

During the last decade, great concern has been raised over the combination of AOP with physico-chemical treatments, which offers another way to ameliorate the OMW detoxification. As has been confirmed in many publications, simple physical processes such as dilution, lagoons of evaporation, sedimentation, filtration and centrifugation, as well as physico-chemical processes including lime treatment, chemical coagulation–floculation and adsorption, cannot attain high removal efficiencies. To overcome these limitations and improve process efficiency, a research program was designed with the aim of investigating the introduction of some AOP. Table 11 provides more details on a selected number of applications carried out by means of AOP combined with physico-chemical treatments.

Ginos et al. (2006) tested the use of coagulation–floculation as pre-treatment of OMW followed by the Fenton process. This study yielded 99.7, 78.8 and 35.5% of TSS, TPh and COD reduction, respectively, while 98.7, 84.9 and 61.4% of TSS, TPh and COD were removed, respectively.

Lucas & Peres (2009b) conducted a similar study, but obtained different results. In the Fenton’s process, almost 96.8% COD were removed, when the pH was 3.5, mass ratio \( R = \frac{H_2O_2}{COD} = 3.0 \) and molar ration \( H_2O_2/Fe^{2+} \) was 15. When coagulation/floculation with lime was used as post-treatment in combination with the Fenton process, more than 99.3% of COD could be degraded effectively, for \( R = \frac{H_2O_2}{COD} = 3.0 \).

Gomec et al. (2007) also used the Fenton reagent in conjunction with acid cracking (AC), lime and anionic/cationic polyelectrolyte (AP, CP). After several combinations were tested, a maximum reduction of COD of 89% was obtained using Fenton’s oxidation after AC and CP (10 ppm) treatment. In another research paper, the AC and Fenton process gave satisfactory treatment efficiencies of around 83, 98.6, 77, and 67% for COD, TPh, color and aromaticity, respectively (Madani et al. 2015). It was found also that the increase in temperature from 25 to 30 °C did not have a significant influence on the efficiency of the process.

More recently, the Fenton’s reagent–ion exchange (IE) system has been studied for detoxification and reduction of pollutants in OMW. Reis et al. (2018) chose Lewatit TP 207 as anionic exchange resin. The Fenton’s process removed 98.2% of TPh and the COD content by 80.7% in 1 h, while the combined system removed the Fe³⁺ completely compared to 35% of Fe²⁺, which allows the authors to conclude that this type of combination is able to avoid Fenton’s main drawback, related to the production of large volumes of sludge.

An innovative application of battery comprising coagulation–floculation, extraction of phenolic compounds and photo-Fenton post-oxidation of OMW was developed by Papaphilippou et al. (2013). The best results were achieved for the photo-Fenton oxidation after coagulation–floculation and solvent extraction, which degraded 73% of COD and 87% of TPh at pH 3, 0.2 g/L Fe²⁺ and 5 g/L \( H_2O_2 \).

Yazdanbakhsh et al. (2015) evaluated the efficiency of the Fenton-like process, coagulation and acid cracking
<table>
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<tr>
<th>Advanced oxidation processes</th>
<th>Physico-chemical processes</th>
<th>Experimental conditions</th>
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<tr>
<td>Fenton’s process</td>
<td>Coagulation–floculation</td>
<td>pH: 5.1–5.3 [Fe^{2+}]: 2.5, 5 and 10 g/L [H_2O_2]: 0.5, 1, 5 and 10 g/L. Lime concentration: 0–230 mg/L</td>
<td>(i) Coagulation–floculation alone leads to 99.7, 78.8 and 35.5% of TSS, TPh and COD reduction, respectively (ii) The combined process leads to 98.7, 84.9 and 61.4% of TSS, TPh and COD reduction, respectively</td>
<td>Ginos et al. (2006)</td>
</tr>
<tr>
<td>Fenton’s process</td>
<td>Coagulation/floculation</td>
<td>pH: 3.5 Temperature: 30 °C [H_2O_2/Fe^{2+}]: 15 [H_2O_2/COD]: 0.25–3</td>
<td>(i) In the Fenton’s process, 96.8% of COD has been achieved (ii) A stronger COD reduction (99.3%) with the combined system</td>
<td>Lucas &amp; Peres (2009a, 2009b)</td>
</tr>
<tr>
<td>Fenton’s process</td>
<td>Acid cracking (AC) + lime + anionic/cationic polyelectrolyte (AP, CP)</td>
<td>pH: 1.7–9.2 [Fe^{2+}]: 2.5, 5 and 10 g/L [H_2O_2]: 750 mg/L</td>
<td>(i) The pre-treatment by AC, AC + AP (5 ppm), AC + AP (10 ppm), lime and lime + AP (9 ppm) leads to a reduction of 72.5, 81.17, 73.85, 56.32 and 41.83% of COD, respectively (ii) Fenton’s oxidation after AC and CP (10 ppm) treatment leads to 89% of COD removal</td>
<td>Gomec et al. (2007)</td>
</tr>
<tr>
<td>Fenton’s process</td>
<td>Acid cracking (AC) + coagulation</td>
<td>pH: 1.5–3.5 treatment time: 4 h Temperature: 25 and 30 °C [H_2O_2]: 0.12–0.5 M [Fe^{2+}]: 0.005–0.03 M</td>
<td>(i) AC removes 47.3, 30.1, 64.3, and 59.1% of COD, TPh, color, and aromaticity, respectively (ii) AC and Fenton process lead to 83, 98.6, 77, and 67% of COD, TPh, color and aromaticity, respectively (iii) The increase in temperature from 25 to 30 °C does not have a significant influence on the efficiency of the process</td>
<td>Madani et al. (2015)</td>
</tr>
<tr>
<td>Fenton’s process</td>
<td>Ion exchange (IE)</td>
<td>pH: 1.5–4.5 [Fe^{2+}]: 0–5 g/L [H_2O_2]: 0–6 g/L</td>
<td>(iv) In the Fenton’s process, 80.7 and 98.2% of COD and TPh have been removed, respectively (v) The tested resin Lewatit TP 207 shows a higher affinity (100% of iron removal efficiency) toward Fe^{3+} when compared with Fe^{2+} (35%)</td>
<td>Reis et al. (2018)</td>
</tr>
<tr>
<td>Photo-Fenton process</td>
<td>Coagulation–floculation</td>
<td>pH: 3 Treatment time: 240 min [FeSO_4], 7H_2O]: 3.33, 5 and 6.67 g/L FLOCAN 23: 0.287, 0.07 and 0.14 [H_2O_2]: 0, 3, 4, 5 and 6 g/L [Fe^{2+}]: 0, 0.2, 0.4 and 0.6 g/L</td>
<td>(i) The coagulation–floculation leads to 97 ± 1.3, 72 ± 1.5, and 40 ± 1.3% of TSS, COD and TPh, respectively (ii) 36% of TPh recovery post-coagulation–floculation was achieved by solvent extraction (iii) 73 ± 2.3 and 87 ± 3.1% removal efficiencies were achieved for COD and TPh, respectively, by combination with photo-Fenton process</td>
<td>Papaphilippou et al. (2015)</td>
</tr>
</tbody>
</table>
| Process Type | Coagulation and acid cracking (AC) | pH: 1.5–4  
Treatment time: 0–400 min  
Alum concentration: 1000–6000 mg/L  
Ferric chloride concentration: 1000–6000 mg/L  
Polyaluminum chloride concentration: 250–1500 mg/L  
$[\text{H}_2\text{O}_2]$ concentration: 250–3000 mg/L  
Zero valent iron concentration: 1–11 g/L |  
(i) Coagulation process removed 91.2% COD, 91.3% TPh, 98.9% TSS and 99.2% turbidity Yazdanbakhsh et al. (2015)  
(ii) The combined process increased the $\text{BOD}_5/\text{COD}$ ratio from 0.14 to 0.83 |
|---|---|---|
| Fenton like process | Coagulation | pH: 4.3–6  
Treatment time: 1–2 h  
$[\text{H}_2\text{O}_2]/[\text{FeSO}_4]$ ratio = 6000/600 and 15,000/1,852 (w/w)  
Coagulant dose: 0–600 mg/L |  
(i) Coagulation by chitosan was shown to remove 81% of TSS Rizzo et al. (2008)  
(ii) The combined photo-Fenton/coagulation system was found to be more efficient for COD removal (91%) compared to Fenton one (81%) Gernjak et al. (2007) |
| Photocatalysis, Fenton and photo-Fenton process | Acidification/coagulation/flocculation | pH: 2.6 and 4.6  
$[\text{H}_2\text{O}_2]$: 0, 15 and 30 g/L  
$[\text{Fe}^{2+}]$: 0, 2, 6 and 10 Mm  
Coagulant dose: 0, 0.25 and 1 (w/w) |  
(i) The acidification followed by Fenton process leads to 15 and 60% of COD and TPh removal, respectively  
(ii) The acidification/coagulation/flocculation/Photo-Fenton system leads to 75 and 100% of COD and TPh removal, respectively Andreozzi et al. (2008) |
| Photo-Fenton Fenton process | Centrifugation | pH: 3  
Treatment time: 60, 90 and 120 min  
Flow-rate: 36 L/h |  
(i) The pre-treatment by centrifugation leads to a reduction of 41.3% of COD  
(ii) Ozonation alone leads to 31.5 and 63.6% of COD and TPh removal, respectively  
(iii) Air/light with Fe(III)/Ozonation system leads to 40.3 and 75% of COD and TPh removal, respectively Ugurlu & Kula (2007) |
| Ozonation Photo-Fenton process (Fe(III))/air/solar light | Lime treatment | pH: 7  
Temperature: 25 °C  
Treatment time: 7 days  
$\text{H}_2\text{O}_2$ (50%) doses: 1–10 mL/100 mL OMW |  
(i) 90% of color, 90% of phenol and 30% of lignin were removed by single UV/H$_2$O$_2$  
(ii) The combination with lime yielded 99, 100 and 40% of color, phenol and lignin removals, respectively Drouiche et al. (2004) |
| UV/H$_2$O$_2$ | Ultrafiltration (UF) | pH: 4.5  
Temperature: 27–37 °C  
$[\text{H}_2\text{O}_2] = 2*10^{-2}$ M |  
(i) 94 and 100% of COD and TSS removal by using UF alone  
(ii) In the combined process, 75% of the initial absorbance vanished after 40 min of irradiation |
(AC) for the treatment of OMW. They found 91.2% COD, 91.3% TPh, 98.9% TSS and 99.2% turbidity removals with a single coagulation stage. After the application of the Fenton-like process with zero valent iron (ZVI) preceded by coagulation and acid cracking pre-treatment, the BOD5/COD ratio was increased from 0.14 to 0.83.

Rizzo et al. (2008) first introduced chitosan as a new coagulant agent to improve removal efficiencies, reaching 81% of TSS removal at natural pH 4.3 and 400 mg chitosan/L. A combined photo-Fenton/coagulation system was then applied to achieve 91% of COD abatement compared to Fenton (81%). Gernjak et al. (2007) could not achieve more than 15% of COD and 60% of TPh removal using acidification followed by the Fenton process. Greater COD removal of 75% and total dephenolization were observed by coupling acidification, coagulation/floculation and photo-Fenton processes. By considering the physical pre-treatment of OMW for COD removal within centrifugation, Andreozzi et al. (2008) found that 41.3% COD was obtained, and after 120 min of treatment with ozone, COD was increased to 31.5% with 63.6% of TPh removal. Moreover, they concluded that air/light with a Fe(III)/Ozonation system was able to reduce the COD and TPh; 40.3 and 75%, respectively.

Many authors have reported high removals of organic pollutants of OMW by coupling photolysis of H2O2 with other physico-chemical processes. Ügurlu & Kula (2007) showed that approximately 99% removal of color, 100% of phenols and 40% of lignin could be achieved by a combination of UV/H2O2 and lime. Drouiche et al. (2004) achieved 94 and 100% of COD and TSS removal using an ultrafiltration process (UF) alone. In addition, it has been shown that the use of a UV/H2O2 process in combination with UF allows the permeate treatment in batch and continuous modes to be completed after 40 min of irradiation.

Kestioglu et al. (2005) examined the utilization of both H2O2/UV and O3/UV oxidation processes combined with acid cracking and ferric coagulation. The results suggested that 99% of both COD and TPh removal efficiencies could be achieved by an acid cracking + ferric coagulation + H2O2/UV system at pH 7, T = 20 °C and 440 min treatment time, while for the other system acid cracking + ferric coagulation + O3/UV, 98% of COD and 99% of TPh removal has been reached. On the other
hand, Lafi et al. (2010) tried to integrate a treatment involving a combination of UV, O₃, O₃/UV, H₂O₂/UV and coagulation process to remove the organic leads of OMW. In this work, a degradation degree of 10, 19, 37 and 39% of COD were removed by UV, O₃, O₃/UV and H₂O₂/UV processes, whereas using the combined systems, coagulation/O₃, coagulation/O₃-UV and coagulation/H₂O₂/UV, led to COD reduction rates of 90, 95 and 94%, respectively.

CONCLUSIONS

The growth of the olive sector around the world over the last decade, combined with an increase in the use of vast amounts of water, has contributed to the large amount of OMW being generated. Different methods to reduce the organic load of OMW have been studied. Among these techniques, AOPs have been successfully applied to achieve a complete detoxification of OMW. These include chemical AOP (Fe³⁺/Fe²⁺/H₂O₂, O₃/H₂O₂, wet air oxidation and catalytic wet air oxidation); photochemical AOP (H₂O₂/UV, O₃/UV, H₂O₂/Fe²⁺ (Fe³⁺)/UV, H₂O₂/O₃/UV, Fe³⁺/UV and TiO₂/UV), sonochemical AOP and electrochemical AOP (anodic oxidation and electro-Fenton) as well as combined systems. This review presents recent information on detoxification of OMW by AOP, either alone or in combination with other methods.

In general, among the combined physical, biological and chemical processes used to decontaminate OMW, the choice of the most appropriate treatment is based on several factors: simplicity, safety, energy efficiency, waste sludge production and operating cost. Given the drawbacks of biological methods, such as the need to dilute many times the effluent, thus increasing their effectiveness, aerobic and anaerobic digestion remains the most convenient technique and least expensive wastewater treatment method, which makes their combination with AOP a suitable solution for the removal of toxic organic pollutants from OMW.

In conclusion, further investigation is required on techno-economical evaluation for future industrialization, as well as studies in reactor design and application. Consequently, great efforts should be made to scale-up AOP experiments from laboratory to industrial size.

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