

Review

Detoxification of Olive Mill Wastewaters by Fenton's Process

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Abstract: Olive mill wastewaters (OMW) constitute an environmental problem affecting mainly Mediterranean Sea area countries where the olive mill industry is a very important economic sector. The strong impact and management issues of these effluents are mainly due to their seasonality, localized production, and high organic load with high toxic features and low biodegradability. As the olive oil industry is highly water demanding, the search for suitable water recovery strategies requires the development and optimization of advanced treatment technologies. The classical Fenton's process is an interesting alternative, as it operates at room conditions of pressure and temperature. However, it shows some drawbacks, such as the generation of iron sludges, which require further management. Nevertheless, because of its features that make it industrially desirable, overcoming these limitations has been the focus of researchers in the last years. Bearing this in mind, this paper focuses on the recent research regarding OMW treatment using Fenton's process. The use of Fenton's peroxidation treatment at homogenous, heterogeneous, and photo-aided conditions is analysed. The use of solid catalysts may be an interesting way to avoid sludge formation. Light-driven Fenton can also reduce the amount of iron needed for effective degradation. Moreover, Fenton's process integration in combined treatment schemes is discussed. Finally, remarks regarding its application at full scale are given.

Keywords: Fenton's reagent; Advanced oxidation processes; Olive mill wastewater; Heterogeneous Fenton's process; Photo-Fenton; Integrated treatment; Real scale application

1. Introduction

Water is an essential resource for life maintenance. The decline in the quantity and quality of the available freshwater because of large drought periods and contamination as a result of human activity is increasing the social and political awareness for water protection. Thus, even more restrictive legislation must be established in order to safeguard the sustainable exploitation of hydric resources. This means that industry will have to accomplish even tighter limits for the quality of discharged wastewater. In this context, there is a need for developing efficient water treatment systems. In fact, one of the basilar stones of the current European commission program regarding water is the development of technological and innovative solutions that are able to lead to safe water for all citizens. Because of the water shortening and increasing supply demanding, liquid effluents must be envisaged as alternative sources of fresh water [1]. In this context, researchers and stakeholders must make efforts so that economically viable technologies can be developed to reach safe water for both ecosystems and human health, from the adequate treatment of contaminated streams. Such a goal will only be reached by combining processes in order to take advantage of their synergies.

Mediterranean Sea area countries suffer from severe drought periods, and water shortening is a particularly serious problem in these countries. Moreover, agro-industries (such as olive mills) are an important part of their industrial network. Even if these industries are a relevant key in their economic development, the wastewaters generated pose major environmental danger. On the one hand, agro-industries are highly water demanding, and, on the other hand, during their operation, a high number of polluted streams are created. Thus, the treatment of these effluents is a major step aimed at environmental preservation and water recovery.

Mediterranean countries are the major producers of olive oil. During olive oil extraction, up to 10 million tons of liquid effluents are generated each year [2]. The composition of olive mill wastewater (OMW) depends on several factors, such as the climate, cultivation, and method of grinding used to produce olive oil. There are several types of processes used in the production of olive oil, such as traditional pressing, and three-phase and two-phase decanting processes [3]. Olive mill wastewaters can be characterized by a strong odour; dark colour; and high organic load, including sugars, tannins, polyalcohols, pectins, and lipids [4,5]. The common treatments based on these biological reactors tend to be inefficient for OMW, because of the presence of toxic compounds in their constitution [6,7]. Moreover, their high organic load (chemical and biochemical oxygen demand may reach up to 100 to 200 g/L) makes these streams hard to manage, as well as making the fulfilment of the legal thresholds for their discharge to the environment difficult [8]. Some recovery strategies were studied in order to take advantage of OMW characteristics. For example, Fabrizio et al. [9] studied integrated microalgae biomass production and olive mill wastewater biodegradation. In fact, OMW can have nutrients like phosphorus and organic carbon that help with microalgae growth. Moreover, aiming at water recovery, robust and efficient treatment approaches are required. In this ambit, advanced oxidation processes are promising technologies to reduce the environmental impact of these effluents [5,10] and to promote water recovery from effluents [11,12]. Among them, ozonation [13] and Fenton's process [14] show interesting potential for the treatment of OMW.

The Fenton's process is based on the production of hydroxyl radicals through the catalytic decomposition of hydrogen peroxide promoted by iron ions. Thus, this technology shows interesting features for full scale application, as it occurs at room temperature and pressure [15], and no sophisticated equipment is required [15,16]. Moreover, there are no safety or environmental issues related to hydrogen peroxide [17]. Consequently, there are several studies involving the application of this process for the treatment of water and wastewater [18–20]. The main drawback of this technology is the need for removing the dissolved iron from the treated effluent (Table 1). In fact, the required amount of catalyst is usually much higher than the legal threshold of iron permitted for an effluent discharge to the natural water courses. Currently, after the oxidation process, the wastewater is alkalized so that insoluble $\text{Fe}(\text{OH})_3$ is produced and precipitates as iron sludge [21]. Typically, these sludges are dried and directed to landfills, which do not allow for catalyst reuse. Furthermore, as the sludges incorporate some organic compounds that coagulate with $\text{Fe}(\text{OH})_3$, they may have a negative environmental impact and may constitute a second source of pollution. In this way, waste minimization and management are technological challenges. Moreover, the possibility of catalyst recovery would reduce the environmental impact and the operating costs of the process.

Table 1. Pros and cons of homogeneous Fenton's process.

Homogeneous Fenton's Process	
Advantages	Disadvantages
<ul style="list-style-type: none"> - Easy operation - Chemical oxygen demand (COD) removal - Biodegradability improvement - Established technology 	<ul style="list-style-type: none"> - Sludge formation - Operation in acidic conditions (pH ~3) - Requires neutralization of pH

Despite these disadvantages, there is much industrial interest on the Fenton's process because of its ability to deal with cumbersome effluents (such as those coming from olive oil extraction), which are unable to be directly managed through the traditional biological systems. In fact, Fenton's process shows a high capacity for improving the biodegradability and reducing the toxicity of bio-refractory effluents [22]. In this context, scientific efforts are in force to overcome the problems associated with iron sludge production. This involves strategies having the iron recovery from the sludge be directly reused in Fenton's reaction [23,24] or as a precursor of solid catalysts [25]. Moreover, the selection of active and stable heterogeneous catalysts for Fenton's peroxidation instead of soluble iron salt is being addressed [26,27]. The use of a light and/or electro driven Fenton's process [28–31] may also reduce the amount of iron required for the reaction.

Bearing in mind the high industrial interest on the Fenton's process, the aim of the present paper is to give a critical overview on the works dealing with this process for the detoxification of olive mill wastewaters. These effluents were selected as case studies because of their high environmental impact, particularly on the Mediterranean basin countries that also suffer from strong water shortening. In this context, Fenton's process can be a suitable alternative for water recovery in this water demanding industry.

2. Homogeneous Fenton's Process

The classic Fenton's process operates in homogeneous conditions, where hydrogen peroxide decomposition into hydroxyl radicals is promoted by the dissolved ferrous iron, according to Equation (1) [32].



However, other reactions can be involved in the global mechanism, such as those described by Equations (2) and (3) [33].



In those reactions, Fenton's main oxidant (hydroxyl radicals) is scavenged, which may reduce the process efficiency. This means that the ratio between $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ must be carefully selected in order to avoid the scavenging effect. Lucas and Peres [34] tested the effect of pH, temperature, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio, and $\text{H}_2\text{O}_2/\text{COD}$ weight ratio for the Fenton's peroxidation of OMW (collected in Portugal and diluted to an initial COD ~ 2 g/L). The best operating conditions (pH 3.5, 30 °C, $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 15$, and $\text{H}_2\text{O}_2/\text{COD} = 1.75$) led to a COD removal of 70%. Moreover, the authors were able to determine the Arrhenius constant (28.2 kJ/mol) for the system that was kinetically well described by a pseudo-first order equation.

One important feature of the Fenton's process is the capability of improving the effluent BOD_5/COD ratio, which means that this chemical process can be followed by a biological system for the further degradation of the effluent [35]. Therefore, if the legal limits for local sewage discharge are accomplished, the pre-treated OMW can be conducted to the municipal wastewater treatment plant (MWTP) for final depuration. Gomec et al. [36] verified that the Fenton's oxidation (2000 mg/L of H_2O_2 and Fe^{2+}) was able to improve the COD removal of OMW after acid cracking and cationic polyelectrolyte coagulation. The COD degradation reached 89% and the wastewater was within the legal limits (regarding the COD and suspended solids) for discharge to the local sewage. However, as the authors refer, information must be collected about the effect of the chemical process over the treated effluent biodegradability and toxicity, so that its impact over the biological systems of the MWTP can be thoroughly assessed. This information can also help with the optimization of the Fenton's process, as this system can be expensive because of the chemical and energy requirements. Hydrogen peroxide is reported to assume up to 75% of the process global operating cost [37]. Moreover, Rivas et al. [37] determined an average stoichiometric ratio of 3 mol of H_2O_2 per mol of COD removed. Thus, instead of seeking large organic matter removal efficiencies, one can be focused on the partial

oxidation of the pollutants, aiming to improve biodegradability and reducing toxicity. Fenton's process has been reported to be able to moderately remove COD, while a large polyphenolic fraction is degraded, leading to an effluent able to be depurated by aerobic biological systems to a high extent [38]. In this way, it can be followed by a biological treatment, for example, in a municipal wastewater treatment plant (MWTP). Thus, the costs associated with the effluent processing may be reduced.

It must be highlighted that Rivas et al. [37] compiled the most important steps in the Fenton's mechanism and gave the kinetic constants for each of them. This may be important when developing mathematical models to simulate the process.

Mert et al. [3] studied physicochemical (acid cracking), Fenton, and Fenton-like processes in the pre-treatment of OMW. The chemical pre-treatment had a positive effect on biodegradability. Acid cracking led to a >67% removal of COD and 72% removal of total-phenols. Fenton's process, with the optimal conditions, namely, pH = 3, $[H_2O_2] = 3500$ mg/L, and $[FeSO_4] = 3000$ mg/L, achieved up to 81% COD removal, 86% phenol removal, and 350 mL/L sludge volume, whereas the Fenton-like process optimal conditions (pH = 3, $[H_2O_2] = 3000$ mg/L, and $[FeCl_3] = 2500$ mg/L) were able to reach an 88% COD removal, 91% phenol removal, and 300 mL/L sludge volume. The authors also studied the costs of the processes in terms of the required chemicals. They found that the Fenton-like process is the most economical and feasible option for the treatment of OMW before discharge into sewage, for the protection of central wastewater treatment plants. Moreover, the OMW inhibitory effect over the activated sludge was truly diminished after the chemical treatment. Thus, Fenton's process may be envisaged as a suitable pre-treatment before a traditional activated sludge reactor.

Fenton's process can also improve the methane production yield during OMW anaerobic digestion (AD). Indeed, the high organic load of OMW makes it an interesting substrate for biogas production using anaerobic digestion. However, its high toxicity may constitute a drawback. Maamir et al. [39] verified that submitting OMW to Fenton's pre-treatment ($[H_2O_2]/[Fe^{2+}] = 1000$ (mol/mol), $[Fe^{2+}] = 1.5$ mM, 120 min, and pH 3) improved the methane yield by up to 24%. Moreover, the highest methane yield after 30 days of AD (63%) was obtained when the Fenton's pre-treated OMW was used without previously precipitated iron. This was attributed to the delignification of the effluent during the Fenton's process. However, the biogas production was reduced when compared with the case where the untreated effluent was applied. This was associated with the production of toxic by-products during oxidation. Thus, following the effluents toxicity during chemical oxidation is crucial if the aim is to afterwards be combined with further biological processing.

Nieto et al. [40] treated an OMW coming from a two-phase olive-oil process industry, as well as the wastewaters from olives and olive-oil washing, with a homogenous Fenton-like reaction (Fe^{3+}/H_2O_2). This process shows an efficiency of more than 90% in the degradation of organic matter and phenolic compounds, with a ratio of catalyst to hydrogen peroxide between 0.02 and 0.04, and pH = 3. The pH 3 was achieved just with the addition of the catalyst when the ratio $[FeCl_3]/[H_2O_2] > 0.01$. The authors were able to obtain the apparent activation energy (E_a) for the Arrhenius equation (8.7 kJ mol⁻¹). At the end of the treatment, the remaining water was ready to be used for irrigation.

Esteves et al. [41] proved the stability of the Fenton's process in continuous conditions using a continuous stirred tank reactor (CSTR) for the degradation of a phenolic mixture (vanillic, caffeic, gallic, 3,4-dihydroxyphenylacetic and coumaric acids, and tyrosol), mimicking the phenolic content of OMW. For a residence time of 120 min, $[Fe^{2+}] = 100$ ppm, $[H_2O_2] = 2.0$ g/L, and $T = 30$ °C, total organic carbon (TOC) and phenolic content removals of 47.5% and 96.9%, were obtained. Moreover, a high toxicity removal as well as biodegradability enhancement was observed, which would allow for the further treatment of wastewater by conventional biological systems. It should be referred that the feed pH of 5 was auto-corrected to 3.2 (which is within the optimal range for Fenton's process) when the reactants were mixed with the wastewater. This will reduce the costs associated with the pH correction before the oxidation.

In order to overcome the drawback associated with iron sludge production, Reis et al. [42] analysed the combination between the Fenton's process and the ion exchange to recover iron. The Fenton's process was able to remove up to 81% of the COD of OMW in 1 h, using pH 3.5, $[\text{Fe}^{2+}] = 50 \text{ mg/L}$, and $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2] = 0.002 (w/w)$. Lewatit TP207 resin removed 90% of the iron from the Fenton's treated stream. Moreover, its efficiency was independent of the load of organic matter in the wastewater. Furthermore, even for large amounts of dissolved iron, it was possible to adapt the ion exchange operating conditions (e.g., increasing the quantity of resin) to maintain the desired efficiency of iron removal. Thus, this sequential treatment seems to be an interesting approach to avoid the formation of iron sludge after Fenton's treatment. Also, Víctor-Ortega et al. [43] concluded that a Dowex Marathon C-cation exchange resin is able to recover iron from Fenton's treated OMW. However, in this case, sludge production was not avoided, as the ion exchange was only applied to remove the dissolved iron remaining after the sludge precipitation. The ion exchange column was able to recover 100% of the iron, even after 10 complete cycles. The treated OMW shows qualities for being used as irrigation water, according to the Food and Agriculture Organization (FAO) when considering the resulting salinity.

The performance of nanofiltration (NF; using DK series membrane) and low-pressure reverse osmosis (RO; AK series membrane) was evaluated for recovering iron from OMW after Fenton's treatment. Up to 99.1% and 100% of the iron recovered was obtained using NF and RO, respectively [44]. The concentrate could be redirected to Fenton's reactor minimizing the catalyst waste. Moreover, the permeate was able to be reused for irrigation. With NF, it was possible to obtain a lower membrane fouling index, which means that longer membrane lifetimes are expected. as well as lower filtration areas.

Despite these interesting results, recovered iron recycling for Fenton's catalyst must be still evaluated. This is an important point, for example, Qiang et al. [45] and Li et al. [46] tested the possibility of directly reusing the iron sludge coming from Fenton's process as a catalyst for this treatment. However, even if high COD removal was obtained, the treated effluent conductivity increased very much because of the high amount of acid used for iron dissolving. Martins et al. [47] verified that the final sludge could be reused without being previously dissolved, even if only by a limited number of times. Table 2 summarizes some of the studies reporting the homogeneous Fenton process in the treatment of OMW.

Table 2. Treatment of olive mill wastewater (OMW) with homogenous Fenton process.

Effluent	Process	Optimal Conditions	Results	Reference
OMW collected in Portugal and diluted to initial COD ~2 g/L	Fenton	pH = 3.5 T = 30 °C $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 15$ $\text{H}_2\text{O}_2/\text{COD} = 1.75$	COD removal of 70%	[34]
OMW after cracking and cationic polyelectrolite coagulation.	Fenton	2000 mg/L of H_2O_2 and Fe^{2+}	COD removal of 89%	[36]
OMW	Fenton	pH = 3 $[\text{H}_2\text{O}_2] = 3500 \text{ mg/L}$ $[\text{FeSO}_4] = 3000 \text{ mg/L}$	81% COD removal 86% phenol removal 350 mL/L sludge volume	[3]
OMW	Fenton-like	pH = 3 $[\text{H}_2\text{O}_2] = 3000 \text{ mg/L}$ $[\text{FeSO}_4] = 2500 \text{ mg/L}$	88% COD removal 91% phenol removal 300 mL/L sludge volume	[3]
OMW	Fenton	pH = 3 $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 1000 (\text{mol/mol})$ $[\text{Fe}^{2+}] = 1.5 \text{ mM}$ t = 120 min	improve methane yield up to 24%	[39]

Table 2. Cont.

Effluent	Process	Optimal Conditions	Results	Reference
OMW coming from a two-phase olive-oil process industry as well as the wastewaters from olives and olive-oil washing	Fenton-like	pH = 3 ratio of catalyst to hydrogen between 0.02 and 0.04	90% in the degradation of organic compounds and phenolic compounds $E_a = 8.7 \text{ kJ mol}^{-1}$	[40]
Phenolic mixture (vanillic, caffeic, gallic, 3,4-dihydroxyphenylecetic, coumeric acids and tyrosol)	Fenton	t = 120 min [Fe ²⁺] = 100 ppm [H ₂ O ₂] = 2.0 g/L T = 30 °C	TOC removal 47.5% phenolic content removals of 96.9%	[41]
OMW	Fenton	t = 1 h pH = 3.5 [Fe ²⁺] = 50 mg/L [Fe ²⁺]/[H ₂ O ₂] = 0.002 (w/w)	81% of COD removal	[42]

3. Heterogeneous Fenton

The use of suitable solid catalysts can overcome the sludge generation shortcoming of the Fenton's process. Moreover, this would allow for catalyst recovery and reuse, which would reduce the operating costs. Furthermore, another drawback of homogeneous Fenton is related with iron solubility. In this context, acid conditions are generally required to ensure iron solubilisation. Moreover, after treatment, alkalisation of the medium is necessary in order to promote iron separation. Whereas in heterogeneous Fenton, a pH change may not be required, so savings can be obtained by this procedure.

In the heterogeneous Fenton's process, iron or other metal(s) are supported, so that ions are not dissolved in the liquid bulk. Several types of solid catalysts were tested for OMW depuration through this process. Rossi et al. [48] tested the efficiency of Fe/Cu oxides prepared by coprecipitation, according to the procedure described by Imamura et al. [49], for the degradation of a phenolic mixture usually present in OMW. Among the tested catalysts, the Fe–Cu–O with a molar proportion of 50/50 was the most efficient in the removal of organic matter. However, a low biodegradability improvement was observed, which may be a drawback of the process. Contrarily, Martins et al. [50] and Rossi et al. [51] concluded that the Fe–Ce–O 70/30 heterogeneous catalyst was able to improve the phenolic mixture biodegradability while reducing toxicity during the Fenton's process. In fact, a chemical process should be envisaged as a pre-treatment to improve the biodegradability of an effluent, so that a further treatment step involving biological degradation may be efficiently applied. In this way, the treatment cost can be reduced.

Kallel et al. [52] studied the applicability of an advanced Fenton process, hydroxyl radicals generated from zero-valent iron and hydrogen peroxide, as a pre-treatment of OMW. They considered the following factors: hydrogen peroxide and zero-valent iron dosages, and initial pH and initial COD. The best conditions achieved were acid pH (2.0–4.0), 5% H₂O₂, and Fe⁰ = 20 g/L. Under these conditions, after 3 h, the colour of the OMW had disappeared and the number of phenolic compounds decreased by 50% compared with the initial charge. The advanced Fenton process has been shown to have several advantages, namely, high efficiency, the fact that specific equipment is not necessary, and cheaper systems can be built by comparing the use of metallic iron with iron salts. In fact, the use of zero valent iron enhances the catalyst regeneration, as the Fe³⁺ can be reduced to Fe²⁺ at the Fe⁰ surface, which will improve the process efficiency, avoiding the waste of H₂O₂. Moreover, it would also allow for the use of iron wastes, such as irons shavings coming from metal processing industry, as a low-cost catalyst for this process [53].

The laboratory catalyst Fe–Ce–O 70/30 showed interesting results in the heterogeneous Fenton peroxidation of weathered OMW coming from an evaporation pond [54]. Although the COD removal was not so high (25%), the following operating conditions were selected: pH 4, [H₂O₂] = 115 mM,

and 1.5 g/L of the catalyst. In fact, at those conditions, the final effluent was biodegradable ($BOD_5/COD = 0.54$) and had a low toxicity, which enabled further biological depuration. Moreover, the catalyst showed stability regarding metal leaching, as the concentration of the iron dissolved in the effluent after treatment was below 0.12 mg/L.

Aiming for the remediation of a mixture of six phenolic compounds (4-hydroxy-3,5-dimethoxybenzoic, 4-hydroxy-3-methoxybenzoic, 3,4,5-trimethoxybenzoic, 3,4-dimethoxybenzoic, 3,4-dihydrobenzoic, and 4-hydroxybenzoic), usually present in real OMW, Martins and Quinta-Ferreira [55] compared the efficiency of a homogenous Fenton's process and the heterogeneous process over the solid Fe–Ce–O 70/30. For the homogenous Fenton's process, the most favourable conditions of reaction were 0.9 g/L of Fe^{2+} and $[H_2O_2] = 310$ mM, whereas for the heterogeneous Fenton's process, the best conditions were 1g/L of Fe–Ce–O 30/70 and $[H_2O_2] = 244$ mM. Both processes were carried out at pH 3, as suggested by Neyens and Bayens [33]. When analysing the results in terms of the total phenolic content (TPh) removal, the results pointed out that both processes are efficient, although for the homogeneous process, the first 15 min of the reaction were enough for total TPh degradation, while for the heterogeneous process, 120 min were required. Regarding TOC and COD, the homogenous Fenton process achieved a much greater reduction in the first 15 min, from 46% and 60%, compared to 31% and 48%, respectively, attained by the heterogeneous system. At the end of the reaction, the performance of both processes was very similar concerning TOC removal, obtaining an approximate reduction of 57%. The homogeneous process had a better performance in COD removal, corresponding to 60% compared with 49% for heterogeneous Fenton. Although the homogeneous Fenton process is quite efficient in COD removal, the Fe–Ce–O heterogeneous catalyst requires a lower hydrogen peroxide charge, further rendering the final effluent more suitable for bio-processing. Table 3 summarizes the results of the studies focused on the application of the heterogeneous Fenton's process in the treatment of OMW.

Table 3. Treatment of OMW with heterogenous Fenton process.

Effluent	Process	Optimal Conditions	Results	Reference
OMW	Heterogenous Fenton: H_2O_2 and zero-valent iron	pH = 2.0–4.0 5% of H_2O_2 $Fe^0 = 20$ g/L t = 3 h	Total color removal. 50% of phenolic content removal	[52]
Weathered OMW	Heterogenous Fenton: H_2O_2 and Fe–Ce–O	pH = 4 $[H_2O_2] = 115$ mM $[Fe-Ce-O] = 1.5$ g/L	25% of COD removal Final effluent biodegradable (BOD_5/COD) = 0.54 and low toxicity	[54]
OMW	Heterogenous Fenton: H_2O_2 and Fe–Ce–O	pH = 3 $[H_2O_2] = 224$ mM $[Fe-Ce-O] = 1.0$ g/L	31% of TOC removed 48% of COD removed Total TPh degradation after 120 min	[55]

4. Photo-Fenton

The use of light may enhance the Fenton's process efficiency (Table 4). During the Fenton's reaction, Fe^{3+} ions accumulate, which reduces the process efficiency, as Fe^{2+} ions are more effective on the catalytic decomposition of hydrogen peroxide into hydroxyl radicals. However, in the presence of light, the photo reduction of ferric ions may occur (Equation (4)), and the regenerated ferrous ions may continue the hydroxyl radicals production cycle [56]. Moreover, at some conditions, the direct photolysis of hydrogen peroxide may lead to HO^\bullet , according to Equations (4) and (5).



Table 4. Treatment of OMW using the photo-Fenton process.

Effluent	Process	Optimal conditions	Results	Reference
OMW	Photo-Fenton: different medium pressure commercial UV-lamps	pH = 3 [H ₂ O ₂] >8 g/L FeCl ₃ solution 3 g/L t = 5–30 min T = 20 °C	90% of COD, total organic carbon, total phenolic compounds, and turbidity removals	[57]
OMW (tyrosol, vanillic acid, caffeic acid, coumaric acid, and ferulic acid)	Photo-Fenton: FeS ₂ and CuFeS ₂ ; UV LED (maximum emission wavelength of 395 nm)		CuFeS ₂ led to total phenolic compounds depletion; 98% of TOC removal. pH autocorrection (~3). High toxicity towards <i>Aliivibrio fischeri</i> due to Fe and Cu leaching.	[60]
OMW	Solar photo-Fenton after coagulation/flocculation		95% of COD removal Removed OMW phytotoxicity High dilution required.	[61]

Garcia and Hodaifa [57] treated OMW using the photo-Fenton reaction in a batch reactor, and using a FeCl₃ solution (3.0 g/L) as a catalyst precursor at 20 °C and pH 3. They studied different H₂O₂ concentrations and different medium pressure mercury commercial UV-lamps. A concentration of H₂O₂ >8 g/L and a short reaction time (5–30 min) allowed for a 90% COD degradation, as well as for the removal of the total organic carbon, total phenolic compounds, and turbidity. All of the tested UV-lamps presented virtually the same removal percentages. After the treatment, the obtained water can be used for different ends according to the achieved parametric values, as follows: for olive irrigation (pH = 6–9, COD <1 g O₂/L) or for discharge into urban effluent treatment plants (pH = 6–9, final COD 0.5 g O₂/L). It should be noted that these limit values are according to the Spanish Standards.

The use of chelating agents such as oxalate, citrate, and EDTA may widen the operational pH range of the Fenton's process, as no iron precipitation occurs this way. The use of 60 mg/L of oxalate promotes solar photo-Fenton of a mixture of phenolic compounds found in OMW (protocatechuic, gallic and p-coumaric acids), leading to the total removal of the initial compounds in 5 min, and up to 94% of mineralization in 194 min [58]. This efficiency increase is related to the photo-sensitivity of ferrioxalate complexes, which can absorb radiation up to 550 nm, in this way enlarging the useful spectrum of solar radiation. A stoichiometric ratio between the consumed hydrogen peroxide and TOC removed within 1 and 3 was always determined. Moreover, the analysis of the role of the oxidant species revealed that besides HO• and O₂•⁻, singlet oxygen may also play an important role in mineralization.

In addition, some compounds already present in wastewaters, such as phenolic compounds, may be used as iron chelating agents. OMW is rich in these substances, and therefore can be used as a chelating agents source, avoiding the use of additional chemicals. Davididou et al. [59] verified that highly diluted OMW, even if with a lower efficiency than typical chelates, like ethylenediamine-N, N-disuccinic acid (EDDS), was a suitable alternative for chelating iron during the photo-Fenton oxidation of saccharin.

The use of natural materials as low-cost catalysts in the Fenton's process reduces the costs of catalyst preparation (Figure 1). Moreover, if those materials present photo-activity, they can be used in photo-Fenton's processes. In this context, Ltaïef et al. [60] studied the catalytic potential of mined pyrite (FeS₂) and chalcopyrite (CuFeS₂) in the photo-Fenton's oxidation of phenolic compounds present in OMW (tyrosol, vanillic acid, caffeic acid, coumaric acid, and ferulic acid). Photo-Fenton was promoted by high intensity UV-LED (maximum emission wavelength of 395 nm). The results showed that chalcopyrite was a suitable catalyst for this process, as a total depletion of the phenolic compounds was

observed while 98% of the TOC was removed. Furthermore, the catalysts were able to spontaneously correct the wastewater pH for the proper value required for Fenton's oxidation (~ 3). The drawback is the high toxicity of the resultant treated samples to *Aliivibrio fischeri*, which was attributed to the Fe and Cu dissolved during the reaction.

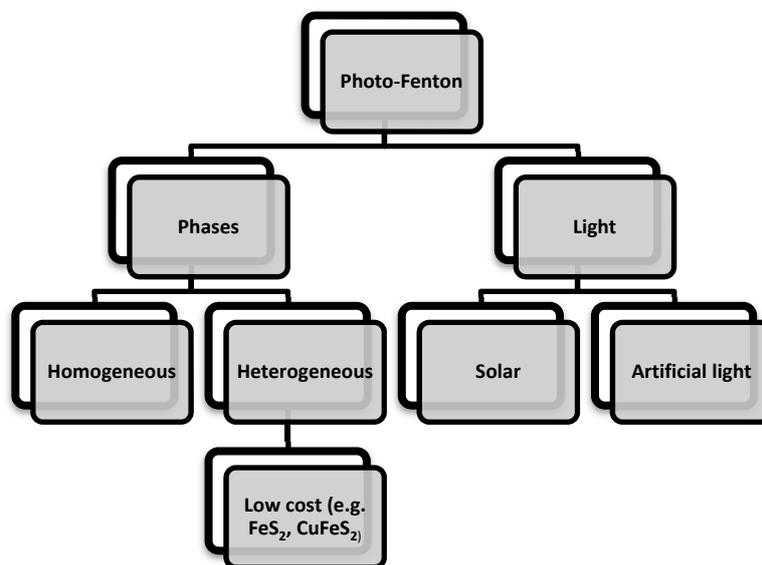


Figure 1. Photo-Fenton methodology.

The efficiency of biological oxidation, the photo-Fenton's process, and filtration for the treatment of OMW was analysed [61]. Solar photo-Fenton after coagulation/flocculation reached up to 95% COD removal. Moreover, such a procedure removed the OMW phytotoxicity. As olive oil production is mainly concentrated at the Mediterranean region where sun light is plentifully available, the operating costs of this treatment would be reduced. However, a shortcoming of this procedure is related to the high dilution of the initial OMW required for the application of such a management strategy. According to the strengths, weaknesses, opportunities, and threats (SWOT) analysis performed, one of the main strengths/opportunities of this technology is related with the possibility of safely using the treated water for the agricultural fields irrigation, which would reduce the water stress provoked by this industry. However, this implies a broad analysis of the potential ecological and human health impacts of such streams. As for the weaknesses, these are mainly related to the operating costs associated with the low incomes of the small olive mills. Moreover, the lack of strict legislation regarding the disposal of OMWs may also constitute a threat for the wide spread of efficient wastewater treatment technologies.

5. Integrated Systems

An important aspect of OMWs is their high content in polyphenolic compounds. These substances are well known for their anti-oxidant potential [62], making them highly valuable compounds for cosmetic pharmaceutical and food industries, with prices ranging 2000 €/g. In this context, OMW can be an interesting source for these substances. Thus, an OMW treatment strategy may encompass a recovery step before oxidation (Table 5). Papaphilippou et al. [63] proposed an integrated treatment scheme involving coagulation–flocculation for the removal of solids, followed by extraction with ethyl acetate for the recovery of phenolic compounds (caffeic acid, tyrosol, gallic acid, and oleuropein). The remaining OMW still possessed a high organic charge. Thus, the authors proposed a solar photo-Fenton step, which, at the optimal conditions (200 mg/L Fe^{2+} ; 5000 mg/L H_2O_2 and pH 3), led to a 73% COD removal. However, the oxidized samples showed a higher toxic character than the raw OMW towards *Daphnia magna*, because of the intermediates formed. This means that further

depuration is required in order to reach a safely treated stream. Moreover, the integrated treatment system's economic viability must be deeply assessed before proposing such an approach (Figure 2).

Table 5. Treatment of OMW with integrated processes.

Effluent	Process	Optimal conditions	Results	Reference
OMW	Integrated treatment scheme involving coagulation-flocculation for the removal of solids followed by extraction with ethyl acetate for the recovery of phenolic compounds (caffeic acid, tyrosol, gallic acid, and oleuropein). Thus, a solar photo-Fenton step	200 mg/L of Fe ²⁺ 5000 mg/L H ₂ O ₂ pH 3	73% of COD removal High toxicity (<i>Daphnia magna</i>) because of the intermediates formed.	[63]
OMW	Integrating coagulation and Fenton oxidation	pH = 3 Fe ²⁺ = 2.5 g/L H ₂ O ₂ = 1 g/L Fe ²⁺ /H ₂ O ₂ = 2.5	Pre-coagulation had a good impact in the degradation of organic matter through the following Fenton's process step.	[64]
OMW	Pre-treatment process involved Fenton-like oxidation, flocculation-sedimentation and filtration through olive stones and after membrane process		The pre-treatment decreased COD and polyphenols concentration and acts in the particle size distribution reducing membrane fouling	[65]
OMW	Integrated system of wet hydrogen peroxide catalytic oxidation (WHPCO) followed by two stage upflow anaerobic sludge blanket (UASB) reactor	Fenton's reaction: diluted wastewater (10MW:1 tap water) pH = 3.0 COD:H ₂ O ₂ = 1.0:1.1 Fe ²⁺ :H ₂ O ₂ = 1:50	Fenton's reaction improves the efficiency of anaerobic digestion	[66]
OMW	Combined treatment by Fenton's reagent and anaerobic biological process	H ₂ O ₂ /COD ratio of 0.20 pH 3.5 H ₂ O ₂ /Fe ²⁺ molar ratio of 15:1	Pre-treatment: 17.6% of COD and 82.5% total polyphenols removal. Biodegradability was improved.	[67]
OMW	Combined treatment by coagulation with natural organic coagulant, chitosan and advanced oxidation processes, namely, photocatalysis, Fenton, and photo-Fenton	—	Coagulation: removed 81% of total suspended solids Photo-Fenton: efficient in COD and aromaticity removal, (93% after 0.5 h) Fenton process reduced 81% of COD after 1 h reaction TiO ₂ photocatalysis: no significant COD removal Chitosan coagulation combined with Fenton or photo-Fenton could be a good alternative.	[68]

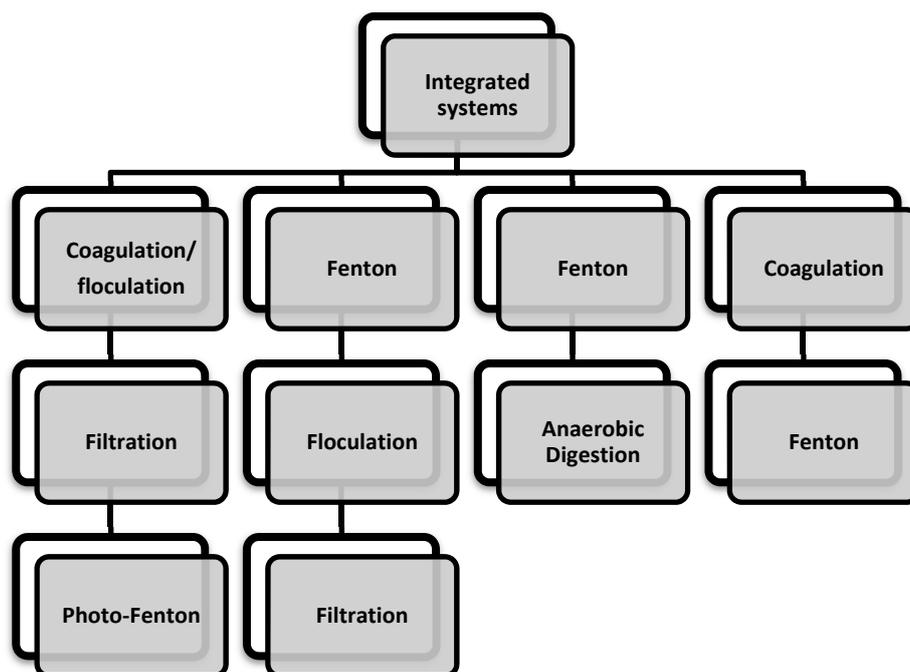


Figure 2. Examples of integrated treatment systems involving Fenton's processes.

Alver et al. [64] studied the olive mill effluent treatment by integrating coagulation and Fenton oxidation. They concluded that the best operating conditions for the Fenton process were $\text{pH} = 3$, $\text{Fe}^{2+} = 2.5 \text{ g/L}$, $\text{H}_2\text{O}_2 = 1 \text{ g/L}$, and $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 2.5$. Pre-coagulation had a good impact in the degradation of organic matter through the following Fenton's process step, but by itself, it was not able to substantially remove the COD and total-phenol.

Membrane processes are usually suitable management strategies when water reuse is intended, as water of a high quality can be obtained. Nevertheless, the main disadvantage of such approaches is related to the membrane fouling, which will imply that the membrane frequent regeneration or even substitution and the pressure required will increase the process costs. In this ambit, Ochando-Pulido et al. [65] studied a pre-treatment before the membrane process, to decrease the fouling formation during the processing of olive mill wastewater. The purpose was to recirculate the treated effluent to the manufacture process, or alternatively in the olives washing machines, so as to close the water loop. Pre-treatment processes involved Fenton-like oxidation, flocculation-sedimentation, and filtration through olive stones. The pre-treatment decreased the COD and polyphenols concentration, also acting in the particle size distribution of the nanometric suspended matter, which means near-zero membrane fouling. This pre-treatment was also shown to be efficient for the composite osmosis reverse membrane operation, which achieved a baseline after the initial flux decay because of concentration polarization.

With the objective of developing an economical solution for the treatment of OMW, El-Goahary et al. [66] studied the integrated system of wet hydrogen peroxide catalytic oxidation (WHPCO), followed by two stages of an up flow anaerobic sludge blanket (UASB) reactor (10 L each). The Fenton's reaction was used as a pre-treatment with diluted wastewater (1 OMW:1 tap water). The optimum operating conditions were $\text{pH} = 3.0$, $\text{COD}:\text{H}_2\text{O}_2 = 1.0:1.1$, and $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1:5.0$. The results showed that the use of Fenton's as a primary treatment of OMW improved the efficiency of anaerobic digestion and could degrade an important part of the toxic compounds present in OMW. In the final effluent residual concentration of p-hydroxy-benzaldehyde (0.432 mg/L and 3.273 mg/L), cinnamic acid was detected. The authors concluded that the anaerobic systems have a high potential to tolerate the abrupt organic load and the toxic compounds present in this kind of wastewater.

Amor et al. [67] proposed a combined treatment of olive mill wastewater by Fenton's reagent and anaerobic biological process. For the Fenton's process, they used a fixed $\text{H}_2\text{O}_2/\text{COD}$ ratio of 0.20, pH 3.5, and a $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio of 15:1. This pre-treatment allows for achieving a reduction of 17.6 of the chemical oxygen demand and 82.5% on the total polyphenols. In anaerobic digestion, the authors used previously adapted microorganisms immobilized in *Sepiolite*, and performed the biological tests with a variation of the substrate concentration supplied to the reactor, which allowed for an increase in COD removal from 52% to 74%. The combination of the Fenton's reaction with an anaerobic biological process compared with single anaerobic degradation is better, because an increase in the organic matter degradation is observed. In fact, the biokinetics constant is higher in the combined process ($k_N = 0.036 \text{ h}^{-1}$ compared with $k_N = 0.017 \text{ h}^{-1}$ for the single process). The authors concluded that the combination of the Fenton process with anaerobic digestion is a good option in the treatment of OMW. Rizzo et al. [68] investigated the combined treatment by coagulation with natural organic coagulant, chitosan, and advanced oxidation processes, namely photocatalysis, Fenton, and photo-Fenton, in order to improve the biodegradability of OMW. In optimal conditions (pH 4.3, 400 mg chitosan L^{-1}), coagulation removed 81% of the total suspended solids. Photo-Fenton showed to be very efficient in COD and aromaticity removal, with a rate of 93% after 0.5 h. The Fenton process reduced 81% of the COD after 1 h of the reaction. The TiO_2 photocatalysis tests did not show a significant organic matter removal in the investigated conditions. According to the results, an initial COD removal was observed at the first stages of TiO_2 photocatalysis. However, the COD increases afterwards, which was attributed to the formation of partial oxidized by-products, which are only detectable at those conditions through COD analysis. Even after 350 min of reaction, this process was not able to totally oxidize organic compounds, probably because of the high pollutant load of the effluent when compared with the radiation flux, as well as the strong color of the wastewater, which reduced the catalyst irradiation. Chitosan coagulation combined with Fenton or photo-Fenton could be a good alternative, considering the good removal of organic matter and its aromatic fraction by Fenton and photo-Fenton processes, and the potential reuse of the organic sludge produced by chitosan coagulation. Still, one must bear in mind the costs of chitosan that may be prohibitive for industrial application. Nevertheless, the economic viability will depend on the way the organic sludge may be reused. In fact, the use of this biomaterial instead of the traditional metal-based coagulants will reduce the formed sludge potential toxicity. Thus, it may potentially be used (after stabilization through anaerobic digestion and/or composting) as a soil amendment.

6. Industrial Applications

There are some reports regarding the industrial application of the homogeneous Fenton's process for the remediation of OMW. Amaral-Silva et al. [10] evaluated, first at a bench and then industrial scale, the integration between coagulation using iron (III) sulphate, followed by the Fenton's process. The coagulation step reduced the suspended solids and removed some COD, leading to enough dissolved iron to be used as a catalyst in the following oxidation step. At an industrial scale, such an approach led to an effluent with 200 mgO_2/L in COD. Furthermore, the biodegradability enhancement obtained (BOD_5/COD increased from 0.03 to 0.42) enabled a successful activated sludge post-treatment, which could further refine the effluent. An average operating cost of 2.70 $\text{€}/\text{m}^3$ of the treated effluent was estimated.

Martins et al. [69] verified that the use of the Fenton's process (pH 3, $[\text{H}_2\text{O}_2] = 88 \text{ mmol/L}$ and $[\text{Fe}^{2+}] = 60 \text{ mmol/L}$) enhanced the further treatment of OMW by ozonation at the industrial scale. Moreover, through respirometric tests, it was concluded that the resulting effluent was biodegradable. Moreover, the legal limits for discharge in the municipal wastewater treatment plant were accomplished. This means that further biological treatment can be applied to further polish the treated water.

Hodaifa et al. [70] studied the effect of operating conditions such as pH, space-time, H_2O_2 , and Fe(III) doses, as well as the $[\text{FeCl}_3]/[\text{H}_2\text{O}_2]$ ratio on the efficacy of the Fenton's process in a

continuous reactor at a pilot scale for OMW treatment. With optimum conditions (pH 3, 3 h and $[\text{FeCl}_3]/[\text{H}_2\text{O}_2]$ between 0.026 and 0.058 *w/w* upon Fe(III) concentrations, ranging from 0.35 to 0.40 g dm⁻³ and ambient temperature), the Fenton's process reached 97% organic matter degradation and 99% phenolic compounds removal. The obtained effluent can be used as irrigation water or can be discharged directly into the municipal wastewater system for further tertiary treatment.

7. Concluding Remarks

Fenton's process shows interesting features that make it industrially desirable, whenever the traditional biological systems fail to accomplish the parameters imposed for wastewater treatment. This happens when the effluent to be treated presents low biodegradability or a strong seasonality, which is the case of OMW. Fenton's process is able to operate at room conditions of pressure and temperature, and does not involve dangerous reactants or sophisticated equipment. In this ambit, several works have been reported regarding its application for the abatement of the pollutant in OMW. However, the fulfilment of the treated water standards for reuse may imply harsh operating conditions involving high loads of reactants. This may limit its application, as the operating costs could be prohibitive. Nevertheless, Fenton's process may be envisaged as a pre-treatment preceding a biologic system. In fact, usually, the by-products formed during the chemical reaction tend to be more biologically amenable than the initial pollutants. Thus, the effluents' biodegradability increases while its toxicity reduces, which enables further bio-processing. Still, the major drawback associated with this process is related with the iron sludge produced at the end of the treatment, which will require management, as it constitutes a second environmental problem. Moreover, this traditional approach does not allow for catalyst recovery. In this ambit, the use of light to enhance the process can be an option, as it allows for a reduction of the amount of catalyst required. Moreover, the development of heterogeneous catalysts is an interesting alternative, as their recovery and reuse would be easier. However, the major drawback is associated with their stability regarding the leaching of the metals. Recently the integration of Fenton's process with ion-exchange resins showed promising results, aimed at homogeneous catalyst recovery and reuse.

Still, even if the drawbacks related with this technology are not fully overcome, its industrial interest is remarkable, as some full-scale applications are already implemented. Namely, in what regards the treatment of olive mill wastewaters this technology (in homogeneous phase) is able to fulfil the legal parameters established for wastewater treatment in the regions where those plants are installed.

Also, the olive oil mill production is changing, which is reflected in the wastes produced. Now, two-phase systems are being preferred, as they are less water demanding. However, a large amount of solid wastes with a high toxic character [71] are produced. Furthermore, from this wet waste, a high organic concentrated leach is produced. In this context, the Fenton's process can be optimized to deal with these new challenges regarding both liquid and solid contaminants [72].

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