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Chapter 15

A Brief Review on Recent Processes for the Treatment of Olive Mill Effluents

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Additional information is available at the end of the chapter

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Abstract

During the last few decades, olive oil industrial sector has grown as a result of the modernization of olive oil mills, in response to the increasing demand of olive oil worldwide. As an undesired side effect, the amount of olive mill effluents (OME) increased, especially as a result of changing old batch press method for the continuous centrifugation-based olive oil production processes currently used, which ensure higher productivity. This chapter presents the state of the art of OME management, with focus on biological and advanced oxidation processes, either alone or in combination, varying in complexity, ease of operation and costs associated. Up to this moment, there isn't a management strategy that can be adopted in a global scale, feasible in different socio-economic contexts and production scales. The most reasonable approach is to regard OME valorisation as a regional problem, defining decentralized treatment that in some cases can be implemented for a group of olive oil mills in the same geographic area. This aspect is receiving strong attention as European Commission is promoting the transition towards a circular economy, which aims at "closing the production loop" by recycling and reusing resources, bringing benefits for the environment, society and the economy.

Keywords: olive mill wastewater, integral wastewater management, biological processes, advanced oxidation processes

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1. Introduction

The production of olive oil employs a very significant number of people and is one of the main industrial activities in countries of the Mediterranean Basin: Italy, Portugal, Greece and Northern African countries—Algeria, Morocco, Tunisia, Libya and Egypt. Other countries such as France, Serbia and Montenegro, the former Yugoslav Republic of Macedonia (FYROM) (Cyprus, Syria, Turkey, Israel and Jordan) also produce a considerable olive oil amount (International Olive Oil Council, IOOC, 2013–2014).

Olive oil production is also rapidly becoming an emergent agro-food industry in China and other countries such as the USA, Australia and the Middle East. It is worth mentioning the case of China, which exhibits favourable edaphoclimatic conditions for the growth of olive trees, and is expected to develop a considerable olive oil production potential in the near future. Hence, the treatment of olive mill effluents (OME), including olive washing wastewater (OWW), olive mill wastewater (OMW, only for press and three phase mills) and wastewater from olive oil washing (OOW), is now a task of global concern.

During the last few decades, a very significant growth of the olive oil industrial sector has been experienced as a result of the modernization of olive oil mills, in response to the increasing demand of olive oil worldwide. Spain is the biggest European Union (EU) producer, with more than 1700 olive mills with licence for operating. Production of olive oil in the Iberian Peninsula accounts for 91,600 tons in Portugal and more than 1,400,000 tons in Spain during the 2013–2014 campaign. In Spain, 70% of the olive oil was obtained in Andalucía where there are 850 olive mills, which yielded a production of 1,022,000 tons of olive oil and 4,778,451 tons of table olives.

The significant boost of this industrial sector in the last years has brought an undesired side effect; the amounts of OME have increased significantly, especially as a result of the change from the older batch press method to the continuous centrifugation-based production processes currently used, which ensure much higher productivity. These continuous systems guarantee a higher yield in recovering olive oil from the olives, up to 21%, but they lead to an increased production of wastewater streams. An average-sized modern olive oil mill currently generates daily several cubic meters of wastewater from the extraction process (OMW), wastewater derived from the washing of the olives (OWW) as well as from olive oil washing process (OOW). These practices have a relevant environmental impact due to water consumption and the production of a huge amount of highly contaminant wastewaters.

The current necessity to maximize the production processes often excludes the planning of the environment protection. Wastewater treatment for ulterior uses in multiple applications contributes to sustainable water consumption and conservation of the water bodies and the ecosystems. In this scenario, the European Directive 2000/60/CE took the lead in establishing the legal framework to confer utmost protection to water, highlighting the reuse of treated wastewater. This strategy can improve the status of the environment both quantitatively, minimizing water abstraction, and qualitatively, preventing pollution; for this reason, it is a top priority in the Strategic Implementation Plan of the European Innovation Partnership (EIP) on Water.

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Direct discharge of OME has been reported to cause strong odour nuisance, soil contamination, plants growth inhibition, leaks to the underground, water body pollution and hindrance of self-purification processes, as well as severe impacts to aquatic fauna and to ecological status [1–5]. Discharge of untreated OME is prohibited in Spain, whereas Italian law (L. 574/96) restricts the maximum amount of OME to be disposed on soil to 50 and to 80 m^3ha^{-1}, for wastewater arising from a press or a continuous mill, and in Portugal, irrigation of tree and bush crops with OME is allowed up to 80 m^3 ha^{-1} $year^{-1}$, as long as there has been pH correction (Despacho Conjunto n° 626/2000). Due to the presence of high levels of organic pollutants and refractory compounds, direct disposal of these effluents to the municipal sewage collection systems is also prohibited. Legal limits are established in order to prevent inhibitions of the biological treatment processes that take place in wastewater treatment plants.

OME exhibit several characteristics that make their reclamation by conventional physico-chemical treatments utterly difficult. The presence of phytotoxic recalcitrant pollutants—such as phenolic compounds, long-chain fatty acids, tannins and organohalogenated contaminants—makes these effluents resistant to biological degradation. The physico-chemical composition of OMW is extremely variable as it depends on several factors such as the extraction process, edaphoclimatic and cultivation parameters, as well as the type, quality and maturity of the processed olives. OME typically exhibit intense violet-dark colour, acid pH, strong odour, considerable saline toxicity reflected by high electric conductivity values, and very heavy organic pollutants load.

Process	Effluent	COD (g L^{-1})	BOD_5 (g L^{-1})	TSS (g L^{-1})	pH	EC (mS cm^{-1})	TP (g L^{-1})
Olives washing	OWW	0.8–2.2	0.3–1.5	8–18	5.5–6.6	2.5–3.0	0–0.1
Batch press	OMW-P	30–130	90–100	10–12	4.5–5.0	2.0–5.0	1.0–2.4
Three phase	OMW-3	30–200	5–45	5–35	3.5–5.5	2.0–7.9	0.3–7.5
Olive oil washing	OOW	4–16	0.8–6.0	2–7	4.9–6.1	1.5–2.5	0.1–1.0

COD, chemical oxygen demand; BOD_5, biological oxygen demand; TSS, total suspended solids; EC, electric conductivity; TP, total phenolic compounds.

Table 1. Characteristics of the effluents of batch and continuous olive oil extraction processes.

As it can be seen, OWW is commonly composed of high concentration of suspended solids (mainly peel, pulp, ground, branches and leaves debris) derived from the washing procedure of the olive fruit. The concentration of dissolved organic matter depends on the water flow exchange rate in the washing machines—and usually is below standard limits for discharge on suitable soils (e.g. Guadalquivir Hydrographical Confederation, 2006–2014: total suspended solids (TSS) < 500 mg L^{-1} and chemical oxygen demand (COD) < 1000 mg O_2 L^{-1}).

Table 1 presents the physico-chemical characteristics of the effluents of batch and continuous olive oil extraction processes.

Major organic pollutants load is present in the effluent coming out of the three-phase centrifuge (OMW-3), mostly phytotoxic compounds recalcitrant to biological degradation. Therefore, the presence of these substances would be hardly reflected in biological oxygen demand (BOD_5)

measurements; for this reason, COD seems a more appropriate parameter together with total phenolic (TP) compounds concentration. In the continuous two-phase extraction process, water injection is only performed in the final vertical centrifugation step, therefore the volume of liquid effluent derived from the production process is reduced by one-third on average if compared to the amount required for the three phase.

Much of the organic matter remains in the solid waste, which contains more moisture than the pomace from the three-phase system (60–70% in two-phase system vs. 30–45% in three-phase one). OOW exhibits lower pollutants degree, with COD commonly in the range 4–16 gL^{-1}, when compared with OMW. Inorganic compounds including chloride, sulphate and phosphoric salts of potassium, calcium, iron, magnesium, sodium, copper and traces of other elements are also common traits of OMW and OOW [6, 7].

From this analysis, it is clear that the wastewater streams produced during olive oil production have considerable different characteristics that, along with the final quality requirements, should be taken into account when selecting the most appropriate treatment strategy.

2. Biological treatments

Along the years, several studies have been developed on biological treatment processes for OME, from the simplest lagooning systems to more complex and high technological treatments [8]. This section reviews the aerobic, anaerobic, combined processes and the new trends in recovering added-value compounds from OME.

Aerobic biological treatments have long been proposed for OME treatment using several microorganisms as Pleurotus ostreatus, Bacillus pumilus, Phanerochaete chrysosporium, Aspergillus niger, Aspergillus terreus, Geotrichum candidum, etc. [9–11]. Ehaliotis et al. [12] used Azotobacter vinelandii ability to fix nitrogen to produce a fertilizer from OMW.

Amaral et al. [13] used a strain of Candida oleophila isolated from OMW for its detoxification. Results showed a removal around 50% of the organic load and 83% of total polyphenol content. Germination index increased up to 32% when compared to the values obtained with untreated OMW. Therefore, C. oleophila isolate was able to detoxify OMW and can be used for future application in biological treatments.

Recently, Chiavola et al. [14] investigated the efficiency of a sequencing batch reactor (SBR) in the biological treatment of previously sieved and diluted OMW. Four dilution ratios were tested (OMW/tap water, v/v): 1:25, 1:32, 1:16 and 1:10. Results showed that there was a complete removal of the biodegradable organic content at all the investigated influent loadings (0.08, 0.11, 0.19 and 0.69 mg COD mg $MLVSS^{-1}$ d^{-1}), with average efficiencies around 90 and 60% for COD and TP, respectively. The authors also tested adding a pre- or a post-treatment using membrane technologies: ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The introduction of the membrane separation allowed achieving a treated wastewater that complies with Italian legislation limits regarding COD, pH and electrical conductivity. TP concentration did not achieve the limit required for reuse. In view of a full-scale application,

it can be considered the option to mix the OMWs with other liquid streams so as to provide required nutrients along with dilution of the influent loading.

2.1. Bioconversion processes with energy production

Anaerobic digestion technology not only allows the treatment of wastewaters but also produces biogas that can be used as a primary energy resource locally. It is known that for an efficient anaerobic bioconversion process, the wastewater should have a balanced carbon-to-nitrogen-to-phosphorus (C/N/P) ratio and a pH in the range 6.5–7.5. Although OME has unbalanced C/N/P ratio, there are studies of anaerobic digestion of OMW as mono-substrate [15], but its mixture with nutrient-rich streams, co-substrates, significantly enhances process performance. This is not only due to balancing nutrient and alkalinity levels but also because it minimizes the inhibitory effect of phenolic compounds and lipids present in OME. Several studies assess the use of pretreatments for removal of recalcitrant compounds before anaerobic digestion process, for example, advanced oxidation processes (AOPs that will be further presented in this chapter) or coagulation-flocculation.

Gunay et al. [16] reviewed recent developments in OMW anaerobic digestion, addressing co-digestion with different streams (slaughterhouse wastewater, whey, manures, wastewater treatment plant sludge and microalgae waste), focusing on process performance but also including different possible pretreatment technologies.

González-González et al. [17] ran an aerobic pretreatment before anaerobic digestion in order to remove phenolic compounds and decrease COD. They observed a reduction in 78 and 90% of polyphenols and 18 and 21% of COD for aeration periods of 5 and 7 days, respectively. The best methane yield (0.39 m^3methane/kg COD removed) was obtained with OMW aerated for 5 days and was 2.4 times higher than that for untreated OMW.

One of the most studied pretreatments is the use of ultrasound for biomass deconstruction; Oz et al. [18] investigated the applicability of low-frequency ultrasound technology to OMW prior to anaerobic digestion in batch reactors. Results showed that the application of 20 kHz, 0.4 W/mL for 10 min to diluted OMW increased soluble chemical oxygen demand (SCOD)/total chemical oxygen demand (TCOD) ratio from 0.59 to 0.79. This fact led to 20% enhancement in biogas and methane production in trials using pretreated diluted OMW.

An important aspect to be taken into account when selecting a pretreatment is the net energy balance; the increase in biogas production should clearly offset the energy input. Ruggeri et al. [19] present an interesting approach, comparing several pretreatment processes based on scoring the biochemical methane potential (BMP) and the Energy Sustainability Index (ESI). ESI considers direct energy use (heat and electricity) and indirect energy use, the energy needed to produce chemicals reagents applied in pretreatments. Results showed that the most effective pretreatment was the addition of $CaCO_3$, with a biogas production of 21.6 NL/L and an ESI of 14 (i.e., the energy obtained in the form of methane is 14 times that of the energy spent).

Regarding the co-substrates studied for OMW co-digestion, manure is one of the most used as it contributes to nutrients balance, has high pH and has high buffering capacity. An example

of a recent study is the research of Khoufi et al. [20] that investigated the co-digestion of OMW with liquid poultry manure (LPM) in batch condition and semi-continuous jet-loop reactor. Authors concluded that the addition of 30% (v/v) LPM gives the best methane yield, and process stability was shown until an organic loading rate (OLR) of 9.5 g COD L^{-1} reactor day^{-1}. Process improvement is probably related to a more balanced nutrients mixture and minimization of the inhibitory effect of ammonia and phenolic compounds. Swine manure has also been used as co-substrate in several anaerobic co-digestion studies. Recently, Kougias et al. [21] carried out batch and semi-continuous mode trials with different mixtures of OMW and swine manure. The best results were obtained using 40% OMW in a semi-continuous reactor, achieving a methane yield of 373 mL CH_4 g^{-1} volatile solids (VS)

Sampaio et al. [22] tested the use of an up-flow anaerobic hybrid digester reactor for OMW digestion. An organic loading rate of 8 kg COD m^{-3} d^{-1} provided 3.7–3.8 m^3 biogas m^{-3} d^{-1} (63–64% CH_4) and 81–82% COD removal. They also tested feeding the reactor with pig slurry and OMW alternately, achieving a biogas production of 3.0–3.4 m^3 m^{-3} d^{-1} (63–69% CH_4).

Another interesting approach for bioconversion of OMW to energy is its use for hydrogen and bioethanol production through anaerobic fermentation. Eroğlu et al. [23] studied Rhodobacter sphaeroides for the photofermentation of OMW under anaerobic conditions, achieving a biohydrogen production of 16 L H_2 L^{-1}. More recently, Battista et al. [24] used a mixture of OMW and olive pomace to produce hydrogen and bioethanol by Saccharomyces cerevisiae anaerobic fermentation. They also tested different pretreatments (ultrasounds, alkaline hydrolysis, and calcium carbonate addition), concluding that ultrasounds and alkaline pretreatment lead to the hydrolysis of the lignin and cellulose. This fact leads to the increase in soluble organic matter (namely sugars) enhancing methane production. Calcium carbonate addition contributed to optimize the process by removing polyphenols, which are inhibitory for the fermentation process.

2.2. Bioconversion into high-added value products

There has been a change of paradigm regarding the economy; the linear vision was replaced by a circular vision, where waste is regarded as a potential source of resources to be reintroduced in the production cycle. Food production chain is one of the main waste producers. Recent studies on food waste valorization have suggested a wide range of possible bioproducts, namely biofuels, enzymes, bioactive compounds, biodegradable plastics and nanoparticles.

Regarding OMW, it has been seen as a source of biologically active phenols (biophenols) due to its high content in phenolic compounds, widely recognized as antioxidants which can be used in several industries, for example, food and pharmaceuticals production. A recent study by Kaleh and Geißen [25] describe the use of acidification, sedimentation and membrane filtration of OMW for biophenols recovery, namely hydroxytyrosol, tyrosol, caffeic acid, oleuropein and luteolin. Synthetic resins and molecularly imprinted polymers were tested as sorbents and results showed that by combining different pretreatments with sorbent options, it is possible to selectively adsorb a specific biophenols.

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Goula and Lazarides [26] present an integrated approach aiming at the complete recovering of OMW valuable compounds and reuse of depolluted water stream in the olive mill. Specially designed fermentation, spray drying and encapsulation technologies are addressed producing a number of valuable bioproducts, such as olive paste spread or olive powder (to be included in food formulations) and encapsulated phenols.

Federici et al. [27] discussed several strategies for OMW such as the recovery of antioxidants by chemical methods and the fermentative production of enzymes of commercial interest.

Mateo and Maicas [28] reviewed the most promising microbiological processes for the valorization of by-products from olive oil production. According to these authors', microbiological processes have an interesting potential as they have less environmental impact and, in most cases, can be cost-effective. Relevant to this analysis is the fact that they lead to added value products such as enzymes, biofuels, biopolymers, etc.

In fact, OMW due to its characteristics has been used in several studies as a medium to grow microbial species that consume organic matter and, simultaneously, produce biomass and other bioproducts, for example, enzymes and organic acids.

Laccases are known to efficiently degrade recalcitrant compounds; their production costs are still a drawback to their wider use. Therefore, there have been some experiments to assess the potential of using waste/wastewaters as a growth medium. White-rot fungi have been reported as efficient for phenolic compounds degradation because their extracellular ligninolytic enzymes (e.g. laccase, manganese peroxidase and lignin peroxidase) are able to catalyze lignin-like structures and promote recalcitrant compounds oxidation [29, 30].

More recently, Mann et al. [31] studied the production of laccases from white-rot fungi grown in OMW. The study showed that it was possible to reduce phenols content and phytotoxicity. Furthermore, results point out to the fact that OMW is a source of laccase mediators, since the efficiency of removal of phenols increased when 1% OMW was added to the solution.

Ntougias et al. [32] also focused on microbial depuration of OMW, assessing the use of 49 white-rot fungi strains belonging to 38 species of Basidiomycota. Results showed a reduction in total phenols up to 60% and colour up to 70%.

Nogueira et al. [33] assessed the efficiency of combining photocatalytic oxidation, using two nanomaterials as catalysts (TiO_2 and Fe_2O_3), with biological degradation by fungi (Pleurotus sajor caju and P. chrysosporium). Results showed that biological treatment with fungi after pretreatment with nanomaterials allowing COD, TP and ecotoxicity removal. The highest removal of COD and TP was achieved with the combination of the system Fe_2O_3/UV and Pleurotus sajor caju, respectively, around 60 and 98%, but only a decrease in around 9% in ecotoxicity. The most efficient detoxifying process was the combination of Fe_2O_3/UV with P. chrysosporium, with a reduction around 37%, and 52 and 96% for COD and TP, respectively.

OMW has also been used for production of algal biomass, which accumulates lipids and carbohydrates and therefore can be used for the production of biofuels or recovery of compound. Di Caprio et al. [34] used OMW supplemented with nitrates (to prevent reduction in

the specific growth rate) for the cultivation of Scenedesmus sp. achieving biomass production and depuration of OMW.

3. Physico-chemical and advanced oxidation processes

3.1. Wet oxidation, Fenton advanced oxidation, ozone

Pham Minh et al. [35] studied the catalytic wet air oxidation (CWAO) of OMW with self laboratory-prepared platinum- and ruthenium-supported titanium or zirconium, coupled with anaerobic digestion. The authors reported the effective elimination of the total organic carbon (TOC), up to 97%, and a nearly complete removal of the phenolic content in CWAO at 190°C and 70-bar total air pressure. Moreover, a decrease in the phytotoxicity of the OMW effluent was observed towards Vibrio fischeri. The ruthenium catalysts were proved to be stable over a long operating period. A high mineralization level of the effluent was achieved, and the methane production yield was enhanced in the subsequent anaerobic treatment. However, experiments were conducted on actual diluted OMW (two times dilutions).

Azaboua et al. [36] examined a compact process for the treatment of OMW comprising catalytic oxidation with wet hydrogen peroxide (WHPCO) followed by different biological techniques. WHPCO catalytic processes were performed using a montmorillonite-based aluminium-iron-pillared interlayer clay [(Al-Fe) PILC] as heterogeneous catalyst. The authors examined [(Al-Fe) PILC]/H_2O_2 under ultraviolet irradiations at 25 or 50°C, both under atmospheric pressure. The results obtained revealed that the raw OMW stream was resistant to the photocatalytic process, but a considerable reduction in the COD, colour and total phenolic compounds concentrations was attained throughout the latter process. As a result, a decrease in the inhibition of Vibrio fischeri luminescence of around 70% was reported. Otherwise, a higher methane production was obtained in the biomethanization of OMW when [(Al-Fe) PILC]/H_2O_2 for 2 h was carried out.

Martínez-Nieto et al. [3] studied an advanced oxidation process based on Fenton's reaction for the degradation of the organic matter load present in olive oil mill wastewater from two-phase olive oil extraction process. The authors examined several methods on a laboratory scale in order to use the cheaper Fe^{3+} salts rather than Fe^{2+} salts, examining the performance of several catalysts—Mohr salt [$(NH_4)_2Fe(SO_4)_2$ $6H_2O$, ferric perchlorate and ferric chloride—as well as the best catalyst/oxidant ratio and operating conditions. It was shown that organic matter is efficiently degraded through Fenton-like reaction using $FeCl_3$ as catalyst in the presence of hydrogen peroxide. Organic matter and phenolic compounds removal efficiencies above 95% were attained. Moreover, ferric ions (Fe^{3+}) helped avoid the consumption of the oxidant (H_2O_2) in transforming ferrous ions into ferric ones, which occurs in unproductive parallel reactions. These results revealed Fenton-like reaction as a solution, relatively cheap, for the treatment of these wastewaters. The treated water from this process was ready for irrigation.

In a subsequent research study, Hodaifa et al. [4] optimized the reclamation of OMW by Fenton-like process in a continuous stirred tank reactor (CSTR) at pilot scale. In the start-up

stage, Fenton reaction reached steady state within 3 h. Oxidation of organic matter in OMW was pH dependent. The final values of COD and total phenols at the outlet of the pilot plant were close to 129 and 0.5 mg/L, respectively. Finally, the produced water was apt for irrigation or to be discharged directly into the municipal wastewater system.

Finally, Martínez-Nieto et al. [37] tested Fenton chemical oxidation process using ferric chloride or potassium permanganate as catalysts for the activation of H_2O_2 on an industrial scale. By using potassium permanganate in the system, the final water was transparent with a slight yellow tinge, but odourless with a low total phenol content. The sediments in the decanter were rich in manganese dioxide (MnO_2), which, though non-toxic, would need further management. Finally, the versatile design of the plant offers the possibility to work with both oxidation systems, without the need to make changes in the process. The water produced could be used for irrigation or discharged directly into the municipal wastewater system.

3.2. Combined treatments

Sarika et al. [38] studied the pretreatment of OMW by flocculation with cationic and anionic polyelectrolytes. The majority of the tested flocculants completely removed the TSS and reduced considerably the COD and the BOD_5. The minimum flocculant dosage to attain solid-liquid separation was 2.5–3 g L^{-1}. Authors suggest the post-treatment of the liquid phase by means of high-power ultrasound, advanced oxidation, biological processes or a combination of them, whereas for the solid fraction, they stated that various solid agro-wastes may be composted to yield soil fertilizers (Manios, 2004), as reported in a study by García-Gómez et al. (2003).

Stoller and Chianese [39, 40] studied the purification of OWW to comply with discharge standards in municipal sewers (Italy). The authors proposed a treatment process comprising an initial coagulation-flocculation with aluminium sulphate (AS) or aluminium hydroxide (AH), followed by batch UF and NF in series with composite thin-film spiral-wound membranes. The two pretreatment processes yielded similar COD and BOD_5 rejection efficiencies. However, higher productivity was attained in the subsequent membranes-in-series process after flocculation with AS. Following this, Stoller [41] conducted a deeper study on flocculation as pretreatment of microfiltration (MF), UF, NF and RO membranes in the treatment of three-phase OMW, by examining the particle size distribution in the effluent at the outlet of each stage. Stoller underlined the effect created by a secondary flocculation induced by the AS flocculant-derived salts accumulating near the membrane surface. This fact enhances the particles to be carried away by the tangential flow, thus sensibly reducing fouling. In a following research work, Stoller and Bravi [42] applied the same coagulant-flocculants to pretreat three-phase OMW before batch MF, UF, NF and RO membranes in sequence. In addition, they examined photocatalysis (PC) with nanometric titanium dioxide in anatase form irradiated by UV light and aerobic treatment. All pretreatment processes provided final RO permeate streams complying with irrigation quality standards (COD ranging from 242 to 456 mg/L). However, UV/TiO_2 photocatalysis showed the highest membrane productivity within the shortest residence time (24 h).

As previously described coagulation-flocculation is a common pretreatment, and research works have studied alternatives to conventional chemicals, using biopolymers as chitosan [43] or residues from other industrial activities. For example, Fragoso et al. [44] studied the use of a sludge produced at water treatment plants (drinking-water treatment sludge—DWTS) with similarities to bentonite (namely the presence of aluminium silicate, alkaline pH and particle size), as an alternative to conventional coagulation-flocculation process. Results showed that it was possible to reduce 40–50% of COD, 45–50% of TP, a maximum of nearly 70% TSS and 45% for total solids (TS) and total volatile solids (TVS). This strategy would represent an integrated management of OMW and DWTS, contributing to a decrease in the environmental impact of two industrial activities, olive oil production and drinking water treatment.

In another study, Rizzo et al. [43] addressed the reclamation of OMW by coagulation with a natural organic coagulant, chitosan, followed by advanced oxidation processes: PC, Fenton (F) and photo-Fenton (PF). The maximum organic matter removal efficiencies were achieved after 2.0 and 1.0 h.

El-Gohary et al. [45] studied the integration of wet hydrogen peroxide catalytic oxidation (WHPCO) prior to a two-stage up-flow anaerobic sludge blanket (UASB) for the treatment of OMW. The raw OMW stream was diluted (1:1 v: v) with tap water and pretreated by Fenton's reaction with $FeSO_4$

In a similar line, Walid et al. [46] investigated different combined processes for OMW treatment, including advanced oxidation by UV and/or O_3, and an aerobic biodegradation. Results showed that for both single-stage O_3 treatment and O_3/UV two-stage treatment, the COD remained quite high. The combination of the advanced oxidation by UV/O_3 followed by biodegradation process ensured the highest COD reduction efficiencies, up to 91%.

Martínez-Nieto et al. [47] examined the efficiency of different flocculants—high molecular weight anionic polyelectrolytes—such as commercial QG-2001, QG-2002, DQGALFLOC-130H and Nalco-77171. The optimum dosage of each flocculant, 150, 2.5, 66 and 6 mg L^{-1}, respectively, was determined. The results revealed that 13.5% v/v final sludge separation and 86.5% v/v final clarified water can be obtained

In a recent study, Alver et al. [48] investigated a sequential system comprising coagulation and Fenton reaction. Higher treatment efficiency was achieved by the sequential coagulation and Fenton system. This study demonstrated that the integrated coagulation and Fenton process could be a potential solution for efficient removal of phenolic pollutants from this type of wastewaters.

3.3. Electrochemical, solar-driven and heterogeneous photocatalytic treatments

Several electrochemical treatments have already been applied for the treatment of OMW, such as electrocoagulation, electro-Fenton, electrochemical oxidation with polialuminium chloride (PAC), conductive diamond electrochemical oxidation (CDEO), electrooxidation with in situ generated active chlorine, as well as by means of cyclic voltammetry and bulk electrolysis with Ti/RuO_2 or Ti/IrO_2 anodes.

Tezcan et al. [49] applied electrochemical oxidation with PAC in the presence of H_2O_2 on fresh OMW (COD 45,000 mg L^{-1}). The obtained results revealed that the Fe electrode was more effective than the Al electrode. Up to 62–86% COD removal efficiency as well as 100% turbidity and oil and grease abatement could be achieved upon 20–75 mA cm^{-2} current density range. Afterwards, Tezcan et al. [50] investigated the electrochemical oxidation of OMW using Ti/RuO_2 anode on OMW samples from an olive oil mill operating with the three-phase technology. The removal rates of organics increased with the increase in the applied current density, sodium chloride concentration, recirculation rate and temperature. The specific energy consumption (SEC) was found to be in the range 5.35–27.02 kWh kg^{-1}. The treated OMW effluent presented a final COD around 167 mg L^{-1} (99.6% removal efficiency) and almost complete abatement of phenolic compounds. The running costs estimated by the authors were equal to 0.78 €/kg^{-1} COD.

Khoufi et al. [51] studied the reclamation of OMW for agricultural purposes by means of electro-Fenton followed by anaerobic digestion. Up to 65.8% of the total phenolic compounds concentration could be removed by electro-Fenton, and a decrease in the toxicity of 33.1% was ensured. Electrocoagulation of the anaerobically digested effluent provided complete detoxification.

Cañizares et al. [52] evaluated and compared the technical and economic feasibilities of three AOPs: CDEO, ozonation and Fenton oxidation, for wastewaters polluted with different types of organic compounds, including OMW. According to their results, only CDEO could achieve complete organic matter abatement (mineralization) of the pollutants for all the wastes. However, the efficiencies were found to depend on the concentration of the specific pollutants, whereas oxidation with ozone (at pH 12) or by Fenton's reagent was found to depend on the nature of the pollutants. The average estimated operation costs were in the range 2.4–4.0 €/kg^{-1} equivalent O_2 for the CDEO process, 8.5–10.0 €/kg^{-1} equivalent O_2 for ozonation, whereas 0.7–3.0 €/kg equivalent O_2 for Fenton oxidation. Moreover, the expected capital investment for Fenton (approximately 16,000 €) was much lower than that needed for CDEO.

Papastefanakis et al. [53] studied the reclamation of OMW through electrochemical oxidation by means of cyclic voltammetry and bulk electrolysis with Ti/RuO_2 and Ti/IrO_2 anodes. Elimination of the ecotoxicity and up to 86 and 84% colour and phenols removal, as well as 52 and 38% COD and total organic carbon reduction, could be successfully achieved upon oxidation at 28 AhL^{-1} and 50 $mAcm^{-2}$. The authors conclude that Ti/RuO_2 and Ti/IrO_2 stable anode-type electrodes show good activity for the treatment of agroindustrial effluents like OMW, despite the complex effluent composition that could have compromised both the activity and stability of the used anodes.

Moreover, Chatzisymeon et al. [54] studied the photocatalytic treatment of three-phase OMW with TiO_2 in a batch laboratory-scale photoreactor. They found that COD removal was enhanced by the contact time and also affected by the influent COD, whilst all other variables had no significant statistical importance on the COD removal. The energy consumption per unit mass of pollutant removed was noted to be lower for higher influent COD, indicating that TiO_2 photocatalysis can be a promising process for OMW treatment. OMW was almost

completely detoxified at low influent COD, though toxicity was only slightly reduced at major organic loadings.

Justino et al. [55] examined the efficiency of a combined treatment process comprising sequentially fungi with Pleurotus sajor caju and photo-Fenton oxidation or vice versa. The treatment with fungi was carried out on diluted OMW samples, after which the reduction in OMW acute toxicity towards Daphnia longispina was confirmed, providing 72.9% total phenolic compounds removal along with 77% organic matter (COD) abatement. The treatment sequence comprising first photo-Fenton oxidation followed by biological treatment with fungi was found to be more efficient, mainly given by the fact that no dilution of the raw OMW effluent was needed.

Ochando-Pulido et al. [56] studied the photocatalytic degradation of OOW at laboratory scale. The main technical-economical handicap relies on the difficulty in recovering the catalyst. To solve this, a novel nano-photocatalyst with ferromagnetic properties was developed. The photocatalyst offered good results in comparison with other commercial ones. Up to 58.3% COD removal, 27.5% total phenols removal and 25.0% total suspended solids removal were attained. Also, if a pH-temperature flocculation pretreatment was performed, the overall COD removal efficiency increased up to 91%. According to the results obtained in this investigation, the photocatalytic degradation process is an alternative with high possibilities in the treatment of OMW.

Ruzmanova et al. [57] recently examined the treatment of three-phase OMW by photocatalysis with N-doped TiO_2 sol-gel material [57–61]. The adopted doping procedure was validated under visible light, exhibiting higher performances if compared to those obtained with non-doped particles, achieving more than 60% COD removal. The photocatalysis assisted by TiO_2 catalyst sensitive to visible light may represent a very promising solution for the degradation of the organic compounds in OMW and similar effluents.

In a different research work, Papaphilippou et al. [62] proposed an integrated treatment process for OMW consisting sequentially of coagulation-flocculation, extraction of phenolic compounds and post-oxidation by photo-Fenton. After photo-Fenton advanced oxidation, COD removal about 73 ± 2.3% and total phenols of 87 ± 3.1% were, respectively, found. Furthermore, comparative phytotoxicity tests revealed that more biologically potent products were obtained during oxidation.

Michael et al. [63] addressed the depuration of three-phase OMW by means of a solar-driven advanced oxidation process combined with previous coagulation/flocculation, achieving high COD removal (87%) and elimination of the bio-recalcitrant polyphenolic fraction. The overall cost of solar Fenton oxidation was 2.11 €m^{-3}.

4. Conclusions

As it was shown, there are several alternatives for OME treatment, comprising biological and physico-chemical processes, either alone or in combination, varying in complexity, ease of

operation and costs. OME has been a challenge for researchers due to its difficult treatability which motivated the development of new approaches and technologies mainly at laboratory scale but also to a lesser extent at pilot scale. Up to this moment, no strategy is available that can be adopted in a global scale. The most reasonable approach is to regard OME treatment/valorization as a regional problem, defining decentralized treatment that in some cases can be implemented for a group of olive oil mills in the same geographic area. This will lead to an economy of scale, allowing the adoption of more expensive technologies, unaffordable by individual mills, complying with environmental regulations and optimizing resource recovery from OME. This aspect is receiving strong attention as European Commission is promoting the transition towards a circular economy which aims at "closing the loop" of product lifecycle through greater recycling and reuse, bringing benefits for both the environment and the economy. It seems that a stepwise strategy is becoming a new research trend: firstly, promoting the recovery of all valuable compounds from OME; and secondly, treating the partially depurated effluent.

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References

[1] Karaouzas I., Skoulikidis N. T., Giannakou U., Albanis T. A. Spatial and temporal effects of olive mill wastewaters to stream macroinvertebrates and aquatic ecosystems status. Water Research 45 (19) (2011) 6334–6346.

[2] Danellakis D., Ntaikou I., Kornaros M., Dailianis S. Olive oil mill wastewater toxicity in the marine environment: Alterations of stress indices in tissues of mussel Mytilus galloprovincialis. Aquatic Toxicology 101 (2) (2011) 358–366.

[3] Martínez Nieto L., Hodaifa G., Rodríguez Vives S., Giménez J. A., Ochando J. Degradation of organic matter in olive-oil mill wastewater through homogeneous Fenton-like reaction. Chemical Engineering Journal 173 (2011) 503–510.

[4] Hodaifa G., Ochando J., Rodríguez S., Martínez-Férez A. Optimization of continuous reactor at pilot scale for olive-oil mill wastewater treatment by Fenton-like process. Chemical Engineering Journal 220 (2013) 117–124.

[5] Ntougias S., Gaitis F., Katsaris P., Skoulika S., Iliopoulos N., Zervakis G. I. The effects of olives harvest period and production year on olive mill wastewater properties—Evaluation of Pleurotus strains as bioindicators of the effluent's toxicity. Chemosphere 92 (2013) 399–405.

[6] Niaounakis M., Halvadakis C. P. Olive processing waste management literature review and patent survey, 2nd ed., Elsevier: Waste Management Series, vol. 5 (2006) 23–64.

[7] Paraskeva P., Diamadopoulos E. Technologies for olive mill wastewater (OMW) treatment: A review. Journal of Chemical Technology and Biotechnology 81 (2006) 1475–1485.

[8] Azbar, N., Bayram, A., Filibeli, A., Muezzinoglu, A., Sengul, F., Ozer, A. A review of waste management options in olive oil production. Critical Reviews in Environmental Science and Technology 34 (2004) 209–247.

[9] Aggelis G., Iconomou D., Christou M., Bokas D., Kotzailias S., Christou G., Tsagou V., Papanikolaou S. Phenolic removal in a model olive oil mill wastewater using Pleurotus ostreatus in bioreactor cultures and biological evaluation of the process. Water Research 37 (2003) 3897–904.S.

[10] Garcia I., Jiménez Peña P. R., Bonilla Venceslada J. L., Martín A., Martín Santos M. A., Gómez Ramos E. Removal of phenol compounds from olive mill wastewater using Phanerochaete chrysosporium, Aspergillus niger, Aspergillus terreus and Geotrichum candidum. Process Biochemistry 35 (2000) 751–758.

[11] Tsioulpas A., Dimou D., Iconomou D., Aggelis G. Phenolic removal in olive mill wastewater by strains of Pleurotus spp in respect to their phenol oxidase (laccase) activity. Bioresource Technology 84 (2002) 251–257.

[12] Ehaliotis C., Papadopoulou K., Kotsou M., Mari I., Balis C. Adaptation and population dynamics of Azotobacter vinelandii during aerobic biological treatment of olive-mill wastewater. FEMS Microbiology Ecology 30 (1999) 301–311.

[13] Amaral C., Lucas M. S., Sampaio A., Peres J. A., Dias A. A., Peixoto F., Rosário Anjos M., Pais C. Biodegradation of olive mill wastewaters by a wild isolate of Candida oleophila. International Biodeterioration & Biodegradation 68 (2012) 45–50.

[14] Chiavola A., Farabegoli G., Antonetti F. Biological treatment of olive mill wastewater in a sequencing batch reactor. Biochemical Engineering Journal 85 (2014) 71–78.

[15] Ammary B. Treatment of olive mill wastewater using an anaerobic sequencing batch reactor. Desalination 177 (2005) 157–165.

[16] Gunay A., Karadag D. Recent developments in the anaerobic digestion of olive mill effluents. Process Biochemistry 50 (2015) 1893–1903.

[17] González-González A., Cuadros F. Effect of aerobic pretreatment on anaerobic digestion of olive mill wastewater (OMWW): An ecoefficient treatment. Food and Bioproducts Processing 95 (2015) 339–345.

[18] Oz N. A., Uzun A. C. Ultrasound pretreatment for enhanced biogas production from olive mill wastewater. Ultrasonics Sonochemistry 22 (2015) 565–572.

[19] Ruggeri B., Battista F., Bernardi M., Fino D., Mancini G. The selection of pretreatment options for anaerobic digestion (AD): A case study in olive oil waste production. Chemical Engineering Journal 259 (2015) 630–639.

[20] Khoufi S., Louhichi A., Sayadi S. Optimization of anaerobic co-digestion of olive mill wastewater and liquid poultry manure in batch condition and semi-continuous jet-loop reactor. Bioresource Technology 182 (2015) 67–74.

[21] Kougias P. G., Kotsopoulos T. A., Martzopoulos G. G. Effect of feedstock composition and organic loading rate during the mesophilic co-digestion of olive mill wastewater and swine manure. Renewable Energy 69 (2014) 202–207.

[22] Sampaio M. A., Gonçalves M. R., Marques I. P. Anaerobic digestion challenge of raw olive mill wastewater. Bioresource Technology 102 (23) (2011) 10810–10818.

[23] Eroglu E., Eroglu I., Gunduz U., Yucel M. Effect of clay pretreatment on photofermentative hydrogen production from olive mill wastewater. Bioresource Technology 99 (2008) 6799–6808.

[24] Battista F., Mancini G., Ruggeri B., Fino D. Selection of the best pretreatment for hydrogen and bioethanol production from olive oil waste products. Renewable Energy 88 (2016) 401–407.

[25] Kaleh Z., Geißen S. U. Selective isolation of valuable biophenols from olive mill wastewater. Journal of Environmental Chemical Engineering 4 (2016) 373–384.

[26] Goula A. M., Lazarides H. N. Integrated processes can turn industrial food waste into valuable food by-products and/or ingredients: The cases of olive mill and pomegranate wastes. Journal of Food Engineering 167 (2015) 45–50.

[27] Federici F., Fava F., Kalogerakis N., Mantzavinos D. Valorisation of agroindustrial by-products, effluents and waste: Concept, opportunities and the case of olive mill waste waters. Journal of Chemical Technology and Biotechnology 84 (2009) 895–900.

[28] Mateo J. J., Maicas S. Valorization of winery and oil mill wastes by microbial technologies. Food Research International 73 (2015) 13–25.

[29] Baldrian P. Fungal laccases-occurrence and properties. FEMS Microbiology Reviews 30 (2006) 215–242. doi:10.1111/j.1574-4976.2005.00010.x.

[30] Morillo J., Antizar-Ladislao B., Monteoliva-Sánchez M., Ramos-Cormenzana A., Russell N. Bioremediation and biovalorisation of olive-mill wastes. Applied Microbiology and Biotechnology 82 (2009) 25–39. doi:10.1007/s00253-008-1801-y.

[31] Mann J., Markham J. L., Peiris P., Spooner-Hart R. N., Holford P., Nair N. G. Use of olive mill wastewater as a suitable substrate for the production of laccase by Cerrena consors. International Biodeterioration & Biodegradation 99 (2015) 138–145

[32] Ntougias S., Baldrian P., Ehaliotis C., Nerud F., Merhautova V., Zervakis G. I. Olive mill wastewater biodegradation potential of white-rot fungi—Mode of action of fungal culture extracts and effects of ligninolytic enzymes. Bioresource Technology 189 (2015) 121–130.

[33] Nogueira V., Lopes I., Freitas A. C., Rocha-Santos T. A. P., Gonçalves F., Duarte A. C., Pereira R. Biological treatment with fungi of olive mill wastewater pre-treated by photocatalytic oxidation with nanomaterials. Ecotoxicology and Environmental Safety 115 (2015) 234–242.

[34] Di Caprio F., Altimari P., Pagnanelli F. Integrated biomass production and biodegradation of olive mill wastewater by cultivation of Scenedesmus sp. Algal Research 9 (2015) 306–311.

[35] Minh D. P., Gallezot P., Azabou S., Sayadi S., Besson M. Catalytic wet air oxidation of olive oil mill effluents 4. Treatment and detoxification of real effluents. Applied Catalysis B: Environmental 84 (2008) 749–757.

[36] Azaboua S., Najjar W., Bouaziz M., Ghorbel A., Sayadi S. A compact process for the treatment of olive mill wastewater by combining wet hydrogen peroxide catalytic oxidation and biological techniques. Journal of Hazardous Materials 183 (2010) 62–69.

[37] Martínez Nieto L., Hodaifa G., Rodríguez S., Giménez J. A. Industrial plant for OMW from two-phase treatment by chemical oxidation. Journal of Environmental Engineering 136 (2010) 1309–1313.

[38] Sarika R., Kalogerakis N., Mantzavinos D. Treatment of olive mill effluents Part II. Complete removal of solids by direct flocculation with poly-electrolytes. Environment International 31 (2005) 297–304.

[39] Stoller M., Chianese A. Optimization of membrane batch processes by means of the critical flux theory. Desalination 191 (2006) 62–70.

[40] Stoller M., Chianese A. Technical optimization of a batch olive wash wastewater treatment membrane plant. Desalination 200 (1–3) (2006) 734–736.

[41] Stoller M. On the effect of flocculation as pretreatment process and particle size distribution for membrane fouling reduction. Desalination 240 (2009) 209–217.

[42] Stoller M., Bravi M. Critical flux analyses on differently pretreated olive vegetation wastewater streams: Some case studies. Desalination 250 (2010) 578–582.

[43] Rizzo L., Lofrano G., Grassi M., Belgiorno V. Pretreatment of olive mill wastewater by chitosan coagulation and advanced oxidation processes. Separation and Purification Technology 63 (3) (2008) 648–653.

[44] Fragoso R., Duarte E. Reuse of drinking water treatment sludge for olive oil wastewater treatment. Water Science and Technology 66 (4) (2012) 887–894.

[45] El-Gohary F. A., Badawy M. I., El-Khateeb M. A., El-Kalliny A. S. Integrated treatment of olive mill wastewater (OMW) by the combination of Fenton's reaction and anaerobic treatment. Journal of Hazardous Materials 162 (2009) 1536–1541.

[46] Lafi W. K., Benbella Shannak B., Al-Shannag M., Al-Anber Z., Al-Hasan M. Treatment of olive mill wastewater by combined advanced oxidation and biodegradation. Separation and Purification Technology 70 (2009) 141–146.

[47] Martínez Nieto L., Hodaifa G., Rodríguez S., Giménez J. A., Ochando J. Flocculation–sedimentation combined with chemical oxidation process. Clean – Soil, Air, Water 39 (10) (2011) 949–955.

[48] Alver A., Bastürk E., Kılıc A., Karatas M. Use of advance oxidation process to improve the biodegradability of olive oil mill effluents. Process Safety and Environmental Protection 98 (2015) 319–324.

[49] Tezcan Un U., Ugur S., Koparal A. S., Bakır Ogutveren U. Electrocoagulation of olive mill wastewaters. Separation and Purification Technology 52 (2006) 136–141.

[50] Tezcan Un U., Altay U., Koparal A. S., Bakir Ogutveren U. Complete treatment of olive mill wastewaters by electrooxidation. Chemical Engineering Journal 139 (2008) 445–452.

[51] Khoufi S., Aloui F., Sayadi S. Treatment of olive oil mill wastewater by combined process electro-Fenton reaction and anaerobic digestion. Water Research 40 (2006) 2007–2016.

[52] Cañizares P., Paz R., Sáez C., Rodrigo M. A. Costs of the electrochemical oxidation of wastewaters: A comparison with ozonation and Fenton oxidation processes. Journal of Environmental Management 90 (2009) 410–420.

[53] Papastefanakis N., Mantzavinos D., Katsaounis A. DSA electrochemical treatment of olive mill wastewater on Ti/RuO_2 anode. Journal of Applied Electrochemistry 40 (2010) 729–737.

[54] Chatzisymeon E., Xekoukoulotakis N. P., Mantzavinos D. Determination of key operating conditions for the photocatalytic treatment of olive mill wastewaters. Catalysis Today 144 (2009) 143–148.

[55] Justino C. I., Duarte K., Loureiro F., Pereira R., Antunes S. C., Marques S. M., Gonçalves F., Rocha-Santos T. A. P., Freitas A. C. Toxicity and organic content characterization of olive oil mill wastewater undergoing a sequential treatment with fungi and photo-Fenton oxidation. Journal of Hazardous Materials 172 (2009) 1560–1572.

[56] Ochando-Pulido J. M., Hodaifa G., Víctor-Ortega M. D., Martínez-Férez A. A novel photocatalyst with ferromagnetic core used for the treatment of olive oil mill effluents from two-phase production process. The Scientific World Journal 2013 (2013) 196470. doi:10.1155/2013/196470.

[57] Ruzmanova Y., Ustundas M., Stoller M., Chianese A. Photocatalytic treatment of olive mill wastewater by N-doped titanium dioxide nanoparticles under visible light. Chemical Engineering Transactions 32 (2013) 2233–2238.

[58] Bangkedphol S., Keenan H. E., Davidson C. M., Sakultantimetha A., Sirisiksoontorn W., Songsasen A. Enhancement of tributyltin degradation under natural light by N-doped TiO_2 photocatalyst. Journal of Hazardous Materials 184 (2010) 533–537.

[59] Chen D., Jiang Z., Geng J., Wang Q., Yang D. Carbon and nitrogen co-doped TiO_2 with enhanced visible-light photocatalytic activity. Industrial and Engineering Chemistry Research 46 (9) (2007) 2741–2746.

[60] Chatterjee D., Dasgupta S. Visible light induced photocatalytic degradation of organic pollutants. Journal of Photochemistry and Photobiology 6 (2–3) (2005) 86–205.

[61] Hu S., Wang A., Li X., Löwe H. Hydrothermal synthesis of well-dispersed ultrafine N-doped TiO_2 nanoparticles with enhanced photocatalytic activity under visible light. Journal of Physics and Chemistry of Solids 71 (2010) 156–162.

[62] Papaphilippou P. C., Yiannapas C., Politi M., Daskalaki V. M., Michael C., Kalogerakis N., Mantzavinos D., Fatta-Kassinos D. Sequential coagulation–flocculation, solvent extraction and photo-Fenton oxidation for the valorization and treatment of olive mill effluent. Chemical Engineering Journal 224 (2013) 82–88.

[63] Michael I., Panagi A., Ioannou L. A., Frontistis Z., Fatta-Kassinos D. Utilizing solar energy for the purification of olive mill wastewater using a pilot-scale photocatalytic reactor after coagulation-flocculation. Water Research 60 (2014) 28–40.