

## REVIEW PAPER

# Study on Olive Oil Wastewater Treatment: Nanotechnology Impact

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### ABSTRACT

The olive mill wastewater (OMW) is generated from olive oil extraction in olive mills. It contains a very high organic load and considerable quantities of phytotoxicity compounds. Comprehensive articles with different methods have been published about the treatment of OMW. This paper reviews the recent reports on the variety methods of OMW treatment. Biological process, containing aerobic pre-treatment by using different cultures and anaerobic co-digestion with other sewage and also added external nutrient with optimum ratio attracted much attention in the treatment of OMW. However, advanced oxidation process (AOP) due to the high oxidation potential which causes destruction of organic pollutants, toxic and chlorinated compounds have been considered. Furthermore, membrane technologies consist of microfiltration, ultrafiltration and especially nanofiltration in wastewater treatment are growing in recent years. They offer high efficiency and mediocre investments owing to novel membrane materials, membrane design technics, module figures and improvement of the skills. In addition, fouling reduces the membrane performances in time, which is a main problem of cost efficiency.

**KEYWORDS:** *Advanced Oxidation Process; Biological Process; Membrane Technologies; Nanofiltration; Olive Oil Wastewater*

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## INTRODUCTION

In recent decades olive oil has been considered as one of the most important industry in agro-industrial section among Mediterranean countries[1]. Spain, by having 1700 olive factories could succeed to produce, supply and also spread more than 45% of the world's olive oil. Amazingly, one-third of the world's olive oil productions are centralized in Andalusia, a region located in south of Spain which has 850 olive factories and produces 1,400,000 tons of olive oil of the world [2, 3]. Spain, Italy, Greece, Syria, Turkey, Morocco, Tunisia, Portugal and Algeria are evidently the

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main Mediterranean countries in olive oil's production in the world (Fig. 1.).

Furthermore, some countries like France, Macedonia, Cyprus and Serbia have the significant annual producing of olive oil. In addition, some countries such as China, Middle East and for example north of Iran have the potential weather for planting olive trees and olive oil production[4]. The level of waste pollution of wood, paper, yeast processing, winery, organic chemistry and olive oil mill (OMW) factories are sadly causing frequent ecological problems[5]. Among these, the waste of untreated olive oil factory is seen as a huge

Table 1. Amount of pollutants in various industrial wastewaters

Wastewater types	BOD <sub>5</sub>	COD	TSS	Ref.
Pulp and paper	100-13300	500-40000	100-23300	[123]
Tannery effluents	800-4000	2000-23000	1500-42500	[124, 125]
Refinery effluent	10-1000	50-4000	10-300	[126]
Winery	500-40000	500-45000	1000-7300	[127-130]
Brewery	500-64000	750-80000	100-3000	[131-135]
Sugar mill	4000-7000	3500-10000	350	[131, 136]
Soft drink	770	1400-33000	140-5000	[131, 137]
Meat processing	600-4600	400-11200	200-9300	[131, 138]
Yeast processing	3000-21000	10000-30000	50-2400	[131]
Dairy/cheese factory	1400-50000	2000-95000	20-22000	[131, 139, 140]
Olive oil mill	10000-150000	37000-318000	6000-83700	[118, 141]

ecological problem due to high toxic organic load, high Chemical Oxygen Demand (COD > 110 g/l), low PH and Biological oxygen demand (BOD > 170 g/l). Although, the high necessity of OMW treatment is an unavoidable and obvious matter, finding the proper and economic method for this process is more important and significant [6] (Table 1).

By developing the technology the discontinuous pressure system for extracting olive oil is replaced by continuous centrifugation method. The high efficiency of these methods persuades the factories to produce by-products in their industries. The OMW with high dense of suspend solids are as same as pulp, branches, leaves and peel. The specifications of solid residue in 2-phase extraction are different in comparison with three-phase and traditional process. The sludge in 2-phase method is including some stone, pulp and vegetation water with 65-75% moisture, whereas the 3-phase and traditional system have 40-45% and 22-25% moisture respectively [7, 8]. In 1996, Alba Mendoza, *et al* studied on differentiation between the amount of water in 2-phase and 3-phase methods and they found out the amount of water in 3-phase method is 5 times more than the amount of water in 2-phase method [9].

Furthermore, the amount of COD in 2-phase method is 4-6 g/l, whereas this amount is 30-200 g/l in 3-phase. For this reason, it is shown that the level of pollution in 2-phase method is less.

OMWW is generally in violet-brown color and sometimes up to black water color [8, 10]. Whether by quality nor quantity, the materials in OMWW are considered by the kind of olive, the method of planting, the weather condition, the process of

olive oil extraction and the time of storing [11, 12].

In fact, along with the water in OMWW, organic acids, phenolic combinations and sugar are the main materials in OMWW. In addition, OMWW is the combination of different valuable resources, such as mineral nutrients and potassium which have the potential of being used as fertilizers. Regarding to the OMWW conditions, the olive species, extraction process and origin of the olives are seen differently in olive pomace chemicals. Besides, there are a noticeable amount of lignin, cellulose, hemicellulose, fat and protein in olive pomace [13].

What's more, OMWW is presenting too much undeniable harm to the environment, such as the serious effect of ground and surface water pollution which cause the toxicity on aquatic fauna life, the changes of soil quality, coloring natural water, phytotoxicity and annoying odors [14-16].

The olives factories dispersal and their seasonal productions have the high level of OMW in Mediterranean countries, specially on November and March. Because of biodegradable pollutions such as tannins, organohalogenated pollutants, fatty acids, phenolic compounds discharged untreated wastewater in surface water and soil and also refractory organic compounds, the direct discharge of OMW to the urban sewages in Spain is forbidden. This despite the fact that in European countries, Italy and Portugal small discharge is allowed in a suitable framework [17].

The characteristic of phytotoxicity in OMW shows that this substance should not discharge directly in soil, on the other hand, the organic materials, nutrients and high amount of water in these wastes make a lot of researchers to study

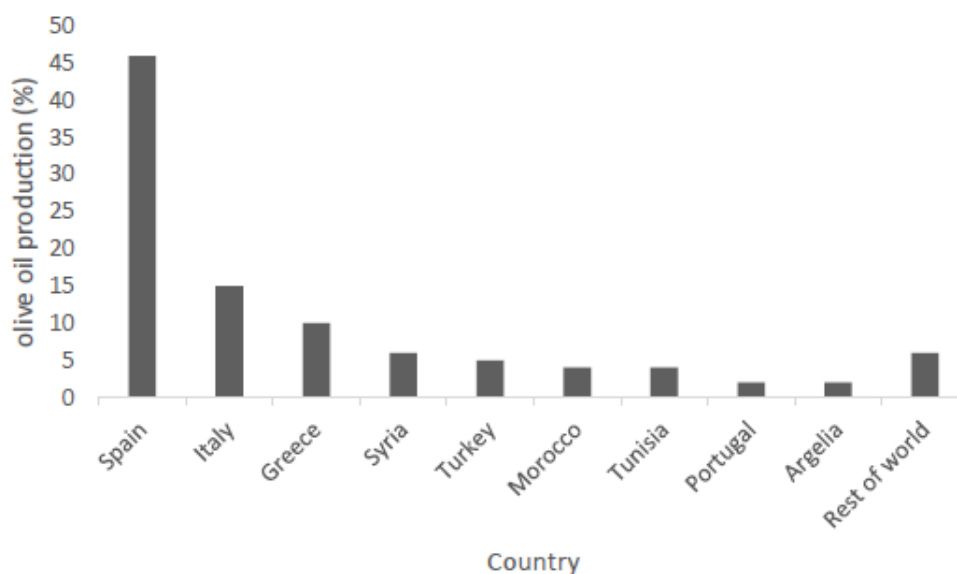


Fig. 1. Comparison of live oil production in world [4]

about the efficiency of these wastes as a valuable resource in agriculture and fertilizer productions. For this reason, phytotoxicity can be used as a fertilizer after removing its organic materials [18-20].

Till now, the vast number of stand-alone and integrated process had been recommended by the huge number of researchers, but unfortunately, none of them were perfectly satisfying such as natural evaporation and thermal concentration[7, 21], treatment with clay[22], treatment with lime[23], composting[24-26], physic-chemical procedures like coagulation-flocculation[27, 28], electrocoagulation[29, 30] and biosorption[6, 31, 32], biological treatment containing active sludge[7, 33, 34], aerobic[35, 36] and anaerobic treatment[37-40], advanced oxidation process comprising ozonation[41-43], Fenton's reaction[44-46]and photocatalysis[43, 47], hybrid process[48-52] and membrane technologies including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis(RO). [53-58].

In this work, the different proposed methods of reclamation of the wastewater generated in olive mills operation were gathered. The different ways of extraction olive oil are including batch-press, 2-phase and 3-phase methods. What's more, biological methods, AOP process and membrane technologies were presented as OMW treatments.

#### OLIVE OIL EXTRACTION PROCESS AND ITS OTHER ASSOCIATED PRODUCTS

Dealing with an economical and ecological problems in extracting olive oil has always had a significant effect on inventing new methods in extracting oil. However, the rate of physical and chemical waste materials directly depends on the ways of how the oil was extracted from olives. There are two known methods for extracting oil including discontinuous process (pressing) and continues process(centrifugation) that are described in Fig. 2. Traditional or pressing system is one of the oldest methods that have been used for centuries. In this method every things has been remained unchanged for many years except hydraulic pressure. Tanks to new technology, traditional method has become obsolete in many countries. Fig. 2. Although, the pressing method has been using in a few countries such as Italy with almost 5000 to 6000 and Portugal with 10000 olive firms[8]. To look profoundly, this method has some advantages such as inexpensive equipment and technology that could seem lucrative for many companies. In these methods, after extracting oil under pressure, considerable solid amounts of some materials such as olive residue, water, stone and skin would be remained left that are known as olive cake. This substance and olive emulsion compounds are separated from waste water by decanter. Moreover, using pressing method requires less water. As a result, it

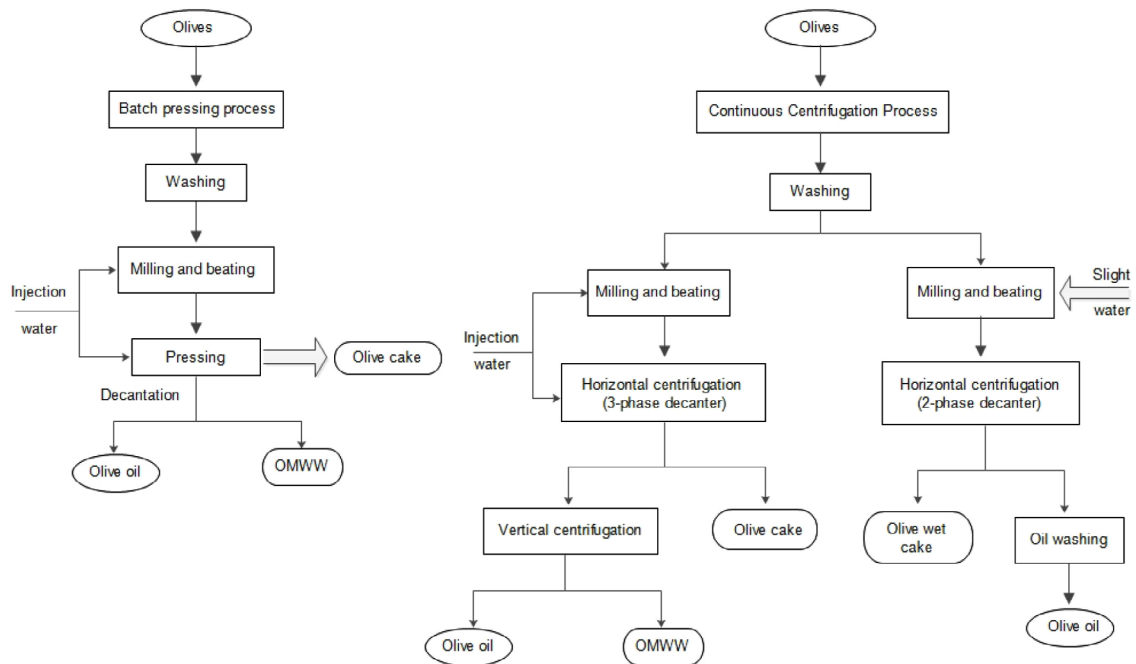


Fig. 2. Conventional and new processes for olive oil extraction

produces less waste water(40 to 60 lit/100kg olive) [59]. However, pressing system requires more manpower for its disconnected procedure and due to this characteristic, the economic recession of the early 1970s forced many factories to change their traditional methods into new methods[60]. In two ways mentioned above, one similar procedure is being used for extracting oil from olive including, washing, milling and beating. The olives get crushed and some water would be added sequentially until it becomes pulp. However, there are some methods for detachment of oil from water that differ among companies. Fig. 2.

Three phase method for separating of olive mixed materials including one phase containing 30% solid substance or olive husk, two phase containing 50% waste water and 20% oil, would be separated according to their difference densities. The whole operation would be done by a de counter with a centrifuge that works in a continues way. Comparing with traditional methods, this method have some advantages consist of changing manual manufacturing process into completely automatic systems, high quality oil and requiring less space for equipment. In other hand, using this method increases the cost of installing and requires high

amount of water and energy. Ergo, the amount of waste water produced by this kind of factories would increase significantly.

In many countries such as Italy, Malta, Cyprus, and Greece, three phase method are still being used. Fig. 3. Since the growing production of wastewater has been increasing in recent years. Therefore, releasing waste water into rivers and increasing the density of COD and other organic substances in water tables has become a matter of concern in many areas. Though, many research about finding convenient solution for solving these problems have been done. Among many researches done in the case of managing waste water, an evaporation pond has been taken into account as a supreme solution. To look profoundly, Mediterranean country's high temperature in summer provides a prone condition for natural evaporation of water. Hence, the residual solid materials reminded could be used for making fertilizer. Otherwise, none insulated construction of these ponds could expose the waste water penetrating into water table and produces a bad smell that attracts many insects. Therefore, another technology called "ecological technology" has been taken into account in order to consume less water, so two phase system developed in 1990s. By employing this method the amount of waste

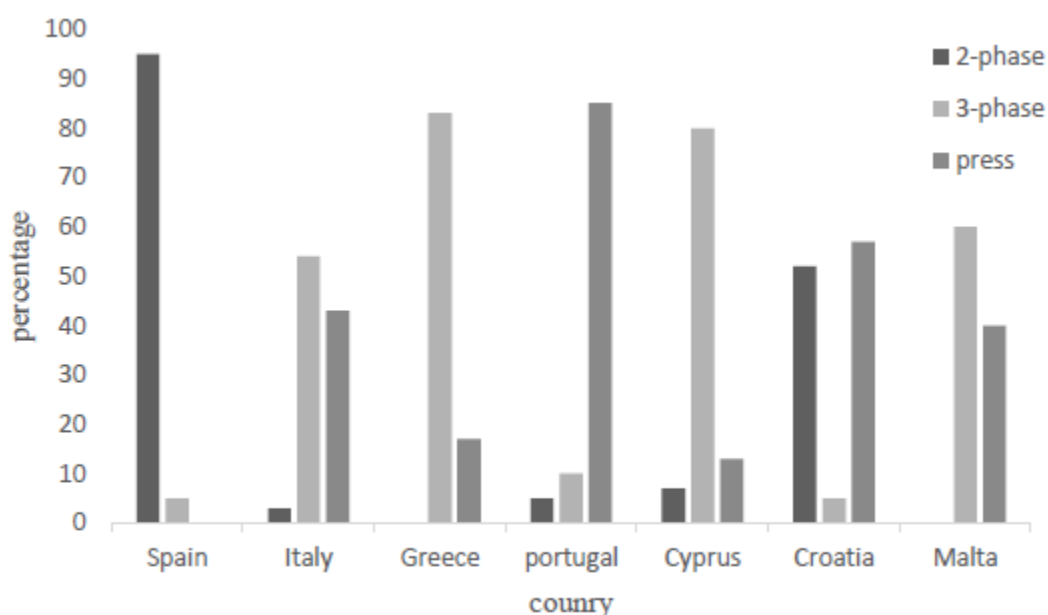


Fig. 3. Technologies used by some countries in olive oil extraction [61]

water produced by factories has reduced almost 75%. Spain and Croatia were the only countries used this method broadly. In spite of producing less waste water, the residue reminded by this operation had much more wet capacity than three phase method and this flaw makes some problems to be occurred. (Fig. 3.)

There are two parts for two phase method; solid phase (alperujo or wet pomace) and liquid phase or olive oil. In solid phase part, residual oil on wet bases requires chemical or mechanical process to be purified. Therefore, the cost for drying process of wet bases would be increased considerably. However, in three phase method this problem has been solved efficiently. To elucidate on, there are many ways for extracting oil in three phase method but all of them would be performed by following operation. First, extracted olive oil obtained is approximately between 40 to 50%. This operation would be done by centrifuge. In the second part, it should be heated in an oven with 400 to 800c temperature in order to decrease the moisture from 60 or 70% to 8% and finally, the rest oil would be extracted by a solvent named Hexane. The whole oil extracted in final procedure could be utilized in many ways. For instance, it could be used in combustion-turbine cycle or providing sufficient energy to trigger dryer ovens in oil extraction firms[61].

## BIOLOGICAL PROCESSES

Two of the best ways consistent with environment in biological processes are aerobic and aerobic processes.

### *Aerobic Pre-treatment:*

For reducing and elimination of phenol compounds and its associated toxics, the aerobic treatment is being used for improving the operation of anaerobic digestions. PH in aerobic methods has some restrictions that must be controlled for performing successful operation but it can easily be used in temperature between 25 to 30°C. The effect of aerobic pretreatment before anaerobic digestion had been studied by a scientist named Borja[62] with three different cultures such as *Geotrichum candidum*, *Aspergillus Terreus* and *Azotobacter chroococcum*. After this operation, he concluded that the number of anaerobic degradation was approximately 2.5, 4 and five times greater than the anaerobic digestions without pretreatments which had been used. As a result, pre-treatment reduced the amount of COD up to 63-75%, toxicity of 59-87% and total phenol concentration about 65-95%. González-González et al.[63] aerated OMWW by the use of indigenous microorganisms. So, they achieved to 56% polyphenol removal after the first day of aeration, with its increasing to 90% by day 7, the later, did not contribute any remarkable advancement.

Table 2. Aerobic treatment of OMW

Culture	COD reduction (%)	Phenol reduction (%)	Ref.
Various strains of <i>Penicillium</i>	25-38	32-45	[146]
Various strains of <i>Pleurotus</i>	-	69-76	[147]
<i>Aspergillus terreus</i>	66	-	[34]
<i>Candida oleophila</i>	55	83	[148]
<i>Candida tropicalis</i>	62.8	51.7	[36]
<i>Penicillium sp</i>	65	65	[149]
<i>Lentinula edodes</i>	67	88	[150]
<i>Lentinula edodes</i>	-	75	[151]

Many reaserches[63-65] Studied on the effects of different microorganisms on the aeration OMW pre-treatment and the given results showed that the time when *G.candidum* removed 75% of COD from the OMWW, aeration with *P.chryso sporium* was effective on the degradation of low molecular polyphenols and it caused thededuction of COD by 20-50% and toxicity by 5%. Several other studies are summarized in Table 2.

#### The Anaerobic Treatment of OMW:

Actually maintaining anaerobic reactors stability is probable by adequate alkalinity levels in the reactor. Most of the time, the OMWs are lack of alkalinity. To enrich them, two different ways are recommended. First of all, the external alkaline chemicals such as  $\text{Ca}(\text{OH})_2$ ,  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{NaHCO}_3$  are added to OMWs[65, 66]. Second, the OMW is mixed with the other wastes which are enriching by alkaline. This composition causes the increase of essential nutrients in microorganisms and furthermore it is a low-cost task[67]. An anaerobic treatment of OMW has normally been done in mesophilic temperature (32-40°C) and in special cases, it is conducted in thermophilic temperature (55°C) [68-70]. Sometimes in a purpose of decreasing operational cost and reaching to a specific ratio of C/N/P (carbon-to-nitrogen-to-phosphorus), other wastes such as whey, slaughterhouse, municipal, manures, microalgae and plant sludge are added to OMW streams. It is noticeable that for having better co-digestion efficiency, the wastes ought to be combined with optimum ratio. For this reason, co-digestions can cause to the dilution of toxic substances [67, 71].

Kougias *et al.*[72] showed that the optimum mixing ratio of OMWW and manure for the co-digestion was 0.4:0.6 and that ratio produce 277 ml  $\text{CH}_4/\text{g}$  COD (79% of the theoretical yield).

The increase of the OMW ratio causes to an accumulation of long-chain fatty acid (LCFA) that prevents methane production. The further study by Ağdağ *et al.*[73] explained that the co-digestion of olive mill pomace (OMP) with municipal solid waste (MSW) had the highest treatment efficiency at a ratio of 0.7:0.3. The treatment performance and  $\text{CH}_4$  productivity is increased by the recirculation of leachate generated during the digestion into reactor.

#### Anaerobic Reactors:

In last 15 years, the anaerobic reactors have been used for OMW treatment because of their high various advantages. The studied about anaerobic reactors are commonly in same laboratory scales. The different types of anaerobic reactors including complete stirred tank reactor (CSTR), anaerobic sequencing batch reactor (ASBR), periodic anaerobic baffled reactor (PABR), up-flow anaerobic reactor filter (UAF), up-flow sludge blanket reactor (UASB) and Hybrid reactors are used prevalently. The functions of some of these anaerobic reactors are shown in Table 3.

CSTRs are the famous suspended-biomass reactors and have been broadly used in anaerobic treatment of OMW. In comparison to other COD removal and  $\text{CH}_4$  production gained by reactors, CSTR provided comparable COD and  $\text{CH}_4$  production and it also has a lower biomass concentration.

Dareioti *et al.*[74] suggested that anaerobic digestion potential for the treatment of a mixture containing OMW (20%) and LCM (liquid cow manure 80% v/v) is using a two-stage process which has been evaluated by using two CSTRs under mesophilic conditions at 35°C for the purpose of monitoring and controlling the processes of acidogenesis and methanogenesis. All process was studied with 19 days hydraulic retention

Table 3. Performances of various anaerobic reactors in OMW treatment

Reactor	Effluent	Operational conditions and Efficiency	Ref.
CSTR	OMSR	15-215 HRT (d) 0.8-11 OLR (g COD/l d) 44.5-97% COD removal 0.2-1.7 CH <sub>4</sub> production rate (l/l d)	[142]
CSTR	OMWW+ cheese wastewater+ manure	19 HRT(d) 4.5-5.5 OLR (g COD/l d) 75.5-85.2% COD removal 30-41% TS removal 1.35 CH <sub>4</sub> production rate (l/l d)	[143]
CSTR	OMWW+ manure	16 HRT(d) 3.63 OLR (g COD/l d) 50% COD removal 34.2% VS removal 0.91 CH <sub>4</sub> production rate (l/l d)	[74]
ASBR	OMWW	0.5-3 HRT (d) 5.3-31.8 OLR (g COD/l d) 53-83% COD removal	[48]
PABR	OMWW	3.75-17.5 HRT (d) 1.46-6.0 5 OLR (g COD/l d) 58.2-81.6% COD removal	[144]
UAF	OMWW + piggery slurry	11-45 HRT (d) 0.2-5.0 OLR (g COD/l d) 62-89% COD removal	[76]
UAF	OMWW + cheese wastewater	0.2-3 OLR (g COD/l d) 83% COD removal 1.25 CH <sub>4</sub> production rate (l/l d)	[145]
UASB	OMWW + manure	1.4-7.6 HRT (d) 38-110 OLR (g COD/l d) 85-95% COD removal	[77]
UASB	Pomace leachate	3 HRT (d) 0.33-1.67 OLR (g COD/l d)  35-70% COD removal 0.12 CH <sub>4</sub> production rate (l/l d)	[68]
Hybrid UASB	OMWW	2.5-10 HRT (d) 4.55-109.8 OLR (g COD/l d) 50-95% COD removal 19-37% SS removal	[66]

time (HRT). The average removal of dissolved was 63.2% and also total COD removal was 50% and at the steady state methane production rate reached to 250.9 L CH<sub>4</sub> at standard temperature. On the other hand they reported 20% and 10.3% removal efficiency of phenol and suspended solid respectively.

UAFs have been completely operated for the treatment of OMW and they considered it as biofilm reactors. Different types of packing materials, such as activated carbon, foam, PVC ring, silica and wood chips are being used but the activated carbon cab is seen as a superior method to all, because of its fabulous surface area for biofilm development



coupled with noticeable adsorption capacity of the phenolic compounds[75]. During the co-digestion of aerobically treated OMWs and piggery slurry, Martinez-Garcia *et al.*[76] obtained high COD removal with methane-rich biogases at an HRT between 11 to 45 days by an UAF reactor.

The well-known UASB is part of granular bioreactor which has proven effective and economical treatment for OMW. Undiluted wastewater can be pleasantly treated by UASB reactors under boosted organic load. In comparison to other reactors, UASB can be operated under higher organic loads during the treatment of OMW. UASB have provided high treatment performance for the co-digestion of OMW. The combination of OMWW and swine manure at a ratio of 1:1 prevented anaerobic treatment, on the other hand, co-digestion at a ratio of 1:2 resulted in a fantastic COD removal efficiency between 85% and 95% and also biogas production of 550 L CH<sub>4</sub>/g COD. (As the time the sulphate was reduced within the structure of the granules, it has the ability to convert phenol to CH<sub>4</sub> which is shown the high promising phenol removal potential in UASB).

In spite of an interesting feature that most of these methods have, we cannot turn blind eyes on this fact that it cannot be used in industrial size. The main problem with this method is its high consumption of energy in long term that increases the cost of operation [77].

Since the anaerobic digestions have more advantages than aerobic purification, they have been considered as a basis for purifying the OMW. Among many reasons supporting the claim, producing less sludge, generation of energy into biogas and high consistency of microorganisms, which makes them more resistant in dealing with seasonal wastewater, can be mentioned as other advantages. Moreover, anaerobic digestions can be reactivated after several months shut downing. Otherwise, aerobic processes in high organic loads need to be diluted in several stages for biological purifying (70 to 100 time's dilution) that increases the costs of operation considerably. On the other hand, because of some compounds such as phenol, organic acids and fats, the anaerobic method cannot directly be used without pretreatment owing to these compounds cannot be used with methanogenic bacteria (the methanogenic bacteria do not have the ability to deal with compounds).

#### ADVANCED OXIDATION PROCESS (AOP)

AOP in a broad sense is a set of chemical treatment method to remove organic material in water and wastewater, consisting reaction with hydroxyl radicals, OH (active and unstable species), which cause destruction of organic pollutants, toxic and chlorinated compounds. Fenton's reagent[10, 44-46, 78], photocatalysis[47, 79, 80], UV irradiation[81], wet air oxidation[82-84], electrochemical oxidation[29, 68, 85-87] and also different compounds of given methods are part of these processes. AOP is used for the full mineralization of most organic compounds and their transformation to carbon dioxide and water. It is used to remove bio-resistant pollutants and also transform them to biodegradable intermediates [88, 89].

Fenton's reagent is a simple and cost-effective chemical oxidation process. In this method, ferrous ion reacts as a catalyst with oxidant in an acidic ambient and produces hydroxyl radical (metal ion accepts an electron transfer, so it is oxidation-reduction reaction). The effective factors on Fenton processes efficiency are temperature, ferrous concentration, PH, hydrogen peroxide and reaction time [90]. Diluted OMW with COD 19g/lit by using of zero-valent Fe/H<sub>2</sub>O<sub>2</sub> reached to high removal efficiency of organic compounds. Empirical results represent that 0.06 M H<sub>2</sub>O<sub>2</sub> removals 1 gr of COD and eventually after 1 h at PH 1, maximum COD removal 78% was obtained, whereas maximum COD removal 92% was achieved within 2 and 4 value[78]. In another study, Alver *et al.*[46] studied on sequential coagulation and Fenton system in OMW for removing TPh (total phenol) and organic matter. The optimum conditions in this study were consist of PH=3, [Fe<sup>2+</sup>] = 2.5 g/l and [Fe<sup>2+</sup>]/[H<sub>2</sub>O<sub>2</sub>] = 2.5. while a high treatment efficiency at sequential coagulation and Fenton system were reached to 65% removal and 87.7% TPh, coagulation process was only able to remove 51.4% COD, 38.6% TOC and 52.1%TN. In recent years, Hodaifa *et al.*[44] suggested the use of Fenton-like process in reclamation of OMW (from 2-phase extraction) with CSTR. They showed that the Fenton process is effective on organic matter removal. The optimum operational conditions caused the removal of 97% organic matter and 99% phenolic compound load.

Electrochemical oxidation is offered as an economical procedure with high potential of



destroying OMW. Ti/Pt was used as anode in this technique and stainless steel 304 as cathode. Added electrolyte to OMW was sodium chloride 4% (w/v), COD was reduced by 93% at 0.26 A/cm<sup>2</sup> after 10 h of electrolysis and total phenolic compound were decreased by 99.4% [91].

A novel method was developed for OMW treatment by Hanafi *et al.* [87] in order to exploit the fertilizer value of OMW. Electrocoagulation was first used by aluminum electrode in order to pre-treat the OMW and then by using a selected strain of *Aspergillus niger van Tieghem* in biological process. The effect of treatments was assessed by the use of durum wheat (*Triticum durum*) seeds. This treatment scheme was capable enough to remove the phytotoxicity completely and the germination index was 106% of OMW.

Wet air oxidation (WAO) contains high percentage of COD removals (more than 10000 mg/lit) in high temperature (200-350°C) and high pressure (50-150 bar) by short time treatment. It has a high potential for changing complex resistant components to simple and biological degradable components. A major disadvantage of this process is the high number of equipments required and expensive operation costs, because of high pressure necessity, it is not economical [92]. Efficiency of the process has been shown in a recent work. In 2007, Minh, D Pham, studied two important pollutants; *p*-hydroxyphenylacetic acid and *P*-hydroxybenzoic acid; in OMW. In a batch reactor at 140 °C and 50 bar of total air pressure, platinum and ruthenium catalyst were used to support titanium and zirconium oxides. They presented the reaction pathways for the oxidation of two substrates by the formation of different aromatic compounds and short-chain organic acid within hydroxylation and decarboxylation reactions. In 7-8 hrs by preparing a catalysts on zirconia from Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, they could achieved to the total elimination of *P*-hydroxyphenylacetic acid with a 65% TOC removal and approximate total elimination of *P*-hydroxybenzoic acid with up to 70% TOC removal [84]. However, OMW with resistant biological degradation were treated in a continuous trickle-bed reactor and a batch reactor. Titania or Zirconia, which were supported by platinum and ruthenium as catalytic wet air oxidation (CWAO), were studied in the next year (2008) by Minh, D Pham. Removal efficiency

of the phenolic content and of the total organic carbon (TOC) at 190°C and 70 bar was approved by CWAO experiments. A reduction in phytotoxicity took place, in the meantime, toxicity towards *vibriofischeri* was decreased. This study examined the feasibility of coupling CWAO and an anaerobic digestion treatment. The total phenolic contents of the wastewater in pretreatment of the OMW was reduced by the presence of a ruthenium catalyst and compared to the untreated effluent, it produced an effluent proper to be treated by anaerobic treatment by increasing biomethane production [82].

Ozone is an unsteady solution with strong oxidizing that is sparingly soluble in water. Therefore it does not have the proper outcome in high OMW concentrations (according to various studies of ozonation method, it was proved that the extent of COD removal could not be more than 30%) [93-95]. Ozonation process is either alone or a combination with other techniques like: integrated ozone and hydrogen peroxide (“O<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>”) and integrated ozone and target catalyst. The method above are non-photochemical methods identified for production of hydroxyl radicals without the using of solar energy but in some cases common oxidation of organic compounds by using hydrogen peroxide or ozone, produces intermediate products that may be even more toxic than initial components. In this case UV irradiations such as (O<sub>3</sub>-UV), (H<sub>2</sub>O<sub>2</sub>-UV), (H<sub>2</sub>O<sub>2</sub>-O<sub>3</sub>-UV), (UV-TiO<sub>2</sub>) are used in order to complete oxidation reactions [96]. For example Speltini *et al.* [81] used OMW as sacrificial agent for the photocatalytic H<sub>2</sub> evolution from water (at ambient temperature and pressure). From aqueous sample, under the optimum condition, 4 h UV-A irradiation, 2 g/l Pt/TiO<sub>2</sub>, OMW 3.3% v/v, COD 944 mg/l and PH 3 were generated.

#### WASTEWATER TREATMENT BY MEMBRANE

The use of membrane for the treatment of wastewater emerged three decades ago. As a matter of the fact, due to membrane fouling the technology was not qualified enough to maintain the performances as a function of time. So, the membrane technologies were not noticeable on the last 20 years. Recently, availability of membrane fouling mechanism, Novel membrane materials, membrane design technics, module figures and the improvement of the skills in general have allowed

the engineers and investors of this technologies to reach their purposes of wastewater treatment. The increase number of using membrane technologies in urban wastewater treatment facilities is making these technologies to play a significant worldwide role in market for membrane every year. In comparison with conventional process, membrane process are showing high selectivity value by displaying the high water quality, costly standard value, less area requirement and the perfect replacement of several units treatment processes by a single one[17, 97]. MF, UF, NF and also RO membranes, in the past years have been used in water treatment process[98], desalination[99], pulp and paper[100-102], textile and tannery[103, 104], pharmaceutical[105], yeast processing[106], slaughterhouse[107], dairy[108, 109] and olive oil[56, 110, 111].

#### *Fouling in Membrane Operations:*

The main reasons of membrane operation limitations are sparingly soluble salts, irreversible fouling and biofouling which decrease the usage and development of desalination and sewage treatment. Concentration polarization can be responsible for scaling. The higher soluble concentration near the membrane surface decreases the effective driving force and thereby the trans-membrane flux. Scaling is happening because of high concentration at the membrane surface. The membrane is possible to act as a heterogeneous surface for making crystallization and making severe precipitation on the surface of membrane. In thermal membrane operations which can also be responsible for scaling, can have a positive and a negative effect by considering the nature of the solute (in terms of solubility). Other classes of fouling are absorption, pore blocking and deposition. In fact, high recovery RO operations are limited because of high energy consumption needed in fouling and concentration polarization.

Fouling can be controlled with different types of methods such as pretreatment of the feed, the expansion of improved membrane materials ranging from carbon nanotubes[112, 113] and aquaporin membrane[114], zeolite, use of proper chemical agents for the cleaning and hydrodynamic optimization of the membrane module[115].

Particulate fouling is prevented by mechanical pretreatment of the feed water by using sand

filtration cartridge filters and screens or membrane pretreatment. What's more, biological fouling which is produced by microorganism makes a gel-like layer. The truth is, this gel is a serious problem and it must be inhibited for example by the process of chlorination during pretreatment. Quist-Jensen *et al.*[115] recommended that fouling cannot be prevented completely even with pretreatment optimizing so, membrane cleaning time ought to be performed. Furthermore, it is not possible to fully remove the fouling and it has to tolerate the decrease of mass flux up to 75%of the original flux. As a matter of the fact, OMW include high concentration of suspended solids and colloidal particles which have high potential of membrane fouling (are amenable to cause membrane fouling) for instanceorganic pollutants and inorganic matter that would also lead to damaging scaling problems. According to this, for preventing high fouling rates which quickly lead to zero flux - if no pretreatment is conducted on the raw wastewater stream the membrane operation- pretreatment process are required.

#### *OMW Treatment by Membrane and Nanotechnology:*

The main concern about the technical implementation of membrane technologies can be the high fouling potential in wastewater treatment plants.

Actually, colloids, microorganisms and soluble organic compounds lead the main causes of membrane fouling which increases the feed pressure (liquid feed pressure). For membrane cleaning the force frequent plant shut down is obligated.

Paraskeva *et al.* [116] using membrane technology makes it probable to complete the fractionation of olive oil. The combination of variety membrane processes were used in OMW fraction into by-products which may happen to reduce the expenses involved in process. UF in combination with NF and RO were so effective in treatment and OMW fraction. The further parametric study about the optimum fractionation yield of OMW had variety of operational system parameters such as trans-membrane pressure and temperature. So the final obtained effluent was a transparent including low content of organic compound and dissolved ionic salts. The chemical compounds in the post-treatment effluent presented that it was proper for irrigation purpose and aquaticreceivers'

disposal. The separation of high molecular weight constituents was the outcome of UF process that is included suspended solid particles. Using the NF step make it possible to remove the phenols in OMW to an amount of more than 95% of the initial value. The obtained concentrate was very rich in phenol at this stage. Better result of OMW treatment was gained when the RO were applied after UF.

Garcia-Castello *et al.*[117] had studied on the analysis of integrated membrane system potentials such as MF, NF, osmotic distillation (OD) and VMD for the recovery, purification and concentration of polyphenols from OMW. At the beginning, the OMW without any preliminary centrifugation was directly submitted to a MF operation which ensured to achieve a 91% and 26% decrease of suspended solid and total organic carbon (TOC) respectively. also, the permeate stream was recovered by 78% of the initial content of polyphenols. Subsequently, the MF permeate was submitted to a NF treatment. While Toc was reduced from 15 g/l to 5.6 g/l, almost all polyphenols were recovered in the permeate stream which was enriched by ulterior treatment by OD. Especially, a solution containing about 0.5 g/l of free low molecular weight (LMW) polyphenols with hydroxytyrosol representing 56% of the total was produced by using a calcium chloride dehydrate solution as brine. The prepared NF permeate stream can be used in food, cosmetic and pharmaceutical industry.

Coskun *et al.*[118] studied about the OMW by membrane methods. The centrifugation of OMW and its filtration through one step UF membrane ( UC010 ) was proceeded by filtration via 3 steps NF ( NP010, NP030 and also NF270 ) and 2 steps RO ( XLE and BW30 ). What's more, except the UF step, the purpose of OMW centrifugation through NP010 and NP030 filtration was to evaluate the performance of centrifuging process as a pretreatment option. They claimed that the membrane fluxes reached the values of UP to 21.2, 5.2, 28.3, 15.5 and 12.6  $\text{lm}^{-2}\text{h}^{-1}$ . Three different steps of NF are followed by two steps RO respectively in the OMW permeate via ultrafiltration membranes. The maximum COD removal efficiencies obtained were 60.1%, 59.4% and 79.2% for NF membranes respectively at 10 bars. And also it was 96.3% and 96.2% for two steps of RO membranes .conductivity removal efficiencies obtained were 93.2% and

94.8% for osmosis membrane different steps at 25 bars. As a result, the obtained efficiencies in comparison with other treatment methods is higher than other processes. Therefore, membrane processes are a well replacement for treatment of OMWs. Furthermore, the centrifuging process seemed helpful pre-treatment method.

El-Abbassi *et al.*[119] investigated that a commercial flat-sheet polytetrafluoroethylene membrane were used for direct contact membrane distillation (DCMD) which was applied for OMW with 0.2 $\mu\text{m}$  mean pore size.(the effects of the temperature and mean temperature difference on the DCMD permeate flux were studied). The influences of microfiltration (MF) and coagulation/filtration processes were investigated as pretreatment on the DCMD performance. The MF was found in a purpose of optimizing the pretreatment to combine with DCMD for OMW. The DCMD permeate flux was increased with the increase of the feed temperature while the permeate temperature was keeping at 20 $^{\circ}\text{c}$  constantly. As regards, the feed phenol concentration of OMW was decreased by permeate flux and also, the concentration factor of phenolic compositions were different from 1.56 to 2.93. The hydroxytyrosol was found as the main phenolic compound in the OMW test which was focused by DCMD for more than 2times from 4.01 g/l to 8.16 g/l after 10hr of OMW processing. Then the result of the integrated MF/DCMD can be an effective process for clean water and phenolic concentrate in concentration treatment of OMW.

Many researches[120, 121] figured out the potential of the integrated system by two UF membrane and final NF in sequence. Three different fractions were received. The first one was the concentrated stream through the retentate of both UF membrane process that is contained of high molecular weight organic substances in which the depleted of polyphenolic compounds can be exposed to an anaerobic digestion for biogas production. NF is another concentrated stream that is enriched in LMW polyphenolic compounds and can be used for cosmetic, food and pharmaceutical industries as liquid dried or lyophilized formulation and frozen and a final NF permeate (treated water stream) is suitable to be reused. The integrated membrane system processor water that is proper as membrane cleaning solution. However, after

cleaning, revealing deleterious irreversible fouling shaped on the membrane, only 87% flux could be recovered.

Zirehpour *et al.*[56] studied on the construction of integrated (UF-NF) membrane system for OMW purification irrigation reuse target. Wastewater was pre-filtered by three steps (MF) membranes with nominal pore size of 50, 5 and 0.2  $\mu\text{m}$  respectively. Indeed, filtration experiments in concentration mode were performed in laboratory scale by using two UF and three NF membranes. Affecting of the filtration treatments was determined by the evaluation of several parameters that are named COD, UV absorbance at 254 nm, total phenols, color and conductivity. In UF membrane, the commercial UF membrane had presented higher permeate flux than self-made UF membrane, likewise, the self-made UF membrane was dominantly better in antifouling properties and rejection efficiency. In NF membranes, the NF-270 in comparison with other NF membranes that were examined, had resulted higher permeate flux, while the rejection efficiency of both NF-90 and self-made NF were better than NF-270. Finally, they reached to 98.8% COD removal in whole integrated system.

Conidi *et al.*[122] investigated the selective recovery of valuable biophenols of OMWs by an integrated membranes system. MF (with a pore size of 0.2  $\mu\text{m}$ ) and UF (with 10kDa molecular weight cut-off) as pressure driven membrane processes were used as pre-treatment stage to produce a permeate stream including phenolic compounds. After that by using a biocatalytic membrane reactor, it was submitted to a bioconversion step. In fact, by  $\beta$ -glucosidase immobilized in a polymeric membrane, the oleuropein is converted to oleuropein aglycon in this last system (UF permeate). A multiphasic biocatalytic membrane reactor (MBMR) were used to direct the transformation of biophenols to the isomer of oleuropein aglycon and the simultaneous isolation in the organic phase. What's more, by a chosen flat-sheet MF membrane (cellulose acetate), the pre-treatment of raw OMWs produced a total removal of suspended solids and a permeate solution was presented to an UF treatment (with a polysulphone flat-sheet membrane). Due to the low rejection the most displayed low molecular weight phenolic compound was in the UF permeate oleuropein. Two different fractions were produced by the MBMR in the next steps: an aqueous phase includes

water soluble biophenols and organic phases were contained the isomer of oleuropein aglycon. The maximum oleuropein conversion reached was about 45.7% and the reaction rate was approximately  $2 \times 10^{-4}$  mmol/min  $\text{cm}^3$ . Furthermore, in all steps of the integrated membrane system, a steady-state flux could be seen. Same catalytic performance and a constant residence time are assured particularly in the MBMR.

## CONCLUSION

Olive oil industry is one of the most important industry in agro-industrial section among the Mediterranean countries or the countries with Mediterranean climate like north of Iran. A large amount of water is used in this industry and for this reason the high percentages of organic pollutant phenols, lipids are produced. The produced wastewater makes the terrific ecological issues, so for reaching to the standard value and getting the evacuation permission it should be treated and recycled again. Many research have been done about this field and also the effects of different technologies were studied. However, OMW treatment is a complicated problem, which has the least relation to the technological reason.

In this work, a review was done regarding to the treatment and disposal of OMW with different types of common treatment methods such as biological treatment, AOP processed and membrane technologies especially nanofiltration membranes. In fact, the complicated compounds in OMW are called the aerobic treatment in order to not reach to their suitable disposal standard. On the other hand, anaerobic treatment has a high advantage and suitable method for OMW treatment. Co-digestion with other wastewater streams or by adding external nutrients cause the dilution toxins and enriched the OMW. What's more, AOP process is another technology that causes the elimination of bio-resistant, it also converted them to biodegradable intermediate. As a matter of the fact, membrane processes like nanofiltration membrane, because of their high advantages, are considered as another method of OMW treatment. Although, the membrane technologies have the high advantages, fouling as a main challenge reduces the function of the membranes which are increased the operation costs. It is considering the fact that all these mentioned methods are showing the attractive



ways in OMW treatment. But unfortunately, the significant methods have not been presented yet in industrial scaling which needs to be economic and at the same time increases the percentages of treatment.

### CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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