8

Olive Mill Wastewater Treatment

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8.1. INTRODUCTION

The cultivation of olive trees and the production and use of olive oil has been a well-known and established practice in the Mediterranean region for more than 7000 years. The consumption of olive oil is rapidly increasing worldwide, due to its high dietetic and nutritional value. According to the IOOC (2004), the production of olive oil increased from 1.85 million tons in 1984 to 3.17 million tons in 2003 (70% increase) (Table 8.1).

There are approximately 750 million productive olive trees worldwide, 98% of them located in the Mediterranean region, where more than 97% of olive oil is produced. The three major olive oil producers worldwide are Spain, Italy, and Greece, followed by Turkey, Tunisia, and to a lesser extent Portugal, Morocco, and Algeria. The data presented in Figure 8.1 reflect the importance of the olive oil sector in the Mediterranean area and consequently the magnitude of the problems related with the disposal of large amounts of wastes produced during olive oil production.

The traditional press extraction method as well as the continuous three-phase decanter process, which is most widely used for the production of olive oil, generate three products: olive oil (20%) and two streams of waste: a wet solid waste (30%) called ''crude olive cake'' or ''olive husk'' and an aqueous waste called ''olive mill wastewater'' or ''olive mill effluent'' or ''alpechin'' (50%). The solid waste (crude olive cake) is the residue that remains after the first pressing of the olives and is a mixture of olive pulp and olive stones. At present, olive husk is processed in seed oil factories in order to extract the small amount of oil remaining in the waste. Both crude and exhausted olive cake can be used as solid fuels (due to their high heating

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Table 8.1. Olive oil production in the last decade in thousand metric tones (International Olive Oil Council, 2004)

1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
1,846	1,736	2,595	2,466	2,403	2,375	2,566	2,826	2,494	3,165	2,766

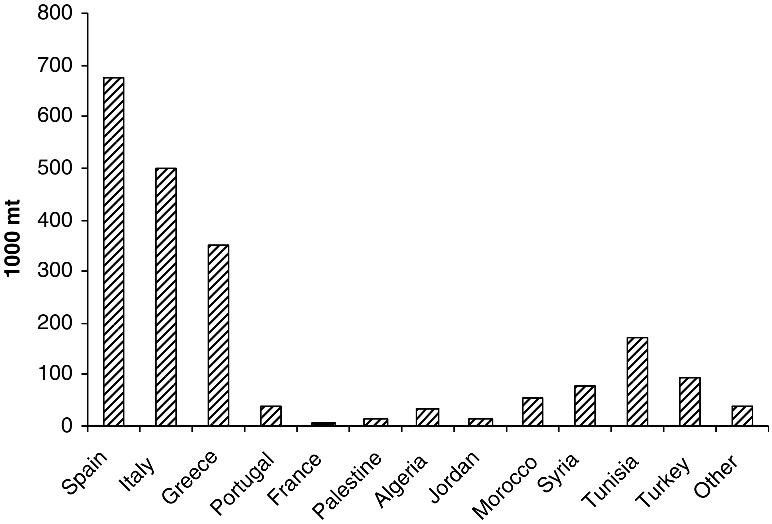

Figure 8.1. Olive oil-producing countries (International Olive Oil Council, 2004).

value), for animal feed supplement, or return to the olive grove as mulch. While economic concerns regarding the profitability of seed oil production now are being questioned, the problem of disposal of olive husk is adequately solved by one of these three alternatives.

On the other hand, as far as olive mill wastewater (OMWW) treatment and disposal is concerned, the situation is much more complicated in practice. Attempts to alleviate the problem, especially in the major olive oil-producing countries, are more than 50 years old; yet, there has been little success in finding an environmentally friendly and economically viable solution to be generally adopted.

8.2. THE DIMENSIONS OF THE PROBLEM

OMWW is a mixture of vegetation water and soft tissues of the olive fruit and the water used in the various stages of the oil extraction process, i.e., water added during centrifugation, water from filtering disks, and from washing rooms and equipment. It contains olive pulp, mucilage, pectin, oil, etc., suspended in a relatively stable emulsion.

The annual world OMWW production is estimated from 7 to over 30 million m^3. Although the quantity of the waste produced is still much smaller than other types of waste (i.e., domestic sewage) and its production is seasonal, the contribution of OMWW to environmental pollution is important, because of some ''peculiarities'' of the case that have to do with both the chemical synthesis of the waste and some aspects of the current situation in the olive oil sector.

8.2.1. Problems Arising from OMWW Synthesis

As far as its chemical synthesis is concerned, OMWW basic characteristics that prove its ''strong'' nature as industrial waste are:

- Strong offensive smell.
- Extremely high degree of organic pollution (COD values up to 220 g/L) and a COD/BOD_5 ratio between 2.5 and 5 (hardly degradable).
- pH between 3 and 5.9.
- High content of polyphenols (up to 80 g/L) which are not easily biodegradable and toxic to most microorganisms.
- High content of solid matter (total solids up to 20 g/L).

In terms of pollution effect, 1 m^3 of OMWW is equivalent to 100–200 m^3 of domestic sewage. Its uncontrolled disposal in water reservoirs leads to severe problems for the whole ecosystem and especially for the natural water bodies (ground water reservoirs, surface aquatic reservoirs, seashores, and sea). The most visible effect is discoloration, a result of oxidation and subsequent polymerization of tannins. OMWW also has a considerable content of reduced sugars, high phosphorus content, and phenolic load that has a toxic action to some organisms. Some microorganisms that metabolize sugars develop more rapidly at the expense of other living organisms. The high phosphorus content accelerates the growth of algae resulting in eutrophication. Some aquatic organisms (i.e., the river fish *Gambusia affinis* and some crustaceans) become severely intoxicated even at exposures corresponding to 1 liter of unprocessed OMWW into 100,000 liter of circulating water (Fiorentino et al., 2004).

OMWW dispersion on the ground and its subsequent metabolization (by microorganisms, insects, earthworms, etc.) to humic extracts or acids also could lead to soil enrichment with nutrients (i.e., organic matter, nitrogen, phosphorus, and potassium) and a low-cost source of water. However, OMWW high concentration of potassium affects the cation exchange capacity of the soil, leading to change of environmental conditions for soil microorganisms and consequently to changes in the fertility of the soil. Soil porosity also could be affected. Other possible negative effects include the immobilization of available nitrogen and decreased available magnesium, perhaps because of the antagonistic effect on potassium.

Finally, no land disposal of OMWW should be done without taking under consideration its severe phytotoxic and antimicrobial properties that may damage the existing crops (Cox et al., 1997; Paredes et al., 1999; Sierra et al., 2001).

The phytotoxic and antimicrobial properties of OMWW have been mainly attributed to its phenolic content and some organic acids, such as acetic and formic acid, that are accumulated as microbial metabolites during storage. Its direct application on plants inhibits the germination of different seeds and early plant growth of different vegetable species and may cause leaf and fruit abscission as well. Different types of crops show different reactions to OMWW spreading and some of them may tolerate a certain amount of OMWW during early growing stages (Rinaldi et al., 2003).

As far as its antimicrobial activity is concerned, catechol, 4-methyl-catechol, and hydroxytyrosol are its most active compounds against a number of bacteria and fungi. Several authors have reported OMWW activity against soil gram(+) spore bacteria like *Bacillus megaterium ATCC 33085, Geotrichum, Rhizopus, Rhizoctonia, Bactrocera oleae,* and *Pseudomonas syringe* (Oikonomou et al., 1994) .

These biotoxic properties of phenols in OMWW constitute a significant inhibitor of the biological processes that take place in common wastewater treatment plants. Such plants do not present the desired performance with treatment of OMWW. Thus, the treatment of straight OMWW together with domestic sewage is not economically feasible, because of serious overload of the sewage treatment plant. So, research is oriented toward more complex treatment methods that usually demand higher capital or operational costs.

8.2.2. Other Problematic Characteristics of OMWW

The problems mentioned above make the technological design of an OMWW treatment plant difficult. Factors that make the economic design of such a plant difficult is the intense and seasonal production of the waste (maximum 4 months each winter), the great variability both of synthesis and quantity, the high regional scattering of olive mills, and the small size of the majority of them in the olive oil-producing regions.

Because of its highly variable input and seasonal production, storage facilities for the excess quantities of waste produced during winter months should be considered during design of a treatment plant. Similar design problems would arise in holiday resorts, where the population also can increase by an order of magnitude.

Olive mills are usually small-scale enterprises that cannot afford the costs of a proper wastewater treatment unless the treatment is a very simple and cheap procedure. Most treatment technologies, however, require high investment costs and a high level of technological know-how. Thus the design of centralized treatment plants is considered more suitable to treat OMWW produced by several mills. This creates a burden to operational costs, as high transportation costs due to high geographic scattering must be taken into account. In some cases, local conditions may call for separate treatment plants. Finally, serious nuisance due to the unpleasant odors and insects from OMWW may cause a serious difficulty at finding a suitable location of a treatment plant. All these factors introduce economic, technical, and organizational constraints that vary greatly from place to place, making the adoption of an environmentally compatible approach on a wide scale very difficult.

8.2.3. The Current Situation

As mentioned above, in all countries that produce olive oil the direct discharge of OMWW into the receiving natural water bodies is strictly forbidden, because of its detrimental effects on ecological balance. Direct discharge of OMWW in public sewers is also formally forbidden, because it causes corrosion to the pipes and builds up sediments. Nevertheless, because of the problems mentioned in the previous chapter, the most common practice followed today from the olive mills is the illegal, direct disposal of OMWW into nearby aquatic bodies, i.e. rivers, lakes, or even the sea.

In Spain, the government subsidized and promoted the construction of storage ponds to promote evaporation during the summer period. Around 1,000 evaporation ponds were constructed, which definitely improved the water quality but caused odor problems for the inhabitants of the region.

According to Italian environmental legislation, OMWW has to undergo treatment before their release into the environment. OMWW spreading on land is permitted under controlled conditions. Taking into account the potential considerable fertilizing value of OMWW, the possibility of using them as soil conditioners is also permitted. A new regulation allowing the reuse of OMWW in agriculture is now the only state regulation in force regarding OMWW and permits use of wet solid waste from the two-phase process as fertilizers on croplands. Such spreading on land must be known to the authorities and supported by a technical report.

In Greece, small olive mills serving local communities are extensively widespread. Extensive research is underway in research organizations and universities in order to safely dispose of the produced wastewater within a maximum period of 3 months after the campaign (Azbar et al., 2004).

8.3. QUANTITY AND SYNTHESIS OF THE WASTE

8.3.1. The Effect of the Production Process

As mentioned before, one of the major problems regarding OMWW disposal is that both its quantity as well as its synthesis show great variability depending on a number of unpredictable and diverse factors such as:

- type of olives,
- area under cultivation or arable soil,

- use of pesticides and fertilizers,
- harvest time, stage of maturity,
- climate, weather conditions, and
- type of olive oil extraction process.

In modern olive mills, the most common methods for extracting olive oil from the olive paste are the following:

- Pressing (traditional or classical batch system).
- Centrifugation (continuous).
  - Three-phase decanter.
  - Two-phase decanter.

A brief presentation of the two major continuous oil extraction systems is shown in Figure 8.2.

At the *traditional batch press process*, the quantity of added water during oil extraction is small (3–5 L/100 kg of olives processed). Thus the smallest quantity of liquid waste is produced, but the most concentrated as well. Besides, this technology gives higher levels of COD, polyphenols, and total solids compared to the waste produced from other processes. Due to the low temperature of extraction, the olive oil produced with this method is of very high quality.

During the *continuous three-phase decanter process*, the addition of warm water is required at the centrifugation stage (1.25–1.75 times more than at the press extraction) resulting in the production of increased volumes of OMWW and loss of

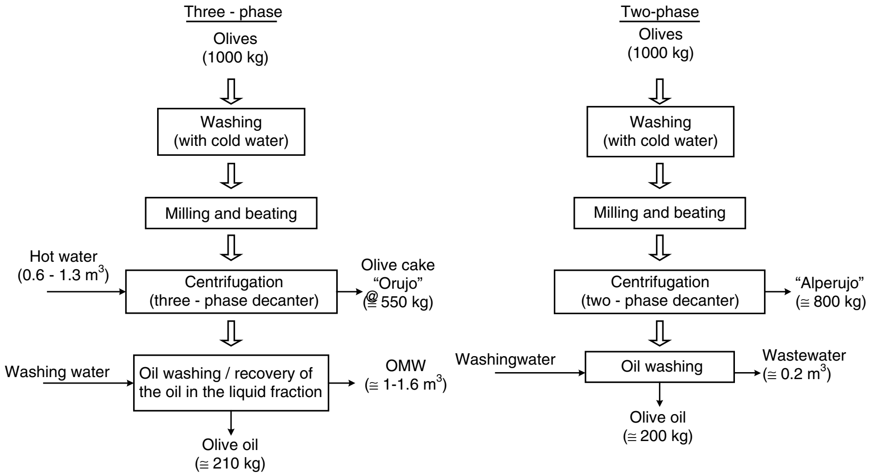

Figure 8.2. Comparison of the three- and two-phase centrifugation systems for olive oil extraction (Alburquerque et al., 2004).

valuable components (i.e., polyphenols) with the wastewater. The total solids content of the waste is approximately twice more than in classic press method and it is in suspended form.

The *two-phase extraction system* was developed during the 1990s in an attempt to minimize the volume of the waste produced and is widely adopted in Spain, where approximately 90% of the country's olive mills use this technology. The philosophy is the same as at the three-phase centrifugation system. The difference is that it uses no process water and delivers only two streams: olive oil and a single waste, a combination of olive husk and OMWW, i.e., a very wet olive cake, which is called ''alpeorujo.''

This modified extraction system is less complicated, consumes less energy, and yields higher-quality olive oil than the three-phase decanter. Nevertheless, although it is called ''*the ecological system*,'' because it reduces wastewater generation up to 80%, the problem remains unsolved, since a new, not yet fully characterized waste is produced with new difficulties in its treatment and disposal. Alpeorujo has much higher moisture content than olive husk (55–70% versus 20–25% for traditional press systems and 40–45% for the three-phase decanter) and a lot of polyphenols and polysaccharides that are absent from the olive husk produced with the other two processes. The high moisture content makes the drying of alpeorujo at seed oil refineries an economic burden. Polyphenols and polysaccharides cause problems to dryers because of caramelization and agglomeration effects. These problems during the seed oil extraction have forced manufacturers to perform a further purification step before drying alpeorujo, which greatly increases seed oil production costs. The new waste generated at this chemical extraction step is called ''orujillo'' and could be used as a fuel but more precise data are needed. So, the problem of alpeorujo disposal has not been fully resolved and research into new technological procedures that permit its profitable use is needed. The influence of the production process on OMWW characteristics is reflected in Table 8.2.

8.3.2. OMWW Synthesis

In Table 8.3 a compilation of literature data on synthesis of OMWW is presented. The most important organic constituents of OMWW are phenolic compounds, sugars, and some organic acids. Sugars vary from 1.6–4% w/v depending on the variety of olives, the climatic conditions and the production method used. The most commonly found sugars, in decreasing quantities are fructose, mannose, glucose, saccharose, sucrose, and some pentoses (Niaounakis and Halvadakis, 2004).

OMWW also contains exploitable quantities of oleanolic and maslinic acid, both acids with various biological effects (carcinogenic promoter-inhibitor effect, antihistamic effect, etc.). As far as inorganic compounds are concerned, it has high potassium content (≈ 4 g/L) and notable levels of nitrogen, phosphorous, calcium, magnesium, and iron compared to other organic wastes. Main anions are Cl^-, $PO_4^=$, F^-, and $SO_4^=$ depending on the extraction process.

Table 8.2. Influence of the production process on OMWW characteristics

Parameter	Press process	3-phase	2-phase	Reference
L OMWW/tn of olives		900–1,500	50–70	Aktas et al. (2001)
		500–1,500		Rozzi and Malpei (1996)
		500–1,400		Sierra et al. (2001)
	400	1,000		Improlive (2000)
	400–600	1,000–1,200	85–110	Caputo et al. (2003)
(% of weight of olives)	50	80–110		Mulinacci et al. (2001)
pH	4.5–5	4.7–5.2		Azbar et al. (2004)
	4.5 ± 0.3	4.8 ± 0.3		Aktas et al. (2001)
	4.5–5	4.5–5		Caputo et al. (2003)
COD (g/L)	120–130	40		Azbar et al. (2004)
	65.7 ± 27.1	103.4 ± 19.5	5–25	Aktas et al. (2001)
	125	50		Caputo et al. (2003)
BOD (g/L)	90–100	33		Azbar et al. (2004)
	90	40		Caputo et al. (2003)
TSS (%)	0.1	0.9		Azbar et al. (2004)
(g/L)	0.1	0.9		Caputo et al. (2003)
	2.7 ± 1.1	27.6 ± 5.1		Aktas et al. (2001)
VSS (%)	10.5	2.6		Azbar et al. (2004)
(g/L)	2.5 ± 1.1	24.5 ± 5		Aktas et al. (2001)
TS (%)	12	3		Azbar et al. (2004)
(g/L)	44.4 ± 13.8	78.2 ± 13.6		Aktas et al. (2001)
Sugars (%)	2–8	1		Azbar et al. (2004)
(g/L)	2.2 ± 1.7	4.7 ± 1.8		Aktas et al. (2001)
	4.5	1.5		
Total N (%)	5–2	0.28		Azbar et al. (2004)
(mg/L)	1.8	0.3		Caputo et al. (2003)
	43.7 ± 33.9	78.8 ± 39.6		Aktas et al. (2001)
Polyalcohols (%)	1–1.5	1		Azbar et al. (2004)
Pectin/tannin (%)	1	0.37		Azbar et al. (2004)
Polyphenols (%)	1–2.4	0.5		Azbar et al. (2004)
	1.7	0.63		Caputo et al. (2003)
(% (w/w) dry residue)		24	20.4	Lesage-Meesen et al. (2001)
(mg/L)		767.1	540.6	Stefanoudaki-Katzouraki and Koutsaftakis (1994)
Oil/grease (%)	0.03–10	0.5–2.3		Azbar et al. (2004)

8.3.2.1. Phenolic Content of OMWW

Olives are rich in simple and complex phenolic compounds, typical secondary plant metabolites, to which several antioxidant and free radical scavenging properties are attributed. During the olive oil extraction process, due to the chemical characteristics of polyphenols that are water-soluble, the partition between water and oil is different and the major proportion of these compounds goes from the olive pulp to the aqueous phase, that is the OMWW (i.e., <1% in the olive oil versus 18% in olives). OMWW phenolic content shows great variability both from the qualitative and quantitative point of view, depending on several factors, such as type of olive,

Table 8.3. Literature data on synthesis of OMWW

	Reference							
Property	Azbar et al. (2004)	Niaounakis and Halvadakis (2004)	Borsani and Ferrando (1996)	Paredes et al. (1999)	Sierra et al. (2001)	Galiatsatou et al. (2002)	Eroglu et al. (2004)	Al-Malah et al. (2000)
pH	3–5.9	4–6		4.8–5.5	4.5–6	4.9–6.5	4.86	4.52
Water (%)			83					
BOD (g/L)	23–100	35–110			35–100	15–120	17.88	13.2
COD (g/L)	40–220	40–220			40–195	30–150	72.20	320
Carbohydrates (%)			2–8	3.37–32.91		2–8		
Polyphenols (g/L)	0.002–80	0.5–24		1.32–3.99%	3–24	1.5–2.4	0.13	3.12
Fats, oils (g/L)	1–23		0.03–1%	0.55–11.37%	0.3–23	1.3		
Pectins (%)			1–1.5			1–1.5		
VOC (g/L)		25–45						
TS (g/L)	1–102.5						42.24	
SS (g/L)							3.48	2.17
N (g/L)	0.3–1.2			0.58–1.13%	5–15	0.5–2%		
K (g/L)		4	0.87% K_2O	3.30–6.94%	2.7–7.2		7.81	
P (g/L)			0.22% P_2O_5	0.06–0.32%	0.3–1.1			
Ca (g/L)				0.32–0.53%	0.12–0.75		0.55	
Na (g/L)				0.04–0.48%	0.04–0.90		0.41	
Mg (g/L)				0.06–0.22%	0.10–0.40		0.28	

stage of maturity, and most important type of production process. The extraction system does not seem to qualitatively alter the phenolic composition of olive oil, but it affects its concentration, with the two-phase decanter OMWW being the richest in quantity (Lesage-Meesen et al., 2001).

More than 30 different phenolic compounds have been detected in OMWW and reported by several authors. As far as their MW is concerned, two major categories are observed.

1. Phenolic monomers, flavonoids, not autoxidated tannins, and other compounds with $MW \leq 10kDa$.
2. Medium and high MW ($MW > 10kDa$) dark colored polymers resulting from the polymerization and autoxidation of phenolic compounds of the first group.

The color of OMWW depends on the ratio between the two groups. Their chemical synthesis divides them into three major categories:

1. Derivatives of cinnamic acid (cinnamic acid, o-, p- coumaric acid, caffeic acid, ferrulic acid).
2. Derivatives of benzoic acid (benzoic acid, protocatechuic acid).
3. β-3,4-dihydroxyphenylethanol derivatives such as tyrosol and hydroxytyrosol.

Other phenols reported to be found in OMWW are catechol, 4-methylcatechol, p-cresol, resorcinol, oleuropein, dimethyloleuropein, verbascoside, and some phenolic acids such as vanillic acid, protocatechuic acid, veratric acid, syringic acid, cinnamic acid. Among the flavonoids contained in OMWW are apigenin, cyanidin flavone, anthocyanin, luteolin, quercetin etc (Ramos-Cormenzana et al., 1996; Lesage-Meesen et al., 2001).

Hydroxytyrosol (3,4-dihydroxyphenylethanol) stands out both because it is the most abundant phenol in OMWW and because of its great bioantioxidant activity. It is produced from the enzymatic hydrolysis (by a glucosidase) of oleuropein, the major polyphenol of the olive fruit. Oleuropein degrades gradually into elenolic acid and hydroxytyrosol, as olives mature, but the majority of hydroxytyrosol quantity in OMWW is produced during the extraction of olive oil. That is why some researchers do not detect oleuropein in OMWW.

8.3.2.2. Properties of Phenols Found in OMWW

Hydroxytyrosol, 2-hydroxytyrosol, tyrosol, oleanolic acid, and maslinic acid, flavonoids, anthocyanins, and tannins that are found in OMWW are considered as natural antioxidants with considerable commercial and economic interest. The most interesting one appears to be hydroxytyrosol, a compound of high added value, due to its antioxidant and potentially beneficial (to human health) properties. Results of *in vitro* research demonstrate that hydroxytyrosol inhibits human LDL oxidation, scavenges free radicals, inhibits platelet aggregation and the production of leucotriene for human neutrofils, and confers cell protection. It also acts against both gram (+) and gram (−) bacteria. It could be used as a food preservative, in agriculture for the protection of olive trees, and in cosmetics industry in antiaging preparations (Allouche et al., 2004; Visioli et al., 1999). Also, phenolic substances are the major contributors to OMWW's antimicrobial properties.

8.4. SUGGESTED OMWW TREATMENT PROCESSES

As can be understood from its synthesis, OMWW possesses a double nature. It is a strong pollutant and at the same time a possible source of valuable components, such as polyphenols, flavonoids, anthocyanins, inorganic trace elements, etc., that could be isolated (removed) and economically exploited.

Research is oriented toward flexible and efficient treatment solutions that could ensure the detoxification of the waste compensating high capital and operating costs with the possibility of recovering and recycling some valuable components. According to these, the numerous treatment processes that have been proposed so far could be classified in the following categories:

- Detoxification processes.
- Processes that aim at the production of various products.
- Integrated processes aiming at energy recovery.
- Combined processes.

8.4.1. Detoxification Processes

These are processes that aim at ''cleaning'' the waste so as to allow its safe, subsequent disposal at water or soil reservoirs. The most important are biological and physicochemical processes.

8.4.1.1. Biological Processes

Biological processes use microorganisms to break down the chemicals present in OMWW. They are divided into *aerobic* and *anaerobic* processes according to the type of the microflora used.

Aerobic processes can operate efficiently only if the concentration of the feed is relatively low; i.e., of the order of 1 g COD/liter. Higher concentrations can be tolerated only if the plant operates at a long hydraulic retention time or/and with high recycle ratio; both possibilities are uneconomical for a treatment plant. Also, the aerobic treatment of concentrated wastewaters yields huge volumes of excess secondary sludge that has to be removed from the system. At last, it is very difficult using aerobic processes to reach the required removal efficiency of pollutants such as polyphenols and lipids. For all the above reasons, aerobic processes are unsuitable for direct and efficient treatment of OMWW. They can be used as pretreatment or posttreatment steps to increase the efficiency of the main treatment process used.

Anaerobic digestion consists of a series of microbiological processes that convert organic compounds into methane and carbon dioxide. Although a pretreatment or posttreatment step is also needed, anaerobic treatment is considered most suitable for OMWW detoxification. The most important reasons for this choice are the feasibility to treat wastewaters with high organic load, such as OMWW, the low energy requirements, the production of methane that may be exploited after suitable treatment, the production of significantly less waste sludge (than aerobic processes), and the ability to restart easily after several months of shut down (Niaounakis and Halvadakis, 2004; Rozzi and Malpei, 1996).

8.4.1.1.a. Anaerobic Processes. Anaerobic processes are driven mostly by bacteria and have three major steps: In the first stage, anaerobic bacteria hydrolyze complex organic compounds, such as polysaccharides and polyphenols to their monomers (simple sugars and phenols, respectively). These molecules are converted into organic acids such as acetic, lactic, and formic acids and alcohol by acetogenic bacteria during the second stage of the process. In the last stage, methanogenic bacteria, which are characterized by their sensitivity to pH and temperature changes, convert the organic acids into biogas (a mixture of 60–80% methane and other gases, mainly carbon dioxide) (Sabbah et al., 2004).

Anaerobic processes are affected by temperature, retention time, pH, H_2 partial pressure, the chemical composition of the wastewater, and the quantity of toxic substances present. The process usually takes place under thermophilic or mesophilic conditions. Retention time varies between 10 and 35 days and pH must be controlled, because acetogenic bacteria tend to lower it and methanogenic bacteria are sensitive to pH variations.

Several technologies have been tested, including upstream anaerobic sludge blanket reactor (UASB), contact reactors, anaerobic filters (upstream and downstream), anaerobic baffled reactors (ABR), and two-stage systems that separate acidogenesis and methanogenesis processes (Azbar et al., 2004; Borja and Gonzalez, 1994; Dalis et al., 1996; Rozzi and Malpei, 1996; Zouari, 1998; Zouari and Ellouz, 1996).

UASB-type reactors and anaerobic filters are suitable for high volumetric pollution loads (5–15 kg COD/m^3 day). COD removals of 80% and 60–65%, respectively, have been reported but in both cases a high dilution ratio is required (1/8 and 1/5) that raises operational costs. Anaerobic filters require very little process control and 75% reduction of phenols has been reported (Dalis et al., 1996). Compared to contact reactors, greater production of methane and elimination of mechanical mixing, settling, and return of the sludge has been reported (Borja and Gonzalez, 1994). Contact reactors can operate at higher feed concentrations (up to 60 g COD/liter) with COD removal efficiencies greater than 80% but only at very low loading rates (<5 kgCOD/m^3 day) (Rozzi and Malpei, 1996).

A general problem encountered with anaerobic digestion of OMWW is that both the addition of alkali substances to neutralize pH and of substances that are sources of nitrogen such as urea or ammonia are necessary. The anaerobic microflora also shows limited efficiency in the removal of aromatics, particularly condensed tannins. Finally, scaling up these processes proves to be extremely difficult. Growth rates of anaerobic microorganisms are appreciably lower than those of aerobic ones and their metabolic degradation pathways require several different microbial populations in series which make process control and stability very delicate (Mechichi and Sayadi, 2004).

All these constraints make the use of pretreatment or posttreatment of anaerobic digestion necessary. Pretreatment methods proposed so far include dilution of the waste, gravity settling, sand filtration, centrifugation, adsorption, membrane processes, physicochemical treatments ($Ca(OH)_2$, NaOH, Na_2CO_3, Fenton's reagent, etc.), and aerobic degradation (Sabbah et al., 2004; Zouari, 1998).

As mentioned before, strong dilution of the waste is necessary in most of the types of anaerobic digesters. Some researchers have proposed that if OMWW is mixed with another organic effluent, definitely a more economic dilution media than water, it will also become enriched in its limiting nutrients such as nitrogen and neutralized without the addition of chemicals. At locations where the polluting load due to olive industry is comparable or lower than domestic sewage load, OMWW can be treated in conventional domestic sewage digesters if mixed with this effluent. Rozzi and Malpei (1996) and Marques (2001) studied the combined treatment of OMWW with piggery effluent, where no chemical correction was needed and 70–80% COD removal was achieved, but decolorization of the waste was not sufficient. The produced effluent could be used as irrigation water.

8.4.1.1.b. Aerobic Processes. The combination of aerobic and anaerobic treatment is extensively studied, as there are aerobic consortia that grow on undiluted or diluted OMWW and are capable of metabolizing and removing its aromatic compounds. In Table 8.4, some data collected from the literature are presented.

Of all the above microorganisms particular interest has been shown in the N_2-fixing bacteria *Azotobacter* and several white rot basidiomycetes, such as *Pleurotus*. Fungi of this kind have ligninolytic enzymes and can degrade phenolic substances of OMWW that have structural relationships with lignin. However, the majority of phenolic compounds removed are simple monomers, whereas polymerized molecules such as tannins degrade more difficultly. This happens because these compounds adsorb strongly to mycelia and extracellular enzymes so that their biodegradation is not possible.

In all cases, a certain pretreatment is necessary (dilution, thermal treatment, etc.) and the resulting effluent always needs additional treatment before it could be safely disposed off. So, aerobic processes alone are not effective enough for the detoxification of OMWW.

Table 8.4. Aerobic microorganisms studied for OMWW degradation

Microorganism	Results	Comments	Reference
Aspergillus niger	35–65% COD reduction	Biofertilization	Cereti et al. (2004) Garcia et al. (2000)
Azotobacter vivelandii	90–96% COD reduction	Biofertilization	Piperidou et al. (2000)
Yarrowia lipolytica	2–42% COD reduction	Production of enzymes and microbial metabolites	Lanciotti et al. (2004)
Pleurotus ostreatus	Up to 78% phenol removal	Diluted or thermally processed OMWW	Fountoulakis et al. (2002) Aggelis et al. (2003)
Phanerochaete chrysosporium		Comparison concerning phenol removal capacity	Garcia et al. (2000)
Aspergillus terreus			
Geotrichum candidum	65% COD removal, 75% color removal	Fresh or stored OMWW	Assas et al. (2002)
Panus tigrinus		Removal of 4-hydroxy substituted simple phenols	D' Annibale et al. (2004)
Pycnosporus coccineus			Jaouani et al. (2003)
Pleurotus sajor caju	75% color removal		Jaouani et al. (2003)
Coriolopsis polyzona	75% color removal		Jaouani et al. (2003)
Lentinus tigrinus			Jaouani et al. (2003)
Candida tropicallis	62.8% COD removal; 51.7% phenols removal		Fadil et al. (2003)
Pleurotus pulmonarium		Production of *Pleurotus basidiomata* only diluted OMWW	Zervakis et al. (1996)
Pleurotus eryngii			
Ankistrodermus braunii	12% phenols reduction	Fresh OMWW or reverse osmosis fraction	Pinto et al. (2003)
Scenedesmus quadric cauda (microalgae)			

8.4.1.2 Physicochemical Processes

8.4.1.2.a. Neutralization, Precipitation/Flocculation. These processes involve the use of additional chemicals in order to destabilize the suspended and colloidal matter of OMWW and form an insoluble solid that can be removed easily from the waste. Oil, suspended solids, COD, and BOD are decreased in this way. Destabilization of these colloids can be achieved either by reducing or increasing pH (neutralization) or by the addition of a precipitate-inducing agent (precipitation/ flocculation).

Reduction of pH to the point of zero charge ($pH = 2–4$) has attracted little attention so far, although apart from colloids destabilization, it also is expected to contribute to the acid hydrolysis of oils to fatty acids which can be easily separated from effluents. On the contrary, the use of lime (CaO) to increase pH at about 11 has been the subject of several studies (Mitrakas et al., 1996).

By treating OMWW with lime, oil, and COD reduction, decolorization, and important reduction in odor emissions are achieved. The liquid obtained after treatment contains no phytotoxic substances and it can be treated further more easily. The major disadvantage of this process is that large quantities of sludge with high pollution load are produced leading to serious disposal problems.

The most important inorganic flocculents that have been used for OMWW treatment are ferric and ferrous chloride, ferric sulfate, and aluminium sulfate. All these reagents should not be used if the precipitated material is to be used as animal feed (Niaounakis and Halvadakis, 2004).

The processes described above, although simple and cheap, are more suitable as pre-treatment methods because the treated liquid still has a high polluting load. Considerations also arise for the disposal of the precipitated material produced.

8.4.1.2.b. Oxidation processes. Several oxidizing agents have been tested for OMWW treatment like hydrogen peroxide, ozone, chlorine, chlorinated derivatives (i.e., chlorine dioxide, sodium hypochloride, etc.), or a combination of them. Ozone and hydrogen peroxide systems are preferred because of their high oxidizing potential and the possibility of operating under atmospheric pressure and ambient temperatures without problematic decomposition products of the oxidizing agent (Niaounakis and Halvadakis, 2004).

In an attempt to increase oxidation rates, advanced oxidation processes have evolved (AOPs) where the combinations of oxidants as well as the combination of oxidants with ultraviolet radiation are used. They are characterized by the production of the highly oxidative $HO^{\cdot}$ radical at ambient temperature via a number of photochemical or non-photochemical pathways. This powerful radical is able to completely transform organic compounds to CO_2.

The principal AOPs used for OMWW treatment are Fenton's reagent reaction (H_2O_2 plus a ferrous salt) (Gernjak et al., 2004; Rivas et al., 2001), O_3 plus UV radiation (Javier-Benitez et al., 1997), H_2O_2 plus UV radiation, H_2O_2/O_3 + UV radiation and photocatalysis, where solar energy also may be used (Gernjak et al., 2004).

Most of the classic oxidation processes lack effectiveness due to either the high cost of antioxidants or the low interval of COD for which the system is suitable. AOPs manage a great COD reduction but their operating costs are considerably high. It could be said that chemical oxidation emerges as a suitable alternative, when biological degradation is not applicable.

8.4.1.3 Thermal Processes

Numerous methods and variations are included in this category and what they have in common is that the concentration of OMWW is achieved either by a manmade heat source or by a natural source of thermal energy (air, sun). The most important thermal processes are evaporation, distillation, lagooning (natural evaporation), combustion, and pyrolysis.

Several distillation and evaporation processes such as vacuum, multiple effect, and flash evaporation already used in desalination and food industry have been tested on OMWW. Although these processes are claimed to reduce significantly the volume of the waste (reduction by 70–75%) great differences exist in bibliography concerning their effectiveness, because it depends on many factors such as extraction process, olive ripening, and especially storage time of the waste (Niaounakis and Halvadakis, 2004).

The main drawback of these processes is related to the posttreatment and disposal of the produced emissions: The distillate/condensate contains, apart from water, an appreciable fraction of volatile compounds such as alcohols and volatile acids. These compounds make the condensate too acidic (pH 4–4.5) and with high BOD (>4 g/liter) and COD (>3 g/liter) values making necessary an additional treatment prior to discharge or reuse. The concentrated paste has a high concentration of the polluting organic load, so its combustion induces air pollution (Niaounakis and Halvadakis, 2004; Rozzi and Malpei, 1996). All these processes also have extremely high costs, due to the great energy consumption necessary and the equipment costs that has to be made of materials resistant to corrosion.

Natural evaporation of OMWW in ambient air with the use of solar energy in evaporation ponds or storage lakes (lagoons) has much lower energy costs and it is a simple procedure. It is one of the first processes used and removal of COD ranging from 20–30% to 75–80% has been reported. The waste has a residence time of 7–8 months in the lagoons and large land surface areas are required (about 1 m^3 for each 2.5 m^3 of OMWW). Several ecological concerns arise including the possibility of groundwater contamination if the bottom of the lagoon is not properly lined against infiltration and leakage and the emissions of methane in the atmosphere due to the anaerobic fermentation of the waste that occurs in the lagoons. These lagoons should be located far enough from residences to avoid the insect and odor nuisances (Azbar et al., 2004; Rozzi and Malpei, 1996).

Combustion and pyrolysis are radical and destructive techniques that eliminate any possibility of further use of OMWW. Both are very expensive methods with high energy requirements, pretreatment of the waste, and posttreatment of the gaseous emissions necessary and expensive equipment needed. For these reasons, they are more suitable for strong wastewaters, concentrated solutions of OMWW, or for olive husk.

In an attempt to minimize the energy costs of thermal processes, several researchers have proposed the combined thermal treatment of OMWW and olive husk. In these processes the required heat for the evaporation of OMWW is produced by the combustion of OMWW concentrated evaporation residue or olive husk or a mixture of these wastes. A critical parameter affecting the feasibility of this disposal approach is the degree of mixing of olive husk and OMWW. As such disposal systems are characterized by a rather high technological level requiring remarkable capital investments and qualified personnel, they are more suitable for centralized treatment plants that serve a large number of mills and gain benefits from the economy of the scale (Caputo et al., 2003; Vitolo et al., 1999).

8.4.1.4 Membrane Processes

Membrane processes also are tested for use in treatment of OMWW because they are effective for separation of oil-water mixtures without adding solvents. Ultrafiltration is the widely considered membrane process for this purpose, while microfiltration and reverse osmosis also have been tested. Two different phases are obtained: the retentate (concentrate) and permeate. Colloidal particles, lipids, and various macromolecules (molecular weights of the order of 10,000 to 100,000 Da) can be prevented from passing through the membrane to the permeate.

With ultrafiltration, only a small amount of retentate (waste) is produced (permeate is 90–95% of the volume of the feed) and very high removal of lipids is achieved. Also, by choosing the appropriate pore size of the membrane used, the composition of the permeate can be controlled. A separation of fats that are rejected by the membrane from salts, sugars, and phenolic substances that pass to the permeate can be achieved, enabling the economic exploitation of these substances.

The capital costs of this operation are extremely high and it is a complicated procedure that needs qualified personnel. The main problem is that severe fouling of the membrane occurs very easily, strongly reducing the membrane efficiency due to gelling substances contained in OMWW. The removal of these substances in a number of pre-treatment steps is therefore absolutely necessary. Also, only a limited concentration factor is achieved and dissolved components such as those determined by the parameter COD are only insufficiently removed and both retentate and permeate still have high COD concentrations and have to be further processed prior to disposal.

For all the reasons stated above, membrane processes are not suitable for the treatment of strong OMWW such as from traditional press systems because of their limited efficiency and their high costs, which make their use just for detoxification purposes economically unprofitable. They can be used as pretreatment steps in processes that aim at the recovery of valuable, expensive components such as polyphenols and flavoring agents from OMWW. Passing through the membrane, the waste becomes concentrated in these substances making their subsequent extraction easier and more economical while the high costs of the membranes are compensated by the high added value of the product. The retentate that has a poor polyphenolic and a high oil content can be used as fertilizer or animal feed after appropriate treatment.

8.4.2. Processes That Aim at the Production of Various Products

OMWW may be regarded as an inexpensive source of inorganic and organic compounds to be recovered because of their potential economic interest or their ability to be transformed into products for use in agriculture, biotechnology, and the pharmaceutics industry as well as in the food industry.

8.4.2.1. Production of Fertilizers (Recycling of the Waste at Land)

8.4.2.1.a. Biofertilization or Bioremediation. OMWW should not be directly applied on soil and crops because of its phytotoxic properties. But with certain treatment it could be converted into a useful fertiliser and soil conditioner, due to its high content of water, organic matter, and plant nutrients. N_2-fixing bacteria of the genus *Azotobacter* utilize phenols, sugars, organic acids, etc., of OMWW as a carbon source, i.e., they degrade them and convert atmospheric nitrogen into several organic nitrogenous compounds.

So, the process of treating OMWW with an enriched aerobic microbial population of this kind results in a nonphytotoxic thick liquid that could be characterized as an organic soil-conditioner biofertilizer with the following characteristics:

1. Contains exopolysaccharides (microbial metabolites) that favor the formation of stable aggregates.
2. Contains all the major and trace plant nutrients that were originally present in OMWW.
3. It is biologically enriched via the N_2-fixation mechanism with organic forms of nitrogen.
4. Contains plant growth-promoting factors such as auxins and cytokinins produced by the bacteria metabolic activity.
5. It is a soil microbial inoculant that allows the establishment of favorable to plants rhizospheric microorganisms and enhances soil suppressiveness.

In this way the waste is fully recycled to land through an environmentally ‘‘clean’’ process while energy and water savings are also achieved at the same time (Chatjipavlidis et al., 1996; Flouri et al., 1994; Ramos-Cormenzana et al., 1995).

8.4.2.1.b. Composting. The term ‘‘composting’’ refers to the process of controlled aerobic biological degradation of organic substrates (wastes, residues, etc.). The microorganisms used for this purpose utilize the organic substrate for growth and multiplication in two stages: A thermophilic stage characterized by the quick growth of bacterial populations and subsequent quick degradation of the organic load and a mesophilic stage where growth of fungi takes place and the rate of organic load degradation is much lower. By this process, stabilized, humic substances and mineral salts-containing material are produced that can be used for soil fertility and plant production improvement.

In the case of OMWW composting, OMWW quantities are added to the solid substrate during the thermophilic stage to replace the water evaporated. In this way, composting time is prolonged, the solid substrate becomes enriched in organic matter (that is necessary for the microbial growth), and OMWW is evaporated or consumed. Either fresh OMWW or sludge from evaporation ponds can be used and OMWW sludge shows greater humification rates, stability, and maturity.

Suitable carriers for OMWW are considered those that have heavy loads of N, so as to compensate the relatively low N content of OMWW and neutral or slightly acid pH to minimize N losses. So far, several plant waste carriers have been studied such as cotton waste, maize straw (Cegarra et al., 1996; Paredes et al., 1999), sugar cane bagasse, spent mushroom compost, barley straw, grape marc, and rice hull (Cegarra et al., 1996). Solid wastes from the olive oil industry and olive orchard operations, such as extracted olive press cake and olive tree leaves and branches also have been used as carriers in a pilot plant and a commercial large-scale plant constructed in Crete, Greece (Manios et al., 2004; Parlavantza et al., 1994). Finally, the use of animals' manure (such as poultry manure) and urban wastes that are rich in N have been studied (Paredes et al., 2001). Although use of OMWW as a fertilizer appears to be a viable alternative, it is not sufficient to cope with the enormous quantities of OMWW produced.

8.4.2.2. Recovery of Antioxidants

The olive fruit is rich in simple and complex water-soluble compounds with potential antioxidant properties. The most important of them are polyphenols, flavonoids, anthocyanins, tannins, oleanolic acid, and maslinic acid.

Polyphenols in OMWW have shown to be antioxidant, antibiotic, antimicrobial, and antifungal activity. Formulas of these olive-derived substances can be used as nutrition supplements or skin cosmetics. Due to their antimicrobial properties, they are also used as antimicrobial agents in detergents and rinsing and cleaning agents. Hydroxytyrosol is the most active component of them and it possesses great economic interest due to its remarkable pharmacological and antioxidant properties. It can be used as a food preservative and in pharmacology and cosmetology in topical preparations with anti-aging and anti-inflammatory action. Oleanolic acid regulates cholesterol levels in blood and balances body weight. Maslinic acid has been widely investigated during the last years and it seems to possess anti-inflammatory and antihistaminic activity. It also could be used in pharmacology as an inhibitor of AIDS virus. Finally, anthocyanins are used as natural food colorants (Ramos-Cormenzana and Monteoliva-Sanchez, 2000).

There are scarce data in the literature concerning methods of extraction of antioxidants of high added value from OMWW because most of these processes are patented. The most widely used are solvent extraction (both liquid–liquid and solid–liquid extraction) and adsorption in adsorbent resins. As a pretreatment step, selective concentration of the waste by ultrafiltration or reverse osmosis can be used. For the purification and separation of these substances from the mixture of antioxidants extracted from OMWW, chromatographic methods are used.

Liquid–liquid extraction is a simple and convenient alternative for this purpose. Polar solvents are best for extraction of polyphenols from OMWW and the yield of extraction increases with increasing polarity of the solvent. Among various polar solvents so tested are methyl isobutyl ketone, methyl ethyl ketone, diethylether, and ethyl acetate, the latter of which is considered the most suitable. Apart from the type of solvent used, other factors affecting the process efficiency are the pH of OMWW (better when acidic), the ratio of solvent/waste, and the number of theoretical steps in batch systems (Allouche et al., 2004; Visioli et al., 1999).

Adsorption is the attachment of dissolved compounds (adsorbate) from polluted waters to a solid substance (adsorbent) as a result of attractive interaction of the molecules of the adsorbate with micropores or macropores of the adsorbent having comparable dimensions to that of the molecules. In the case of OMWW, adsorbates are polyphenols and tannins. The most widely used adsorbents for this purpose are activated carbon, activated clay, and superabsorbent polymers.

Activated carbon adsorption installations are associated with extremely high costs coming from both the high initial cost of the material and from subsequently high operational costs. A possible solution to this economic burden could be the use of activated carbons produced by olive stone and solvent-extracted live pulp, inexpensive by-products of the olive oil industry. In this way, the volume of solid waste also could be reduced (Galliatsatou et al., 2002). The use of activated clay is another cheap alternative with maximum removal of polyphenols about 81% and 71% for organic matter (Al-Malah et al., 2000).

8.4.2.3. Production of Biopolymers

The production of biopolymers from OMWW is a very interesting alternative that has been studied during the last years due to the high added value and excellent properties of these substances. Research is oriented toward two main categories of these substances: exopolysaccharides and polyhydroxyalkanoates.

Exopolysaccharides are extracellular polysaccharides that are derived from specific microorganisms under stress conditions. They possess great rheological properties such as great solubility in water, increase of viscosity of a solution even at small concentrations, pseudoplasticity and good stability in solutions. The most important of them, from the economical point of view, are xanthan and pullulan (Ramos-Cormenzana and Monteoliva-Sanchez, 2000).

Pullulan is produced by the fungus *Aureobasidium pullulans*. OMWW is a good quality substrate for its production and production yield of 8 g/liter of a solution of OMWW/water 1:3 has been reported (Ramos-Cormenzana et al., 1995). Xanthan is produced by *Xanthomonas campestris*. Concentrations of OMWW in the substrate of the microorganism greater than 60% have an inhibitory effect. In more diluted substrates, the maximum xanthan production reported is 7.7 g/liter (Lopez et al., 2001; Lopez and Ramos-Cormenzana, 1996).

Polyhydroxyalkanoates (PHA) are reserve polyesters that are accumulated as intracellular granules in a variety of bacteria under unbalanced growth conditions, i.e., in the excess of a carbon source combined with limited concentration of another vital nutrient such as O_2, N_2, or phosphate. They can be used in the production of completely biodegradable plastics and in the preparation of micro- or nanocapsules that permit the controlled release of an active compound of a medicine so as to prolong its action (Ramos-Cormenzana and Monteoliva-Sanchez, 2000).

The production of these substances is extremely expensive (15–30 $ cost for 1 kg produced) because of the substrates used. The use of OMWW as substrate is a very economical alternative. Strains of *Azotobacter chroococcum* are studied for this purpose. Results report PHA produced up to 50% of the cell dry weight after 24 hours in medium supplemented with OMWW (Gonzalez-Lopez et al., 1996).

8.4.2.4. Production of Biogas

Biogas contains methane and CO_2 and can be used as an energy source like natural gas and other calorific gases. It is produced during the anaerobic fermentation of wastewaters. Almost 80% of organic compounds of OMWW are biomethanizable. Theoretically, a yield of $37\,m^3$ of methane per m^3 of OMWW could be achieved, but on applying anaerobic fermentation to this wastewater, the high concentration of polyphenols inhibits the normal development of biomethanization. As explained in a previous chapter, by combining unaerobic treatment with an aerobic step where specific microorganisms eliminate the phenolic content, the yield of biogas production can be increased (Fiestas Ros de Ursinos and Borja-Padilla, 1996; Niaounakis and Halvadakis, 2004).

8.4.2.5. Production of Animal Feed

Olive cakes or solid residues of various OMWW processes could be used in animal feeding, as they are rich in oil, carbohydrates, and proteins. Problems arise from OMWW's high concentration of potassium and phenolic compounds which are anti-digestive factors.

This problem could be eliminated and the nutritive value of these wastes improved by special chemical treatments such as with sodium hydroxide and ammonia (Molina Alcaide and Nefzaoui, 1996).

8.5. CONCLUSIONS

OMWW treatment and disposal is a problem with great complexity due to the strong nature of the waste and several economical, technical, and organizational constraints involved in the olive oil sector. Practically, all treatment processes developed for domestic and industrial wastewaters have been tested on OMWW but none of them appeared suitable to be generally adopted.

All the approaches so far, although technically successful, lack economic viability. This is because up to now the emphasis has been on treating OMWW like all other wastes, i.e., on reducing polluting loads to legally accepted levels for disposal to the environment. To achieve this goal, sophisticated technical solutions are required that the majority of the small-sized and high geographically scattered olive mills cannot afford.

So, the future olive oil waste management strategy should be toward a combination of detoxifying OMWW and utilizing it, at the same time, for producing valuable by-products. In this way, high costs of detoxification could be compensated. This is the case with the large amounts of phenolic compounds present in OMWW. They constitute the major obstacle in the detoxification of OMWW, while they are products of high added value at the same time. So, the trend now is toward turning this problem to an economic benefit by extracting these compounds. The optimal solution for OMWW treatment will eventually depend on local factors in each and every separate case. However, process approaches that are economically sustainable will constitute the core of the waste treatments.

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