

# 17

## Olive Oil Waste Treatment

**Adel Awad and Hana Salman**

*Tishreen University, Lattakia, Syria*

**Yung-Tse Hung**

*Cleveland State University, Cleveland, Ohio, U.S.A.*

### 17.1 INTRODUCTION

The extraction and use of olive oil has been linked to Mediterranean culture and history since 4000 BC. Several terms used today are reminders of this ancient heritage. For example, the Latin words *olea* (oil) and *olivum* (olive) were derived from the Greek word *elaia*. As a dietary note, olive oil is high in nutrition, and appears to have positive effects in the prevention and reduction of vascular problems, high blood pressure, arteriosclerosis, thrombosis, and even some types of cancer [1].

The social and economic importance of the olive production sector may be observed by considering some representative data. In the European Union (EU), there are about 2 million companies related to olives and olive oil. Worldwide olive oil production is about 2.6 million tons per year, 78% (about 2.03 million tons) of which are produced in the EU (main producers: Spain, Greece, and Italy). Other main producers are Turkey (190,000 tons), Tunisia (170,000 tons), Syria (110,000 tons), and Morocco (70,000 tons). More than 95% of the world's olives are harvested in the Mediterranean region. In Spain alone, more than 200 million olive trees out of the total world number of 800 million are cultivated on an area of approximately 8.5 million ha. Within Spain, 130 million olive trees are found in Andalusia, where about 15% of the total arable land is used for olive cultivation [2].

According to the FAOSTAT database [3], the total waste generated by olive oil production worldwide in 1998 was 7.3 million tons, 80% of which was generated in the EU and 20% generated in other countries. In Spain, the top olive oil producer, the generated waste in 1998 alone was 2.6 million tons, or about 36% of the waste generated worldwide.

Approximately 20 million tons of fresh water are required for olive oil production in the Mediterranean area, resulting in up to 30 million tons of solid–liquid waste (*orujo* and *alpeorujo*) per year. By comparison, the annual amount of sewage sludge in Germany is 55 million m<sup>3</sup>, with 5% dry solid matter content [4].

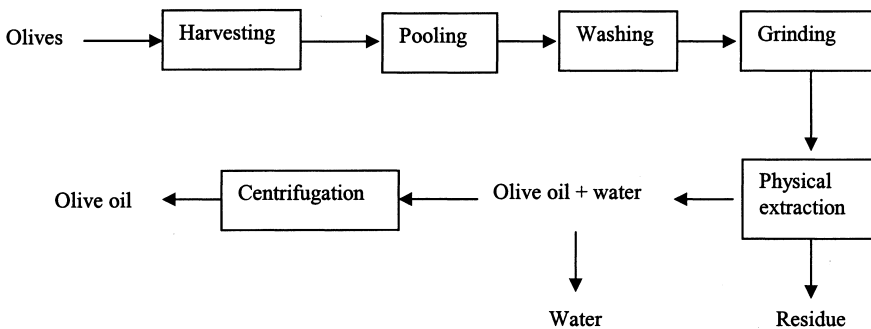
## 17.2 OLIVE OIL MILL TECHNOLOGY

The olive oil extraction industry is principally located around the Mediterranean, Aegean, and Marmara seas, and employs a very simple technology (Fig. 1). First, the olives are washed to remove physical impurities such as leaves, pieces of wood, as well as any pesticides. Afterwards, the olives are ground and mixed into paste. Although a large variety of extracting systems are available, two methods are generally employed: traditional pressing and modern centrifuging. Pressing is a method that has evolved since ancient times, while centrifuging is a relatively new technology. Figures 2 and 3 are schematic drawings of the two systems. Figure 2 represents the traditional discontinuous press of olive oil mills, while Fig. 3 represents more recent continuous solid/liquid decanting system (three-phase decanting mills). Both systems (traditional and three-phase decanter) generate one stream of olive oil and two streams of wastes, an aqueous waste called *alpechin* (black water) and a wet solid called *orujo*. A new method of two-phase decanting, extensively adopted in Spain and growing in popularity in Italy and Greece, produces one stream of olive oil and a single stream of waste formed of a very wet solid called *alpeorujo*.

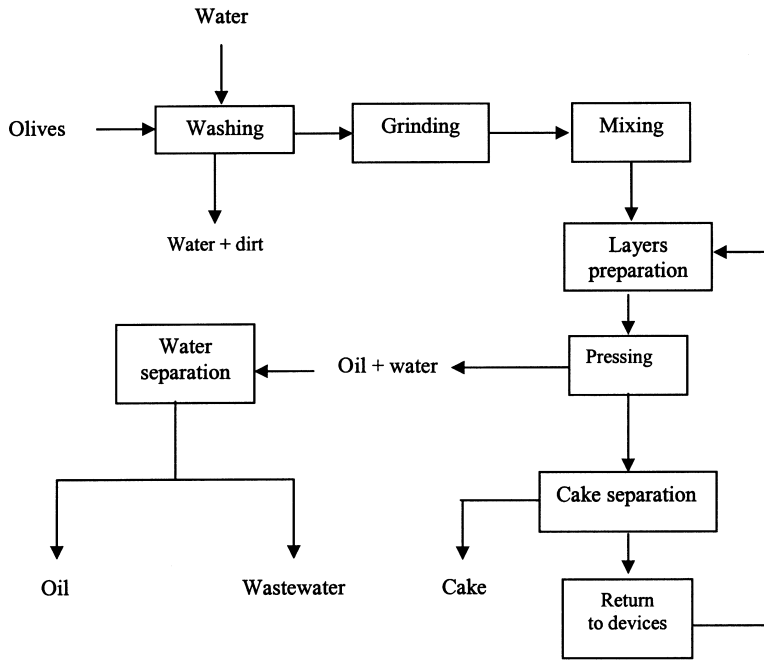
Looking at milling systems employed worldwide, a greater percentage of centrifuge systems are being used compared to pressing systems. Because of the higher productivity of the more modern centrifuge systems, they are capable of processing olives in less time, which is a requisite for a final quality product [5].

Furthermore, in contrast to the three-phase decanter process, the two-phase decanter does not require the addition of water to the ground olives. The three-phase decanter requires up to 50 kg water for 100 kg olive pulp in order to separate the latter into three phases: oil, water, and solid suspension [6]. This is necessary, since a layer of water must be formed with no bonds to the oil and solid phase inside the decanter. Thus, up to 60 kg of *alpechin* may be produced from 100 kg olives. *Alpechin* is a wastewater rich in polyphenols, color, and soluble stuffs such as sugar and salt [7].

In the two-phase decanter, there must be no traces of water inside the decanter to prevent water flowing out with the oil and reducing the paste viscosity, which leads to improved oil extraction [8]. The two-phase decanter process is considered more ecological, not only because it reduces pollution in terms of the *alpechin*, but since it requires less water for processing [9]. Depending on the preparation steps (ripeness, milling, malaxing time, temperature, using enzymes or talcum, etc.), the oil yield using the two-phase decanter may be higher than that using the three-phase decanter [10]. The oil quality is also different in each process. In the case

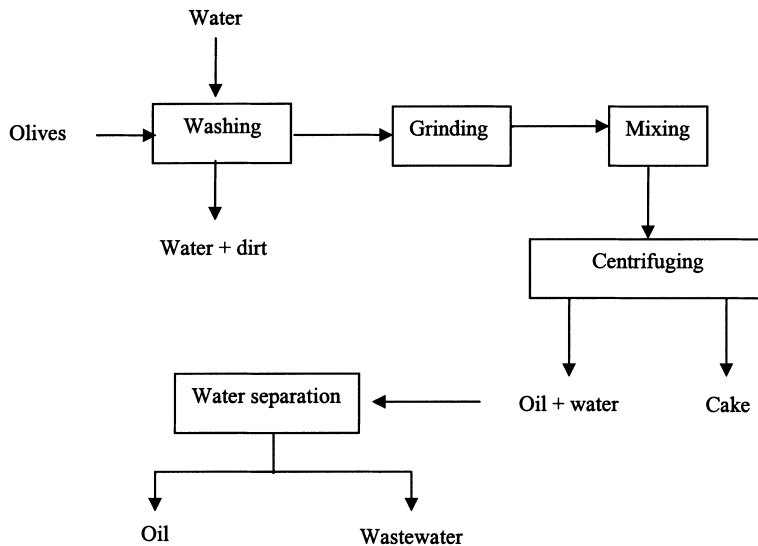


**Figure 1** Technology generally used to produce olive oil (from Ref. 5).



**Figure 2** Traditional pressing for olive oil production (from Ref. 5).

of the three-phase decanter, the main part of the polyphenols will be washed out in the alpechin phase. These chemicals, which also provide antioxidation protection, are sustained in the oil phase using the two-phase decanter; the results are better conditions for a long oil shelf life as well as a more typical fruit taste [11].



**Figure 3** Modern centrifuging for olive oil production (three-phase decanter) (from Ref. 5).

The alpeorujo (solid/liquid waste) has a moisture content of 60–65% at the decanter output while the moisture content of the solid waste using the three-phase decanter is about 50%, and by traditional pressing is about 25%. One drawback is that two-phase alpeorujo is more difficult to store due to its humidity. Comparing the three different solids (orujo press cake, three-phase decanter orujo, and two-phase decanter alpeorujo), the two-phase decanter alpeorujo is the best residue to be reprocessed for oil [9].

### 17.3 OLIVE OIL WASTEWATER CHARACTERISTICS

The olive consists of flesh (75–85% by weight), stone (13–23% by weight) and seed (2–3% by weight) [12]. The chemical composition of the olive is shown in Table 1. The quantities and composition of olive mill waste (OMW) vary considerably, owing to geographical and climatic conditions, tree age, olive type, extraction technology used, use of pesticides and fertilizers, harvest time, and stage of maturity.

In waste generated by olive oil mills, the only constituents found are produced either from the olive or its vegetation water, or from the production process itself. Auxiliary agents, which are hardly used in production, may be influenced and controlled by process management. Therefore, they are not important to the composition of wastewater. However, the composition of the olive and its vegetation wastewater cannot be influenced; thus the constituents of vegetation wastewater are decisive for the expected pollution load. Table 2 summarizes some literature data concerning the constituents of olive oil wastewater [13–25]. The variations of maximum and minimum concentrations of olive oil wastewater resulting from both methods (traditional presses and decanter centrifuge) are also presented, according to the International Olive Oil Council (IOOC) in Madrid [26], in Table 3.

Wastewater from olive oil production is characterized by the following special features and components [27]:

- color ranging from intensive violet–dark brown to black;
- strong olive oil odor;
- high degree of organic pollution (COD values up to 220 g/L, and in some cases reaching 400 g/L) at a COD/BOD<sub>5</sub> ratio between 1.4 and 2.5 and sometimes reaching 5 (difficult to be degraded);

**Table 1** Composition of Olives

Constituents	Pulp	Stone	Seed
Water	50–60	9.3	30
Oil	15–30	0.7	27.3
Constituents containing nitrogen	2–5	3.4	10.2
Sugar	3–7.5	41	26.6
Cellulose	3–6	38	1.9
Minerals	1–2	4.1	1.5
Polyphenol (aromatic substances)	2–2.25	0.1	0.5–1
Others	–	3.4	2.4

Note: Values in percent by weight (%).

Source: Ref. 12.

**Table 2** Summary of the Constituents of Olive Oil Wastewater (Alpechin) According to Different Literature Data

Parameter	Pompei <sup>13</sup> (1974)	Fiestas <sup>14</sup> (1981)	Garcia <sup>18</sup> (1989) <sup>a</sup>	Steggmans <sup>15</sup> (1992)	Hamdi <sup>16</sup> (1993)	Borja <sup>25</sup> (1995)	Beccari <sup>23</sup> (1996) <sup>f</sup>	Ubay <sup>22</sup> (1997) <sup>e</sup>	Zouari <sup>24</sup> (1998) <sup>c</sup>	Andreozzi <sup>17</sup> (1998)	Beltran-Heredia <sup>21</sup> (2000) <sup>d</sup>	Kissi <sup>20</sup> (2001) <sup>b</sup>	Rivas <sup>19</sup> (2001) <sup>a</sup>
pH	–	4.7	–	5.3	3–5.9	5.2	5.06	4.7	–	5.09	13.6	4.2	12.9
Chemical oxygen demand, COD (g/L)	195	–	15–40	108.6	40–220	60	90 (filtered 63)	115–120	225	121.8	6.7	50	24.45
Biochemical oxygen demand in 5 days, BOD <sub>5</sub> (g/L)	38.44	–	9–20	41.3	23–100	–	–	–	58	–	4.3	–	14.8
Total solids, TS (g/L)	–	1–3	–	19.2	1–20	48.6	51.5	8.5–9 (SS)	–	102.5	22.9	4 (SS)	–
Organic total solids (g/L)	–	–	–	16.7	–	41.9	37.2	–	190	81.6	4.6	–	–
Fats (g/L)	–	–	–	2.33	1–23	–	–	7.7	–	9.8	–	–	–
Polyphenols (g/L)	17.5	3–8	0.5	0.002	5–80	0.3	3.3	–	–	6.2	0.12	12	0.833
Volatile organic acids (g/L)	–	5–10	–	0.78	0.8–10	0.64	15.25	–	–	0.96	–	–	–
Total nitrogen (g/L)	0.81	0.3–0.6	–	0.6	0.3–1.2	0.16	0.84	0.18	1.2	0.95	–	–	–
						(N-NH <sub>4</sub> )							

<sup>a</sup>Wastewater generated in the table olive processing industries during different stages including washing of fruits, debittering of green olives (addition of sodium hydroxide), fermentation and packing.

<sup>b</sup>Other parameters were measured such as: color ( $A_{395}$ ) = 16;  $Cl^-$  = 11.9 g/L;  $K^+$  = 2.5 g/L;  $NH_4^+$  = 0.15 g/L.

<sup>c</sup>Since the dark color of olive oil mill effluent was difficult to determine quantitatively, the optical value (OD) at 390 nm was measured; this value was 8.5.

<sup>d</sup>Represents wastewater generated in table olive processing plant (black olives). Aromatic compounds (A) = 17 were determined by measuring the absorbance of the samples at 250 nm (the maximum absorbance wavelength of these organic compounds).

<sup>e</sup>Represents concentrated black water from a traditional olive oil mill plant. Other parameters were measured such as SS = 8.5–9 g/L, Total P = 1.2 g/L.

<sup>f</sup>Other parameters were measured such as TC = 25.5 g/L, Total P = 0.58 g/L, Lipids = 8.6 g/L.

Source: Refs. 13–25.

**Table 3** Maximum and Minimum Concentration Values of Olive Oil Wastewater According to Applied Type of Technology

Parameters	Technology type	
	Centrifuge	Traditional presses
pH	4.55–5.89	4.73–5.73
Dry matter (g/L)	9.5–161.2	15.5–266
Specific weight	1.007–1.046	1.02–1.09
Oil (g/L)	0.41–29.8	0.12–11.5
Reducing sugars (g/L)	1.6–34.7	9.7–67.1
Total polyphenols (g/L)	0.4–7.1	1.4–14.3
O-diphenols (g/L)	0.3–6	0.9–13.3
Hydroxytyrosol (mg/L)	43–426	71–937
Ash (g/L)	0.4–12.5	4–42.6
COD (g/L)	15.2–199.2	42.1–389.5
Organic nitrogen (mg/L)	140–966	154–1106
Total phosphorus (mg/L)	42–495	157–915
Sodium (mg/L)	18–124	38–285
Potassium (mg/L)	630–2500	1500–5000
Calcium (mg/L)	47–200	58–408
Magnesium (mg/L)	60–180	90–337
Iron (mg/L)	8.8–31.5	16.4–86.4
Copper (mg/L)	1.16–3.42	1.10–4.75
Zinc (mg/L)	1.42–4.48	1.6–6.50
Manganese (mg/L)	0.87–5.20	2.16–8.90
Nickel (mg/L)	0.29–1.44	0.44–1.58
Cobalt (mg/L)	0.12–0.48	0.18–0.96
Lead (mg/L)	0.35–0.72	0.40–1.85

Source: Ref. 26.

- pH between 3 and 5.9 (slightly acid);
- high content of polyphenols, up to 80 g/L; other references up to 10 g/L [28];
- high content of solid matter (total solids up to 102.5 g/L);
- high content of oil (up to 30 g/L).

Table 4 compares the composition values of olive oil mill wastewater (A and B) with those of municipal wastewater (C). While the ratio COD/BOD<sub>5</sub> in both types of wastewater is rather close (between 1.5 and 2.5), there is a big difference between the two for the ratio (BOD:N:P); olive oil wastewater (100:1:0.35) highly deviates from that in municipal wastewater (100:20:5).

Based on Tables 2 and 3, the phenols and the organic substances responsible for the high COD value must be considered as problematic for treatment of this wastewater, and the presence of inhibitory or toxic substances may seriously affect the overall treatment system. Therefore, the chemical oxygen demand (COD), the total aromatic content (A), and the total phenolic content (TPh) are mostly selected as representative parameters to follow the overall purification process [19,21,29].

The terms and definitions for the waste resulting from the different oil extraction processes are neither standardized nor country specific [30]. Table 5 shows the nominations found in the Mediterranean countries, while Table 6 shows the most common terminology used in these countries with descriptions.

**Table 4** Comparison of Composition Values of Olive Oil Wastewater from a Small Mill (A) and a Big Mill (B) with Municipal Wastewater (C)

Parameter	Source of liquid waste		
	A	B	C
pH	4.5–5.3	5.3–5.7	7–8
BOD <sub>5</sub> (g/L)	15–65	17–41	0.1–0.4
COD (g/L)	37–150	30–80	0.15–1
Total solids (g/L)	24–115	19–75	0.35–1.2
Volatile solids (g/L)	20–97	17–68	0.18–0.6
Suspended solids (g/L)	5.7–14	0.7–26	0.1–0.35
Fats and oils (g/L)	0.046–0.76	0.1–8.2	0.05–0.1
Total nitrogen (g/L)	0.27–0.51	0.3–0.48	0.02–0.08
Total phosphorus (g/L)	0.1–0.19	0.075–0.12	0.006–0.02
COD/BOD <sub>5</sub>	2.3–2.5	1.8–2	1.5–2.5
BOD <sub>5</sub> : N : P	100 : 0.98 : 0.37	100 : 1.3 : 0.34	100 : 20 : 5

Between 400 and 600 L of liquid waste are generated per ton of processed olives from the traditional presses used for olive oil extraction, which are operated discontinuously. Depending on its size, the capacity of such an olive oil mill is about 10 to 20 tons of olives per day. With a capacity of 20 tons of olives per day and a process-specific wastewater volume of 0.5 m<sup>3</sup> per ton of olives, the daily wastewater can range up to 10 m<sup>3</sup> per day.

Compared to the traditional presses, twice the quantity of wastewater (from 750 to 1200 L per ton of olives) is produced with the three-phase decanting method. Depending on their size, the capacities of the olive oil mills are also between 10 and 20 tons of olives per day. With a capacity of 20 ton of olives per day and a process specific wastewater volume of about 1 m<sup>3</sup> per ton of olives, the daily wastewater volume from a continuous process is up to 20 m<sup>3</sup> per day. The concentration of the constituents in wastewater from traditional presses is therefore twice as high as in the wastewater resulting from three-phase decanting. In general, the organic pollution

**Table 5** Nominations of Waste Resulting from Different Oil Extraction Processes as Found in the Mediterranean Area

	Pressing	Three-phase decanting	Two-phase decanting
Solid	Orujo (Sp) Pirina (Gr, Tk) Hask (It, Tu) Grignons (Fr)	Orujo (Sp) Grignons (Fr) Pirina (Gr, Tk) Hask (It, Tu) Orujillo (Sp) after de-oiling of solid waste	Alpeorujo (in two- phase decanting mainly alpeorujo is produced)
Wastewater	Alpechin (Sp) Margine (Gr) Jamila (It)	Alpechin (Sp) Margine (Gr) Jamila (It)	Alpechin
Oil (from de-oiling of solid waste)	–	Orujooil	Orujooil

Note: Sp, Spanish; Gr, Greek; It, Italian; Tu, Tunisian; Tk, Turkish; Fr, French.

Source: Ref. 30.

**Table 6** Terminology of the Olive Oil Sector Related with Waste

Name	Description
Flesh, pulp (En)	Soft, fleshy part of the olive fruit
Pit, husk, stone (En)	Nut, hard part of the olive
Kernel, seed (En)	Softer, inner part of the olive
Alpeorujo, orujo de dos fases, alperujo (Sp)	Very wet solid waste from the two-phase decanters
Orujo, orujo de tres fases (Sp)	
Pirina (Gr/Tk)	
Pomace (It)	Wet solid waste from the three-phase decanters and presses
Grignons (Fr)	
Husks (It/Tu)	
Orujillo (Sp)	De-oiled orujo, de-oiled alpeorujo
Alpechin (Sp)	Liquid waste from the three-phase decanters and presses
Margine (Gr)	
Jamila (It)	
Alpechin-2 (Sp)	
Margine-2 (Gr)	Liquid fraction from secondary alpeorujo treatment (second decanting, repaso, etc.)
Jamila-2 (It)	

*Note:* En, English; Sp, Spain; Gr, Greek; It, Italian; Tu, Tunisian; Tk, Turkish; Fr, French.

*Source:* Ref. 1.

load in wastewater from olive oil extraction processes is practically independent of the processing method and amounts to 45–55 kg BOD<sub>5</sub> per ton of olives [31].

The input–output analysis of material and energy flows of the three production processes (press, two-phase, and three-phase decanting) is shown in Table 7. The basis of reference is one metric ton of processed olives.

### 17.3.1 Design Example 1

What is the population equivalent (pop. equ.) of the effluents discharged from a medium-sized oil mill processing about 15 tons (33,000 lb) of olives per day by using the two systems of traditional pressing or continuous centrifuging?

#### Solution

Traditional pressing of olives results in a wastewater volume of approximately 600 L (159 gal) per ton of olives; thus wastewater flow rate = 15 T × 0.6 m<sup>3</sup>/T = 9 m<sup>3</sup>/day (2378 gal/day). Assuming a BOD<sub>5</sub> concentration of 40 g/L (0.34 lb/gal), the resulting total BOD<sub>5</sub> discharged per day = 9 m<sup>3</sup>/day × 40 kg/m<sup>3</sup> = 360 kg BOD<sub>5</sub>/day (792 lb/day).

$$\text{BOD}_5 \text{ per person} = 54 - 60 \text{ g/p.day (0.119 - 0.137 lb/p.day)}$$

then

$$\text{Pop. equ.} = \frac{360}{0.06} = 6000 \text{ persons}$$

Continuous centrifuging (three-phase decanting) of olives results in a wastewater volume of approximately 1000 L (264.2 gal) per ton of olives, thus wastewater flow rate =



**Table 7** An Input–Output Analysis of Material and Energy Flows of the Production Processes Related to One Ton of Processed Olives

Production process	Input	Amount of input	Output	Amount of output
Traditional pressing process	Olives	1000 kg	Oil	200 kg
	Washing water	0.1–0.12 m <sup>3</sup>	Solid waste (25% water + 6% oil)	400 kg
	Energy	40–63 kWh	Wastewater (88% water)	600 L <sup>a</sup>
Three-phase decanters	Olives	1000 kg	Oil	200 kg
	Washing water	0.1–0.12 m <sup>3</sup>	Solid waste (50% water + 4% oil)	500–600 kg
	Fresh water for decanter	0.5–1 m <sup>3</sup>	Wastewater (94% water + 1% oil)	1000–1200 L <sup>b</sup>
	Water to polish the impure oil	10 kg		
Two-phase decanter	Energy	90–117 kWh		
	Olives	1000 kg	Oil	200 kg
	Washing water	0.1–0.12 m <sup>3</sup>	Solid waste (60% water + 3% oil)	800–950 kg
	Energy	<90–117 kWh		

<sup>a</sup>According to International Olive Oil Council: (400–550 L/Ton processed olives)

<sup>b</sup>According to International Olive Oil Council: (850–1200 L/Ton processed olives)

Source: Ref. 1.

$15 \text{ T} \times 1 \text{ m}^3/\text{T} = 15 \text{ m}^3/\text{day}$  (3963 gal/day). Assuming a BOD<sub>5</sub> concentration of about 23 g BOD<sub>5</sub>/L (0.192 lb/gal), the resulting total BOD<sub>5</sub> discharged per day is:

$$15 \text{ m}^3/\text{day} \times 23 \text{ kg}/\text{m}^3 = 345 \text{ kg}/\text{day} \text{ (759 lb}/\text{day)}$$

then

$$\text{Pop. equ.} = \frac{345}{0.06} = 5750 \text{ persons}$$

## 17.4 ENVIRONMENTAL RISKS

Olive oil mill wastewaters (OMW) are a major environmental problem, in particular in Mediterranean countries, which are the main manufacturers of olive oil, green and black table olives. In these countries, the extraction and manufacture of olive oil are carried out in numerous small plants that operate seasonally and generate more than 30 million tons of liquid effluents (black water) [16], called “olive oil mill wastewaters” (OMW) each year. These effluents can cause considerable pollution if they are dumped into the environment because of their high organic load, which includes sugar, tannins, polyphenols, polyalcohols, pectins, lipids, and so on. Seasonal operation, which requires storage, is often impossible in small plants [32]. In fact, 2.5 L of waste are released per liter of oil produced [28].

Olive oil mill wastewaters contain large concentrations of highly toxic phenol compounds (can exceed 10 g/L) [33]. Much of the color of OMW is due to the aromatic compounds present, which have phytotoxic and antibacterial effects [34,35].

Despite existing laws and regulations, disposal of untreated liquid waste into the environment is uncontrolled in most cases. When it is treated, the most frequent method used is to retain the effluent in evaporation ponds. However, this procedure causes bad odors and risks polluting surface waters and aquifers. Therefore, this process presents an important environmental problem. Table 8 displays the risks that arise from direct disposal of olive oil mill wastewater (OMW) in the environment (soil, rivers, ground water). Examples of the risks [2] are described in the following sections.

#### 17.4.1 Discoloring of Natural Waters

This is one of the most visible effects of the pollution. Tannins that come from the olive skin remain in the wastewater from the olive oil mill. Although tannins are not harmful to people, animals, or plants, they dye the water coming into contact with them dark black-brown. This undesired effect can be clearly observed in the Mediterranean countries [2].

#### 17.4.2 Degradability of Carbon Compounds

For the degradation of the carbon compounds ( $BOD_5$ ), the bacteria mainly need nitrogen and phosphorus besides some trace elements. The  $BOD_5:N:P$  ratio should be 100:5:1. The optimal ratio is not always given and thus an excess of phosphorus may occur [36].

#### 17.4.3 Threat to Aquatic Life

Wastewater has a considerable content of reduced sugar, which, if discharged directly into natural waters, would increase the number of microorganisms that would use this as a source of

**Table 8** The Environmental Risks Resulting from the Direct Disposal of the Olive Oil Mill Liquid Water Without Treatment

Pollutants	Medium/environment	Effects
Acids	Soil	Destroys the cation exchange capacity of soil
Oil		Reduction of soil fertility
Suspended solids	Water	Bad odors
Organics		Consumption of dissolved oxygen
Oil		Eutrophication phenomena
Suspended solids		Impenetrable film
Acids	Municipal wastewater sewerage	Aesthetic damage
Suspended solids		Corrosion of concrete and metal canals/pipes
Acids	Municipal wastewater treatment plants	Flow hindrance
Organics		Anaerobic fermentation
Nutrient imbalance		Corrosion of concrete and metal canals/pipes
Oil		Sudden and long shocks to activated sludge and trickling filter systems
Organics		
Nutrient imbalance		Shock to sludge digester

Source: Refs 2 and 15.

substrate. The effect of this is reduction of the amount of oxygen available for other living organisms, which may cause an imbalance of the whole ecosystem.

Another similar process can result from the high phosphorus content. Phosphorus encourages and accelerates the growth of algae and increases the chances of eutrophication, destroying the ecological balance in natural waters. In contrast to nitrogen and carbon compounds, which escape as carbon dioxide and atmospheric nitrogen after degradation, phosphorus cannot be degraded but only deposited. This means that phosphorus is taken up only to a small extent via the food chain: plant → invertebrates → fish → prehensile birds.

The presence of such a large quantity of nutrients in the wastewater provides a perfect medium for pathogens to multiply and infect waters. This can have severe effects on the local aquatic life and humans that may come into contact with the water [2].

#### **17.4.4 Impenetrable Film**

The lipids in the wastewater may form an impenetrable film on the surface of rivers, their banks, and surrounding farmlands. This film blocks out sunlight and oxygen to microorganisms in the water, leading to reduced plant growth in the soils and river banks and in turn erosion [2].

#### **17.4.5 Soil Quality**

The waste contains many acids, minerals, and organics that could destroy the cation exchange capacity of the soil. This would lead to destruction of microorganisms, the soil–air and the air–water balance, and therefore a reduction of the soil fertility [15].

#### **17.4.6 Phytotoxicity**

Phenolic compounds and organic acid can cause phytotoxic effects on olive trees. This is of dire importance since wastewater can come into contact with crops due to possible flooding during the winter. The phenols, organic, and inorganic compounds can hinder the natural disinfection process in rivers and creeks [2].

#### **17.4.7 Odors**

Anaerobic fermentation of the wastewater causes methane and other gases (hydrogen sulfide, etc.) to emanate from natural waters and pond evaporation plants. This leads to considerable pollution by odors even at great distances [2].

Other risks could be referred to in this respect, such as agricultural-specific problems arising from pesticides and other chemicals, although their effect in olive cultivation is less pronounced than other fields of agriculture. The main problem is soil erosion caused by rainwater, which results in steeper slopes and increases difficulty in ploughing. Soil quality and structure also influence erosion caused by rain. At present, protective measures such as planting of soil-covering species or abstention from ploughing are hardly used.

### **17.5 LIQUID WASTE TREATMENT METHODS**

Disposal and management of highly contaminated wastewater constitute a serious environmental problem due to the biorecalcitrant nature of these types of effluents, in most cases. Generally, biological treatment (mainly aerobic) is the preferred option for dealing with urban

and industrial effluents because of its relative cost-effectiveness and applicability for treating a wide variety of hazardous substances [19]. Nevertheless, some drawbacks may be found when applying this technology. For instance, some chemical structures, when present at high concentrations, are difficult to biodegrade because of their refractory nature or even toxicity toward microorganisms. Thus, several substances have been found to present inhibitory effects when undergoing biological oxidation. Among them, phenolic compounds constitute one of the most important groups of pollutants present in numerous industrial effluents [37]. Owing to the increasing restrictions in quality control of public river courses, development of suitable technologies and procedures are needed to reduce the pollutant load of discharges, increase the biodegradability of effluent, and minimize the environmental impact to the biota.

Industries that generate nonbiodegradable wastewater showing high concentrations of refractory substances (chiefly phenol-type compounds) include the pharmaceutical industry, refineries, coal-processing plants, and food-stuff manufacturing. The olive oil industry (a common activity in Mediterranean countries), in particular, generates highly contaminated effluents during different stages of mill olive oil production (washing and vegetation waters).

Therefore, most treatment processes used for high-strength industrial wastewaters have been applied to olive oil mill effluents (OME). Yet, OME treatment difficulties are mainly associated with: (a) high organic load (OME are among the strongest industrial effluents, with COD up to 220 g/L and sometimes reaching 400 g/L); (b) seasonal operation, which requires storage (often impossible in small mills); (c) high territorial scattering; and (d) presence of organic compounds that are difficult to degrade by microorganisms (long-chain fatty acids and phenolic compounds of the C-7 and C-9 phenylpropanoic family) [23].

Furthermore, a great variety of components found in liquid waste (alpachin) and solid waste (orujo and alpeorujo) require different technologies to eliminate those with harmful effects on the environment. Most used methods for the treatment of liquid waste from olive oil production are presented in Table 9. They correspond to the current state-of-art-technologies and are economically feasible. These methods are designed to eliminate organic components and to reduce the mass. In some cases, substances belonging to other categories are also partly removed. In practise, these processes are often combined since their effects differ widely [1]. Therefore, methods should be used in combination with each other.

The following key treatment methods are mainly applied to liquid waste. Some of these methods can also be used in the treatment of liquid–solid waste (alpeorujo), for example, treatment by fungi, evaporation/drying, composting, and livestock feeding. However, those methods tested at laboratory scale must be critically examined before applying them at industrial or full-scale, in order to meet the local environmental and economical conditions.

Regarding the olive oil industry, it should always be considered that complicated treatment methods that lack profitable use of the final product are not useful, and all methods should have a control system for the material flows [38].

### 17.5.1 Low-Cost Primitive Methods

These methods are mostly applied in the developing countries producing olive, due to their simplicity and low costs. Of these methods, the most important are:

- Drainage of olive oil mill liquid waste in some types of soils, with rates up to 50 m<sup>3</sup>/ha-year (in the case of traditional mills) and up to 80 m<sup>3</sup>/ha-year (in the case of decanting-based methods), or to apply the olive oil mill liquid wastes to the irrigation water for a rate of less than 3%. These processes are risky because they decrease the fertility of the soil. This calls for greater care and scientific research into these methods prior to agronomic application.

**Table 9** Treatment Methods for the Liquid and Solid Waste from Olive Oil Production

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 Treatment method of (alpechin)
 

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Low-cost primitive methods

- Drainage in soil
- Simple disposal in evaporation ponds
- Mixing with solid waste in sanitary landfills

Aerobic treatment

Anaerobic treatment

Combined biological treatment methods

Wet air oxidation and ozonation

Fungal treatment

Decolorization

Precipitation/flocculation

Adsorption

Filtration (biofiltration, ultrafiltration)

Evaporation/drying

Electrolysis

 Bioremediation and composting<sup>a</sup>

 Livestock feeding<sup>a</sup>

 Submarine outfall
 

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<sup>a</sup> These recycling methods can be used for liquid as well as solid waste from olive oil production.

Products resulting from treatment may be reused, for instance, as fertilizer or fodder in agriculture. For all methods, waste that is not suited for reuse can be disposed at landfills.

- Simple disposal and retention in evaporation ponds (large surface and small depth ponds), preferably in distant regions, to be dried by solar radiation and other climatic factors. This method does not require energy or highly trained personnel. Drawbacks are associated with the evaporation process, which generates odors and additional risks for the aquatic system of the area (filtration phenomena, surface water contamination, etc.). In addition, the disadvantages include: the need for large areas for drying in selected regions with impermeable (clay) soil distant from populated areas; the requirement, in most cases, for taking necessary precautions to prevent pollutants reaching the groundwater through placement of impermeable layers in the ground and walls of ponds; ineffective in higher rainfall regions; emergence of air pollutants caused by decomposition of organic substances (ammonia-hydrocarbon volatile compounds). This method is being applied in many countries of the Mediterranean area. In Spain alone, there are about 1000 evaporation ponds, which improve the water quality, but the ponds themselves caused serious negative environmental impacts. Dried sludge from evaporation ponds can be used as fertilizer, either directly or composted with other agricultural byproducts (e.g., grape seed residues, cotton wastes, bean straw) [39].
- Mixing the olive oil mill liquid wastes with municipal solid wastes in sanitary landfills leads to increased organic load on site. Consideration should be made regarding the pollutants that may reach the groundwater, in addition to the risks of combustion due to generation of combustible hydrocarbon gases. These factors should be taken into account in designing and establishing landfills, not forgetting the necessity to collect

and treat the drainage wastewater resulted from applying this method. This method is cost-effective and is suitable for final disposal of the wastes, with the property of obtaining energy from the generated gases. Nevertheless, there are drawbacks such as the air pollution caused by the decomposition, the need for advanced treatment for the highly polluted collected drainage wastewater, and the need for using large areas of land and particular specifications.

### 17.5.2 Aerobic Treatment

When biodegradable organic pollutants in olive oil mill wastewater (alpechin) are eliminated by oxygen-consuming microorganisms in water to produce energy, the oxygen concentration decreases and the natural balance in the water body is disturbed. To counteract an overloading of the oxygen balance, the largest part of these oxygen-consuming substances (defined as BOD<sub>5</sub>) must be removed before being discharged into the water body. Wastewater treatment processes have therefore been developed with the aim of reducing the BOD<sub>5</sub> concentration as well as eliminating eutrophying inorganic salts, that is, phosphorus and nitrogen compounds, ammonium compounds, nonbiodegradable compounds that are analyzed as part of the COD, and organic and inorganic suspended solids [38].

In aerobic biological wastewater treatment plants, the natural purification processes taking place in rivers are simulated under optimized technical conditions. Bacteria and monocellular organisms (microorganisms) degrade the organic substances dissolved in water and transform them into carbonic acid, water, and cell mass. The microorganisms that are best suited for the purification of a certain wastewater develop in the wastewater independently of external influences and adapt to the respective substrate composition (enzymatic adaptation). Owing to the oxidative degradation processes, oxygen is required for wastewater treatment. The oxygen demand corresponds to the load of the wastewater.

Two types of microorganisms live in waters: suspended organisms, floating in the water, and sessile organisms, which often settle on the surface of stones and form biofilms. Biofilm processes such as fixed-bed or trickling filter processes are examples of the technical application of these natural processes [38].

### Treatment of Olive Oil Mill Wastewaters in Municipal Plants

Municipal wastewater is unique in that a major portion of the organics are present in suspended or colloidal form. Typically, the BOD in municipal sewage consists of 50% suspended, 10% colloidal, and 40% soluble parts. By contrast, most industrial wastewater are almost 100% soluble. In an activated sludge plant treating municipal wastewater, the suspended organics are rapidly enmeshed in the flocs, the colloids are adsorbed on the flocs, and a portion of the soluble organics are absorbed. These reactions occur in the first few minutes of aeration contact. By contrast, for readily degradable wastewaters, that is, food processing, a portion of the BOD is rapidly sorbed and the remainder removed as a function of time and biological solids concentration. Very little sorption occurs in refractory wastewaters. The kinetics of the activated sludge process will therefore vary depending on the percentage and type of industrial wastewater discharged to the municipal plant and must be considered in the design calculations [40].

The percentage of biological solids in the aeration basin will also vary with the amount and nature of the industrial wastewater. Increasing the sludge age increases the biomass percentage as volatile suspended solids undergo degradation and synthesis. Soluble industrial wastewater will increase the biomass percentage in the activated sludge.

A number of factors should be considered when discharging industrial wastewaters, including olive oil mill effluents, into municipal plants [40]:

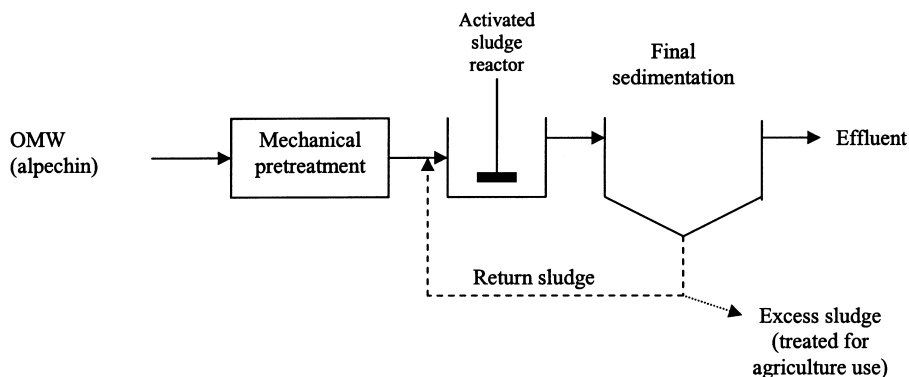
- *Effect on effluent quality.* Soluble industrial wastewaters will affect the reaction rate  $K$ . Refractory wastewaters such as olive oil mills, tannery, and chemical will reduce  $K$ , while readily degradable wastewaters such as food processing and brewery will increase  $K$ .
- *Effect on sludge quality.* Readily degradable wastewaters will stimulate filamentous bulking, depending on basin configuration, while refractory wastewaters will suppress filamentous bulking.
- *Effect of temperature.* An increased industrial wastewater input, that is, soluble organics, will increase the temperature coefficient  $\theta$ , thereby decreasing efficiency at reduced operating temperatures.
- *Sludge handling.* An increase in soluble organics will increase the percentage of biological sludge in the waste sludge mixture. This will generally decrease dewaterability, decrease cake solids, and increase conditioning chemical requirements. One exception is pulp and paper-mill wastewaters in which pulp and fiber serve as a sludge conditioner and enhances dewatering rates.

It is worth pointing out that certain threshold concentrations for inhibiting agent and toxic substances must not be exceeded. Moreover, it should be noted that most industrial wastewaters are nutrient deficient, that is, they lack nitrogen and phosphorus. Municipal wastewater with a surplus of these nutrients will provide the required nutrient balance.

The objective of the activated sludge process is to remove soluble and insoluble organics from a wastewater stream and to convert this material into a flocculent microbial suspension that is readily settleable and permits the use of gravitational solids liquid separation techniques. A number of different modifications or variants of the activated sludge process have been developed since the original experiments of Arden and Lockett in 1914 [40]. These variants, to a large extent, have been developed out of necessity or to suit particular circumstances that have arisen. For the treatment of industrial wastewater, the common generic flow sheet is shown in Fig. 4.

The activated sludge process is a biological wastewater treatment technique in which a mixture of wastewater and biological sludge (microorganisms) is agitated and aerated. The biological solids are subsequently separated from the treated wastewater and returned to the aeration process as needed. The activated sludge process derives its name from the biological mass formed when air is continuously injected into the wastewater. Under such conditions, microorganisms are mixed thoroughly with the organics under conditions that stimulate their growth through use of the organics as food. As the microorganisms grow and are mixed by the agitation of the air, the individual organisms clump together (flocculate) to form an active mass of microbes (biologic floc) called activated sludge [41].

In practise, wastewater flows continuously into an aeration tank where air is injected to mix the activated sludge with the wastewater and to supply the oxygen needed for the organisms to break down the organics. The mixture of activated sludge and wastewater in the aeration tank is called mixed liquor. The mixed liquor flows from the aeration tank to a secondary clarifier where the activated sludge is settled out. Most of the settled sludge is returned to the aeration tank (return sludge) to maintain a high population of microbes to permit rapid breakdown of the organics. Because more activated sludge is produced than is desirable in the process, some of the return sludge is diverted or wasted to the sludge handling system for treatment and disposal.



**Figure 4** Aerobic treatment (activated sludge plant).

Biofilm processes are used when the goal is very far-reaching retention and concentration of the biomass in a system. This is especially the case with slowly reproducing microorganisms in aerobic or anaerobic environments. The growth of sessile microorganisms on a carrier is called biofilm. The filling material (e.g., in a trickling filter stones, lava slag, or plastic bodies) or the filter material (e.g., in a biofilter) serve as carrier. The diffusion processes in biofilm plants are more important than in activated sludge plants because unlike activated sludge flocs the biofilms are shaped approximately two-dimensionally. On the one hand, diffusion is necessary to supply the biofilm with substrate and oxygen; on the other hand, the final metabolic products (e.g.,  $\text{CO}_2$  and nitrate) must be removed from the biofilm.

For treatment of industrial wastewater, trickling filters are often used. A trickling filter is a container filled completely with filling material, such as stones, slats, or plastic materials (media), over which wastewater is applied. Trickling filters are a popular biological treatment process [42]. The most widely used design for many years was simply a bed of stones, 1–3 m deep, through which the wastewater passed. The wastewater is typically distributed over the surface of the rocks by a rotating arm. Rock filter diameters may range up to 60 m. As wastewater trickles through the bed, a microbial growth establishes itself on the surface of the stone or packing in a fixed film. The wastewater passes over the stationary microbial population, providing contact between the microorganisms and the organics. The biomass is supplied with oxygen using outside air, most of the time without additional technical measures. If the wastewater is not free of solid matter (as in the case of alpechin), it should be prescreened to reduce the risk of obstructions.

Excess growths of microorganisms wash from the rock media and would cause undesirably high levels of suspended solids in the plant effluent if not removed. Thus, the flow from the filter is passed through a sedimentation basin to allow these solids to settle out. This sedimentation basin is referred to as a secondary clarifier, or final clarifier, to differentiate it from the sedimentation basin used for primary settling. An important element in trickling filter design is the provision for return of a portion of the effluent (recirculation) to flow through the filter. Owing to seasonal production of wastewater and to the rather slow growth rates of the microorganisms, these processes are less suited for the treatment of alpechin, compared to the activated sludge process.

Another worthwhile aerobic treatment method developed by Balis and his colleagues [38] is the bioremediation process, based on the intrinsic property of an *Azotobacter vinelandii* strain (strain A) to proliferate on limed olive oil mill wastewater. More specifically, the olive mill



wastewater is pretreated with lime to pH 7–8 and then is fed into an aerobic bioreactor equipped with a rotating wheel-type air conductor. The reactor is operated in a repeated fed batch culture fashion with a cycle time of 3 days. During each cycle, the *Azotobacter* population proliferates and fixes molecular nitrogen. It concomitantly produces copious amounts of slime and plant growth promoting substances. The endproduct is a thick, yellow-brown liquid. It has a pH of about 7.5–8.0, it is nonphytotoxic, soluble in water, and can be used as liquid fertilizer over a wide range of cultivated plants (olives, grapes, citrus, vegetables, and ornamentals). Moreover, there is good evidence that the biofertilizer induces soil suppressiveness against root pathogenic fungi, and improves soil structure. A medium-scale pilot plant of 25 m<sup>3</sup> capacity has been constructed in Greece by the Olive Cooperative of Peta near Arta with the financial support of the General Secretariat of Science and Technology of Greece. The plant has been operating since 1997. The local farmers use the liquid biofertilizer that is produced to treat their olive and citrus groves.

In short, it has been demonstrated that free-living N<sub>2</sub>-fixing bacteria of *Azotobacter* grow well in olive mill wastewater and transform the wastes into a useful organic fertilizer and soil conditioner. For further details in this regard, refer to Section 17.5.17 (Bioremediation and Composting).

The following case study explains the influence of aerobic treatments for already fermented olive oil mill wastewater (OMW), on the anaerobic digestion of this waste.

### Case Study

This kinetic study [25] allows intercomparison of the effects of different aerobic pretreatments on the anaerobic digestion of OMW, previously fermented with three microorganisms (*Geotrichum conidium*, *Azotobacter chroococcum*, and *Aspergillus terreus*). The OMW used was obtained from a continuous olive-processing operation. The bioreactor used was batch fed and contained sepiolite as support for the mediating bacteria. The results of the microtox toxicity test expressed as toxic units (TU) for both pretreated and untreated OMW are as follows:

- prior to inoculation (untreated OMW): TU = 156;
- after fermentation with *Geotrichum*: TU = 64;
- after fermentation with *Azotobacter*: TU = 32;
- after fermentation with *Aspergillus*: TU = 20.

The influence of the different aerobic pretreatments on the percentages of elimination of COD and total phenol contents are indicated in Table 10.

**Table 10** Influence of Different Aerobic Pretreatments on the Percentages of Elimination of COD and Total Phenol Contents

Pretreatment	Elimination COD %	Elimination phenols %
<i>Geotrichum</i>	63.3	65.6
<i>Azotobacter</i>	74.5	90.0
<i>Aspergillus</i>	74.0	94.3

Source: Ref. 25.

A kinetic model was developed for the estimation of methane production ( $G$ ) against time ( $t$ ), represented in the following equation:

$$G = G_M \left[ 1 - \exp\left(-\frac{AXt}{S_0}\right) \right], \quad \text{over the COD range studied (3.9 - 14.5 g/L)}$$

where  $G_M$  is the maximum methane volume obtained at the end of digestion time,  $S_0$  is the initial substrate concentration,  $X$  is the microorganism concentration, and  $A$  is the kinetic constant of the process, which was calculated using a nonlinear regression. This kinetic parameter was found to be influenced by the pretreatment carried out, and was 4.6, 4.1, and 2.3 times higher for *Aspergillus*-, *Azotobacter*-, and *Geotrichum*-pretreated OMWs than that obtained in the anaerobic digestion of untreated OMW. The kinetic constant increased as the phenolic compound content and biotoxicity of the pretreated OMWs decreased.

The final conclusion that can be drawn from this work is that aerobic pretreatment of the OMW with different microorganisms (*Geotrichum*, *Azotobacter*, and *Aspergillus*) considerably reduces the COD and the total phenolic compound concentration of waste that is responsible for its biotoxicity. This fact is shown through enhancement of the kinetic constant for the anaerobic digestion process, and a simultaneous increase in the yield coefficient of methane production.

Case studies regarding the role and importance of the aerobic treatment process combined with chemical oxidation such as wet air oxidation (WAO) are found in Section 17.5.9.

### 17.5.3 Design Example 2

An olive oil mill is to treat its wastewater in an extended aeration activated sludge plant. The final effluent should have a maximum soluble BOD<sub>5</sub> of 20 mg/L during the olive mill operation season. This plant is to be designed under the following conditions:  $Q = 60 \text{ m}^3/\text{day}$  (15,850 gal/day);  $S_0$  (diluted) = 800 mg/L;  $S_e = 20 \text{ mg/L}$ ;  $X_v = 3000 \text{ mg/L}$ ;  $a = 0.50$ ;  $a' = 0.6$ ;  $b = 0.10$  at 20°C;  $\theta = 1.065$ ;  $K = 6.0/\text{day}$  at 20°C; and  $b' = 0.12/\text{day}$ .

#### Solution

$$t = \frac{S_0(S_0 - S_e)}{KS_eX_v}$$

$$t = \frac{800(800 - 20)}{6(20)(3000)} = 1.73 \text{ days}$$

$$\frac{F}{M} = \frac{S_0}{X_v t} = \frac{800}{3000 \times 1.73} = 0.154$$

The degradable fraction is determined by:

$$X_d = \frac{0.8}{1 + 0.26\theta_c}$$

Assuming  $\theta_c = 25$  day (SRT)

$$X_d = \frac{0.8}{1 + 0.2 \times 0.1 \times 25} = 0.53$$

The aeration basin volume is:  $60 \text{ m}^3/\text{day} \times 1.73 \text{ day} = 104 \text{ m}^3$  (27,421 gal). The sludge yield can be computed as:

$$\Delta X_v = aS_r - bX_d X_v t$$

$$\Delta X_v = 0.5 \times 780 \text{ mg/L} - 0.10 \times 0.53 \times 3000 \text{ mg/L} \times 1.73$$

$$\Delta X_v = 115 \text{ mg/L}$$

$$\begin{aligned} \Delta X_v &= 115 \text{ mg/L} \times 60 \text{ m}^3/\text{day} \times 10^{-3} \\ &= 7.0 \text{ kg/day} (15.4 \text{ lb/day}) \end{aligned}$$

Check the sludge age:

$$\theta_c = \frac{V X_v}{\Delta X_v} = \frac{104 \times 3000}{7 \times 1000} = 45 \text{ day}$$

or

$$\theta_c = \frac{27,421 \text{ gal} \times 8.34 \times 10^{-6} \times 3000}{15.4} = 45 \text{ day}$$

Compute the oxygen required:

$$\text{O}_2/\text{day} = a'S_r Q + b'X_d X_v V$$

$$\text{O}_2/\text{day} = (0.6 \times 780 \times 60 + 0.12 \times 0.53 \times 3000 \times 104)10^{-3}$$

$$\text{O}_2/\text{day} = 48 \text{ kg/day} = 2 \text{ kg/hour} (4.4 \text{ lb/hour})$$

The oxygen needed can also be calculated directly from the approximate relation:

$$2.0 - 2.5 \text{ kg O}_2/\text{kg BOD}_5$$

$$\text{O}_2/\text{day} = 60 \text{ m}^3/\text{day} \times 800 \text{ g BOD}_5/\text{m}^3 \times 10^{-3} \times 2 \text{ kg O}_2/\text{kg BOD}_5$$

$$\text{O}_2/\text{day} = 96 \text{ kg O}_2/\text{day} (4 \text{ kg/hour}) (8.8 \text{ lb/hour})$$

Compute the effluent quality at 15°C:

$$K_{15}^\circ = 6 \times 1.065^{(15-20)} = 4.38/\text{day}$$

$$S_e = \frac{S_0^2}{KX_v t + S_0} = \frac{800^2}{4.38 \times 3000 \times 1.73 + 800}$$

$$S_e = 27 \text{ mg/L}$$

The effluent quality at 10°C:

$$K_{10}^\circ = 6 \times 1.065^{(10-20)} = 3.19/\text{day}$$

$$S_e = \frac{(800)^2}{3.19 \times 3000 \times 1.73 + 800}$$

$$S_e = 37 \text{ mg/L}$$

### 17.5.4 Anaerobic Treatment

Anaerobic processes are increasingly used for the treatment of industrial wastewaters. They have distinct advantages including energy and chemical efficiency and low biological sludge yield, in addition to the possibility of treating organically high-loaded wastewater ( $\text{COD} > 1500 \text{ mg/L}$ ), with the requirement of only a small reactor volume.

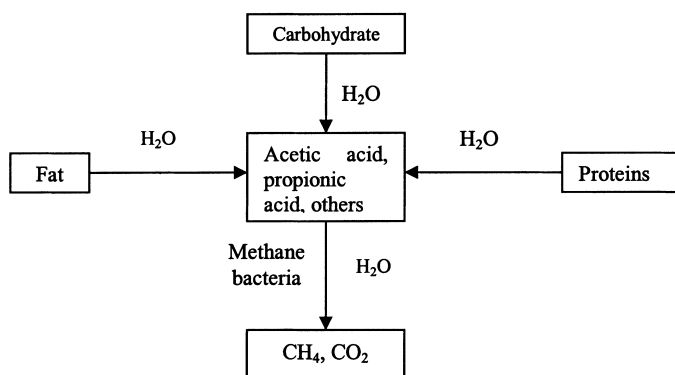
Anaerobic processes can break down a variety of aromatic compounds. It is known that anaerobic breakdown of the benzene nucleus can occur by two different pathways, namely, photometabolism and methanogenic fermentation. It has been shown that benzoate, phenylacetate, phenylpropionate, and annamate were completely degraded to  $\text{CO}_2$  and  $\text{CH}_4$ . While long acclimation periods were required to initiate gas production, the time required could be reduced by adapting the bacteria to an acetic acid and substrate before adapting them to the aromatic.

Chmielowski et al. [43] showed that phenol, p-cresol, and resorcinol yielded complete conversion to  $\text{CH}_4$  and  $\text{CO}_2$ .

#### Principle of Anaerobic Fermentation

In anaerobic fermentation, roughly four groups of microorganisms sequentially degrade organic matter. Hydrolytic microorganisms degrade polymer-type material such as polysaccharides and proteins to monomers. This reduction results in no reduction of COD. The monomers are then converted into fatty acids (VFA) with a small amount of  $\text{H}_2$ . The principal organic acids are acetic, propionic, and butyric with small quantities of valeric. In the acidification stage, there is minimal reduction of COD. Should a large amount of  $\text{H}_2$  occur, some COD reduction will result, seldom exceeding 10%. All formed acids are converted into acetate and  $\text{H}_2$  by acetogenic microorganisms. The breakdown of organic acids to  $\text{CH}_4$  and  $\text{CO}_2$  is shown in Fig. 5. Acetic acid and  $\text{H}_2$  are converted to  $\text{CH}_4$  by methanogenic organisms [40].

The specific biomass loading of typical anaerobic processes treating soluble industrial wastewaters is approximately  $1 \text{ kg COD utilized}/(\text{kg biomass}\cdot\text{day})$ . There are two classes of methanogenes that convert acetate to methane, namely *Methanotrix* and *Methanosarcina*. *Methanotrix* has a low specific activity that allows it to predominate in systems with a low steady-state acetate concentration. In highly loaded systems, *Methanosarcina* will predominate with a higher specific activity (3 to 5 times as high as *Methanotrix*) if trace nutrients are



**Figure 5** Anaerobic degradation of organics (from Ref. 46).

available. At standard temperature and pressure, 1 kg of COD or ultimate BOD removed in the process will yield  $0.35 \text{ m}^3$  of methane [40].

The quantity of cells produced during methane fermentation will depend on the strength and character of the waste, and the retention of the cells in the system.

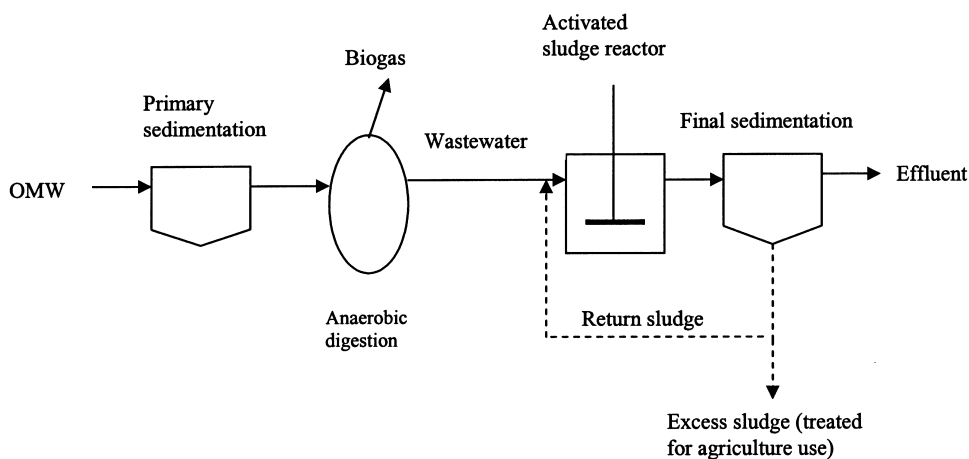
In comparing anaerobic processes and aerobic processes, which require high energy and high capital cost and produce large amounts of secondary biological sludge, the quantity of excess sludge produced is 20 times lower in anaerobic processes. This can be explained by the fact that with the same organic load under oxygen exchange about 20 times less metabolic energy is available for the microorganisms. Anaerobic wastewater treatment methods are mainly used for rather high-loaded wastewaters with a COD of 5000 up to 40,000 mg/L from the food and chemical industry [2]. Unfortunately, these methods are normally employed strictly as pretreatment measures. Aerobic follow-up treatment, for example, in a downstream-arranged activated sludge plant, is possible and recommended (Fig. 6).

### Factors Affecting Anaerobic Process Operation

The anaerobic process functions effectively over two temperature ranges: the mesophilic range of  $85\text{--}100^\circ\text{F}$  ( $29\text{--}38^\circ\text{C}$ ) and the thermophilic range of  $120\text{--}135^\circ\text{F}$  ( $49\text{--}57^\circ\text{C}$ ). Although the rates of reaction are much greater in the thermophilic range, the maintenance of higher temperatures is usually not economically justifiable.

Methane organisms function over a pH range of 6.6–7.6 with an optimum near pH 7.0. When the rate of acid formation exceeds the rate of breakdown to methane, a process unbalance results in which the pH decreases, gas production falls off, and the  $\text{CO}_2$  content increases [40]. pH control is therefore essential to ensure a high rate of methane production. According to German literature, the tolerable pH range for anaerobic microorganisms is between 6.8 and 7.5. This means that the anaerobic biocenosis is very pH-specific [38].

With regard to the influence of initial concentration on anaerobic degradation, preliminary laboratory and pilot-scale experimentation on diluted olive oil mill effluents (OME) [44] showed that the anaerobic contact process was able to provide high organic removal efficiency (80–85%) at  $35^\circ\text{C}$  and at an organic load lower than  $4 \text{ kg COD/m}^3\text{-day}$ ; however, in particular at high feed concentration, the process proved unstable due to the inhibitory effects of substances



**Figure 6** Anaerobic–aerobic treatment method.

such as polyphenols. Moreover, additions of alkalinity to neutralize acidity and ammonia to furnish nitrogen for cellular biosynthesis were required.

To overcome these difficulties and improve process efficiency and stability, there are basically two methods that may be adopted [23]: (a) the treatment of combined OME and sewage sludge in contact bioreactors; and (b) operation with more diluted OME in high-rate bioreactors (such as UASB reactors and fixed-bed filters).

In the first method, conventional digesters can be overloaded with concentrated soluble wastes such as OME, and still operate satisfactorily. Moreover, nutrients such as ammonia and buffers are provided by degradation of proteinoous substances from sludge. On this basis, laboratory-scale experimentation [45] has shown that removal efficiencies of 65 and 37% in terms of COD and VSS, respectively, were obtained at 35°C and at an organic load of 4.2 kg COD/m<sup>3</sup>-day (66% from sewage sludge, 34% from OME). Higher OME additions led to process imbalance due to the inhibitory effects of polyphenols. This method, based on anaerobic contact digestion of combined OME and sewage sludge, seems to be suitable only for those locations where the polluting load due to the OME is lower than the domestic wastewater load. In this regard it is worth considering that during the olive oil milling season, OME pollution largely exceeds that from domestic wastewater [23].

With regard to the second method, based on the use of high-rate bioreactors, experimentation on UASB reactors [46,47] showed that COD removal efficiencies of about 70–75% were obtained at 37°C and at an organic load in the range 12–18 kg COD/m<sup>3</sup>-day by adopting a dilution ratio in the range of 1 : 8 to 1 : 5 (OME: tap water; diluted OME initial concentration in the range 11–19 g COD/L). Slightly less satisfactory results were obtained by using anaerobic filters filled with macroreticulated polyurethane foam [45].

It is important to note that immobilization of methanogenic bacteria may decrease the toxicity of phenolic compounds. Another pilot-scale anaerobic–aerobic treatment of OME mixed with settled domestic wastewater [48] produced a final COD concentration of about 160 mg/L, provided that a dilution ratio of 1 : 60 to 1 : 100 was adopted, corresponding to a COD load ratio equal to 3 : 1 for OME and domestic wastewater, respectively. This ratio is typical for those locations with a high density of olive oil mills. However, in addition to the high value required for the dilution ratio, the final effluent did not comply with legal requirements in terms of color and nitrogen [23].

The aforementioned data clearly show that in the treatment of OME, even when carried out with the use of most appropriate technology, that is, anaerobic digestion, it was difficult to reach the treatment efficiencies required by national regulations throughout the Mediterranean area. In particular, methanogenesis, which represents the limiting step in the anaerobic digestion of soluble compounds, is severely hindered by the inhibition caused by the buildup of volatile fatty acids (VFAs) and/or the presence of a high concentration of phenolic compounds and/or oleic acid in the OME. As for phenol, 1.25 g/L leads to 50% activity reduction of acetate-utilizing methanogens [49]. As for oleic acid, it is reported that 5 mM is toxic to methanogenic bacteria [50].

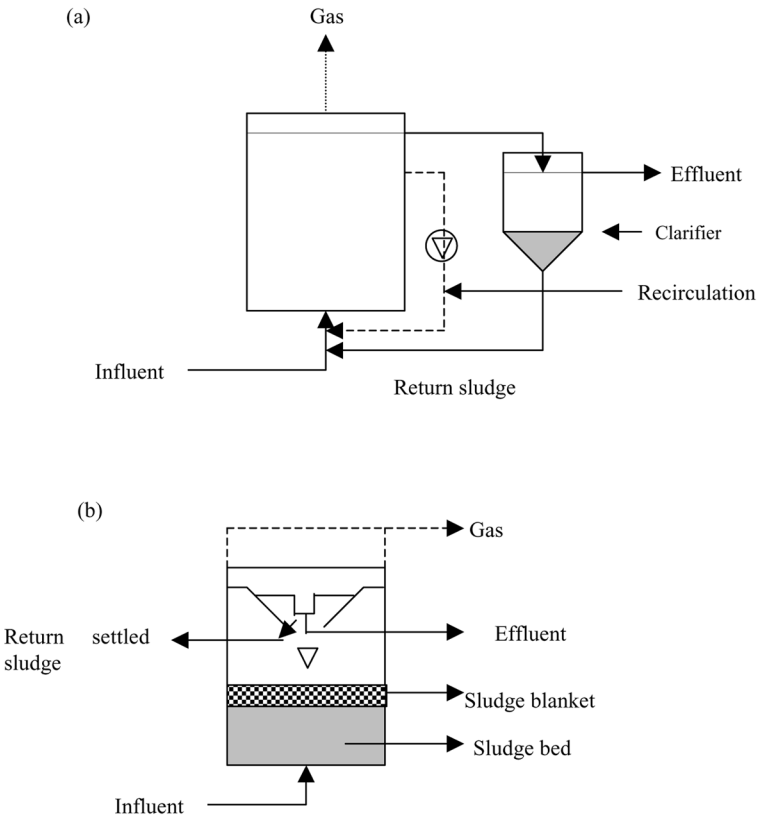
The reader may refer to the following Case Study V to better understand the mechanism of biodegradation of the main compounds contained in the OME in relation to pH, temperature, and initial concentration of effluents, and in particular the mutual coherence of the two successive partial stages occurring in anaerobic digestion of OME, acidogenesis, and methanogenesis.

### **Anaerobic Treatment Systems of Wastewater**

Seasonal operation of olive oil mills is not a disadvantage for anaerobic treatment systems because anaerobic digesters can be easily restarted after several months of mill shutdown [51].

At present there are no large-scale plants. However, the anaerobic contact reactors and upflow sludge-blanket reactors have been mainly studied using several pilot tests (Fig. 7), besides other tested reactors such as anaerobic filters and fluidized-bed reactors.

Sludge retention is decisive for the load capacity and thus the field of application of an anaerobic reactor. In the UASB reactor, favorable sludge retention is realized in a simple way. Wastewater flows into the active space of the reactor, passing from the bottom to the top of the reactor. Owing to the favorable flocculation characteristics of the anaerobic-activated sludge, which in higher-loaded reactors normally leads to the development of activated sludge grains and to its favorable sedimentation capacity, a sludge bed is formed at the reactor bottom with a sludge blanket developing above it. To avoid sludge removal from the reactor and to collect the biogas, a gas-sludge separator (also called a three-phase separator) is fitted into the upper part of the reactor. Through openings in the bottom of this sedimentation unit, the separated sludge returns into the active space of the reactor. Because of this special construction, the UASB reactor has a very high load capacity. In contrast to the contact sludge process, no additional sedimentation tank is necessary, which would require return sludge flow for the anaerobic activated sludge, resulting in a reduction of the effective reactor volume. Several studies on anaerobic treatment of olive oil wastewaters have been carried out, and data from different publications are listed in Table 11.



**Figure 7** Anaerobic treatment processes: (a) Contact sludge reactor; (b) UASB reactor.

**Table 11** Summary of the Data from Different Publications Related to Anaerobic Treatment of Olive Oil Wastewater

	Fiestas (1981) <sup>14</sup>	FIW <sup>38</sup>	Aveni (1984) <sup>44 a</sup>	FIW <sup>38</sup>	FIW <sup>38</sup>	FIW <sup>38</sup>	Steegmans (1992) <sup>15</sup>	Ubay (1997) <sup>22</sup>
Treatment process	Contact process	UASB reactor	Contact process	Conventional reactor	UASB reactor	Packed-bed reactor	UASB reactor	UASB reactor
Influent	33–42 g BOD <sub>5</sub> /L	4–6 g COD/L	–	20–65 g COD/L	5–15 g COD/L	45–50 g COD/L	26.7 g COD/L	5–22.6 g COD/L
Volumetric loading	1.2–1.5 kg BOD/(m <sup>3</sup> *day)	15–20 kg COD/(m <sup>3</sup> *day)	4 kg COD/(m <sup>3</sup> *day)	20–65 kg COD/(m <sup>3</sup> *day)	5–21 kg COD/(m <sup>3</sup> *day)	–	1.59 kg COD/(m <sup>3</sup> *day)	5–18 kg COD/(m <sup>3</sup> *day)
Purification efficiency	80–85% BOD	70% COD	80–85% COD	80–85% COD	70–80% COD	45–55% COD	55.9% COD	70–75% COD
Gas production	700 L/kg BOD <sub>elim</sub>	–	–	550 L/kg COD <sub>elim</sub>	8000 L/(m <sup>3</sup> *day)	300–600 L/kg COD <sub>elim</sub>	50–100 L CH <sub>4</sub> /kg COD <sub>elim</sub>	350 L CH <sub>4</sub> /kg COD <sub>elim</sub>
Methane content	70%	–	–	50–70 %	70–80 %	84 %	70%	–

<sup>a</sup>Based on laboratory and pilot experimentation on diluted olive oil mill effluents.

Source: Refs. 14, 15, 22, 38, 44.



## Case Studies

Many anaerobic pilot plants have been applied successfully in treating OMW in various parts of the world. The following describe some of these pilot plants and tests.

*Case Study I.* The search for an economic treatment process for wastewater from an olive oil extraction plant in Kandano (region of Chania, Crete) led to the concept of a pilot plant. The goal was to study the efficiency of separate anaerobic treatment of the settled sludge and of the sludge liquor from the settling tank (Fig. 8) [38].

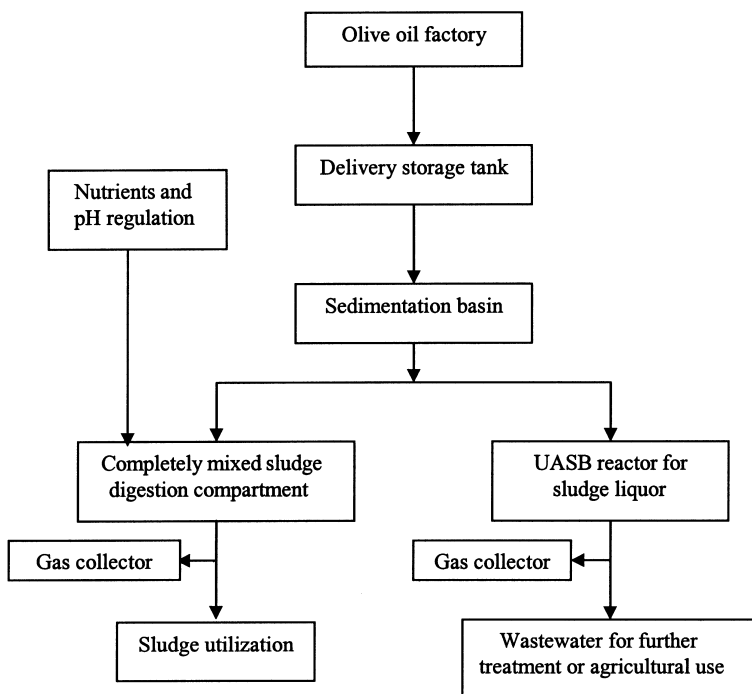
Description of the plant:

- delivery, storage container;
- settling tank with a capacity of 650 m<sup>3</sup>;
- anaerobic digester (volume: 16 m<sup>3</sup>) for the sludge;
- UASB (upflow anaerobic sludge blanket) reactor (volume: 18 m<sup>3</sup>) for the sludge liquor.

The plant can receive one-sixth of the total wastewater volume produced. The daily influent is 30 m<sup>3</sup>. The wastewater is collected in a storage container where its quality and quantity are analyzed. The raw wastewater is then retained for ten days in the settling tank where the particular substances settle.

Two separate zones are formed:

- the supernatant zone;
- the thickening and scraping zone.



**Figure 8** Pilot plant for treatment of wastewater from olive oil extraction in Kandano (a region of Chania, Crete) (from Ref. 38).

Both the preclarified sludge liquor and the primary sludge withdrawn are anaerobically treated in parallel. There is the risk of scum layer formation in the settling tank, which may lead to strong odors. This problem can be solved by covering the tank or using a scraper bridge.

The preclarified sludge liquor is preheated and fed into the UASB reactor. The biogas obtained is withdrawn from the upper part of the reactor and conducted to the gas storage room. The liquid phase is submitted to sedimentation, then stored in a container.

After the addition of nutrients and pH regulation, the primary sludge, showing a high water content (65–80%), is fed into a completely mixed digester. The biogas is again withdrawn from the upper part of the digester and conducted to the gas storage room. The treated liquid phase is conducted to the settling tank and then to the collecting container. At this point, the biogas is incinerated.

To build a plant that treats 30 m<sup>3</sup> per day, a surface of at least 1 ha is necessary, at the cost of about 150,000 Euro. This sum does not include the construction costs for a soil filter or an irrigation system because these strongly depend on the location of the plant. At least 50% of the staff should be skilled workers, including a chemical engineer who is in charge of plant operation. Because of its high realization costs, this method is suited for industrial-scale oil mills, or as a central treatment facility for several oil mills.

The biogas may be used by the plant itself, or it may be fed into the public supply grid. The liquid phase, designated to be spread on agricultural land, is stored in an open pit. After drying, the solids can be sold as soil-improving material or as humus after having been mixed with vegetable residues. There are no odor nuisances from escaping liquids from the digesters, and maintenance costs are moderate. If the treated wastewater is additionally submitted to soil filtration and then used for irrigation or as fertilizer, the water cycle is closed, thus solving the problem of olive oil waste.

*Case Study II.* A pilot plant was operated between January 1993 and April 1994 to treat the wastewater from an oil mill in the region of Kalyvia/Attica (Fig. 9) [38].

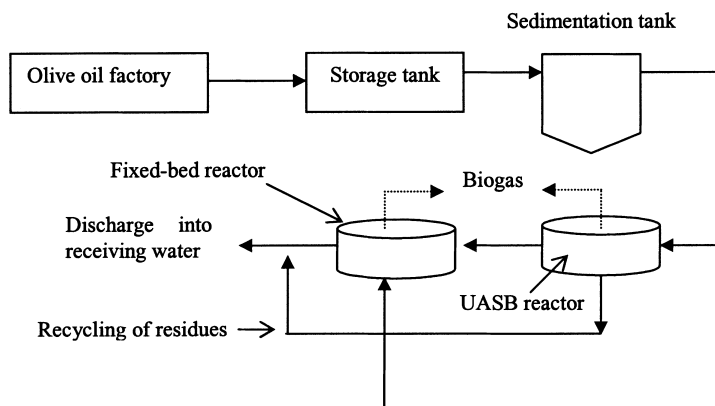
Description of the plant:

- delivery, storage tank with a volume of 20 m<sup>3</sup> for the total quantity of margine produced;
- settling tank with a volume of 4 m<sup>3</sup>;
- UASB reactor with a working volume of 2 m<sup>3</sup>, additionally equipped with a high-performance heat exchanger to maintain the temperature during the mesophile phase;
- fixed-bed reactor with a working volume of 2 m<sup>3</sup>, a high-performance heat exchanger, and recirculation system;
- gas storage room;
- seven tests (mesophile phase) have been carried out under varying operational conditions.

The organic load was degraded by 88–89%. During the fourth test, the phenol content was reduced by 74–75%, while the biogas production was 21–23 L gas per liter of bioreactor volume.

Foregoing the addition of CaO and expensive processing equipment facilitates the treatment for wastewater from oil mills. Plant investments can be quickly amortized by methane production.

*Case Study III.* A pilot test has been carried out in Tunisia with a sludge-bed reactor and an anaerobic contact reactor, followed by a two-stage aerobic treatment [15,38]. To compare the two different anaerobic processes, the semitechnical pilot plant was designed with parallel streams. The goal was not only to determine parameters and values for design and operation of optimal anaerobic–aerobic treatment, dependent on the achievable purification



**Figure 9** Pilot plant for treatment of wastewater from an olive oil mill in the region of Kalyvia, Attica (from Ref. 38).

capacity, but also to examine, modify, and further develop the process technology with regard to optimizing the purification capacity of the single stages, the total purification capacity, and process stability.

The tests determined that both anaerobic–aerobic procedures proved successful in the treatment of liquid waste from olive oil production. Comparing the anaerobic contact process with the bed process, neither is clearly favored. Both procedures lead to nearly the same results with regard to pretreatment of liquid waste from olive oil production.

*Case Study IV.* The anaerobic treatability of olive mill effluent was investigated using a laboratory-scale UASB reactor (with active volume of 10.35 L) operating for about 6 months. The black water collected from a traditional olive oil extraction plant in Gemlik village (Turkey) was used as the feed [22].

Active anaerobic sludge retained in the UASB reactor after a previous study was used as the seed. During the startup, pH was maintained in the range 6.8–8.0 and the average temperature was kept at mesophilic operating conditions (34°C) in the reactor. NaOH solution was added directly to the reactor to maintain the required pH levels when it was necessary. Urea was added to the feed to provide COD : N : P ratio of 350 : 5 : 1 in the system due to N deficiency of the feed.

In the first part of this study, the reactor was operated with feed COD concentrations from 5000 to 19,000 mg/L and a retention time of 1 day, giving organic loading rates (OLR) of 5–18 kg COD/m<sup>3</sup>-day. Soluble COD removal was around 75% under these conditions. In the second part of the study, feed COD was varied from 15,000 to 22,600 mg/L while retention times ranged from 0.83 to 2 days; soluble COD removal was around 70%. A methane conversion rate of 0.35 m<sup>3</sup> per kg COD removed was achieved during the study. The average volatile solids or biomass (VS) concentration in the reactor had increased from 12.75 g/L to 60 g/L by the end of the study. Sludge volume index (SVI) determinations performed to evaluate the settling characteristics of the anaerobic sludge in the reactor indicating excellent settleability with SVI values of generally less than 20 mL/g. Active sludge granules ranging from 3 to 8 mm in diameter were produced in the reactor.

In short, it may be concluded that anaerobic treatment may be a very feasible alternative for olive mill effluents, but additional posttreatment, such as aerobic treatment, would be needed to satisfy discharge standards required for receiving waters (river, lake).

*Case Study V.* This experiment aimed at gaining better insight into the degradation of the main compounds contained in the OME, in particular, the interaction between the two successive stages occurring in the anaerobic digestion: acidogenesis and methanogenesis [23].

Fresh OME was obtained from the olive oil continuous centrifuge processing plant of Montelibretti (Rome). The tests were carried out in 500 mL glass bottles with perforated screw tops with latex underneath, which served to ensure that the bottles were airtight. These bottles were filled with OME diluted in distilled water to obtain the required concentration (in the range of 10–60 g COD/L). The inoculum was obtained from a sludge anaerobic digester at the East Rome wastewater treatment plant. The main results that can be drawn from this study are as follows.

Under the most favorable conditions (pH 8.5, 35°C, initial concentration 10 g COD/L, acclimatized inoculum) the OME were degraded with a high conversion yield (70–80%), both in acidogenic and methanogenic tests. Most of the lipids were degraded both in acidogenesis and methanogenesis tests. On the other hand, polyphenol-like substances were not degraded at all in acidogenic conditions, whereas they were partially removed in methanogenic conditions. Such a difference has been observed both in OME and synthetic solutions. A little methanogenic activity, established in acidogenic conditions because of the partial degradation of the chemical inhibitor, seems to be the key factor determining lipids degradation, even in acidogenesis tests.

It was also experimentally reported that polyphenol degradation is directly related to the presence of an intense methanogenic activity. In addition, bioconversion yields of OME in acidogenesis are remarkably less sensitive to the effect of pH and substrate concentrations than in methanogenesis. This result might lead to adoption of two-phase anaerobic digestion of OME as a suitable process for optimizing its performance. It is our recommendation that further research be conducted in this scope.

### 17.5.5 Design Example 3

The design of an anaerobic contact reactor to achieve 90% removal of COD from a wastewater flow 180 m<sup>3</sup>/day (47,600 gal/day) resulted from a group of neighboring olive mills. The following conditions apply: total influent COD = 13,000 mg/L; nonremovable COD = 2500 mg/L; removable COD (COD<sub>R</sub>) = 10,500 mg/L; and COD to be removed = 90%. The process parameters are: sludge age (SRT) = 15 days (minimum); temperature = 35°C;  $a = 0.14$  mg VSS/mg COD<sub>R</sub>;  $b = 0.02$  mg VSS/mg VSS-day;  $K' = 0.0005$  L/mg-day;  $X_v = 5000$  mg/L.

#### Solution

(a) The digester volume from the kinetic relationship:

$$\text{Detention time, } t = \frac{S_r}{X_v K' S} = \frac{(10,500)(0.9)}{(5000)(0.0005)(1050)} = 3.6 \text{ day}$$

The digester volume is therefore:

$$V = (3.6 \text{ day})(180 \text{ m}^3/\text{day}) = 648 \text{ m}^3 \text{ (0.1712 MG)}$$

Check SRT from the equation:

$$\begin{aligned} \text{SRT} &= \frac{X_v t}{\Delta X_v} = \frac{X_v t}{a S_r - b X_v t} \\ &= \frac{(5000)(3.6)}{(0.14)(9450) - (0.02)(5000)(3.6)} = 18.7 \text{ day} \end{aligned}$$

This is in excess of the recommended SRT of 15 days to ensure the growth of methane formers.

(b) The sludge yield from the process is:

$$\begin{aligned} \Delta X_v &= a S_r - b X_v t \\ &= (0.14)(9450) - (0.02)(5000)(3.6) = 963 \text{ mg/L} \end{aligned}$$

$$\begin{aligned} \Delta X_v &= 963 \text{ mg/L} \times 180 \text{ m}^3/\text{day} \\ &= 173.34 \text{ kg/day} \text{ (381.35 lb/day)} \end{aligned}$$

(c) Gas production:

$$G = 0.351(S_r - 1.42\Delta X_v),$$

where  $G = \text{m}^3$  of  $\text{CH}_4$  produced/day

$$\begin{aligned} G &= 0.351[(9.450)(180) - (1.42)(173.34)] \\ &= 0.351(1701 - 246.14) = 511 \text{ m}^3 \text{ CH}_4/\text{day} \end{aligned}$$

or

$$G = 5.62(S_r - 1.42\Delta X_v),$$

where  $G = \text{ft}^3$  of  $\text{CH}_4$  produced/day

$$\begin{aligned} G &= 5.62[(9450)(0.0476 \text{ MG/day})(8.34) - (1.42)(381.35)] \\ &= 18,040 \text{ ft}^3/\text{day} \text{ (511 m}^3/\text{day)} \end{aligned}$$

Gas production can be also determined by using the approximate estimation, which is 1 kg  $\text{COD}_{\text{elim}}$  yields about 0.3–0.5  $\text{m}^3$  of methane. Therefore, total gas production:

$$\begin{aligned} G &= 9.45 \text{ kg COD/m}^3 \times 180 \text{ m}^3/\text{day} \times 0.3 \text{ m}^3 \text{ CH}_4/\text{kg COD} \\ &= 510 \text{ m}^3 \text{ CH}_4/\text{day} \end{aligned}$$

(d) Heat required can be estimated by calculating the energy required to raise the influent wastewater temperature to 35°C (95°F) and allowing 1°F (0.56°C) heat loss per day of detention time. Average wastewater temperature = 24°C (75.2°F) and heat transfer efficiency = 50%.

$$\begin{aligned} \text{Btu}_{\text{req}} &= \frac{W(T_i - T_e)}{E} \times (\text{specific heat}) \\ &= \frac{(47,600 \text{ gal/day})(8.34 \text{ lb/gal})(95^\circ\text{F} + 3.6^\circ\text{F} - 75.2^\circ\text{F})}{0.5} \times \left( \frac{1 \text{ Btu}}{1 \text{ lb}^\circ\text{F}} \right) \\ &= 18,600,000 \text{ Btu} \text{ (19,625,000 kJ)} \end{aligned}$$

The heat available from gas production is:

$$\begin{aligned} \text{Btu}_{\text{available}} &= (18,040 \text{ ft}^3 \text{ CH}_4/\text{day})(960 \text{ Btu}/\text{ft}^3 \text{ CH}_4) \\ &= 17,320,000 \text{ Btu}/\text{day} \text{ (18,300,000 kJ}/\text{day)} \end{aligned}$$

External heat of  $18,600,000 - 17,320,000 = 1,280,000 \text{ Btu}/\text{day}$

$1,325,000 \text{ kJ}/\text{day}$  should be supplied to maintain the reactor at  $35^\circ\text{C}$  ( $95^\circ\text{F}$ ).

(e) Nutrient required as nitrogen is:

$$\begin{aligned} N &= 0.12\Delta X_v = 0.12 \times 173.34 \text{ kg}/\text{day} \\ &= 20.80 \text{ kg}/\text{day} \text{ (45.8 lb}/\text{day)} \end{aligned}$$

The phosphorus required is:

$$\begin{aligned} P &= 0.025\Delta X_v = 0.025 \times 173.34 \text{ kg}/\text{day} \\ &= 4.33 \text{ kg}/\text{day} \text{ (9.534 lb}/\text{day)} \end{aligned}$$

### Remarks

1. The effluent from the anaerobic plant does not achieve the national quality criteria of the water resources because of the high values of residual  $\text{COD}_R$  ( $10\% = 1050 \text{ mg}/\text{L}$ ) and nonremovable COD ( $2500 \text{ mg}/\text{L}$ ). Therefore, we recommend that an aerobic treatment process (such as activated sludge) follow the anaerobic process to produce an effluent meeting the quality limits.
2. Another suggestion is to apply wet air oxidation (WAO) as a pretreatment step to remove biorecalcitrant compounds, which leads to the reduction of anaerobic reactor volume and also to the reduction of energy consumption. This combined WAO–anaerobic process achieves an overall performance to meet the national regulations of Mediterranean countries.

## 17.5.6 Combined Biological Treatment Processes

The following models are suggested for combined biological treatment processes of OMW. It has been referred to as the combined treatment in order to realize the following: partial treatment by high organic load in the first phase and full treatment by low organic load in the second phase.

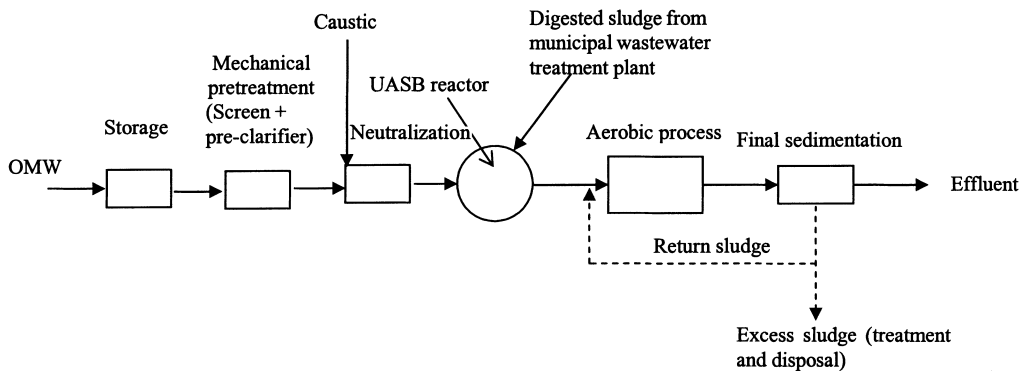
### Treatment on Site

Before discharge to a nearby water recourse, OMW could be subjected to either of the two hereafter proposed complete treatment systems.

*Anaerobic–Aerobic Treatment.* The combined model “anaerobic–aerobic treatment” (Fig. 10) may be considered quite practical, both environmentally and economically. This method can be applied without serious emissions into air, water, and soil, keeping to the key objectives of environmental policy adopted worldwide.

Anaerobic processes are especially suited for the treatment of high-load wastewater with a COD concentration of thousands ( $\text{mg}/\text{L}$ ) in industry. Moreover, the climatic conditions in the olive-growing and production countries are optimal for anaerobic processes.

Combining anaerobic and aerobic processes lessens the disadvantages resulting from separate applications. The first step includes the advantages of the anaerobic process concerning degradation efficiency, energy self-sufficiency, and minimal excess sludge production. The

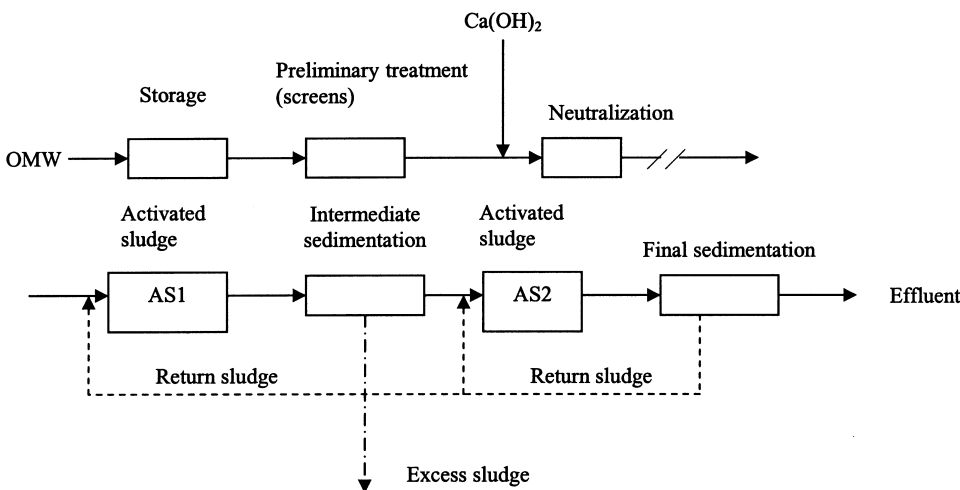


**Figure 10** Combined anaerobic–aerobic treatment model (on site).

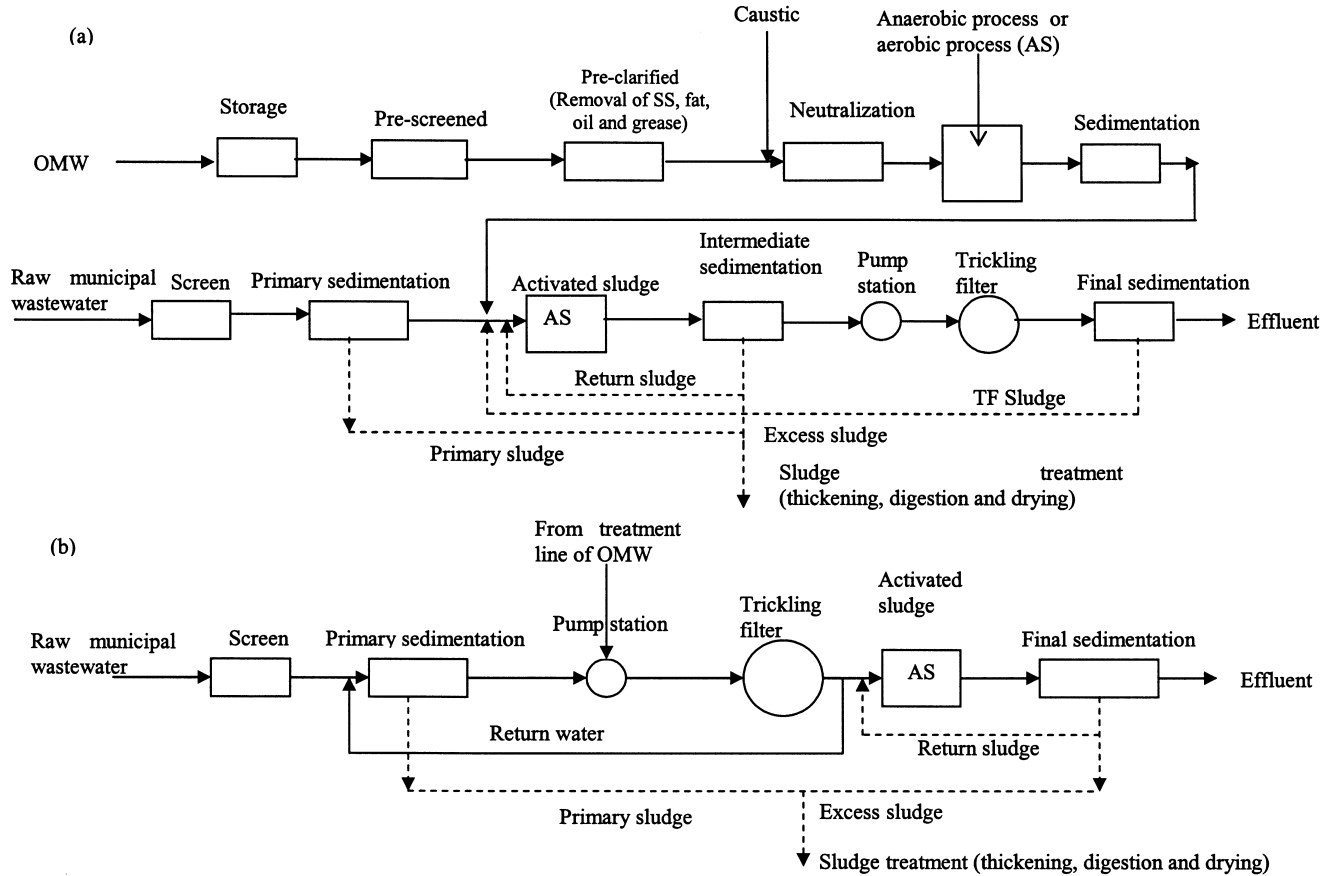
disadvantages of aerobic treatment are nearly compensated by the anaerobic preliminary stage. The high quantity of excess sludge that normally results is strongly reduced. At the same time, the aeration energy needed for the aerobic process is also considerably minimized. With regard to treatment efficiency, plant reliability, and costs, the anaerobic–aerobic model well suits the treatment of olive oil mill wastewater (alpechin) from both ecological and economical aspects [38].

*Two-Stage Aerobic Treatment.* This is a combined treatment model of two-stage aerobic treatment based on an activated sludge process, as illustrated in Fig. 11.

*Treatment in Combination with Municipal Wastewater.* In the case where full treatment onsite is not possible, OMW after pretreatment should be drained to a municipal wastewater treatment plant in the vicinity. Figure 12 illustrates clearly the combined treatment of OMW with municipal wastewater, where two streams (a and b) are suggested.



**Figure 11** Combined treatment model of two-stage activated sludge process (on site). (Note: In dispensing with the primary sedimentation tank, it is recommended here to recirculate the return sludge from the final sedimentation to both the AS1 and AS2. Consequently, excess sludge will be discharged only from the intermediate sedimentation tank.)



**Figure 12** Combined treatment of OMW with municipal wastewater. (Note: Aerobic process may need addition of nutrients in order to maintain the ratio COD : N : P at 100 : 5 : 1, this ratio being commonly satisfactory for microorganism growth and activity.) (a) Where the activated sludge process is before a trickling filter process is preferable to line (b) in general, with the consideration that line (b) (trickling filter-activated sludge combined model) dispenses with the intermediate sedimentation basin.



The aforementioned combined models suggested for treatment of OMW realize different degrees of efficiency depending on the wastewater characteristics, discharge regulations, organic load in each phase, type and number of phases within the treatment line or plant. In this respect it is necessary that the treated wastewater meet the quality criteria of the water resources (drinking, irrigation, recreation, etc.), where it is supposed to be discharged. In the event the treated wastewater is intended to be used directly for irrigation, it should meet local criteria adopted in that country or those adopted by the Food and Agriculture Organization (FAO).

### 17.5.7 Design Example 4

To continue Example 3, assuming that an air-activated sludge plant follows the anaerobic process, a design for this plant is required under the following conditions to produce an effluent with a COD of 30 mg/L. The aerobic process parameters are:  $T = 20^\circ\text{C}$ ;  $a = 0.5$ ;  $F/M = 0.3 \text{ day}^{-1}$ ;  $a' = 0.55$ ;  $X_v = 2500 \text{ mg/L}$ ;  $b = 0.15/\text{day}$  at  $20^\circ\text{C}$ ; power = 1.5 lb  $\text{O}_2/(\text{hp}\cdot\text{hour})$  (0.91 kg  $\text{O}_2/\text{kW}$ ).

#### Solution

$$t = \frac{S_0}{X_v(F/M)} = \frac{1050}{2500 \times 0.3} = 1.4 \text{ day}$$

$$S_r = S_0 - S_e = 1050 - 30 = 1020 \text{ mg/L}$$

$$K = \frac{(S_0 S_r)}{t S_e X_v} = \frac{1050 \times 1020}{1.4 \times 30 \times 2500} = 10.2/\text{day}$$

The aeration tank volume is:

$$V = Q \cdot t = 180 \times 1.4 = 252 \text{ m}^3 \text{ (66,640 gal)}$$

Calculate the degradable fraction  $X_d$  using the following equation:

$$\begin{aligned} X_d &= \frac{aS_r + bX_v t - [(aS_r + bX_v t)^2 - 4bX_v t \times 0.8aS_r]^{1/2}}{2bX_v t} \\ &= \frac{(0.5 \times 1020) + (0.15 \times 2500 \times 1.4) - [\dots\dots\dots]^{1/2}}{2 \times 0.15 \times 2500 \times 1.4} \\ &= \frac{(510 + 525) - [(510 + 525)^2 - (4 \times 525 \times 0.8 \times 510)]^{1/2}}{2 \times 525} \\ &= \frac{1035 - 463}{1050} = 0.545 \end{aligned}$$

The oxygen required is:

$$\begin{aligned} \text{O}_2/\text{day} &= (a'S_r + 1.4bX_dX_v t)Q \\ &= [(0.55 \times 1020) + (1.4 \times 0.15 \times 0.545 \times 2500 \times 1.4)] \times 47,600 \text{ gal} \times 8.34 \times 10^{-6} \\ &= 382 \text{ lb/day} = 16 \text{ lb/hour (7.3 kg/hour)} \end{aligned}$$

The power required is:

$$\begin{aligned} \text{hp} &= \frac{\text{O}_2/\text{hour}}{[1.5 \text{ lb O}_2/(\text{hp}\cdot\text{hour})]} = \frac{16}{1.5} \\ &= 10.7 \text{ hp (8 kW)} \end{aligned}$$

Other olive oil mills wishing to economize their operations would like to join the abovementioned combined anaerobic–aerobic plant for the treatment of their wastewater (45 m<sup>3</sup>/day), without affecting the plant's efficiency.

- Compute the new effluent from the anaerobic process assuming ( $X_v$ ) remains the same; what will the new gas production be?
- What modifications to the aerobic process must be made to maintain the same effluent quality? Assume the sludge settling characteristics are the same as originally and the volatile content of the sludge is 75%.

### Solution

The load to the plant is increased to 225 m<sup>3</sup>/day (59,400 gal/day).

(a) *Anaerobic process.* New effluent concentration; from example 3:  $SRT_{\min} = 15$  days;  $T = 35^\circ\text{C}$ ;  $a = 0.14$ ;  $b = 0.02$ ;  $k' = 0.0005$  L/(mg-day);  $X_v = 5000$  mg/L;  $\text{COD}_R = 10,500$  mg/L; and volume = 648 m<sup>3</sup> (0.1712 MG).

The new detention time is:

$$t' = \frac{V}{Q} = \frac{648}{225} = 2.9 \text{ day}$$

The COD effluent from the anaerobic process can be estimated by:

$$\begin{aligned} \text{COD}_E &= \frac{\text{COD}_{\text{removed}}}{X_v K' t'} = \frac{(\text{COD}_R - \text{COD}_E)}{X_v K' t'} \\ &= \frac{\text{COD}_R}{(1 + X_v K' t')} \\ &= \frac{10,500}{(1 + 5000 \times 0.0005 \times 2.9)} \\ &= 1273 \text{ mg/L} \end{aligned}$$

The COD removed is:

$$\begin{aligned} \text{COD}_{\text{removed}} &= \text{COD}_R - \text{COD}_E \\ &= 10,500 - 1273 \\ &= 9227 \text{ mg/L} \end{aligned}$$

Check SRT using the equation:

$$\begin{aligned} \text{SRT} &= \frac{X_v t'}{\Delta X_v} = \frac{X_v t'}{a\text{COD}_{\text{removed}} - bX_v t'} \\ &= \frac{5000 \times 2.9}{(0.14 \times 9227) - (0.02 \times 5000 \times 2.9)} \\ &= 14.5 \text{ day} \approx 15 \text{ day} \quad \text{OK} \end{aligned}$$

*New gas production.* The sludge yield is:

$$\begin{aligned} \Delta X_v &= (a\text{COD}_{\text{removed}} - bX_v t')Q \\ &= (0.14 \times 9227 - 0.02 \times 5000 \times 2.9) \text{ mg/L} \times 59,400 \text{ gal/day} \\ &\quad \times 8.34 \times 10^{-6} \text{ (lb/MG)/mg/L} \\ &= 496.4 \text{ lb/day (225.36 kg/day)} \end{aligned}$$

The mass of COD removed per day is:

$$\begin{aligned} S_r &= \text{COD}_{\text{removed}} \times Q \\ &= 9227 \text{ mg/L} \times 59,400 \text{ gal/day} \times 8.34 \times 10^{-6} \\ &= 4571 \text{ lb/day (2076 kg/day)} \end{aligned}$$

or

$$S_r = 9227 \text{ mg/L} \times 225 \text{ m}^3/\text{day} \times 10^{-3} = 2076 \text{ kg/day}$$

The methane production can be estimated from:

$$G = 5.62(S_r - 1.42\Delta X_v)$$

where  $G$  is given in  $\text{ft}^3$  of  $\text{CH}_4/\text{day}$

$$\begin{aligned} G &= 5.62(4571 - 1.42 \times 496.4) \\ &= 21,727 \text{ ft}^3/\text{day (615 m}^3/\text{day)} \end{aligned}$$

(b) *Aerobic process.* The new detention time is:

$$t' = \frac{252 \text{ m}^3}{225 \text{ m}^3/\text{day}} = 1.12 \text{ day}$$

The new COD removed:

$$S'_r = S'_0 - S_e = 1273 - 30 = 1243 \text{ mg/L}$$

From the equation:

$$\frac{S_0 - S_e}{X_v t} = K \frac{S_e}{S_0}$$

By rearrangement, the new MLVSS are obtained as

$$\begin{aligned} X'_v &= (S'_0 S'_r) / (t' S_e K) \\ &= (1273) \times (1243) / (1.12 \times 30 \times 10.2) \\ &= 4617 \text{ mg VSS/L} \end{aligned}$$

and the MLSS are:

$$\text{MLSS} = 4617/0.75 = 6156 \text{ mg/L}$$

The new  $F/M$  is:

$$\begin{aligned} (F/M)' &= S'_0/(X'_v t') \\ &= 1273/(4617 \times 1.12) = 0.25/\text{day} \end{aligned}$$

Power increase, the new degradable factor is:

$$X'_d = 0.50$$

The new oxygen required is:

$$\begin{aligned} \text{O}_2/\text{day} &= (a'S'_r + 1.4bX'_dX'_v t')Q \\ &= (0.55 \times 1243 + 1.4 \times 0.15 \times 0.5 \times 4617 \times 1.12) \times 59,400 \text{ gal} \times 8.34 \times 10^{-6} \\ &= 608 \text{ lb/day} = 25.3 \text{ lb/hour} (11.5 \text{ kg/hour}) \end{aligned}$$

The new power required is:

$$h/p = \frac{25.3 \text{ lb/hour}}{1.5} = 16.9 \text{ hp} (12.6 \text{ kW})$$

The power increase is:

$$\text{hp}_{\text{inc.}} = 16.9 - 10.7 = 6.2 \text{ hp} (4.6 \text{ kW})$$

### 17.5.8 Design Example 5

A 7500 m<sup>3</sup>/day (2.0 million gal/day) municipal activated sludge plant operates at an  $F/M$  of 0.3 day<sup>-1</sup>. A group of olive oil mills needs to discharge 450 m<sup>3</sup>/day (0.12 million gal/day) of wastewater with a BOD of 8000 mg/L to the plant. What pretreatment is requested of the mills to reduce the BOD in their wastewater, in order to win the plant's approval?

#### Solution

(a) Municipal sewage: flow = 7500 m<sup>3</sup>/day (2.0 million gal/day);  $S_0$  (BOD) = 300 mg/L; Soluble BOD = 100;  $F/M$  = 0.3;  $X_v$  = 2500 mg/L;  $S_c$  (soluble) = 10 mg/L;  $K$  = 8/day at 20°C. (b) Olive mill wastewater: flow = 450 m<sup>3</sup>/day (0.12 MG/day);  $S_0$  (BOD) = 8000 mg/L;  $K$  = 2.6/day at 20°C; estimated MLVSS = 3500 mg/L.

Detention time is:

$$\begin{aligned} \frac{F}{M} &= \frac{S_0}{X_v t} \\ t &= \frac{300}{2500 \times 0.3} = 0.4 \text{ day} \end{aligned}$$

Average reaction rate  $K$  will be:

$$\frac{7500(8) + 450(2.6)}{7950} = 7.7/\text{day}$$

The new detention time is  $0.4 \times 7500/7950 = 0.38$ . The influent to the plant to meet the permit can be calculated:

$$\frac{S_0 - S_e}{X_v t} = K \frac{S_e}{S_0}$$

$$S_0^2 - S_e S_0 - S_e K X_v t = 0$$

$$S_0 = \frac{S_e + \sqrt{S_e^2 + 4S_e K X_v t}}{2} = \frac{10 + \sqrt{100 + (4 \times 10 \times 7.7 \times 3500 \times 0.38)}}{2}$$

$$= 325 \text{ mg/L of soluble BOD}$$

The concentration of BOD in the pretreated mill wastewater can then be calculated by a material balance:

$$Q_s(S_{0,s}) + Q_l(S_{0,l}) = (Q_s + Q_l)S_{0,s+l}$$

$$7500(100) + 450(S_{0,l}) = 7950(325)$$

or

$$2.0(100) + 0.12(S_{0,l}) = 2.12(325)$$

$$S_{0,l} = 4075 \text{ mg/L}$$

Pretreatment is required to reduce about 50% of the BOD in the mill wastewater.

(c) *Temperature effects*: Determine the change in MLVSS that will be required when the temperature coefficient  $\theta$  increases from 1.015 to 1.04 due to an increase in soluble mill wastewater BOD:

$$\frac{K_{20}}{K_{10}} = (1.015)^{10} = 1.16 \text{ sewage}$$

$$\frac{K_{20}}{K_{10}} = (1.04)^{10} = 1.48 \text{ sewage-mill-wastewater}$$

The increase in MLVSS can be calculated as:

$$\frac{1.48}{1.16} \times 2500 \text{ mg/L} = 3190 \text{ mg/L}$$

## Remarks

1. To achieve the BOD reduction of about 50% in the olive oil mill effluents, the anaerobic process should be recommended as pretreatment.
2. The municipal activated sludge plant could not achieve the quality limits or criteria of the water resources because of the high value of BOD in the mill wastewater (4075 mg/L). In such a case, an additional aerobic degradation stage is needed, such as activated sludge or trickling filter as illustrated in [Figure 12](#).

## 17.5.9 Wet Air Oxidation and Ozonation

The clear advantages of the anaerobic process make it the process of choice for treating olive oil effluents [52]. However, many problems concerning the high toxicity and inhibition of

biodegradation of these wastes have been encountered during anaerobic treatments, because some bacteria, such as methanogens, are particularly sensitive to the organic contaminants present in the OME. The biorecalcitrant and/or inhibiting substances, essentially phenolic compounds (aromatics), severely limit the possibility of using conventional wastewater anaerobic digestions [53] or lead to difficulties in the anaerobic treatment of OME [23].

Moreover, it was proved that the anaerobic sludge digestion of OME in UASB-like reactors was unstable after a relatively short period of activity [54]. Consequently, anaerobic biological treatment as a unique process showed limited efficiency in the removal of aromatics. Therefore, other treatments such as chemical oxidation have been investigated for olive oil mill wastewater and for table olive wastewater purification, with encouraging results.

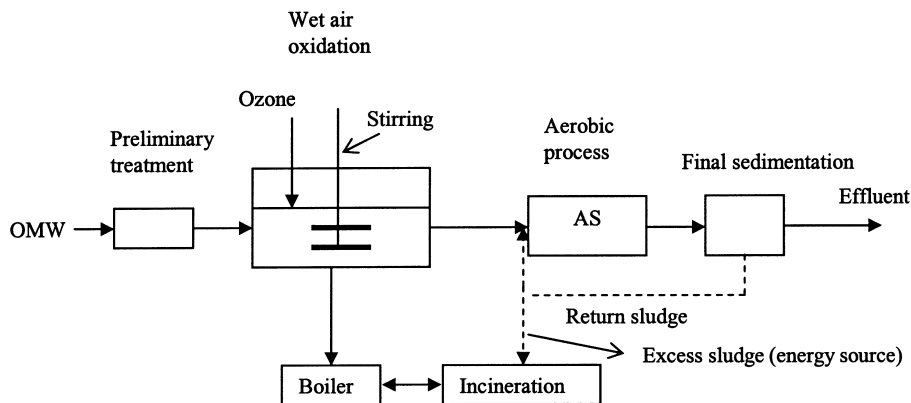
This chemical oxidation proved to be very effective in treating wastewaters that contain large quantities of aromatics [55,56]. Recently, integrated chemico-physical and biological technologies have been developed as efficient processes to achieve high purification levels in wastewaters characterized by difficult biotreatability [57].

The effectiveness of the combination of chemical oxidation and biological degradation relies on the transformation of nonbiodegradable substances into biogenic compounds readily assimilated by microorganisms [57].

### Principle of Wet Air Oxidation (WAO)

The type of chemical preoxidation used in integrated processes is highly dependent on the characteristics and nature of the wastewater to be treated. Thus, in the case of effluents with a high content of phenol-type substances, oxidizing systems based on the use of oxygen or ozone at high temperatures and pressures have been shown to readily degrade phenolic structures [58]. Wet air oxidation (WAO) is an oxidation process, conducted in the liquid phase by means of elevated temperatures (400–600 K) and pressures (0.5–20 MPa). The oxidant source is an oxygen-containing gas (usually air).

As pressure increases, the temperature rises, which leads to an increasing degree of oxidation. With far-reaching material conversion, only the inorganic final stages of  $\text{CO}_2$  and water (and possibly other oxides) are left. With incomplete degradation, the original components (which often are nondegradable) are decomposed to biodegradable fragments. Therefore, it is useful to install a biological treatment stage downstream of the wet oxidation stage (Fig. 13) (Case Study I).



**Figure 13** Wet air oxidation–aerobic process.

On other hand, Beltran-Heredia et al. [21] applied an opposite arrangement, that is, aerobic degradation followed by ozonation, in normal conditions where the temperature and the pH values were varied (Case Study II). Oxidizing chemicals are also used instead of oxygen so that even hardly degradable constituents of liquid waste from olive oil production can be destroyed or attacked. Possible oxidizing agents are ozone ( $O_3$ ) or hydrogen peroxide ( $H_2O_2$ ) [59].

The utilization of  $H_2O_2$  has turned out to be environmentally friendly because this oxidizing agent has no negative effects. However, since  $H_2O_2$  quickly undergoes decomposition, its ability to be stored is limited. The OH radicals formed during  $H_2O_2$  decomposition have oxidative effects. Using suitable agents [e.g., titanium dioxide ( $TiO_2$ )] or UV radiation, the development of radicals can be considerably forced [38].

In oxidation systems, ozone in particular has many of the oxidizing properties desirable for use in water and wastewater treatment; it is a powerful oxidant capable of oxidative degradation of many organic compounds, is readily available, soluble in water, and leaves no byproducts that need to be removed. In addition, it may also be used to destroy bacteria, odors, taste, and coloring substances.

It has been reported in the literature that anions of phenolic compounds are more reactive towards oxidative processes than the noncharged species [58,60].

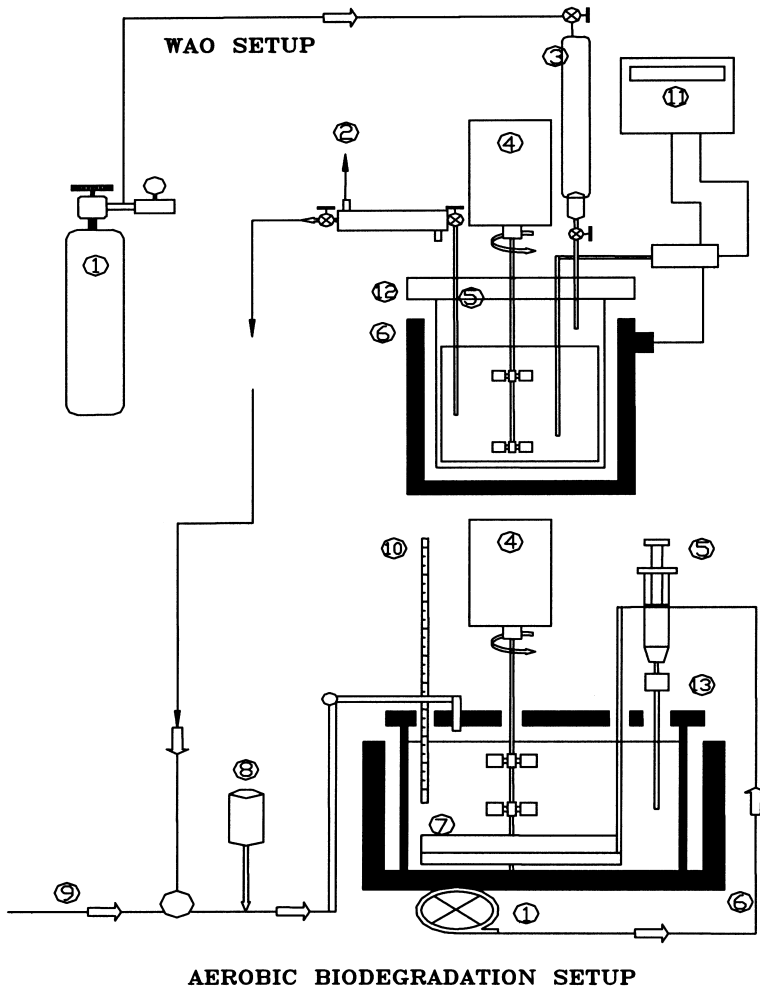
## Case Studies

*Case Study I.* A considerable amount of work has been devoted to the integrated wet air oxidation–aerobic biodegradation process (Fig. 14) in treating olive-processing wastewater in the province of Badajoz, Spain [19]. The most representative parameters are the COD and  $BOD_5$ , with values of 24.45 and 14.8 g  $O_2/L$  respectively, and phenolic content 833 mg phenol/L. Chemical oxygen demand (COD) conversion in the range 30–60% (6 hours of treatment) was achieved by WAO using relatively mild conditions (443–483 K and 3.0–7.0 MPa of total pressure using air). Also noticed was a significant removal of phenolic content at the end of WAO process with conversion values 95%. Use of the homogeneous catalysts such as radical promoters (hydrogen peroxide) resulted in a higher efficiency of the process (between 16 and 33% COD removal improvement, depending on operating conditions). Biodegradability tests conducted after the oxidation pretreatment showed the positive effect of the WAO pretreatment on the aerobic biological oxidation of wastewater. Acclimation of microorganisms to oxygenated species formed in a chemical preoxidation step enhanced the efficiency of the biodegradation.

In conclusion, if WAO is used as a pretreatment step, the advantages associated with the use of the previous oxidation are based on the higher biodegradation rate and better properties of the activated sludge used in the biodegradation process to remove biorecalcitrant compounds.

As inferred and reported from this work [19], the following conclusions may be drawn:

- The WAO process may become thermally self-sustaining, because the COD of the influent is well above 15 g/L. In this case, the wastewater stream would not be diluted and more severe conditions should be applied.
- The seasonal character of these activities (fruit and vegetable related processes) may allow for the use of WAO mobile units, capable of processing up to a maximum of 400–500 L/hour of wastewater (more than needed for these types of industries). As a result, a permanent location is not needed, with subsequent savings in fixed capital costs.
- Use of *in situ* WAO shows additional advantages regarding necessary barreling and hauling to appropriate wastewater plants.



**AEROBIC BIODEGRADATION SETUP**

**Figure 14** Experimental setup of WAO–aerobic processes (from Ref. 19). 1 = Air Cylinder; 2 = Cooling Water; 3 = Injection Port; 4 = Stirring System; 5 = Sampling Port; 6 = Thermostatic Bath; 7 = Porous Plate; 8 = pH Controller; 9 = Dilution Waterline; 10 = Thermometer; 11 = Temperature Controller; 12 = High-Pressure Reaction Vessel; 13 = Glass Bioreactor.

- The consequences of WAO pretreatment may also affect the operability of aerobic biological treatment itself. Thus the benefits are as follows. (a) The biodegradation rate was observed to increase from a nonpretreated effluent to a WAO pretreatment wastewater, which would imply a lower total volume of biological reactor and lower energy consumption (requirements for mixing and aeration) to achieve an overall performance to meet the limits of the environmental legislation. (b) The sludge volume index (SVI) decreased if the WAO pretreatment was applied. An average 20% decrease was observed for biological experiments using pretreated wastewater. This would help to prevent operational problems usually found in activated sludge plants, such as bulking sludge, rising sludge, and nocardia foam, and would allow a wider food-to-microorganisms (F/M) ratio for operation in the aeration tank and lower total volume of the secondary clarifier. (c) An excess of generated sludge as a result of



biological oxidation could be recycled as an energy source by combustion or anaerobic treatment to use in the wastewater treatment plant, or it could even be treated by the same WAO system.

*Case Study II.* The original black-olive wastewater was obtained from a table olive processing plant in the Extremadura community (Spain). The treatment was carried out by ozonation, aerobic biological degradation, and the combination of two successive steps: an aerobic biological process followed by ozonation. For this purpose, the chemical oxygen demand (COD), the total aromatic content (A), and the total phenolic content (Tph), were selected as representative parameters to follow the overall purification process.

The experimental results [21] given for ozonation, where the temperature (10, 20, and 30°C) and the pH (7.9 and 13.6) were varied, are as follows: the COD conversions ranged between 42 and 55% depending on the operating conditions; the conversions of the total phenolic and aromatic compounds are around 75 and 67%, respectively.

A direct influence of temperature and pH on the COD and the phenolic compounds degradation was also observed. Thus, it may be concluded that ozone is an excellent oxidizing agent in the specific destruction of phenolic and aromatic compounds.

The experimental results from the aerobic biological treatment were as follows: the COD conversions ranged between 76 and 90%; the conversions of aromatic compounds ranged between 16 and 35%; and conversions ranged between 53 and 80% for total phenolics.

The combined process of an aerobic degradation followed by an ozonation produced a higher COD, phenolic and aromatic removal efficiency. This combined process reached a degradation level that cannot be obtained by any chemical or biological process individually under the same operating conditions.

There was a clear improvement in the second stage relative to ozonation, and biological pretreatment also led to an increase in the kinetic parameters. This implied that the aerobic pretreatment enhanced the later ozone oxidation by removing most of the biodegradable organic matter, while the ozonation step degraded some of the nonbiodegradable organic matter plus most of the phenolic compounds not removed previously.

*Case Study III.* This research focuses on the degradation of the pollutant organic matter present in wastewater obtained from an olive oil production plant located at the Extremadura Community (Spain), by combining two successive steps: (a) ozonation followed by aerobic degradation, and (b) aerobic degradation followed by ozonation. For this purpose, the chemical oxygen demand (COD), the total aromatic content (A) and the total phenolic content (Tph), were selected as criteria to monitor the overall degradation process [32]. The combined OMW degradation processes were studied with the goal of evaluating the influence of each respective pretreatment on the second stage. The first combined process (C-1) comprised ozone oxidation pretreatment followed by aerobic biodegradation. Table 12 summarizes the operating conditions, the initial and final COD concentrations, and the conversion values obtained ( $X_{\text{COD}}$ ) in each stage individually considered, as well as the conversion achieved by the overall process. The total conversion obtained by the successive stage (C-1) was 84.6%, a higher value than achieved by either single process under the same operating conditions. This suggests that ozone pretreatment enhances the subsequent aerobic process, probably by removing some phenolic compounds capable of inhibiting biological oxidation. Similar to combination (C-1), the overall process achieved, by the second combined process (C-2), 81.8% degradation, which was greater than that obtained by the individual chemical or biological processes under the same operating conditions (Table 12). This suggests that aerobic pretreatment enhanced the subsequent ozone oxidation by removing most of the biodegradable organic matter. The ozonation step then

**Table 12** Treatment of Olive Mill Wastewaters by Ozonation, Aerobic Degradation, and the Combination of Both Treatment Methods

C-1 Ozonation followed by aerobic degradation	C-2 Aerobic degradation followed by ozonation
C-1-A Ozonation stage Operating conditions: $T = 20^{\circ}\text{C}$ ; $P_{\text{O}_3} = 1.73 \text{ kPa}$ ; $\text{pH} = 7$ ; $\text{COD}_0 = 34.05 \text{ g dm}^{-3}$ Substrate removal obtained: $\text{COD}_1 = 29.9 \text{ g dm}^{-3}$ ; $X_{\text{COD}} = 12.2\%$	C-2-A Aerobic degradation stage Operating conditions: $X = 0.53 \text{ g dm}^{-3}$ ; $\text{COD}_0 = 41.95 \text{ g dm}^{-3}$ Substrate removal obtained: $\text{COD}_1 = 11.07 \text{ g dm}^{-3}$ ; $X_{\text{COD}} = 73.6\%$
C-1-B Aerobic degradation stage Operating conditions: $X = 0.59 \text{ g dm}^{-3}$ ; $\text{COD}_0 = 29.85 \text{ g dm}^{-3}$ Substrate removal obtained: $\text{COD}_1 = 5.22 \text{ g dm}^{-3}$ ; $X_{\text{COD}} = 82.5\%$	C-2-B Ozonation stage Operating conditions: $T = 20^{\circ}\text{C}$ ; $P_{\text{O}_3} = 1.69 \text{ kPa}$ ; $\text{pH} = 7$ ; $\text{COD}_0 = 10.95 \text{ g dm}^{-3}$ Substrate removal obtained: $\text{COD}_1 = 7.63 \text{ g dm}^{-3}$ ; $X_{\text{COD}} = 30.3\%$
Total removal in process C-1: $X_{\text{COD}} = 84.6\%$	Total removal in process C-2: $X_{\text{COD}} = 81.8\%$

Source: Ref. 32.

degraded some of the nonbiodegradable organic matter and much of the residual phenolic compounds.

In conclusion, the study shows that ozonation of OMW achieves a moderate reduction in the COD, and significant removal of aromatic and total phenolic compounds. The microbial aerobic treatment achieves significant removal of COD and phenolics but with less elimination of aromatic substances. The two processes combined, as presented in this case study, achieve higher COD removal efficiency than treatment by either stage separately under the same operating conditions. Together, the two processes may be used to treat OMW to meet discharge criteria or norms and reach treatment efficiencies required by national regulations, particularly in Mediterranean countries.

### 17.5.10 Fungal Treatment

Several types of industrial wastes contain phenols. Many of these compounds are extremely harmful as they are highly toxic both towards microorganisms and vertebrates [61]. Enzymatic approaches to removing phenols have been tried for some years as they have several advantages compared with the conventional methods (solvent extraction, chemical oxidation, absorbance on active carbons, etc.) [62].

Recently, results have been obtained for the removal of phenols using phenol oxidizers, which catalyze oxidative coupling reactions of phenol compounds and do not require hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) [63]. Olive oil mill wastewaters (OMW) contain large concentrations of phenol compounds, which are highly toxic. The structure of the aromatic compounds present in OMW can be assimilated to many of the components of lignin [64].

However, some microorganisms actively degrade lignin, among which the “white-rot” fungi are particularly efficient. These organisms utilize mainly peroxidases and phenol oxidizers [65]. Potential applications of white-rot fungi and their enzymes are gaining increasing importance in the detoxification of industrial wastewaters, reducing the toxicity of many aromatic compounds (pesticides, disinfectants, phenols) in several types of polluted environments.

## Case Studies

*Case Study I.* This study investigates the application of “white-rot” basidiomycete *Pleurotus ostreatus* and the phenol oxidizers it produces, for reducing the phenol content and the toxicity of the olive wastewater at an olive oil factory in Abruzzo, Italy [61]. It was found that up to 90% of the phenols present in OMW could be removed by treatment with phenol oxidizer from a mixture containing aromatic compounds extracted from OMW, although no concomitant decrease of toxicity was observed.

Results show that *P. ostreatus* removed phenols and detoxified OMW diluted to 10% in the absence of any external added nutrient; the diluted wastewaters were also clarified from this treatment in a relatively short time (100 hours). The detoxifying activity of *P. ostreatus* was concomitant with a progressively increasing phenol oxidase expression. It was noticed that after 100 hours incubation with *P. ostreatus*, the concentration of phenol compounds decreased by 90% and the toxicity towards *Bacillus cereus* was reduced seven-fold compared with that of untreated waste.

*Case Study II.* This study focused on the ability of white-rot fungi isolated from Moroccan OMW (classified as *Phanerochaete chrysosporium* Burdsall M<sub>1</sub>) to modify the polluting properties of diluted OMW in comparison with that of *P. ostreatus*. Olive oil mill wastewater (OMW) was collected from an olive oil factory in Marrakech, Morocco [20].

In order to study the effects of fungal treatment on OMW, two different white-rot fungi were tested in batch cultures of diluted OMW (20%). The maximum reduction of phenol content and COD was 62 and 52% for *P. ostreatus*, whilst it was 82 and 77% for *Ph. chrysosporium* after 15 days of treatment. The time course of absorbance decrease is similar to that of phenol content and COD reduction for both fungi, suggesting the existence of a correlation between these parameters and the colored components present in OMW. The results obtained indicate that *Ph. chrysosporium* is able to decolorize OMW and to degrade its phenolic component more efficiently than *P. ostreatus* can.

Toxicity tests performed on *B. cereus* revealed that fungal treatment of the waste (20 or 50%) causes the complete loss of OMW toxicity after 15 days of treatment. The optimal decolorization temperature for *Ph. chrysosporium* Burdsall M<sub>1</sub> was 28°C. Furthermore, the optimal pH for *Ph. chrysosporium* OMW treatment was in the 4.0–5.0 range. Since the pH of diluted OMW was between 4.0 and 5.0, the process did not require any pH alteration of the effluent.

Degradation of 20 or 50% OMW, expressed as color, phenol, and COD removal, was almost the same after 15 days of fungal growth. Hence, not only is this fungus able to grow in 50% OMW as the sole carbon source, but the degradation rate of the effluent increases in these cultural conditions. This proves that the isolated *Ph. chrysosporium* strain, which is able to grow using diluted OMW, and to notably reduce color, phenol content, and COD, would be a good candidate for the effective treatment of this wastewater.

### 17.5.11 Decolorization

Investigation of the effect of oxidative coloration on the methanogenic toxicity and anaerobic biodegradability of aromatics showed that their oxidized solutions were less biodegradable in proportion to their color [66]. In contrast, the aerobic processes can have substantial aromatic removal efficiency, but these processes require sizeable energy expenditures in oxygen transfer and sludge handling [67].

An important step in the degradation of olive oil wastewater is the breakdown of colored polymeric phenolics (decolorization) to monomers, which may subsequently be mineralized.

A significant correlation has been demonstrated between sewage decolorization and reduction of total organic carbon and phenolic content. However, decolorization of wastewaters appears to be associated only with a partial depolymerization. A decrease in the content of the lower molecular mass components and an increase in the proportion of components of intermediary molecular mass have also been demonstrated.

Crude oil wastewater and solutions of its brownish pigment change in both color and solubility as the result of pH modification. It appears that sewage decolorization may be produced simply by a process of adsorption or by adsorption associated with subsequent chemical modification of chromophores.

The effluent is acidified as a consequence of fungal growth. A considerable decrease in pH and an elevated adsorption of lignin-derived products onto the biological matrix suggested that the decolorization process was an indirect effect of culture acidification. The sewage decolorization eventually stops with time, suggesting that the putative enzymes responsible for decolorization have a defined lifetime.

Many recalcitrant compounds from olive oil mill wastewater are present in the colored fraction. Optimum culture conditions will be identified for the decolorization of that sewage by *Phanerochaete flavido-alba* for subsequent use in bioremediation assays. Of several media tested, nitrogen-limited *P. flavido-alba* cultures containing 40 µg/mL Mn(II) were the most efficient at decolorizing oil wastewater. Decolorization was accompanied by a 90% decrease in the phenolic content of the wastewater. Concentrated extracellular fluids alone (showing manganese peroxidase, but not lignin peroxidase activity) did not decolorize the major olive oil wastewater, suggesting that mycelium binding forms part of the decolorization process [38].

In batch cultures, or when immobilized on polyurethane, *Ph. chrysosporium* is able to degrade the macromolecular chromophores of oil wastewater and decrease the amount of phenolic compounds with low molecular weight. *Pleurotus ostreatus* and *Lentinus edodes* also decrease the total phenolic content and reduce the color of cultures containing oil wastewater.

Decolorization of juices and wastewaters by Duolite XAD 761 resin is widely used on an industrial scale and is particularly useful for the removal of color, odor, and taste from various organic solutions in the food and pharmaceutical industries. It removes color, protein, iron complexes, tannins, hydroxymethyl furfural and other ingredients responsible for off-flavors, according to the Duolite Company. The degree of adsorption tends to increase with molecular weight in a given homologous series and has more affinity for aromatic than aliphatic compounds. Recovery of coloring compounds and pigments from agroindustrial products is a common practise [24].

The following case study offers detailed information about the efficiency of resin application in decolorization of olive mill effluents.

### Case Study

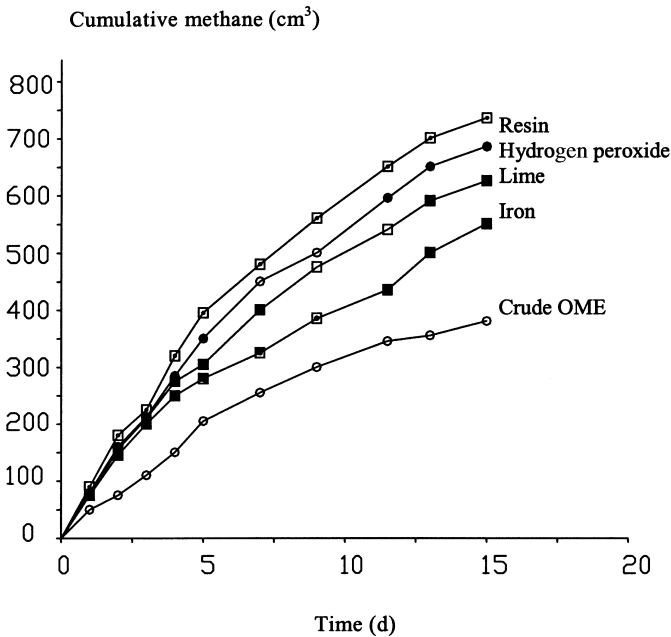
Chemical and physical treatments of olive oil mill effluent (OME) were performed in this study [24]. The goal was to evaluate the efficiency of aromatic removal from undiluted OME through precipitation by iron sulfate and lime, adsorption on a specific resin, and chemical oxidation by hydrogen peroxide prior to anaerobic digestion as the final treatment method, in order to reduce the toxic effect of OME on bacterial growth and to reduce the coloring compounds in undiluted OME. Olive oil mill effluent was obtained from a local olive oil mill in Tunisia and stored at -20°C. The main findings from this case study are as follows:

1. With regard to the decolorization of OME by iron as a complexing agent, it was noticed that many of the organic and inorganic OME components are susceptible to precipitation by iron. The decrease in the color of OME resulted in a decrease in COD.

The maximum amount of COD and OD removal that could be attained was close to 70% by using 30 g/L of ammonium iron(III) sulfate. Moreover, it seems that the removal of OME color corresponded to the same degree of COD removal. This means that COD is mostly due to the aromatic compounds that are responsible for the color. The complexing effect of iron was complete after 3 hours.

2. As for decolorization of OME by lime treatment and pure calcium hydroxide, the removal efficiency increased with increasing lime concentration. In total, 55% of COD and 70% of color ( $OD_{390nm}$ ) removal were reached. However, for economic and biological considerations, treatment with 10 g/L calcium hydroxide was sufficient. The effect of lime was complete after 12 hours. It may be concluded that using only 10 g/L of iron and lime as complexing agents was sufficient to precipitate more than 50% of the initial COD and remove 50% of the initial color within a short contact time.
3. With regard to decolorization of OME by resin treatment, the Duolite XAD 761 resin as aromatic adsorbent was used in a column (28 cm long, 1.5 cm in diameter, and with a total volume of 50 cm<sup>3</sup>). The results obtained after treating one, two, or three bed volumes of OME, were as follows: COD removal varied between 63 and 75%, and color decrease varied between 52 and 66% for  $OD_{280nm}$  and between 51 and 64% for  $OD_{390nm}$ . It was also shown that the coloring components in OME are the compounds most responsible for its pollution potential (COD). It may be concluded that the aromatic adsorbent resin retained more than 50% of the coloring compounds (chromophores) corresponding to removal of more than 60% of the initial COD after treating three bed volumes of crude OME. The efficiency depended on the volume treated.
4. As for oxidation of OME by hydrogen peroxide, it has already been shown before (Section 17.5.9) that chemical oxidation is very effective in treating wastewaters that contain large quantities of aromatics. The study was limited to the use of hydrogen peroxide ( $H_2O_2$ ) concentrations of up to 3%. The effect of  $H_2O_2$  on OME is clear:  $H_2O_2$  removed the substituents of the aromatic rings, which resulted in a decrease in length of the coloring compounds in OME. However, they were not completely degraded, leading to shorter wavelength absorption. This chemical treatment was efficient in color removal but only 19% COD removal was possible. In all cases, simple aromatics were reduced, as determined by GPC analysis.
5. With regard to anaerobic digestion of pretreated OME, the anaerobic digestion of crude and treated OME was elucidated in order to evaluate the efficiency of the physical and chemical pretreatments of OME (Fig. 15). In general, it may be concluded that each pretreatment was efficient in removing the toxic effect in OME. The anaerobic digestibility of OME was improved, with iron and lime, and no inhibition was observed on methanogenic activity. Oxidation of coloring compounds in OME by  $H_2O_2$  removed their toxic effect and did not generate new toxic chemicals to bacterial growth. Separation of aromatics by resin treatment seemed to be the most effective in removing the inhibitory effect of OME prior to anaerobic digestion. Nevertheless, the choice from these different alternatives must be based on economic considerations.

The following process was proposed for reducing environmental pollution by aromatic compounds: Physico-chemical reduction of most toxic compounds of OME, followed by anaerobic microbial decomposition of the main pollutants up to an insignificant amount (see Section 17.5.10 for case studies about the role of fungal treatment in decolorization of OME).



**Figure 15** Methanogenic activity in relation to different treatments of OME (role of different treatments in decolorization of OME) (from Ref. 24).

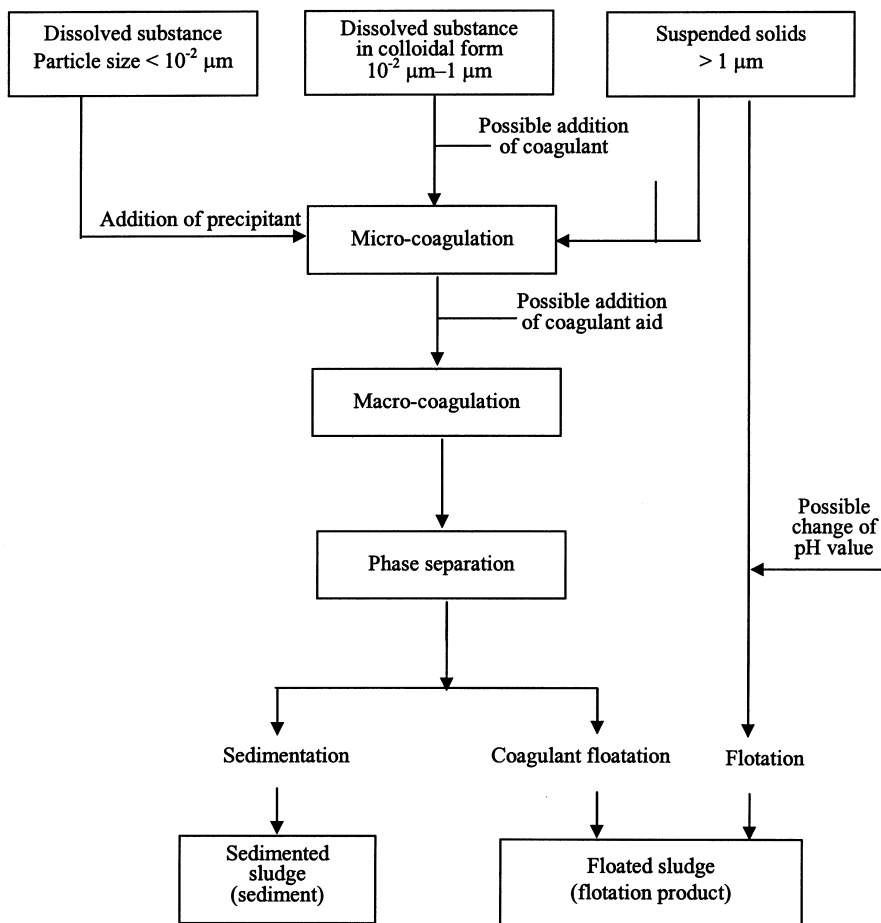
### 17.5.12 Precipitation/Flocculation

Precipitation involves transforming a water-soluble substance into its insoluble particular form by means of a chemical reaction. Certain chemicals cause precipitation when they react with dissolved and suspended organic compounds. By adding flocculants and coagulation aids, the finest suspended compounds or those dissolved in colloidal form are then transformed into a separable form. This means that, in contrast to precipitation, flocculation is not a phase-transition process [38]. The wastewater may be further treated by activated carbon, ultrafiltration, or reverse osmosis. Figure 16 gives a general concept of the precipitation–flocculation process.

Iron sulfate and aluminum sulfate are commonly used as efficient chelating agents of complex organic compounds in certain wastewaters [68]. Their adsorption capacity is complex and depends on the composition of the precipitated molecule. Lime stabilization is a recognized means of treating municipal sludge prior to land application [69]. The addition of lime temporarily halts biological activity. Moreover, lime renders organic molecules more accessible to microorganisms [70].

In wastewater from olive oil mills (OMW), a purification efficiency of almost 70% of the organic and inorganic components could be removed or complexed by lime (calcium hydroxide) [24]. Disadvantages include the high consumption of chemicals and the large quantities of sludge formed in the process (about 20% of treated alpechin) [38]. For more information about the efficiency of lime and iron as complexing agents in removing COD and color from OMW, refer to the case study presented in Section 17.5.11 (Decolorization).

A proposed plant in Madrid for combined precipitation/flocculation treatment of OMW is presented as a good example of a complete treatment system [38]. This system consists of four phases. In the first phase, a flocculent is added, followed by discharge, filtration, or



**Figure 16** Precipitation–flocculation processes in general (from Ref. 38).

centrifugation. The resulting liquid has a dark red color, and its  $\text{BOD}_5$  is about 10,000 mg/L. In the second phase, another flocculation occurs where the smaller size of the flocs are separated through filtration, and its  $\text{BOD}_5$  reaches 8000 mg/L. The sludge from these two stages combined is 12% of the original alpechin. The third phase is biological and occurs in three or four stages in purification towers with a separation device for the solids (biomass) and biomass recirculation. The resulting wastewater has a  $\text{BOD}_5$  of 2000 mg/L. The fourth phase consists of the filtration of the wastewater, ultrafiltration, and reverse osmosis. The concentrated and thickened sludge from the previous phase is then dried by means of band filters for further use as fertilizer.

### 17.5.13 Adsorption

Currently, the most commonly used methodologies for the treatment of aromatic-bearing wastewaters include solvent extraction, physical adsorption separation, and chemical oxidation [67]. The adsorption method, which refers to bonding of dissolved compounds (adsorbate) at the surface of solid matter (adsorbent), for example, activated carbon and bentonite, is used for adsorption of dissolved organic pollutants in water. In the field of olive oil wastewater, these are

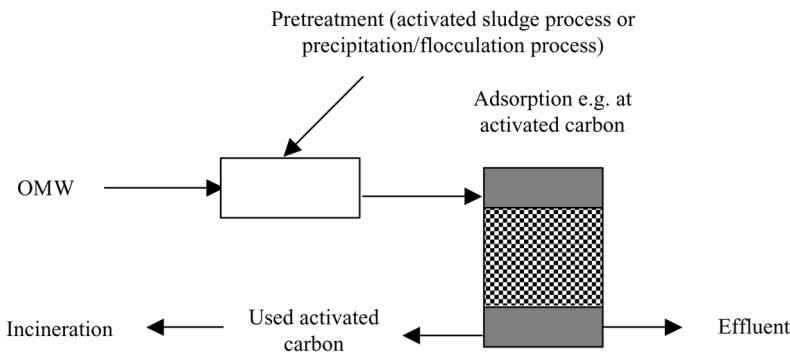
coloring substances (mainly tannic acid), hardly or nonbiodegradable pollutants, bactericidal or inhibiting compounds, which have to be removed. Adsorption not only takes place at the visible surface of the solid, but also in its pores. Activated carbon is especially suited because of its large inner surface ( $500\text{--}1500\text{ m}^2/\text{g}$ ) and its high adsorptive capacity, but unfortunately it cannot be reused. However, the calorific value is very high so it can be incinerated without problems [38]. Activated carbons are the most common adsorbent, and they are made from different plants, animal residues, and bituminous coal [71,72]. Depending on the composition of the industrial wastewater, one type of carbon may be superior to another [73]. Between 60 and 80% of the organic constituents from alpechin can be adsorbed by activated carbon.

Strong contamination has negative effects on the workability of the plant; thus the alpechin should be pretreated, for example in an activated sludge tank (Fig. 17) [38].

The use of bentonite as an adsorbent for cleaning vegetable oils suggests its applications to reduce lipid inhibition on thermophilic anaerobic digestion [74]; bentonite was added to a synthetic substrate (glyceride trioleate, GTO) and turned out to stimulate methane production by binding the substrate on its surface and thus lowering GTO concentration in the liquid phase.

Laboratory-scale experiments were carried out on fresh OME obtained from an olive oil continuous centrifuge processing plant located in Itri, Lazio, Italy, in order to identify pretreatment type and condition capable of optimizing OME anaerobic digestion in terms of both kinetics and methane yield [75]. In this regard, a set of tests was carried out to evaluate the effect of adding bentonite to OME, both untreated and pretreated with  $\text{Ca}(\text{OH})_2$ . Significant results were obtained by adding  $\text{Ca}(\text{OH})_2$  (up to pH 6.5) and 15 g/L of bentonite, and then feeding the mixture to the anaerobic biological treatment without providing an intermediate phase separation. Indeed, the biodegradable matter adsorbed on the surface of bentonite was gradually released during the biotreatability test, thus allowing the same methane yield (referred to the total COD contained in untreated OME) both in scarcely diluted (1 : 1.5) pretreated OMW and in very diluted (1 : 12) untreated OME.

These results suggest the application of a continuous process combining pretreatment [with  $\text{Ca}(\text{OH})_2$  and bentonite] and anaerobic digestion without intermediate phase separation [75]. Specific resin is an economic adsorbent alternative for separating complex organic compounds from wastewater. The Duolite XAD 761 resin is used industrially for the adsorption of mono- and polyaromatic compounds. A considerable number of experiments have focused on removal of coloring compounds in OME by resin treatment [24]. Crude OME was passed through a resin (Duolite XAD 761) column (28 cm long, 1.5 cm in diameter, and with a total volume of  $50\text{ cm}^3$ ) according to the suggested operating conditions reported by the Duolite



**Figure 17** Adsorption process for treatment of olive oil mill wastewater (from Ref. 38).



Company. The pH of the resin was almost 4, and the pH of OME was corrected to 4 using 2 mol/L HCl. The OME was passed through the resin bed at a rate of 50 cm<sup>3</sup>/hour. Table 13 shows the results obtained after treating one, two, and three bed volumes of OME. With such treatment, it is clear that the removal of COD up to 75% and decrease in color (OD<sub>280nm</sub> and OD<sub>390nm</sub>) up to 66.3 and 63.5%, respectively, could be achieved. Efficiency of the resin treatment decreased with OME volume, due to the saturation of the resin. Moreover, the ratio OD<sub>280nm</sub>/OD<sub>390nm</sub> remained constant (almost 5) in crude and treated OME, which meant that adsorption of organic compounds on the resin occurred with the same degree of affinity. On the other hand, the decrease in OME color corresponded to the same degree of COD removal. (For more information about this process, refer to Section 17.5.11).

#### 17.5.14 Biofiltration and Ultrafiltration

Physical processes including filtration, centrifugation, sedimentation, and ultrafiltration are highly efficient methods for phase separation. Filtration processes are used to remove solid material as far as possible from the wastewater. Particles and liquid are separated as a result of pressure difference between both sides of the filter, which enables the transport of water through the filter. During the filtering process, the solids accumulate in the filter and reduce the pore volume, resulting in a change of resistance to filtration and of the filtrate quality. As soon as the admissible resistance to filtration is reached, the filter must be backwashed by forcing clean water backwards through the filter bed. The washwater is a waste stream that must be treated [76].

Compounds that are already dissolved cannot be treated, except by biofiltration. In this case, the filter serves also as nutrient for bacteria so that dissolved organic substance can be aerobically degraded. The purification capacity of biofiltration plants is between 70 and 80%. Up to 100% of the solids can be reduced.

A prerequisite for biofiltration is sufficient oxygen supply. If the alpechin is insufficiently treated, the filter will be quickly clogged. The material kept back in the filter can be used in agriculture (Fig. 18).

A promising alternative method is based on a chemico-physical pretreatment that removes lipids and polyphenols as selectively as possible before biological treatment. In this regard, the potential of filtration applied with other techniques for removal of COD, lipids, and polyphenols from OME has been studied in the following example [75].

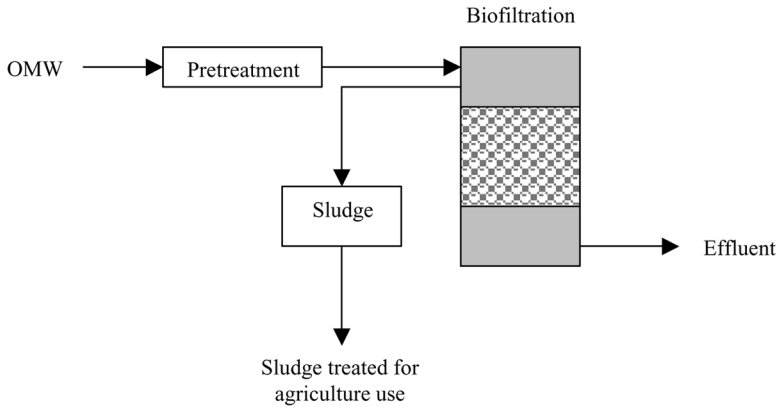
A laboratory-scale experiment was carried out in order to choose the pretreatment operating conditions capable of optimizing the anaerobic digestion of OME in terms both of

**Table 13** Treatment of OME Through Duolite XAD 761 Resin

OME	OD (280 nm)	OD (280 nm) removal (%)	OD (390 nm)	OD (390 nm) removal (%)	OD (280 nm)/OD (390 nm) ratio	COD (g/dm <sup>3</sup> )	COD removal (%)
Crude OME	45.1	–	8.5	–	5.3	147	–
[V(o)/V(r)] = 1	15.2	66.3	3.1	63.5	4.9	37	75
[V(o)/V(r)] = 2	18.7	58.5	3.6	57.6	5.2	43.4	70.1
[V(o)/V(r)] = 3	21.7	51.8	4.2	50.6	5.1	54	63.2

*Note:* OD: optical density measures qualitatively the color darkness of OME. The OD values were measured at 390 nm and 280 nm.

*Source:* Ref. 24



**Figure 18** Biofiltration process for treatment of olive oil mill wastewater (from Ref. 38).

kinetics and biomethane yield. Fresh OME was obtained from an olive oil continuous centrifuge processing plant located in Itri, Italy. The OME (pH 4.4, total COD = 92.6 g/L) contained 5.1 g/L of polyphenols, 3.1 g/L of oleic acid, and 11.1 g/L of lipids. The first set of pretreatment tests was carried out by using only physical methods of phase separation: sedimentation, centrifugation, filtration, and ultrafiltration. In the sedimentation phase, after two hours of magnetic stirring, 50 mL of OME were left undisturbed for 24 hours. Afterwards, the OME were centrifuged at 4600 rpm for 15 minutes. The resulting intermediate phase was filtered under vacuum on filter at several pore sizes (25, 11, 6, and 0.45  $\mu\text{m}$ ). After filtration on 0.45  $\mu\text{m}$  filters, 20 mL of OME were ultrafiltered on membranes at 1000 and 10,000 D cutoff threshold (a micron ultrafiltration cell; operating pressure, 4 bar by nitrogen gas).

Table 14 shows the results obtained. The highest removals of oleic acid (99.9%) and polyphenols (60.2%) were obtained through ultrafiltration (at 1000 D). However, COD removed by this technique (65.1%) was much higher than COD associated to lipids and polyphenols removal. While very efficient as a separation technique, ultrafiltration subtracts too much biodegradable COD from the pretreated OME, thus lowering the potential for methane production.

**Table 14** Removal of COD, Oleic Acid, and Polyphenols from OME by Means of Physical Methods of Separation

Method of separation	Removal of COD (%)	Removal of oleic acid (%)	Removal of polyphenols (%)
Sedimentation	38.4	96.1	0
Centrifugation	38.6	95.4	10.2
Filtration [pore size ( $\mu\text{m}$ )]			
25	36.7	96.6	12.2
11	37.6	97.6	13.4
6	38.9	98.1	13.4
0.45	40.3	99.0	13.1
Ultrafiltration [cutoff (D)]			
10,000	51.5	99.8	37.2
1000	65.1	99.9	60.2

Source: Ref. 75.

Therefore, ultrafiltration is considered here as a separation technique with poor selectivity. Moreover, the application of ultrafiltration to OME pretreatment might encounter serious problems of membrane fouling as well as of treatment of the concentrated stream. Among the other separation techniques, centrifugation demonstrated the important advantages of producing smaller volumes of separated phases. Further details about this and other sets of pretreatment tests in connection with anaerobic biotreatability may be found in Ref. 75.

### 17.5.15 Evaporation/Drying

Evaporation is a method used to concentrate non-steam-volatile wastewater components. The evaporation plant contains a vapor condenser by which vapor and steam-volatile compounds are separated from the concentrate. While the concentrate is then recycled into the evaporator, the exhaust steam can be used for indirect heating of other evaporator stages (Fig. 19).

The degree of concentration of the wastewater components depends on different factors, for example [38]:

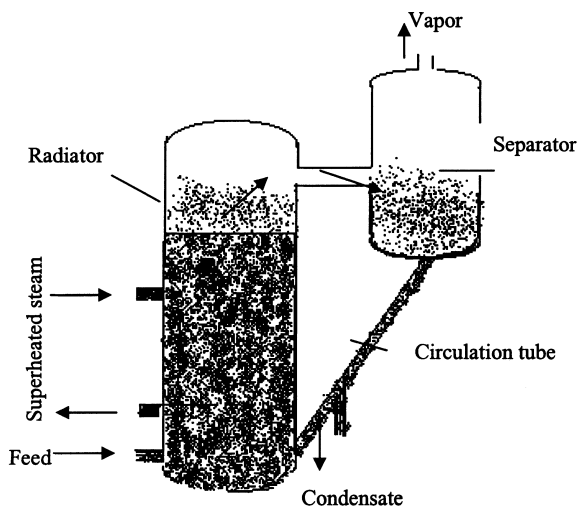
- reuse of the concentrate (e.g., reuse in production, use as fodder, recovery of recyclable material);
- type of disposal of the concentrate (e.g., incineration, landfill)
- properties of the concentrate (e.g., viscosity, propensity to form incrustation, chemical stability).

Advantages of this method include:

- the residue (dried oil wastes) can be reused as fodder and fertilizer;
- only a small area is needed;
- exhaust steam can be reused as energy;
- considered state of the art in the food industry [38].

Disadvantages are:

- the exhaust steam from evaporation is organically polluted and needs treatment;
- rather high operation and maintenance costs;



**Figure 19** Evaporation/drying processes for treatment of olive oil mill wastewater (from Ref. 38).

- requires high energy;
- requires trained personnel.

Details about drying processes, including case studies for the treatment of olive oil mill wastes, are discussed in Section 17.6.2.

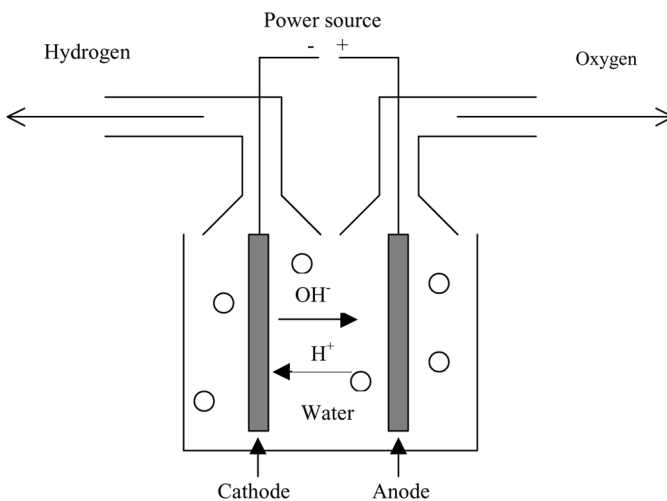
### 17.5.16 Electrolysis

There are methods still in the experimental stage for treatment of olive oil mill wastewater, one of which is electrolysis. This method is based on electrolytic oxidation of margine constituents, using titanium/platinum for the anode and stainless steel for the cathode. The following data are drawn from laboratory experience (Fig. 20) [38].

The process has the following components:

- electrolytical cell;
- recirculation reactor;
- margine input;
- pH control;
- cooling system.

The performance of the electrolytic cell was tested with a 4% NaCl density in the margine (alpechin) at 42°C, with the temperature remaining constant during the course of the experiment. Four tests lasting 10 hours each were carried out under the same conditions. After 10 hours of electrolysis, the organic load was reduced by 93% in COD and by 80.4% in TOC (total organic carbon). The greatest disadvantage of this method is its high energy consumption (12.5 kW per kg of margine). Therefore it should be applied only as part of the biological pretreatment of the wastewater. Energy consumption then reaches 4.73 kW/kg within the first three hours [38].



**Figure 20** Experimental setup of electrolysis for olive oil wastewater treatment (from Ref. 38).

### 17.5.17 Bioremediation and Composting

The aim of bioremediation is to repurpose the liquid waste (alpechin) or the liquid fraction of alpeorujo (aqueous fraction that can be separated from fresh alpeorujo by percolation or soft pressing) by diverse aerobic fermentation. The composting of the solid waste (orujo) or the solid fraction of alpeorujo produces a useful material for plant growth.

Several years' research work at the Laboratory for Microbiology of the Athens University has shown that margine (alpechin) is a good substrate for certain microbial fauna. It is especially useful for producing fertilizer for agricultural purposes. Under aerobic conditions, the margine content aids the qualitative breeding of nitrogen-consuming bacteria, especially of acetobacter. This feature was taken into consideration when developing a treatment method for the wastewaters from olive oil production with high organic load. Using this method, a substrate for soil improvement with high nutrient content is obtained from the wastewaters.

#### Case Studies

*Case study 1.* A pilot plant was put into operation in an oil mill of the Romano-Pylas region. The first big treatment unit was built in 1997 within the framework of the LIFE program for a total of six oil mills in the region of Kalamata (Peloponnes). In addition, a second plant with lower performance was built to treat wastewater from the oil mill in the Arta district. The method consists of two phases [38]. In Phase 1, the margine is neutralized by adding CaO at a pH between 7 and 8. The substrate is mixed in a reactor, which is equipped with a mechanical stirring device. The undiluted residues from the decanter are fed into the stirring reactor. In Phase 2, the contents of the stirring reactor are fed into the bioreactor where sessile microorganisms (especially *Acetobacter vinelandii*) degrade the substances with phytotoxic effect. These bacteria consume nitrogen and take in oxygen from atmospheric air, which is provided by a turntable air distribution system. This leads to increased nitrogen consumption of the bacteria, degradation of the phytotoxic substances, formation of polymers, and secretion of reproduction factors like auxines, cytokinines, which support plant growth.

Retention time in the reactor is 3 days (repeated fed batch culture). The advantages of this method lie in the possibility of applying it directly to olive oil mill wastewater without oil separation, and the high removal efficiency of COD and decolorization.

We propose the possibility of replacing the bioreactor (Phase 2) with the process of natural composting, where the content of Phase 1 is to be mixed, in a well studied way, with municipal solid waste. On the other hand, the main disadvantages here are the long duration (one month or more) needed for aerobic degradation and the need for a large area to conduct the aerobic process.

The final product from the bioreactor or from the natural waste composting plant has a pH of 7.5–8, and, mixed with any quantity of water, can be used to improve soil. Moreover, it has the following characteristics:

- It shows a high content of organic nitrogen (by consumption of atmospheric nitrogen), and substances like auxines support plant growth.
- All nutrients and trace elements present in the olive can be found again in the substrate improved soils.
- The product is able to improve the soil structure and to increase its water retention capacity, due to the biopolymers contained therein.

*Case study II.* A study was carried out on isolating bacteria from the alpeorujo composting system at Kalamata, Greece [77]. The main results were:

- Identifying bacterial diversity using biochemical techniques of lipid analysis and the molecular biological techniques.
- Demonstration of detoxification of compost by indigenous bacteria.
- Possibility of using a combination of traditional microbiological and modern molecular biological approaches, to follow the changes in microbial flora within the composting material in a qualitative manner.

Strain A of *Azotobacter vinelandii* was used as an agent in the bioremediation process, which was studied in an aerobic, biowheel-type bioreactor, under nonsterile conditions. Before inoculation, the pH of the liquid fraction of alpeorujo was adjusted to 8.5 by adding CaO. The inoculation was then added at a rate of  $10^5$  cells/cm<sup>3</sup>. The main experimental findings were:

- The alpeorujo liquid fraction (ALF) is very phytotoxic, and inhibitory to the growth of pleurotus and other fungi and many bacteria.
- When ALF is diluted with water (10-fold or more) it can be used as substrate for *Azotobacter*, *Fusarium*, *Pleurotus* and some yeasts (*Candida*).
- *A. vinelandii* (strain A), while it can degrade and utilize phenolic compounds, grows slowly during the first three days because of the antimicrobial properties of OMW.

Standard bioremediation conditions are of major importance, since (a) the OMW quality is largely dependent on the olive mill machinery and storage facilities and on the quality of the raw material (olives); and (b) bioremediation cycles are performed during wintertime in plants that are exposed to variable environmental conditions.

A continuous composting process was followed. It was observed that alpeorujo, unlike the extracted press cake of the three-phase decanters, is highly unsuitable and cannot be used as a pleurotus substrate. This is due to its high concentration of phenolics. This toxicity is more acute in the pulp fraction of alpeorujo. The wet olive pulp represents 60% of alpeorujo. It is acidic (pH 4.6–4.8), almost black in color mass with moisture content of 65–67% (wet basis), having a smooth doughlike structure. It is also rich in organic and inorganic constituents, especially potassium. Nevertheless its chemical composition is not compatible with the composting process, and so the olive pulp poses quite a serious obstacle to waste treatment and hinders alpeorujo recycling efforts.

In the course of this case study, the possibility of composting both alpeorujo and pulp was also investigated. The major experimental findings were:

- Composting of alpeorujo is feasible when it is mixed with bulky material at a proportion of 3 : 1.
- The mature alpeorujo compost or compost taken from the end of the thermophilic phase offers an ideal microbial consortium to act as starter.
- For alpeorujo and deoiled alpeorujo a self-sustainable composting process was elaborated. Bulky material is only required for the initiation of the process.

In addition, a novel thermophilic process of composting based on the use of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was developed, due to the fact that hydrogen peroxide exerts a triggering effect on the composting process. The key points include:

- The long-term rise of temperature reflects intensification of microbiological activity in the catabolic processes.

- The formation of glucose from cellulose yields hydrogen peroxide, hydroxyl, and superoxide radicals that are needed to initiate in a snowball reaction the breakdown of the lignin skeleton.
- Similar evidence has been reported in the case of the brown rot fungus *Gloeophyllum trabeum*.

These findings have led to the establishment of a new method for assessing compost stability [77].

With regard to positive effect on plant growth and control of soil fungal pathogens, it was noticed that *A. vinelandii* possesses the ability to inducing soil suppressiveness against some notorious soil-borne root pathogens such as *Pythium*, *Phytophthora*, and *Rhizoctonia* species through its intrinsic ability to produce siderophores.

At the end of this project, the compost produced satisfied farmers, who expressed commercial interest in its use. The compost extract gave similar or even better control against potato blight when compared with commercial organic preparations. Therefore, composting and subsequent utilization in agriculture appears to be the most suitable procedure for treatment of (solid–liquid) waste (alpeorujo). However, large-scale application and more intensive investigation must follow before these procedures may be introduced to the market.

### 17.5.18 Livestock Feeding

Several methods may be used to enrich OMW with fungi and yeasts so that it becomes suitable for animal feed. The following is a summary of successful experiments performed in Greece as part of the Improlive project, an “International Project to Improve Environmental Compatibility in Olive Oil Production” (during the period 1997–1999) within the European FAIR Programme “Quality of Life and Management of Living Resources.”

#### Case Study

Research [78] was conducted by the University of Athens (1997–1999) with the objective of enriching the two-phase system waste “alpeorujo” with fungal or yeast protein through microbial fermentation and subsequent amino acid production. To give a clear picture of the microorganisms (such as fungi, yeasts, and bacteria) present in the alpeorujo, various techniques and methodologies were applied: serial dilution and selective culture media, application of different inoculation techniques and enrichment of cultures and subcultures, as well as variation in growth temperature and anaerobic conditions. The isolated microorganisms were analyzed for their morphological and biochemical features, then classified into 27 bacteria strains, nine yeasts and three more fungal strains. In order to study the fermentation of bacteria and yeasts, the microcosm system was selected, while a solid-state fermentation bioreactor was used for the fungal strain of *Paecilomyces variotii*. In the microcosm system, and as for as the bacteria concerned, their population declined immediately after inoculation and showed no survival after 72 hours. Total sugars and tannins of the fermented products decreased shortly after each growth cycle of the inoculums. Total lipid content increased after fermentation in all cases.

The microcosm system was followed by solid-state fermentation experiments, which were used to study the growth and activity of selected strains of yeasts and fungi and relevant control conditions, leading to findings such as (a) protein content increased after fermenting the substrate (alpeorujo) with *P. variotii*; (b) the best growth temperature is 35°C for *P. variotii*; (c) long-term experiments are suitable for the best fermentation of alpeorujo substrate. Another step performed was the enrichment of alpeorujo with molasses, which is an inexpensive, renewable industrial byproduct with a very high sugar concentration.

The following conclusions may be drawn from the case study:

- The main constituents of alpeorujo are tannins, lipids, proteins, sugars, and lignocellulosic materials. The chemical profile of alpeorujo makes it adequate for supporting microbial growth by providing plenty of carbon, nitrogen, and energy sources. The results confirm this assumption: alpeorujo is a suitable substrate for the growth of fungi and yeasts and metabolite production.
- Apart from the aerobic bacteria growing at 30°C, several thermophilic bacteria have been isolated and identified, in addition to yeasts (for example, *Candida* genus) and fungi such as *Rhizopus* and *Penicillium*.
- The enrichment of alpeorujo with molasses produced satisfactory results. The increase in the final protein content is around 45%. This increase is a very positive result for the use of the waste material.
- The industrial application of *P. variotii* as a means of increasing the protein content seem feasible, giving the excellent ability to grow in a variety of high-polluted industrial effluents, such as molasses, wood hydrolysates, and spent sulfite liquor. This fungus has an optimum growth at 35°C, while the optimum pH was 4.

The enrichment of alpeorujo with molasses could be a good solution to increase the final protein content and for the optimization of waste materials to be used as animal feed or food additives.

The final conclusion is that *P. variotii* is a fungus that can better utilize the substrate and grows well in it. The resulting increase in the final protein content allows for the possibility of using it as an animal feed or as a feed additive. In addition, not only the fresh but also dried (solid/liquid) waste can be used for fermentation experiments. It is more convenient, however, to use the latter since it is easily handled as a substrate. Further experiments are needed to test the nutrition value of the derived products and their safety for animal consumption.

### 17.5.19 Ocean Outfalls

The authors proposed for study and application the following method for disposal of olive oil mill wastewaters through submarine outfalls. This section will introduce this method and present its advantages, defects, success conditions, quality limits of sea water, design criteria of marine outfalls, and the required specific pretreatment.

#### Significance of Submarine Outfalls

Discharge of sewage to the sea through sea outfalls was introduced more than 50 years ago. Outfalls can range in length from a few hundred meters up to more than 15 km; diameters typically vary from 0.5 m up to 8 m and the number of diffuser ports can range from one to several hundred. Sea conditions vary significantly from protected estuaries to open coasts with strong currents and breaking waves [79].

The discharge of industrial and domestic wastewater through submarine outfalls and diffuser systems is one of the most economic solutions for the final disposal process in coastal areas. This disposal system represents a viable alternative for the many population and industrial centers of the world located on sea coasts, particularly for developing countries where financial resources are limited. The capital costs of constructing inland treatment works are often similar to those for an equivalent marine treatment scheme. However, the operational cost of inland treatment is much greater.



Diffusion of industrial and domestic wastewater into marine receiving water, after the degree of treatment deemed necessary for a location, from a properly designed and sited marine outfall system is one of the most environmentally safe options for populations near open coast areas. Such systems can make maximum utilization of the natural assimilating capacity of the sea water environment, which serves as a treatment and disposal facility, and when properly planned, will not produce an undesirable impact upon marine water.

### Specific Pretreatments and Quality Limits

Marine treatment via a sea outfall must be considered as a part of the wastewater treatment in conjunction with land treatment, and is one of the most efficient processes to treat effluents with high contaminations. However, since wastewater discharged from inadequately designed or poorly maintained sea outfalls can be a major source of pollution in many coastal areas, the EPA and the EEC have developed some restrictive legislation regarding this issue [80].

In some cases, sea outfalls are used to discharge toxic effluents without proper pretreatment and consequently are responsible for some ecological damage. However, it is widely accepted by scientists and engineers that the use of long sea outfall with an adequate control of the discharged effluent quality is an environmentally safe, waste disposal option.

Materials diffused through marine outfalls may or may not affect the ecology of the receiving water area. Consequently, the oceanography, biology, and ecology of receiving water areas were studied to determine sensitivities to contaminants and design allowing diffusion below sensitivity levels. By satisfying these requirements, marine outfalls could have a positive impact on the coastal water including the presence of fertilizers, such as nitrogen, phosphorus, and carbon in wastewater that maintain life productivity [81].

Sea discharge of industrial and municipal effluents should meet the quality limits of coastal waters used for fisheries, swimming, and recreational purposes, and meet the design criteria given at national level. If a coastal country has no such limits or standards, it may benefit from other countries' experience in this respect. Turkey is a good example in the Mediterranean area (Tables 15 and 16).

**Table 15** Required Characteristics of Industrial Wastewater for Sea Discharge in Turkey

Parameter	Value	Remarks
pH	6–9	
Temperature (°C)	35	
SS (mg/L)	350	
Oil and grease (mg/L)	10	
Floating matter	None	
BOD <sub>5</sub> (mg/L)	250	
COD (mg/L)	400	
Total N (mg/L)	40	
Total P (mg/L)	10	
Surface active agents (mg/L)	10	
Other parameters	–	Special care for hazardous wastes

Source: Ref. 82.

**Table 16** Design Criteria for Marine Outfalls Systems in Turkey

Parameter	Limits
Temperature	2°C (max) increase after initial dilution
Total coliform (fecal coliform bacteria/100 mL)	1000 in 90% of samples
Initial dilution ( $D_x$ )	40 (min)
Discharge depth (m)	20 (min)
Discharge length (m)	1300 m (min) for discharge depth less than 20 m

Source: Ref. 82.

If the receiving water body and/or wastewater characteristics are not deemed acceptable, then marine outfall is not permitted [82]. Table 17 shows the necessity for pretreating some polluting constituents such as particle, oil, grease, and floatables prior to sea discharge through submarine outfalls, with special concentration on refractory substances and heavy metals that require specific treatment at source in conformity with the quality limits of the sea water.

Table 18 presents the removal of significant constituents by pretreatments (milliscreens or rotary screens and by primary sedimentation) [83]. It is noted that the main differences in effluent characteristics relate to the removal of settleable solids and suspended solids and, to a lesser extent, to removal of grease. However, milliscreens remove floatables and particulate fat, which is the material of significance regarding aesthetic impact on the marine environment. The only adverse impact of the discharge of grease relates to slick formation, but when initial dilution is sufficient, the concentration of such material in the mixed effluent/sea water plume is very low and this problem is eliminated [84].

In addition, the data show that screens with openings of less than 1.0 mm require extensive maintenance for cleaning whereas those of 1.0 mm do not.

### Disposal of OME Through Submarine Outfalls

With regard to olive industry wastewater, which is mainly characterized by a high content of polyphenols, fats, COD, and solid matters, Table 17 shows that sea water can play a role in the treatment and disposal of biodegradable organics. Refractory organics should be subjected to proper treatment at the source (mill). Fats, floatables, settleable and suspended solids should be pretreated by rotary screens or milliscreens and primary sedimentation. It is possible to treat polyphenols by the decolorization process, which has demonstrated significant correlation

**Table 17** The Role of Sea Water in Removal of Wastewater Constituents and the Required Pretreatment Process Prior to Sea Discharge Through Submarine Outfalls

Constituent	Pretreatment	The required process
Particle	Partly needed	Mechanical pretreatment (preliminary treatment + primary sedimentation)
Oil, fats, and floatables	Needed	
Biodegradable organics	Not needed	–
Nutrients	Not needed	–
Pathogenic bacteria	Not needed	–
Refractory organics	Needed	Proper treatment at source
Heavy metals	Needed	Proper treatment at source

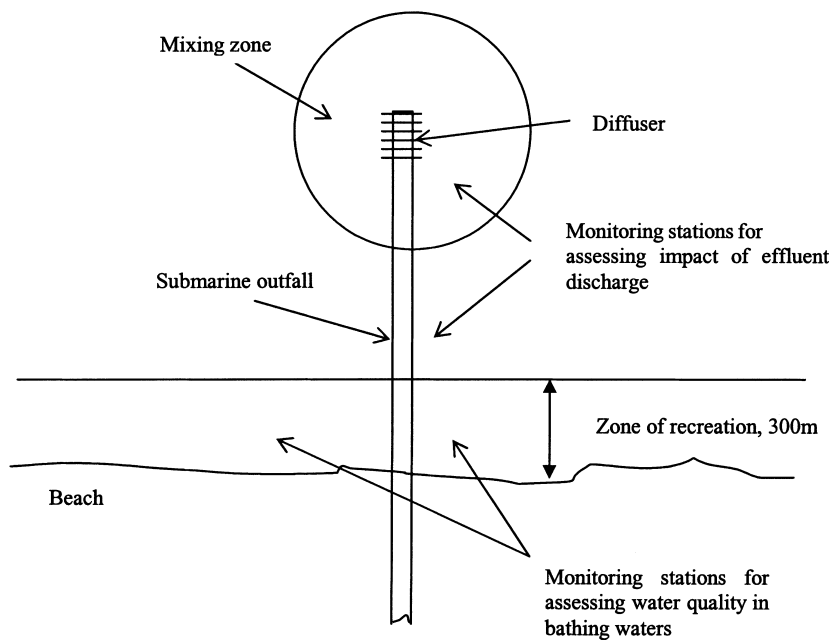
**Table 18** Removal of Wastewater Constituents by Milliscreens and Primary Treatment

Constituent	Percentage removal		
	Milliscreens		Primary treatment
	0.5 mm apertures	1.0 mm apertures	
Settleable solids	43	23	95–100
Suspended solids	15	10	50
Oil and grease	43	30	50–55
Floatable solids	99	96	95–100

Source: Ref. 82.

between the sewage decolorization and reduction of total organic carbon and phenolic content. It is also advisable to conduct intensive research about sea water’s role in reducing these compounds. In cases where pH is less than or equal to 5, it is necessary to apply neutralization within the pretreatment. The criteria given in Table 16 can be referred to for planning and designing the submarine outfalls. Other references provide further details about design criteria and modeling [85]. For economic reasons, it is recommended that several neighboring mills associate in one submarine outfall.

The possible impact of effluents on public health and the environment (aesthetic) should be assessed through monitoring stations for effluent discharge and bathing water (Fig. 21) to achieve national or international standards (fats, COD, and polyphenols).



**Figure 21** Monitoring stations location for olive oil mill wastewater discharge through submarine outfalls (from Ref. 48).

## 17.6 SOLID WASTE TREATMENT METHODS

Many of the abovementioned treatment methods for liquid waste are suitable for the treatment of solid/liquid waste arising from the two-phase decanter (alpeorujo). Some of these methods are also appropriate for the treatment of solid waste (orujo), such as recycling methods (composting and livestock feeding). In this respect, a distinction should be made between aerobic treatment systems for liquid waste (such as activated sludge, trickling filter, bioremediation) and aerobic treatment systems for solid waste (such as composting).

Based on the various experiments and published research for waste, especially solid waste and liquid–solid waste, we can propose suitable methods for treating waste from olive oil mills (Table 19). These treatments are classified into three groups: physical, biotechnological, and chemical processes [1]. At the same time, it should be realized that no specific treatment or solution can be generalized. Each case must be studied and evaluated according to local circumstances.

### 17.6.1 Biotechnological Processes

Biotechnological processes mainly include aerobic (composting), anaerobic (mixed fermentation), solid fermentation, and fungal treatments. A detailed description of methodologies, results, and case studies related to these processes was discussed in Section 17.5.

Other points of considerable importance can be added in this respect [1]:

- Because olive oil mills are operated over limited periods, that is, about three months only per year, an ideal treatment method would be one that could be shifted for treating other types of waste after the end of the olive oil production season.
- The composting method for solid waste treatment is preferable to other methods. This process takes place without serious emissions into air, water, or soil and therefore conforms to the key objectives of Mediterranean environmental policy. Since operational and personnel costs are rather low, this process might also be accepted by plant operators.

**Table 19** Treatment Methods for the Solid Waste from Olive Oil Production

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Treatment method of orujo and alpeorujo

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Physical processes

- Drying
- Evaporation
- Thermal treatment

Biotechnological treatment

- Aerobic (composting)
- Solid fermentation
- Anaerobic/mixed fermentation
- Fungal treatment

Chemical processes

- Incineration
  - Combustion
  - Pyrolysis
  - Gasification
- 

Adapted from Ref. 1.

- The costs of a composting plant strongly depend on the sales potential for the final product in the individual countries. In Greece, for example, higher receipts from compost selling are possible than in Spain. As a result the total costs of a plant also change [2].
- The start-up time of the compost process is only two weeks. It runs in a cycle, which means that additional structuring material is required only in the beginning, and the compost itself is used later as structuring material. The final product is of a high quality and well suited to be used as fertilizer in agriculture.
- Anaerobic treatment by itself is not suitable for solid waste because of its low water content. Problems with mixing and clogging may arise during treatment. Moreover, anaerobic treatment requires further treatment measures, causing additional costs. Another problem is the long start-up time of the process after a longer shutdown period. These problems were behind the breakdown of anaerobic plants in Greece. In the meantime, these plants have been shut down. An economically reasonable solution is to combine this treatment for existing fermentation plants. For this purpose, however, the local situation must be suitable, that is, the fermentation plant should have free capacity and be situated near the olive oil production to avoid high transportation costs and start of digestion of the solid waste.

### 17.6.2 Physical Processes

Evaporation/drying processes and their advantages and disadvantages in liquid waste treatment have already been discussed. In solid waste treatment, these processes can be discussed in detail as follows. Two of the most important problems related with the treatment of solid waste or solid/liquid waste (alpeorujo) are the optimization of drying and oil recovery by physical means (to get, as much as possible, olive oil instead of orujo oil).

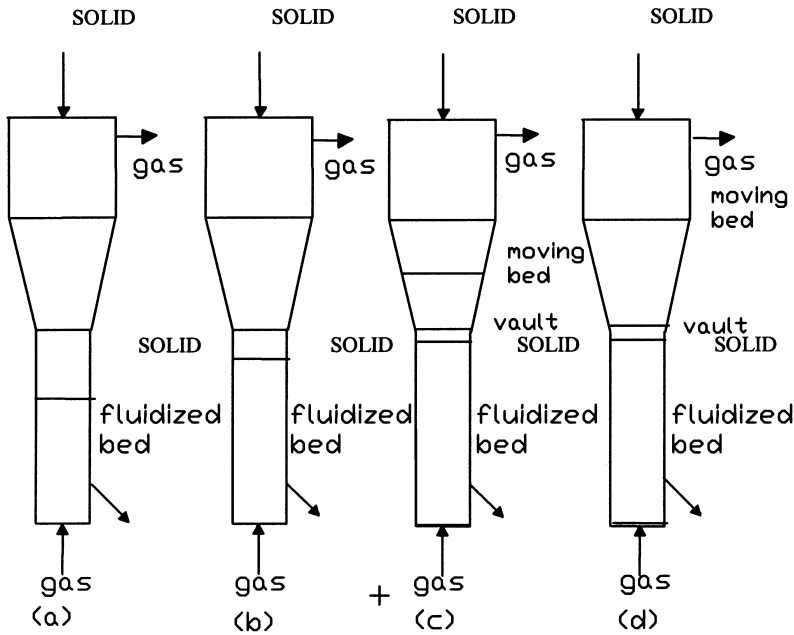
The following case studies discuss new driers based on the combination of fluidized and moving beds, in addition to different pilot-plant treatments of pit separation, drying in a ring drier, and deoiling solid waste in oil mills.

#### Principle of Fluidized/Moving Beds (Flumov)

The fluidized/moving bed (flumov) combines a fluidized bed with a top section in the form of a fixed/moving bed. The main problem that must be dealt with is the control of the circulation of solids to obtain almost-perfect mixing flow of the solids through the fluidized bed and a plug-flow of the solids in the moving bed (Fig. 22).

The drying of solid waste (or alpeorujo) is required before this waste may be used to recover orujo oil by extraction with hexane and for other processes such as the production of compost, activated coal, biopolymers, and so on. The classical driers, for example, rotary kilns (trommels) and trays, have a low thermal efficiency due to the poor air–solid contact and can present several problems because of the high moisture and sugar contents of the alpeorujo. The presence of the moving zone in flumov allows the fresh product feed to have a higher degree of moisture. Moreover, it favors the solid transport to the fluidized bed contactor, since part of the water is eliminated in the moving zone and the solid enters into the fluidized zone with a relatively low level of moisture [86].

We were particularly interested in confirming the filtering action of the moving bed zone. The filter effectiveness would improve the performance of conventional filtering units usually required for eliminating the suspended solids in the outgoing gas, and even eliminate the necessity of using these units. The stability of the vault, which forms between both beds, requires the input of secondary air into the conical zone to regulate the flow rate of solids from moving

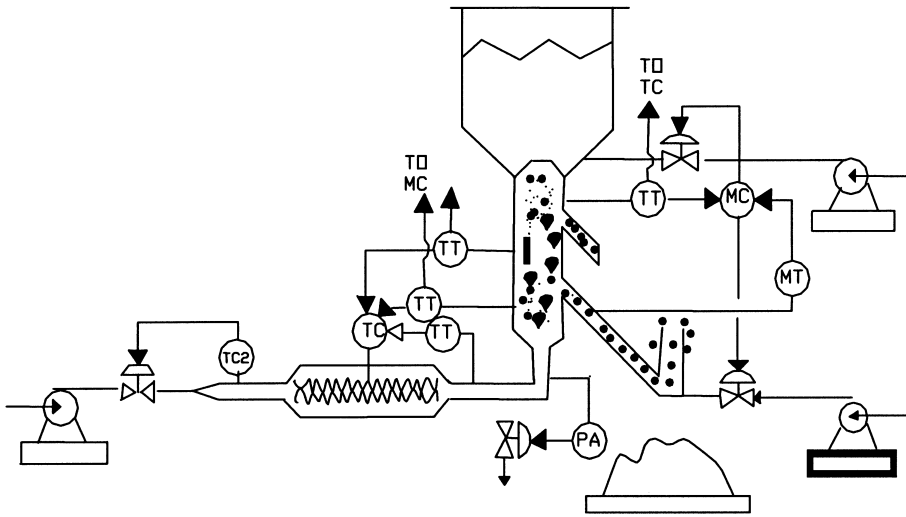


**Figure 22** Concept of the flumov state: (a) fluidized bed; (b) expanded fluidized bed; (c) formation of vault; (d) fluidized moving bed (from Ref. 1).

bed to the fluidized bed. The experimental results of residence time distribution of the solid agree with combined models of flow and illustrate the almost plug-flow in the moving bed and the perfect mixing in the fluidized zone of the flumov. The filtering effectiveness of the moving zone is very high and the fines in the output air are mostly eliminated.

## Case Studies

*Case Study I: Flumov Drier.* A fluidized/moving bed drier was constructed and operated [87,88]. It consisted of a cylinder 5.4 cm (inner diameter) and 40 cm height (fluidized bed zone) jointed by a conical device to an upper cylinder 19.2 cm (inner diameter) and 30 cm height (moving bed zone). The feed and removal of solids is made with the aid of J-valves especially designed for this work [89]. The system is a small pilot plant capable of treating up to 5 kg/hour of solid or solid-liquid waste (alpeorujo) (Fig. 23). The drying of waste was studied in batch, semibatch, and continuous operation. Several runs were made in both a conventional fluidized bed drier and a flumov drier with input air between 70 and 200°C and temperature inside the beds between 50 and 150°C. Fresh alpeorujo contained 50–60% moisture (wet basis) and the dried alpeorujo obtained was rather homogeneous. The extracted oil had the same quality as the oil obtained from dried alpeorujo obtained by other drying methods. The filtering effectiveness of the moving bed was very high. In order to solve the operative problems derived from the high moisture content of alpeorujo and the high viscosity of the semidried one, two solutions were found: mixing dry and wet alpeorujo and using pulses of a secondary air injection into the conical zone. Using these two conditions, the dry/wet mixture circulated more effectively along the whole system than the fresh wet alpeorujo. The feeding from the moving bed to the fluidized zone was also well controlled, the air-solid contact improved and the flumov drier was able to operate at a low temperature, about 60°C, inside the fluidized zone (implying a better thermal efficiency balance and allowed for improvement in the dry solid characteristics).



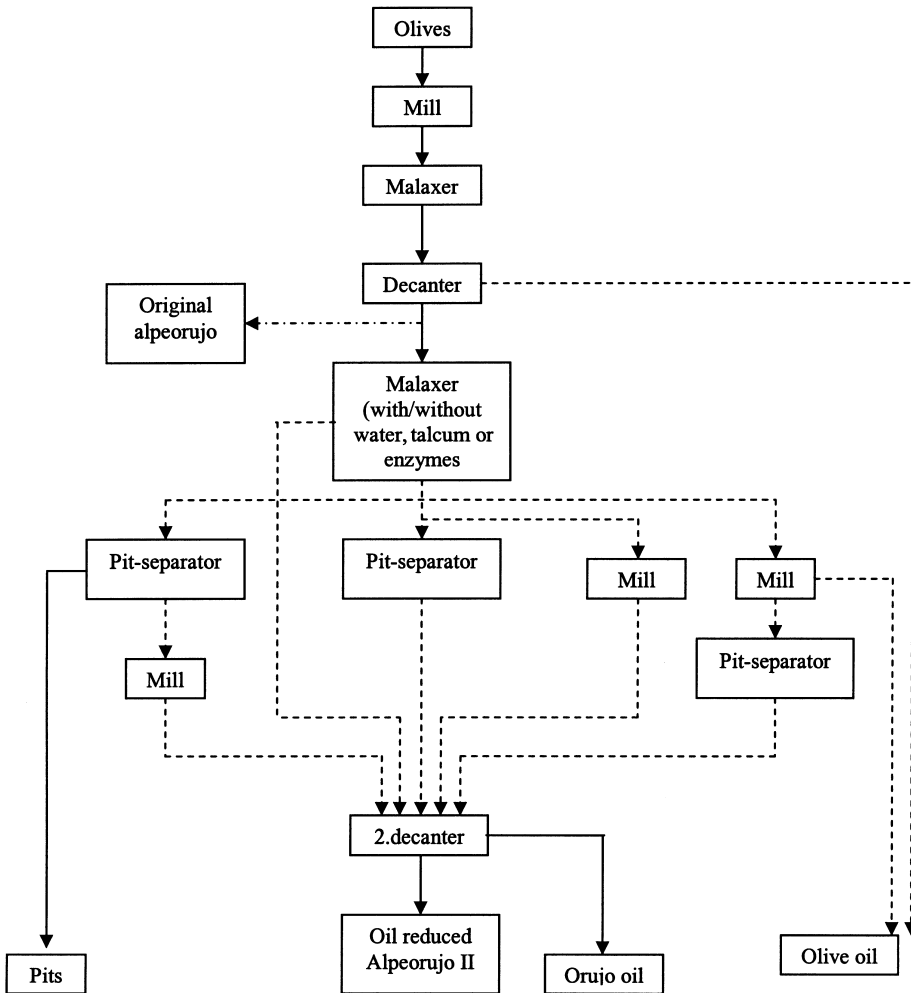
**Figure 23** Drier with the implemented advanced control prototype (from Ref. 1). Temperature (TC) and Moisture (MC) control system; Pressure alarm (PA) and temperature transmitters (TT). Control prototype designed by Cognito Quam Electrotechnologies Ltd.

The energy consumption of the flumov drier was between 0.71 and 1.11 kWh/kg water. The mechanical power consumption was similar to other industrial driers, 0.05 kWh/kg water. From the results obtained in the small pilot plant, the flumov drier is a feasible and competitive solution for drying waste. The possibility of drying at low temperatures resulted in a better thermal efficiency balance, lower operating and energetic costs, and improved solid characteristics in use of subsequent solid treatments (high quality of the orujo oil extracted). The main advantages of the system are: reduced total volume, filtering capacity, and ability of using low temperature sources to recover heat from several systems, for example, combined cycle systems and exhaust gases. The details about the control system and prototype, and moisture sensor are in the reference materials [1,89].

*Case Study II: Ring Drier.* (a) Deoiling of the waste. In southern Spain, Westfalia Separator A.G. installed a batch pilot plant with a capacity of approximately 1 m<sup>3</sup> per batch (Fig. 24) [1]. This plant allowed for an efficient pretreatment of solid/liquid waste (alpeorujo), the separation of the phases as well as a subsequent drying. Owing to product variation, the actual daily quality of the waste was determined as a basis for the planning of the tests. Thus, for each sample a standard test was carried out and several runs were carried out under different process combinations in order to reach a better deoiling of the fresh waste. For this aim, the pits were partially separated, different malaxing times were tested, enzymes or talcum were added to the malaxing process, small quantities of water were added, or other measures were tested for an improvement of the oil yield.

All these measures changed the characteristics of the raw material and consequently contributed in improving the drying process of the deoiled waste. After the deoiling, different intermediate products were generated, that is, partially deoiled orujo and partially depitted orujo. The following parameters were adjusted or the following aids were used [1].

- Enzymes: combination of pectinase and cellulase;
- Talcum: type “talco” 2%;



**Figure 24** Flow sheet of deoiling pilot plants (from Ref. 1).

- Mill: 2.5, 3, and 4 mm screen;
- Pit separator: 3 mm and 4 mm screen;
- Storage tank: 2 m<sup>3</sup>;
- Malaxer: 1 m<sup>3</sup>;
- Feed rate: up to 500 kg/h (waste).

(b) Drying of the waste. For the drying, a ring drier was installed to dry different alpeorujos. The intermediate products generated by the deoiling pilot plant were stored and dried. This drier was fueled by propane gas, and hot air was produced with this gas heater. The temperature of this hot air can be varied between 160 and 400°C. With the help of the horizontal screw, one part of the dried waste was mixed with the raw stuff. Both pit-reduced waste and simple deoiled waste were dried as a result. By using the ring drier, the humidity of the waste (alpeorujo) was reduced to approximately 10–15%. The dried material is a powder, the fractions of which are: pit fragments, skin, fruit flesh particles, or agglomerates. The thermal energy



requirement for the drier is 1.13 kWh/kg evaporated water. After drying, the oil content vs. drying substance (DS) is sometimes higher than the original material. Another conclusion can be drawn here from deoiling and drying of waste in ring drier. Pit separation before processing is a good solution, in order to produce pit that can be used as a fuel directly in the oil mill, and can raise the throughput. On the other hand, the oil yield is a little bit lower than in the basic version. It is worth noting that drying of solid or solid/liquid waste (alpeorujo) is supposed to precede composting or combustion, and is even indispensable for the latter.

### 17.6.3 Chemical Processes

Incineration plants are widely known as the conventional means for municipal solid waste treatment for many decades up to the present day. This method, which consists of oxidation of organic substances in high temperatures, has its advantages and disadvantages. Pyrolysis, in contrast to incineration, is a thermic-decomposed reaction of materials containing a high percentage of carbon (without oxygen) in high temperatures. Thus, pyrolysis is a reduction process that might trigger degasification. It is possible to introduce gasification when there is a partial reaction of coke and water with oxygen. These substances react to carbon oxide and hydrogen. The heat obtained in this process helps to crack heavy molecules. Although the pyrolysis can be used to recycle solid residuals and produce heat, it has not become widespread for technical and/or economical reasons [90]. Additionally, there are no known successful applications, even at pilot plant scale of either incineration or pyrolysis in treatment of olive oil mill waste.

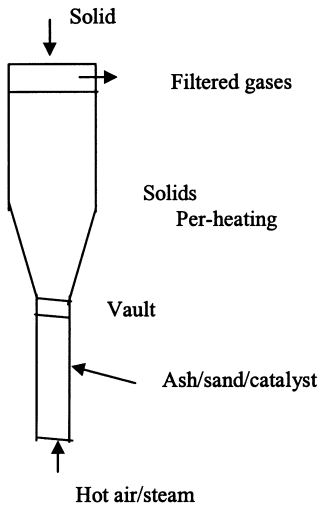
We will discuss a new technique that applies combustion and gasification together in a pilot plant, and has tested successfully in treatment of olive oil mill solid waste concentration [1]. This technique depends on a fluidized moving system, which is a good concept of the gasifier because of the special configuration of the reactor zones. In the bottom part of the gasifier, the fluidized bed permits the required combustion, which represents exothermic reactions, necessary to maintain the thermal balance inside the whole reactor. In the upper part, the moving bed zone does not allow the combustion process to occur but only the endothermic gasification processes. This is due to the fact that the rising gas that reaches the moving bed contains a very low concentration of oxygen and has a high temperature (800–850°C). So only the gasification process can be performed in the moving bed.

#### Case Study

A fluidized/moving bed reactor was designed to serve as combustor and gasifier. The pilot plant was capable of processing 1–5 kg/hour of solids. The control system in the reactor could regulate the mass flow of air, temperature, and level in the fluidized bed and solid feed. The gasifier is a flumov system, a rather new concept of reactor, and was based on a combination of (a) fluidized bed in the bottom part, where mainly combustion processes take part, and (b) moving bed in the upper part, where the solids are preheated and gasified (Fig. 25) [86]. A special characteristic of the flumov system is that the moving bed filters the flue gases.

The solid used for gasification was orijullo (deoiled orujo and deoiled alpeorujo) of mean particle size 1.4 mm, and pits (ground stone) of mean particle size 2.57 mm. The fluidized bed was filled with sand of mean particle size 0.21 mm, or in some runs, with dolomite with a mean particle size 0.35 mm.

The ultimate analysis of orujillo and stone showed that both have the same composition (dry ash free analysis: 47% C, 6% H, 1% N, 46% O, and <0.01% S). The content of ash is about 3.2% by weight. One of the main elements in ash is potassium (8–30% in K<sub>2</sub>O), the ingredient



**Figure 25** Flumov gasifier (from Ref. 86).

that makes the ashes useful as fertilizer additives. The main process operation variables were temperature, air/water ratio, and equivalent ratio (ER). The presence of sand and dolomite in the fluidized bed had no positive effect on the tar production in the moving bed nor on the flue gas composition (10% H<sub>2</sub>, 2% CH<sub>4</sub>, 8% CO). Many runs were carried out to find out the best operating conditions, both in combustion and in gasification to obtain the best thermal efficiency. The optimal operating conditions for obtaining the best flue gas were:

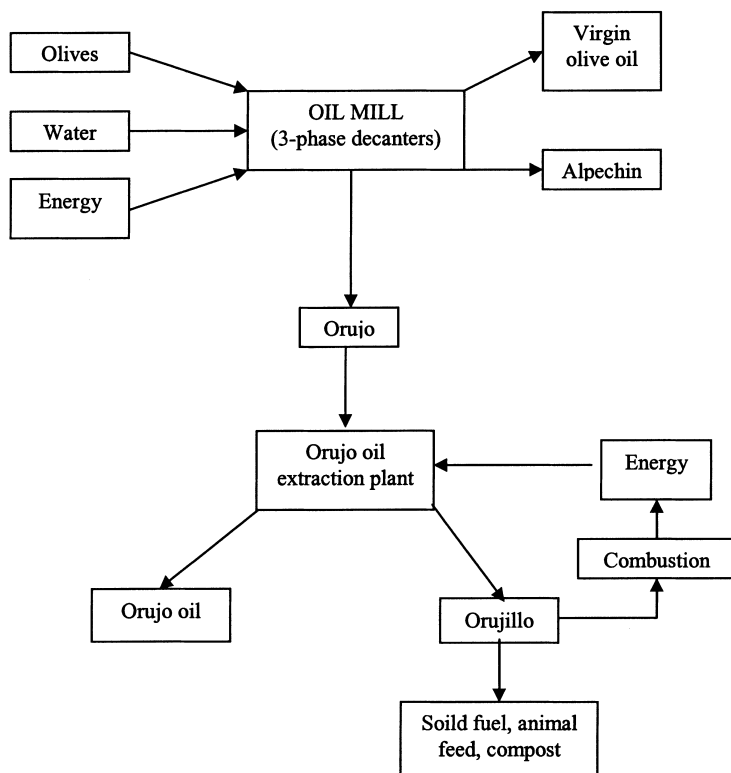
- Equivalent ratio (ER = actual air/stoichiometric): 0.20–0.30;
- Temperature in the moving bed: 750–800°C;
- Temperature in the fluidized bed: 800–824°C;
- Throughput: 400–500 kg solid/hm<sup>2</sup> fluidized bed;
- Airflow rate: 1.3 Nm<sup>3</sup>/hour;
- Water/air ratio: 0.2 kg water/kg air.

An assessment of the energetic validation by combustion and gasification of orujillo and pits was made. The gas produced in the fluidized/moving bed gasifier supported the expected composition of gasification flue gases and could be suitable for applications in the electrical power production by means of classical explosion motors.

#### 17.6.4 Examples of Technologies and Treatments

After reviewing various case studies applied in different regions, we can conclude that the most appropriate treatment depends not only on intrinsic factors but also on the capacity and system of production of the plants (olive mills and extraction plants and other industries or activities) [1].

As an example, the present practise in Greece and Italy is decanting in three-phase conditions (Fig. 26) with generation of alpechin and treatment of orujo in extraction plants that use hexane to extract the orujo oil. Part of the deoiled orujo (orujillo) is used to dry wet orujo in its own extraction plant. The excess orujillo is sold as solid fuel (ceramic manufacture furnaces, cement kilns, domestic heating), or used as raw material for composting and as additive for animal feed.

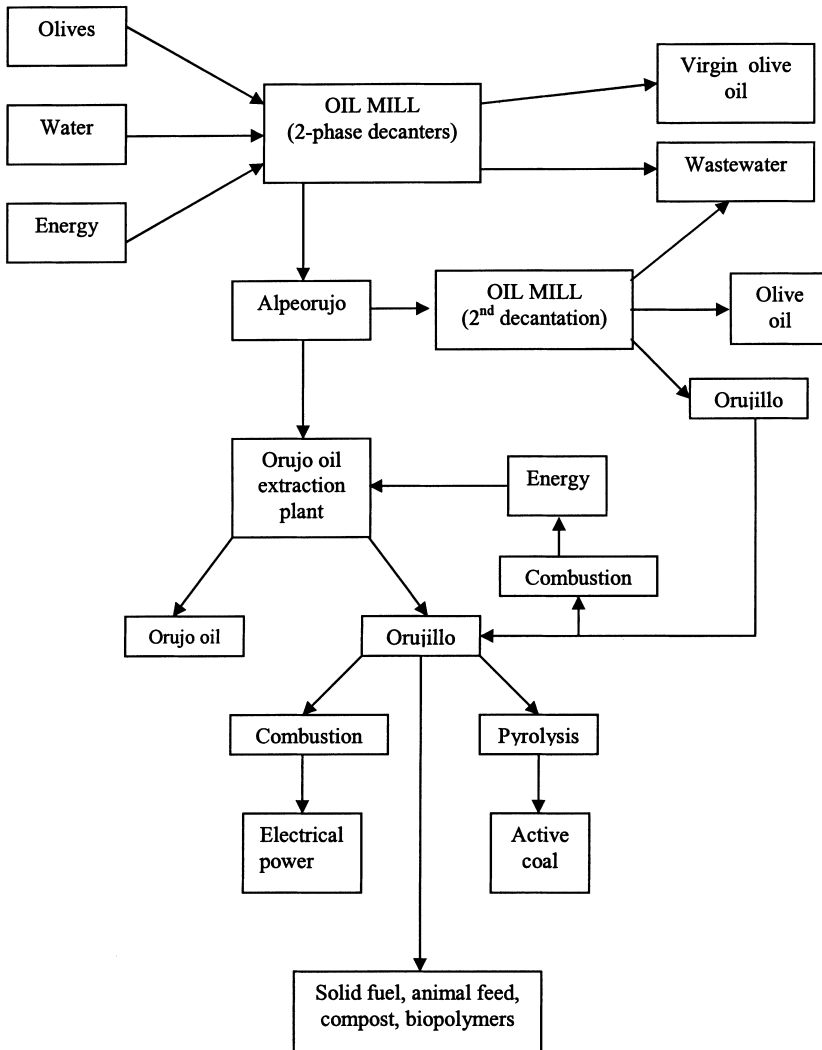


**Figure 26** Common integration of treatments for orujo from three-phase decanting method (from Ref. 1).

Spain is a different case, especially in the southern regions, where production is carried out almost exclusively by medium and big cooperatives, and where the two-phase decanting method has been adopted by more than 95% of producers (Fig. 27). The main waste is alpeorujo. Nowadays the “repaso” or second decanting of alpeorujo in the same oil mill is producing a new kind of wastewater, not equal to alpachin but nevertheless representing a growing environmental problem. The orujo oil can still be extracted by extraction plants, but the oil content decreases over time due to the deoiling of alpeorujo made in the oil mills. This means that some producers have decided to burn deoiled alpeorujo to produce electricity. Recent normative, with assured advantages for producers of energy from biomass, has also contributed to the use of orujillo as fuel in small electrical power plants (15 MW). Other new applications such as the production of active coal are also emerging [1].

Currently there is a tendency in some countries to move from the traditional pressing system to the three-phase system and from three-phase to the two-phase system, so the use of different models is constantly changing. Since there are no general unified solutions, every case should be studied according to the local conditions.

As we have seen in the previous section, in the case of waste resulting from the two-phase decanting process, separation into pulp, alpeorujo liquid fraction (ALF), and pits allows for the application of selective treatments and techniques such as composting, bioremediation, and gasification. Another valuable point is worth mentioning here: mixing alpeorujo with other wastes such as molasses improves the production of animal feed with a high protein content.



**Figure 27** Common integration of treatments for orujo from two-phase decanting method (from Ref. 1).

With regard to the energy value of wastes, it is important to consider that the integration of energy cycles will optimize costs and environmental impacts, for example, by burning pits dry, or predry the waste or alpeorujo, and combustion/gasification of it to recover energy and combustible gases to obtain and use electrical energy [1].

Furthermore, there should be always specific training programs for operators and supervisors in oil mills and related waste treatment units.

## 17.7 ECONOMY OF TREATMENT PROCESSES

Many food-processing-related industries, including the manufacture of olive oil and table olives, are of a seasonal nature, and consequently waste is not generated throughout the entire year.

Capital and operating costs of an *in situ* complete treatment (physical-chemical and biological processes) of these waste streams are inevitably high [91]. Thus, if a factory is located in an urban area, the most common practise for dealing with these kinds of effluents is to deliver the industrial effluent to the nearest municipal wastewater treatment plant and to pay the appropriate fee. However, the presence of inhibitory or toxic substances may have a serious effect on the overall treatment system, particularly the biological treatment process, from an operational and economical viewpoint. Thus, in the activated sludge process, phenol-type compounds in concentrations of  $>200$  mg/L and  $>10$  mg/L are known to inhibit carbonaceous removal and nitrification respectively [92]. As a result, some action must be taken before discharging these industrial effluents into municipal sewers and treatment facilities.

As discussed before, several anaerobic processes or techniques have been applied only to the treatments of diluted OME, such as an upflow anaerobic sludge blanket (UASB) reactor, a combined sludge blanket reactor with fixed-bed filter, anaerobic contact reactors, and anaerobic filters. In these biological treatments, OME has to be diluted prior to biological digestion, otherwise the bioreactors need high volumes due to the relatively low loading rates that could be applied and the high pollution potential of OME. At the same time, physical and chemical methods are widespread and applied for treatment of OME. These methods, as discussed before (treatment sections), are considered partial treatments, for example, precipitation by iron and lime, adsorption on a specific resin, and chemical oxidations by hydrogen peroxide and ozone. It was noticed that each pretreatment was efficient in removing the toxic effect of OME. Furthermore, the aerobic pretreatment of OME with different microorganisms (such as *Azotobacter* and *Aspergillus*) reduces considerably the COD and the total phenolic compounds concentration of the waste, which is responsible for its biotoxicity.

It is important to consider that any of these alternatives (physical, chemical, biological) must depend on economic factors, taking into account the possible combination of two or more alternatives. The physical or chemical pretreatment of OME could resolve the problems of time-variable composition and of pollution potential [24]. As a result, dilution for further biological treatment could be reduced, which is an important factor in the evaluation of its economy. The precise evaluation of the cost and feasibility of each of these treatment alternatives depends on several factors, such as capacity of production, waste amount, waste state (liquid or solid), site requirements, specific training of the workers, noise and odor emissions, industrial and agriculture–ecological surroundings, local laws [93].

As reported in the literature, wet air oxidation (WAO) is an economically acceptable technology used to treat aqueous wastes containing oxidizable pollutants at concentrations too high or too toxic for aerobic biological treatment [94]. An exhaustive economic evaluation of WAO is a rather difficult task, given the high number of parameters involved in the process. Thus for a continuous process, there are several operating variables (influent flow rate, temperature, pressure, contamination level, cooling and steam process water temperature, effluent temperature, final contamination level, biodegradability, etc.). Obviously, kinetic and thermodynamic data of the wastewater to be processed must also be considered (specific heat, heat of reaction, rate constants, etc.). These parameters will determine the residence time of the wastewater in the reactor and the energy needed and released in the process [19,95].

An economic assessment compared WAO and incineration processes for treatment of industrial liquid waste with a high content of phenol-type substances. The outcome was that incineration resulted in roughly four times the expense of WAO [96,97].

Another example focuses on solid waste treatment by gasifier/combustion flumov system to produce the optimal flue gas. Economic and industrial estimations were made of the gasifier's industrial design. The size and cost of a gasifier for treating 15 T/hour of solids capacity was estimated at 3.6 million euro (fluidized bed  $2.6 \times 8$  m, moving bed  $8 \times 8$  m) [1].

As previously discussed, it is important from an economic perspective to develop profitable uses for the final waste product, such as organic fertilizer, soil conditioner, and livestock feed. In this regard, it is worth pointing out that an opportunity exists to obtain a new type of renewable and low-cost activated carbon (J-carbon) from the processed solid residue of olive mill products. This is due to the fact that olive mills generate a huge amount of waste, which can be suitable as a raw material with economic value, and as a supportive means for pollutant removal from wastewater [98]. A study was performed to compare the capability of J-carbon with commercial activated carbon to remove ammonia ( $\text{NH}_3$ ), total organic carbon (TOC), and some special organics from Flexsy's (Rubber) wastewater treatment plant as tertiary treatment [99].

In this regard the final result was that the J-carbon has almost similar behavior and efficiency as the commercial activated carbons (powder activated carbon and granular activated carbon). Therefore, it was concluded that the J-carbon, as well as other commercial activated carbons, could be used in the treatment of industrial wastewater to improve efficiency of the treatment plant. The exhausted carbon would be settled by gravity and disposed of with the sludge as a carbon–sludge mixture. Thus, there would be no need for regeneration since the J-carbon is a renewable and very low-cost adsorbent.

## 17.8 SUMMARY

This chapter is based around the fact that the olive oil industry is in continuous growth due to its nutritious and economic importance, particularly for Mediterranean countries. This is accompanied by vast waste generation from different olive oil technologies (traditional and pressing decanting processes). The wastewater is mainly characterized by a high degree of organic pollution, polyphenols, and aromatics forming inhibitor or toxic substances, which constitute a serious environmental problem for soil, rivers, and groundwater.

The great variety of components found in liquid waste and solid waste requires different appropriate technologies to eliminate those that have harmful effects on the environment. From an economic perspective it is important to develop profitable uses for the final waste product such as organic fertilizer, soil conditioner, and livestock feed.

The optimal disposal and management of olive oil mill waste should be viewed within a multidisciplinary integrated frame that comprises specific procedures such as extraction by decanter centrifuge, liquid/solid waste treatments, aerobic bioremediation and composting, enrichment of waste with fungal/yeast protein, drying and gasification in fluidized moving beds, recovery of orujo oil, and recovery of energy and combustible gases.

Prospective researches should take into consideration the new advances in biotechnology, treatment reactors, control, new products and processes, composting from different wastes mixtures, all for the service of minimizing the impact on the environment, and reducing the use of valuable natural and living resources within the course of sustainable development.

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