

An Overview on Olive Mill Wastes and Their Valorisation Methods.

Roig*, A., Cayuela, M.L., Sánchez-Monedero, M.A.

Department of Soil and Water Conservation and Waste Management.

CEBAS CSIC. Campus Universitario de Espinardo. 30100 Murcia

Spain

*Corresponding author:

Phone: +34 968 396333

Fax: + 34 968 396213

Email: aroig@cebas.csic.es

INDEX

Abstract

- 1. Introduction.**
 - 2. Olive oil extraction systems and wastes produced.**
 - 3. Olive mill wastewater. Proposed valorisation methods.**
 - 3.1. Evaporation.*
 - 3.2. Direct application on soil.*
 - 3.3. Physicochemical treatments*
 - 3.4. Biotechnological transformations.*
 - 3.4.1 Microbiological treatments.*
 - 3.4.2. Composting.*
 - 3.4.3 Anaerobic digestion.*
 - 3.5. Extraction of valuable products.*
 - 4. Two-phase olive mill waste. Proposed valorisation methods.**
 - 4.1. Physicochemical treatments.*
 - 4.1.1. Drying and second extraction of oil.*
 - 4.1.2 Energetic revalorisation.*
 - 4.2. Biotechnological transformations..*
 - 4.2.1. Composting*
 - 4.2.2. Anaerobic digestion*
 - 4.2.3. Solid fermentation*
 - 4.3.. Direct soil application.*
 - 4.4. Extraction of valuable products.*
 - 4.5. Other valorisation options.*
 - 5. Other solid by-products.**
 - 6. Conclusions.**
- Acknowledgements.**
- References.**

Abstract

Olive mill wastes represent an important environmental problem in Mediterranean areas where they are generated in huge quantities in short periods of time. Their high phenol, lipid and organic acid concentrations turn them into phytotoxic materials, but these wastes also contain valuable resources such as a large proportion of organic matter and a wide range of nutrients that could be recycled. In this article recent research studies for the valorisation of olive mill wastes performed by several authors were reviewed: second oil extraction, combustion, gasification, anaerobic digestion, composting and solid fermentation are some of the methods proposed. Special attention was paid to the new solid waste generated during the extraction of olive oil by the two-phase system. The peculiar physicochemical properties of the new solid waste, called two-phase olive mill waste, caused specific management problems in the olive mills that has led to the adaptation and transformation of the traditional valorisation strategies. The selection of the most suitable or appropriate valorisation strategy will depend on the social, agricultural or industrial environment of the olive mill. Although some methods are strongly consolidated in this sector, other options, more respectful with the environment, should also be considered.

Keywords: olive mill waste, olive husk, olive mill wastewater, revalorisation.

1. Introduction

Olive oil industry is very important in Mediterranean countries, both in terms of wealth and tradition. Spain is the main world producer followed by Italy, Greece, Turkey, Syria and Tunisia. One third of the total world olive oil production is concentrated in Andalusia, a region in the South of Spain. This corresponds to nearly 80% of the Spanish and to more than 40% of the European olive oil production, that represents more than 75% of the global oil production. Hence, this area is especially affected by olive mill waste pollution. However, many other countries such as Argentina, Australia or South Africa are becoming emergent producers since they are promoting intensive olive tree cultivation.

The extraction of olive oil generates huge quantities of wastes that may cause a great impact on land and water environments because of their high phytotoxicity. Several studies have proved the negative effects of these wastes on soil microbial populations (Paredes *et al.*, 1987), on aquatic ecosystems (DellaGreca *et al.*, 2001) and even in air medium (Rana *et al.*, 2003). Therefore there is a need for guidelines to manage these wastes through technologies which minimise their environmental impact and lead to a sustainable use of resources.

For many years, olive mill wastewater (OMW) has been the most pollutant and troublesome waste produced by olive mills in all Mediterranean countries. Thus, the management of this liquid residue has been extensively investigated and some extensive and detailed reviews, which focus mainly on its management, have been recently published (Niaounakis and Halvadakis, 2004; Azbar *et al.*, 2004). However,

from the early nineties, the implementation of a new extraction system (two-phase technology) in some countries, has introduced a new solid waste, called two-phase olive mill waste (TPOMW), with specific management problems. This study provides a summary of updated information on research works that propose different valorisation methods based on scientific studies, laying special emphasis on TPOMW.

2. Olive Oil Extraction Systems and Wastes Produced.

Olive oil extraction involves different processes such as olive washing, grinding, beating and the extraction itself, that constitutes the basic stage of the whole process. The amount and physico-chemical properties of the wastes produced will depend on the method used for the extraction.

There are two ways of extracting the oil: traditional pressing, used for many centuries with only minor modifications, and centrifugation, that the olive oil industry has taken over in the last decades. There are also two centrifugation systems, called three-phase and two-phase systems, that are described in figure 1.

Even though traditional pressing is a relatively obsolete technology it is still in use for some olive oil producers (figure 2). After the extraction by pressing, a solid fraction, called olive husk, is obtained as by-product, alongside with an emulsion containing the olive oil, that is separated by decantation from the remaining olive mill wastewater.

The three-phase system generates three fractions at the end of the process: a solid (olive husk or olive pomace) and two liquids (oil and wastewater). In spite of the advantages of this system compared to pressing (complete automation, better oil quality, smaller area needed) it also presents some inconveniences (greater water and energy consumption, higher wastewaters production and more expensive installations).

Olive mill wastewater, generated by both systems (traditional and the three-phase system mills) have been illegally dumped to the soil or into a nearer stream or river for many years. The continuous dumping and the rapid increase in the amount of wastes generated have brought about serious environmental problems in the Mediterranean area due to its high organic matter concentration and its phytotoxicity. To avoid these environmental impacts, olive mills were enforced to treat or eliminate their wastes. One of the most accepted management options was the use of storage ponds that allowed natural evaporation of the wastewater and, more recently, specific wastewater treatment plants were developed. However, they did not consolidate in the olive oil sector because of technical and economical reasons.

In recent years olive mill technology has been aimed at saving water during the extraction stage. Thus, at the end of 1991/92 olive oil campaign, a new centrifugation system was developed which reduced by 75% the olive mill wastes. This system was launched to the market with the denominations of “ecological”, because of the reduction in water consumption, and of “two-phase”, because it produced two fractions: a solid one (called in different ways: alperujo, olive wet husk, wet pomace or two-phase olive mill waste) and a liquid one (olive oil).

In Spain the new two-phase system quickly replaced the three-phase method. Therefore a new waste, with peculiar physico-chemical properties, was generated in huge quantities leading to serious management problems. This sudden replacement has not happened in other countries, probably due to the management difficulties arisen with the new waste. In Europe, besides Spain, only Croatia has a high proportion of two-phase systems (figure 2).

Usually, the olive husk from the three-phase system had a second oil extraction with organic solvents after its drying. However, when two-phase olive mill waste was intended to be treated similarly, great difficulties appeared owing to its high moisture and carbohydrate concentration. Thus, the new waste tends to stick to the furnace walls blocking the gaseous stream and causing an explosion hazard (Arjona *et al.*, 1999). Besides, because of its high moisture, the drying process demands a lot of energy that significantly increases costs.

Moreover, the higher temperatures necessary for drying the two-phase olive mill waste, compared to the conventional olive husk, may also alter the material composition reducing the oil quality. Hence, in July 2001, benzopyrenes, which are recognised as carcinogenic substances, were detected in a husk-oil batch. This fact caused a great concern in Spain and the Health Ministry decided to temporarily withdraw it from the market. The sector came to a standstill for several months. Finally, a new legislation (BOE, 2001), that limits the higher concentration of benzopyrenes in 5µg/kg oil), came into force and husk-oil was back on the market

again. However, the sector is undergoing a recession since then, and two-phase olive mill waste became a new waste to be disposed of.

3. Olive mill wastewaters. Proposed valorisation methods.

Olive mill wastewaters (OMW) are the main pollutant from three-phase extraction systems and traditional mills. They are constituted by vegetable water of the fruit and the water used in different stages of oil extraction. They hold olive pulp, mucilage, pectin, oil, etc., suspended in a relatively stable emulsion (Paredes *et al.*, 1999). Their chemical composition is variable depending on olive varieties, growing techniques, harvesting period and especially the technology used for oil extraction.

The main characteristic of OMW is the presence of organic compounds such as organic acids, lipids, alcohols and polyphenols that turn OMW into phytotoxic materials, representing a great environmental hazard when it is not managed properly. However, OMW also contain valuable resources such as a high organic matter concentration and a number of nutrients, especially potassium, that could be recycled as a potential fertiliser. Table 1 shows the main chemical characteristics given by several authors.

In recent years many management options have been proposed for the treatment and valorisation of OMW. Most of these methods aim to the reduction of the phytotoxicity in order to reuse it for agricultural purposes, but more recently other alternative methods have also been proposed.

3.1. Evaporation

In practice, the most common elimination method is through evaporation in storage ponds in the open because of the low investment required and the favourable climatic conditions in Mediterranean countries. However, this method needs large areas and produces several problems such as bad odour, infiltration and insect proliferation.

The evaporation of OMW produces sludge. The majority of the sludge produced in evaporation ponds is disposed of in landfill sites, although it may be used also either in agriculture or as a heat source owing to its oil content. Most of the studies about revalorisation of OMW sludge focus on composting. Paredes *et al.* (2002) studied the composting process of OMW sludge with maize straw and cotton waste and concluded that this can be an environment-friendly alternative to OMW sludge disposal. Vitolo *et al.* (1999) proposed the preparation of a fuel by mixing the solid residue of OMW with olive husk. Another imaginative way of recycling this waste was proposed by Hytiris *et al.* (2004) who investigated the potential of using OMW sludge as an additive for the development of construction materials.

3.2. Direct application on soil.

Many researchers have applied OMW directly on soil and have tested its effect as an organic fertiliser showing positive and negative effects. Beneficial effects are related to its high nutrients concentration, especially K and its potential for mobilizing soil ions, whereas, negative effects are associated with its high

mineral salt content, low pH and the presence of phytotoxic compounds, especially polyphenols (Paredes *et al.*, 1999). Rinaldi *et al.* (2003) applied OMW without pre-treatment on a wheat crop during three years and observed some necrotic spots on the leaves and a reduction in secondary stems emergence. However, at harvest no significant differences were observed for grain yield.

OMW may reduce the mobility of certain organic compounds in soil. Cox *et al* (1997) suggested its use to attenuate leaching of toxic organic chemical such as herbicides (clopyralid and metamitron) in cultivated lands.

Another characteristic of OMW is its high antimicrobial capacity, which can be used for soil sanitation against certain pathogens. Thus, Kotsou *et al* (2004) verified the OMW suppressiveness against the plant pathogen *Rhizoctonia solani*. Therefore its addition prior to plantation could be a good prevention method.

3.3. Physico-chemical treatments.

These treatments consist in the addition of chemical substances which produce the coagulation, precipitation or destruction of dissolved organic compounds. Tsonis *et al.* (1989) used calcium hydroxide and aluminium sulphate to reduce COD (carbon oxygen demand) to 20-30% of initial values. On the other hand, Aktas *et al.* (2001) proposed a pre-treatment with lime to reduce the polluting effect of OMW since lime can easily be purchased and it is cheaper than other chemicals.

A new technology developed by several companies consists in the flocculation of the organic matter of OMW with an organic commercial polyelectrolyte. This process produces water that can be used for irrigation and a sludge which is called the solid fraction of OMW. This waste has been successfully composted with other agricultural by-products (Negro and Solano, 1996; García-Gómez *et al.*, 2003).

3.4. Biotechnological transformations.

3.4.1. Microbiological treatments.

Several authors have performed microbiological treatments of OMW for production of biopolymers such as xanthan (López and Ramos-Cormenzana, 1996), pullulan (Ramos-Cormenzana *et al.*, 1995) or polyhydroxyalkanoates (González-López *et al.*, 1995).

Aerobic treatment with micro-organisms has also been used to remove the pollution effect of OMW. These studies are nowadays focused on the degradation of phenolic compounds, the main responsible for phytotoxicity. Many microorganisms have been tested: the fungus *Pleurotus ostreatus*, *Bacillus pumilus*, the yeast *Yarrowia Lipolytica*, etc. (Tomati *et al.*, 1991; Ramos-Cormenzana *et al.*, 1996; Scioli and Vollaro, 1997).

The use of OMW as substrate for *Azotobacter vinelandii* growth and application of the treated effluent to cultivated soils as fertiliser was recently proposed by Ehaliotis *et al.* (1999) and Piperidou *et al.* (2000).

Although all these methods are very interesting from a scientific point of view, they are not usually used at industrial scale.

3.4.2. Composting

Composting is one of the main technologies for recycling OMW and transforming it into a fertiliser. This process allows the return of nutrients to cropland. Besides, composting avoids the negative effects often observed when these wastes are directly applied to soil.

The OMW has to be absorbed in a solid substrate before proceeding the composting, such as lignocellulosic waste. Tomati *et al.* (1995) found that a fertiliser with a high level of humification and no phytotoxic effects was obtained by composting OMW with wheat straw. Also, Paredes *et al.* (2000) tested different substrates with OMW and evaluated the evolution of organic matter and nitrogen during the composting process.

Cegarra *et al.* (1996) applied OMW composts to cultivate horticultural and other crops and found that yields obtained with compost fertilisation were similar, and sometimes higher to those obtained with mineral fertilisers. Tomati *et al.* (1996)

also observed an enhancement of activities in the plant-soil system after the addition of OMW composts.

3.4.3. Anaerobic digestion.

The main interest of anaerobic digestion is the production of energy (biogas) and the potential re-use of the effluent in irrigation (Marques, 2001). The major limitation of this treatment is the inhibition of methanogenic bacteria by the phenolic compounds and the organic acids present in the olive mill waste waters (Hamdi, 1996). According to Azbar et al (2004) anaerobic filter or up-flow anaerobic sludge bed reactor are suitable systems to treat OMW but a pre-treatment is necessary to remove undesirable compounds. Filidei *et al* (2003) proposed sedimentation-filtration pre-treatment prior to anaerobic digestion as a profitable way of OMW disposal.

3.5. Extraction of valuable products.

There are valuable compounds in the OMW, such as antioxidant substances and phenols, which can be used in pharmaceutical and cosmetic industry. The most important marketable antioxidants found in the pulp of olives are tyrosol, hydroxytyrosol and oluropein. Briante *et al.* (2004) proposed a bioreactor for the production of highly purified antioxidants which could be converted into pharmacologically active compounds. Moreover, Turano *et al.* (2002) proposed an integrated centrifugation-ultrafiltration system that allows the reduction of pollution and the selective separation of some useful products (lipid, sugar, polyphenol).

Many other wastewaters valorisation methods have been studied: reverse osmosis (Amirante and Di Renzo, 1991), photochemical degradation of phenols (Cermola *et al.*, 2004), electrocoagulation (Adhoum and Monser, 2004) etc...

Despite all the proposed solutions, olive mill wastewater was in 2001 the main pollutant in Guadiamar (Andalusia), a river which had become severely polluted by mine spillage at Aznalcóllar (Macpherson *et al.*, 2001). This fact shows the magnitude of the problem and proves that none of these approaches appears as a true solution.

4. Two-phase Olive Mill Waste. Proposed Valorisation Methods

Two-phase olive mill waste, TPOMW, (also called alperujo, olive wet husk, olive wet pomace or olive wet cake) is a solid waste with a strong odour and a doughy texture that makes its management and transport difficult. Olive vegetation waters (which in three-phase systems made up waste waters) are included now in TOMW and this characteristic causes the most important problem for its revalorisation because of its high moisture (65 %). Thus, this residue has become a serious trouble for olive mills nowadays, because its management requires specific facilities (storage tanks with special valves, mass pumps and tank trucks). The reduced profitability of this waste compared to the olive husk has lead to a deeper study on TPOMW and its new valorisation alternatives.

Table 2 shows some chemical characteristics given by several authors. TPOMW shows a slightly acidic pH, a high organic matter concentration (mainly fibres) and also it is especially rich in potassium. Lipid concentration is high but it depends on the extraction yield. Polyphenols are other valuable compounds present in TPOMW. Some recent studies have proved that these compounds (oleuropein, hydroxytyrosol and caffeic acid) exert a protective effect in human erythrocytes and DNA against oxidative damages (Manna et al., 1999; Quiles et al., 2002). Unlike other organic residues (sewage sludge, municipal solid wastes) that have been proposed for agricultural aims, the concentration of heavy metals in TPOMW is almost non-existent. Madejón *et al.* (1998) provided data of the toxic heavy metals, showing a concentration lower than 1 mg/kg for Pb, Cd, Cr and Hg.

4.1. Physicochemical treatments.

4.1.1. Drying and second extraction of oil.

TPOMW was thought to be valorised just as olive husk; that is by drying it and performing a second extraction of oil with solvents. The high moisture content of the new TPOMW caused technical problems during the drying process in traditional husk-extraction mills. These problems led to the research of new drying methods. Thus, Arjona *et al.* (1999), based on a description of the different stages that make up the whole drying process, developed a useful procedure to determine the operation conditions at which the residue could ignite. Afterwards, Krokida et al (2002) proposed a design for an appropriate industrial rotary dryer and discussed economic

feasibility. More recently, Arjona et al (2005) developed a control system that increases automation and improves the energetic efficiency.

However, the increase in the cost of the drying process due to greater required energy together with the low demand for husk oil have led to consider alternative technologies for its valorisation.

4.1.2. Energetic revalorisation.

After the second extraction, the exhausted olive cake is usually used as fuel in the husk mill to obtain thermal or electric energy through combustion (Masghouoni and Hassairi, 2000; Caputo *et al.*, 2003). This method is currently used in most of the olive mills since the dried olive husk presents a relative high calorific power (400 kcal/kg). However, most of the energy obtained by combustion is used for dryness of the fresh TPOMW and therefore the total energy recovery is low (Azbar et al.,2004).

Biomass gasification is a new physicochemical method especially for the de-oiled TPOMW. This process transforms solid biomass in synthetic gas (called “syngas”), a mixture of CO and H₂. Synthetic gas is used for obtaining important chemical products such as CH₃OH or NH₃ and for preparation of synthetic fuel. Jurado *et al.* (2003) propose olive cake to produce syngas with energetic aims.

4.2. Direct soil application

TPOWM has been assayed directly as soil amendment considering its high potassium concentration, its low economical value and that it is produced near application lands and, therefore, no transport is required. Nevertheless, several experiences have shown that, though it is less phytotoxic than wastewaters, it causes great nutritional imbalances, since it modifies nitrogen cycle in soil due to its high C/N ratio (Thompson and Nogales, 1999).

Saviozzi *et al.* (2001) evaluated the suitability of TPOWM as soil amendment adding mineral nitrogen and they concluded that its mineralisation largely depended on the type of soil, being temporarily inhibited in acidic soils. Also Ordoñez *et al.* (1999) advised to add nitrogen fertilisers together with the TPOMW and emphasised the increase produced in available K in soil.

4.3. Biotechnological transformations

4.3.1. Anaerobic digestion.

Biogas (a mixture of CH₄ and CO₂) and partially stabilised organic matter can be obtained through anaerobic digestion. Biogas can be used to obtain energy and organic matter can be applied as soil conditioner. Tekin *et al.* (2000) proposed biogas production from olive husk and found that the methane content was in the range of 75-80%. Borja *et al.* (2003) conducted a laboratory-scale experiment on the mesophilic anaerobic digestion of two-phase olive mill waste and found that methane production was reproducible within 10% deviations. However, they remarked the high level of phenolic compounds as a limiting factor.

4.3.2. Solid state fermentation.

TPOMW has also been proposed as livestock feed (Molina-Alcaide and Nefzaoui, 1996). However, due to its high proportion of low digestible fibres and its low concentration of proteins, especially lysine, it is recommendable to use protein supplements (Molina-Alcaide *et al.*, 2003). It is also possible to improve its nutritional properties through solid fermentation. This process, performed by microorganisms in a solid medium, has been successfully exploited for production of animal feeds, fuel, and enzymes. Haddadin *et al* (1999) increased protein percentage in olive husk from 5.9% to 40.3% with this treatment.

4.3.3. Composting.

Several authors have studied the co-composting of TPOMW with other agricultural wastes. Due to its semi-solid consistence, it needs to be mixed with bulking agents before composting. Unlike OMW, the new residue is added at once at the beginning of the process, whereas OMW is added repeatedly during the thermophilic phase.

Some suitable material used as bulking agents were straw (Madejón *et al.* 1998), cotton waste (Cegarra *et al.*, 2000), poplar sawdust and bark chips (Filippi *et al.*, 2002). In all cases the final product showed good humification degree, no phytotoxic effect and considerable amounts of mineral nutrients. They suggested that composting may be a suitable low-cost strategy for the recycling of olive oil by-

products with a complete detoxification of starting materials, representing an alternative to combustion.

Physical characteristics of TPOMW make difficult its composting by forced aeration systems because of the generation of preferential flow paths for the air that dried the material forming aggregates (Cayuela, 2004). Baeta-Hall *et al.* (2005) compared two different aeration processes for the co-composting of TPOMW and grape stalks and recommended mechanical turning better than forced aeration.

Olive mill wastes composts may play an important role on organic agriculture. The high purity of olive mill wastes (lacking in recalcitrant toxic substances) guarantees the quality and competitiveness of composts made from the biological transformation of these residues. Cayuela *et al.* (2004) proposed its industrial composting with manure as a good method to revalorise this residue in the olive mills surrounding area.

Olive by-products composts have been assayed as fertilisers in horticultural crops (Madejón *et al.*, 2001). However, high pH reached during composting of TPOMW with other agricultural wastes may represent a limitation for its soil application. In order to solve this problem, Roig *et al.* (2004) suggested the addition of elemental sulphur as a suitable strategy for pH control during the composting process under the organic farming regulations.

4.4. Extraction of valuable products.

TPOMW has been proposed as a low-cost substrate for the production of valuable compounds. For instance, it has been suggested for the extraction of pectins. These are natural hydrocolloids widely used as gelling agents, stabilizers and emulsifiers in the food industry that currently are available from two important sources: apple pomace and citrus peel. However, there is an intense search for other pectin sources, specially using waste products as raw materials. Thus, Cardoso *et al* (2003) studied the profit for the extraction of pectins from TPOMW showing positive results.

TPOMW is a potentially rich source of a great range of phenols with a wide array of biological activities. Recently, a detailed review on bioactivity and analysis of bio-phenols from olive mill waste has been published (Obied *et al.*, 2005). In this article, it is shown that olive mill waste is rich in polyphenols and typically contains 98% of the total phenols in the olive fruit. Hydroxytyrosol, tyrosol, oleuropein and caffeic acid are the major phenolic components. A wide number of scientific articles prove the antioxidant, cardioprotective, antimicrobial, antihypertensive, anticarcinogenic activities of these compounds, which could be used in pharmaceutical, cosmetic and food industries. Some authors have developed new technologies for the improvement of their extraction methods (Fernandez-Bolaños *et al.*, 2002; Bouzid *et al.*, 2005).

5.6. Other valorisation options.

Other less common, but also very interesting ways of valorisation have been proposed: its use as heavy metal sorbent material for the treatment of aqueous solutions (Pagnanelli *et al.*, 2002); its application to agricultural soils to extend and

strength sorption of herbicides (simazine) and insecticides (imidacloprid) to reduce their biodegradation and to retard their leaching, reducing the risk of groundwater contamination (Albarrán *et al.*, 2004; Cox *et al.*, 2004). Siracusa *et al.* (2001) studied the possibility of recycling TPOMW by mixing it with thermoplastic polymers to produce new materials for manufacturer of containers.

In a recent study, Vlyssides *et al.* (2004) proposed an integrated method for reusing olive oil extraction by-products. Extraction of valuable compounds which may be marketable in pharmaceutical and cosmetic industry, wastewater purification and composting of solid residues for its use as fertilisers in olive orchard are included in this integrated approach.

5. Other solid by-products.

A limited amount of solid wastes (leaves and small twigs) is produced during the cleaning of the olives prior to milling. Nevertheless, these by-products do not involve any management problem since they can be used as animal feed or calorific source. Olive leaves are a well-known source of antioxidant compounds and are marketed as herbal teas with diuretic, antihypertensive and antioxidant activity.

Some olive mills are provided with a system able to remove stones from the olive pulp. This process is often used to improve the oil extraction yield. Besides, stones, also called pits, are a valuable product because of their high calorific power. They are currently used as an energy source, but they have been proposed for other interesting uses such as soil-less substrate for hydroponics (Melgar *et al.*, 2001) and

to produce activated carbon (El Sheikh *et al.*, 2004). Moreover, Fernández-Bolaños *et al.* (2001) proposed steam-explosion of olive stones to obtain high-value-added products such as hydroxytyrosol xylo-oligosaccharides and high quality lignin. Furthermore, Montané *et al.* (2002) produced furfural through high-temperature acid hydrolysis of olive stones.

7. Concluding remarks.

The replacement of three-phase extraction systems by the two-phase technology has considerably reduced water needs during the oil extraction process. This fact could have an important repercussion in many countries of the Mediterranean area, since they suffer severe water restrictions. Furthermore, the volume of wastes produced has undergone a considerable decrease. However, a new solid waste with specific physicochemical characteristics has appeared and although less water is needed, two-phase process does not completely eliminate the environmental problems. Thus, TPOMW presents more disposal problems than the olive husk of the three-phase system and it demands for new environmental and economically viable management options.

Many solutions have been suggested for the valorisation of olive mill wastes but many factors should be considered when selecting the best revalorisation method. For instance, total amount of waste, investment required to perform the treatment, available land, industrial or agronomic environment, local laws and most important needs. There is no a unique solution but it will depend on the specific needs of the local area. The majority of olive oil producer countries in Mediterranean area are

exposed to desertification processes, so organic matter application would be beneficial to improve the soil fertility and control the erosion processes. Also in organic agriculture, the use of these by-products could represent an important source of nutrients, closing the cycle residues-resources. Therefore, the use of olive mill wastes as soil conditioners or fertilisers can play a fundamental role in the maintenance of the olive tree ecosystem and on sustainable agriculture.

Acknowledgements

The authors wish to thank the Spanish Comisión Interministerial de Ciencia y Tecnología (CICYT) for financing this work through the PETRI project nº ref PTR1995-0458-OP.

References.

Adhoum, N. and Monser, L., 2004. Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation. *Chemical Engineering and Processing* 43(10), 1281-1287.

Aktas, E.S., Imre, S., Ersoym L., 2001. Characterization and lime treatment of olive mill wastewater. *Water Research* 35(9), 2336-2340.

Albarrán, A., Celis, R., Hermosín, M.C., López- Piñeiro, A., Cornejo, J., 2004. Behaviour of simazine in soil amended with the final residue of the olive oil extraction process. *Chemosphere* 54, 717-724.

Alburquerque, J.A., González, J., García, D., Cegarra, J., 2004. Agrochemical characterisation of “alperujo”, a solid by-product of the two phase centrifugation method for olive oil extraction. *Bioresource Technology* 92 (2), 195-200.

Amirante, P., Di Renzo, G.C., 1991. Tecnologías e instalaciones para la depuración de alpechines por medio de procesos físicos de concentración y ósmosis. *Actas Reunión Internacional sobre Tratamiento de Alpechines*. Córdoba. Spain. pp: 49-61.

Arjona, R., García, A., Ollero, P., 1999. The drying of alpeorujo, a waste product of the olive oil mill industry. *Journal of Food Engineering* 41, 229-234.

Arjona, R., Ollero, P., Vidal, F., 2005. Automation of an olive waste industrial rotary dryer. *Journal of Food Engineering* 68, 239-247.

Azbar, N., Bayram, A., Filibeli, A., Muezzinoglu, A., Sengul, F., Ozer, A., 2004. A review of wastes management options in olive oil production. *Critical reviews on environmental science and technology* 34 (3), 209-247.

Baeta-Hall, L., Sàágua, M.C., Bartolomeu, M.L., Anselmo, A.M., Rosa, M.F., 2005. Biodegradation of olive oil husks in composting aerated piles. *Bioresource Technology* 96(1), 69-78.

BOE, 2001. Orden de 25 de Julio de 2001 por la que se establecen límites de determinación de hidrocarburos aromáticos policíclicos en aceite de orujo de oliva. *Boletín Oficial del Estado* N° 178.

Borja, Rincón, B., Raposo, F., Alba, J., Martín, A., 2003. Kinetics of mesophilic anaerobic digestion of the two-phase olive mill solid waste. *Biochemical Engineering journal* 15(2), 139-145.

Boucid, O., Navarro, D., Roche, M., Asther, M., Haon, M., Delattre, M., Lorquin, J., Labat, M., Asther, M., Lesage-Meessen, L., 2005. Fungal enzymes as a powerful tool to release simple phenolic compounds from olive oil by-product. *Process Biochemistry* 40 , 1855-1862.

Briante, R., Patumi, M., Febbraio, F., Nucci, R., 2004. Production of highly purified hydroxytyrosol from *Olea Europaea* leaf extract biotransformed by hyperthermophilic β -glycosidase. *Journal of Biotechnology* 111, 67-77.

Caputo, A.C., Scacchia, F., Pelagagge, P., 2003. Disposal of by-products in olive oil industry: waste to energy solutions. *Applied Thermal Engineering* 23, 197-214.

Cardoso, S.M., Coimbra, M.A., Lopes da Silva, J.A., 2003. Calcium-mediated gelation of an olive pomace pectic extract. *Carbohydrate polymers* 52, 125-133.

Cayuela, M.L. 2004. "Producción Industrial de compost ecológico a partir de residuos de almazara". Ph.D. Thesis. University of Murcia. Spain

Cayuela, M.L. Bernal, M.P., Roig, A., 2004. Composting olive mill wastes and sheep manure for orchard use. *Compost Science and Utilization* 12(2), 130-136.

Cegarra J., Amor J.B., González J., Bernal M.P., Roig A., 2000. Characteristics of a new solid olive-mill-by-product ("alperujo") and its suitability for composting. In: Warman, P.R., Taylor, B.R. (Eds.), *Proceedings of the International Composting Symposium ICS'99*, vol. 1. CBA Press Inc., pp. 124-140.

Cegarra, J., Paredes, C., Roig, A., Bernal. M.P. and García, D., 1996. Use of olive mill wastewater compost for crop production. *International Biodeterioration and Biodegradation* 38, 193-203.

Cermola, F., DellaGreca, M., Iesce, M.R., Montella, S., Pollio, A., Temussi, F., 2004. A mild photochemical approach to the degradation of phenols from olive oil mill wastewater. *Chemosphere* 55, 1035-1041.

Cox, L., Celis, R., Hermosin, M.C., Becker, A., Cornejo, J., 1997. Porosity and herbicide leaching in soils amended with olive-mill wastewater. *Agriculture, Ecosystems and Environment* 65, 151-161.

Cox, L., Hermosín, M.C., Cornejo, J., 2004. Influence of organic amendments on sorption and dissipation of imidacloprid in soil. *International Journal of Environmental and Analytical Chemistry* 84, 95-102.

DellaGreca, M., Monaco, P., Pinto, G., Pollio, A., Previtiera, L., Temussi, F., 2001. Phytotoxicity of low-molecular-weight phenols from olive mill wastewaters. *Bulletin of Environmental Contamination and Toxicology* 67, 352-359.

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

El-Sheikh, A.H., Newman, A.P., Al-Daffae, H.K., Phull, S., Cresswell, N., 2004. Characterization of activated carbon prepared from a single cultivar of Jordanian Olive stones by chemical and physicochemical techniques *Journal of Analytical and Applied Pyrolysis* 71(1), 151-164.

Fernández-Bolaños, J., Felizón, B., Heredia, A., Rodríguez, R., Guillén, R., Jiménez, A., 2001. Steam-explosion of olive stones: hemicellulose solubilization and enhancement of enzymatic hydrolysis of cellulose. *Bioresource Technology* 79, 53-61.

Fernandez-Bolaños, J., Rodriguez, G., Rodriguez, R., Heredia, A., Guillén, R., Jiménez, A., 2002. Production in large quantities of highly purified hydroxytyrosol from liquid-solid waste of the two-phase olive oil processing or "alperujo". *Journal of Agricultural and Food Chemistry* 50, 6804-6811.

Filidei, S., Masciandaro, G., Ceccanti, B., 2003. Anaerobic digestion of olive oil mill effluents: evaluation of wastewater organic load and phytotoxicity reduction. *Water, Air and Soil Pollution* 145, 79-94.

Filippi, C., Bedini, S., Levi-Minzi, R., Cardelli, R., Saviozzi, A., 2002. Cocomposting of olive oil mill by-products: chemical and microbiological evaluations. *Compost Science and Utilization* 10 (1), 63-71.

García-Gómez, A., Roig, A., Bernal, M.P., 2003. Composting of the solid fraction of olive mill wastewater with olive leaves: organic matter degradation and biological activity. *Bioresource Technology* 86, 59-64.

González-López, J., Pozo, C., Martínez-Toledo, M.V., Rodelas, B., Salmerón, V., 1995. Producción de polihidroxialcanoatos por *Azotobacter chroococcum* H23 en

alpechín. Simposium Obtención del aceite de Oliva y reciclado de Subproductos. Granada, España. pp.43.

Haddadin, M.S., Abdulrahim, S.M., Al-Khawaldeh, G.Y., Robinson, R.K., 1999. Solid state fermentation of waste pomace from olive processing. *Journal of Chemical Technology and Biotechnology* 74, 613-618.

Hamdi, M., 1996. Anaerobic digestion of olive mill wastewaters. *Process biochemistry* 31(2), 105-110.

Hytiris, N., Kapellakis, I.E., de La Roij, R., Tsagarakis, K.P., 2004. The potential use of olive mill sludge in solidification process. *Resources, Conservation and Recycling* 40, 129-139.

IMPEL, 2003. IMPEL Olive Oil Project Report. European Union Network for the implementation and enforcement of Environmental Law. http://europa.eu.int/comm/environment/impel/olive_oil_project.htm

Jurado, F., Cano, A., Carpio, J., 2003. Modelling of combined cycle power plants using biomass. *Renewable Energy* 28(5): 743-753.

Kotsou, M., Mari, I., Lasaridi, K., Chatzipavlidis, I., Balis, C., Kyriacou, A., 2004. The effect of olive oil mill wastewater (OMW) on soil microbial communities and suppressiveness against *Rhizoctonia solani*. *Applied Soil Ecology* 26, 113-121.

Krokida, M.K., Maroulis, Z.B., Kremalis, C., 2002. Process design of rotatory dryers for olive cake. *Drying technology* 20(4): 771-787.

López, M.J., Ramos-Cormenzana, A., 1996. Xanthan production from olive-mill wastewaters. *International Biodeterioration & Biodegradation* 38(3/4), 263-270.

Madejón, E., Galli, E., Tomati, U., 1998. Composting of wastes produced by low water consuming olive mill technology. *Agrochimica* 42,135-146.

Madejón, E., López, R., Murillo, J.M., Cabrera, F., 2001. Agricultural use of three (sugar- beet) vinasse compost: effect on crops and chemical properties of a Cambisol soil in the Guadalquivir river Valley (SW Spain). *Agriculture, Ecosystems & Environment* 84(1), 55-65.

Manna, C., Galletti, P., Cucciolla, V., Monteodoro, G.F., Zappia, V. 1999. Olive oil hydroxytyrosol protects human erythrocytes against oxidative damages. *Journal of Nutritional Biochemistry* 10, 159-165.

Marques, I.P., 2001. Anaerobic digestion treatment of olive mill wastewater for effluent re-use in irrigation. *Desalination* 137, 233-239.

Masghouni, M., Hassairi, M., 2000. Energy applications of olive-oil industry by-products: I. The exhaust foot cake. *Biomass & Bioenergy* 18, 257-262.

Mcpherson, E., Ferrer, E., Grimalt, J., 2001. El accidente de las minas de Aznalcollar. *Investigación y Ciencia*. October 2001. 24-35.

Melgar, R., Gómez, M., Benítez, E., Polo, A., Molina, E., Nogales, R., 2001. Posibilidades de utilización de los huesos triturados de aceituna como sustrato de cultivos hidropónicos. Resultados preliminares. *I Encuentro Internacional de Gestión de Residuos Orgánicos en el Ámbito Rural Mediterráneo*. Pamplona, España.

Molina Alcaide, E. Y Nefzaoui, A., 1996. Recycling of olive oil by-products: possibilities of utilization in animal nutrition. *International Biodeterioration and Biodegradation* 38 (3/4), 227-235.

Molina Alcaide, E., Yáñez Ruiz, D. R., Moumen, A., Martín García, A. I. 2003. Ruminant degradability and in vitro intestinal digestibility of sunflower meal and in vitro digestibility of olive by-products supplemented with urea or sunflower meal: Comparison between goats and sheep. *Animal Feed Science and Technology* 110 (1-4), 3-15.

Montané, D., Salvadó, J., Torras, C., Farriol, X., 2002. High-temperature dilute-acid hydrolysis of olive stones for furfural production. *Biomass & Bioenergy* 22, 195-304.

Moreno, E., Pérez, J., Ramos-Cormenzana, A., Martínez, J., 1987. Antimicrobial effect of wastewater from olive oil extraction plants selecting soil bacteria after incubation with diluted waste. *Microbios* 51, 169-174.

Negro, M.J. and Solano, M.L., 1996. Laboratory composting assays of the solid residue resulting from the flocculation of oil mill wastewater with different lignocellulosic residues. *Compost Science and Utilization* 62-71.

Niaounakis, M., Halvadakis, C. P., 2004. Olive-mill waste management: literature review and patent survey. *Typhito- George Dardanos Publications*. Athens. ISBN 960-402-123-0.

Ordoñez, R., González, P., Giráldez, J.V., García-Ortiz, A., 1999. Efecto de la enmienda con alperujo sobre los principales nutrientes de un suelo agrícola. In: *Estudios de la Zona no Saturada*. Eds. R. Muñoz-Carpena, A. Ritter, C. Tascón. ISBN 84-699-1258-5.

Obied, H.K., Allen, M.S., Bedgood, D.R., Prenzler, P.D., Robards, K., Stockmann, R., 2005. Bioactivity and analysis of biophenols recovered from olive mill waste. *Journal of Agricultural and Food Chemistry* 53, 823-837.

Pagnanelli, F., Toro, L., Veglio, F., 2002. Olive mill solid residues as heavy metal sorbent material: a preliminary study. *Waste Management* 22, 901-907.

Paredes, C., Bernal, M.P., Cegarra, J., Roig, A., 2002. Bio-degradation of olive mill wastewater sludge by its co-composting with agricultural wastes. *Bioresource Technology* 85, 1-8.

Paredes, C., Cegarra, J., Roig, A., Sánchez-Monedero, M.A., Bernal, M.P., 1999. Characterization of olive-mill wastewater (alpechín) and its sludge for agricultural purposes. *Bioresource Technology* 67, 111-115.

Paredes, C., Roig, A., Bernal, M.P., Sánchez-Monedero, M.A., Cegarra, J., 2000. Evolution of organic matter and nitrogen during co-composting of olive mill wastewater with solid organic wastes. *Biology and Fertility of Soils* 32, 222-227.

Paredes, M.J., Moreno, E., Ramos-Cormenzana, A., Martínez, J., 1987. Characteristics of soil after pollution with wastewaters from olive oil extraction plants. *Chemosphere* 16(7), 1557-1564.

Piperidou, C.I., Chaidou, C.I., Stalikas, D., Soulti, K., Pilidis, G.A., Balis, C., 2000. Bioremediation of olive mill wastewater: chemical alterations induced by *Azotobacter vinelandii*. *Journal of Agricultural and Food Chemistry* 48, 1941-1948.

Quiles, J.L., Farquharson, A.J., Simpson, D.K., Grant, I, Whale, K.W., 2002. Olive oil phenolics: effects on DNA oxidation and redox enzyme mRNA in prostate cells. *British Journal of Nutrition* 88, 225-234.

Ramos-Cormenzana, A., Juárez-Jimenez, B., García-Pareja, M.P., 1996. Antimicrobial activity of olive mill wastewaters (alpechín) and biotransformed olive oil mill wastewater. *International Biodeterioration and Biodegradation* 38, 283-290.

Ramos-Cormenzana, A., Monteoliva-Sánchez, M., López, M.J., 1995. Bioremediation of alpechín. *International Biodeterioration and Biodegradation* 35(1/3), 249-268.

Rana, G., Rinaldi, M., Introna, M., 2003. Volatilisation of substances alter spreading olive oil waste water on the soil in a Mediterranean environment. *Agriculture, Ecosystems and Environment* 96, 49-58.

Raposo, F., Borja, R., Sánchez, E., Martín, M. A., Martín, A., 2004. Performance and kinetic evaluation of the anaerobic digestion of two-phase olive mill effluents in reactors with suspended and immobilized biomass. *Water Research* 38, 2017-2026.

Rinaldi, M., Rana, G., Introna, M., 2003. Olive mill wastewater spreading in southern Italy: effects on a durum wheat crop. *Field Crops Research* 84, 319-326.

Roig, A., Cayuela, M.L., Sánchez-Monedero, M.A. 2004. The use of elemental sulphur as organic alternative to control pH during composting of olive mill wastes. *Chemosphere* 57, 1099-1105.

Saviozzi, A., Levi-Minzi, R., Cardelli, R., Biasci, A., Riffaldi, R., 2001. Suitability of moist olive pomace as soil amendment. *Water, Air and Soil Pollution* 128, 13-22.

Saviozzi, A., Levi-Minzi, R., Riffaldi, R., Lupetti, A., 1991. Effetti dello spandimento di acque di vegetazione sul terreno agrario. *Agrochimica* 35, 135-148.

Scioli, C. and Vollaro, L., 1997. The use of *yarrowia lilytica* to reduce pollution in olive mill wastewaters. *Water Research* 31(10), 2520-2524.

Siracusa, G., La Rosa, A.D., Siracusa, V., Trovato, M. 2001. Eco-compatible use of olive husk as filler in thermoplastic composites. *Journals of Polymers and the Environment* 9(4), 157-161.

Tejada, M., Gonzalez, J.L., 2004. Effect of foliar application of a by-product of the two-step olive oil mill process on rice yield. *European journal of Agronomy* 21, 31-40.

Tekin, A.R., Dalgıç, A.C., 2000. Biogas production from olive pomace. *Resources, Conservation and Recycling* 30, 301-313.

Thompson, R.B. and Nogales, R. 1999. Nitrogen and carbon mineralization in soil of vermi-composted and unprocessed dry olive cake ("orujo seco") produced from two-stage centrifugation for olive oil extraction. *Journal of Environmental Science and Health B34* 917-928.

Tomati, U., Galli, E., Fiorelli, F., Pasetti, L., 1996. Fertilizers from composting of olive-mill wastewaters. *International Biodeterioration and Biodegradation* 44, 155-162.

Tomati, U., Galli, E., Di Lena, G., Buffone, R., 1991. Induction of laccase in *Pleurotus ostreatus* mycelium grown in olive oil wastewaters. *Agrochimica* 35, 273-279.

Tomati, U., Galli, E., Pasetti, L., Volterra, E., 1995. Bioremediation of olive mill waste-waters by composting. *Waste Management and Research* 13, 509-518.

Tsonis, S.P., Tsola, V.P., Grigoropoulos, S.G., 1989. Systematic characterization and chemical treatment of olive oil mill wastewater. *Toxicological and Environmental Chemistry* 20-21, 437-457.

Turano, E., Curcio, S., De Paola, M.G., Calabrò, V., Iorio, G., 2002. An integrated centrifugation-ultrafiltration system in the treatment of olive mill wastewater. *Journal of Membrane Science* 209, 519-531.

Vitolo, S., Petarca, L., Bresci, B., 1999. Treatment of olive oil industry wastes. *Bioresource Technology* 67, 129-137.

Vlyssides, A.G., Bouranis, D.L., Loizidou, M., Karvouni, G., 1996. Study of a demonstration plant for the co-composting of olive-oil-processing wastewater and solid residue. *Bioresource Technology* 56, 187-193.

Vlyssides, A.G., Loizides, M., Karlis, P.K., 2004. Integrated strategic approach for reusing olive oil extraction by-products. *Journal of Cleaner Production* 12(6), 603-611.

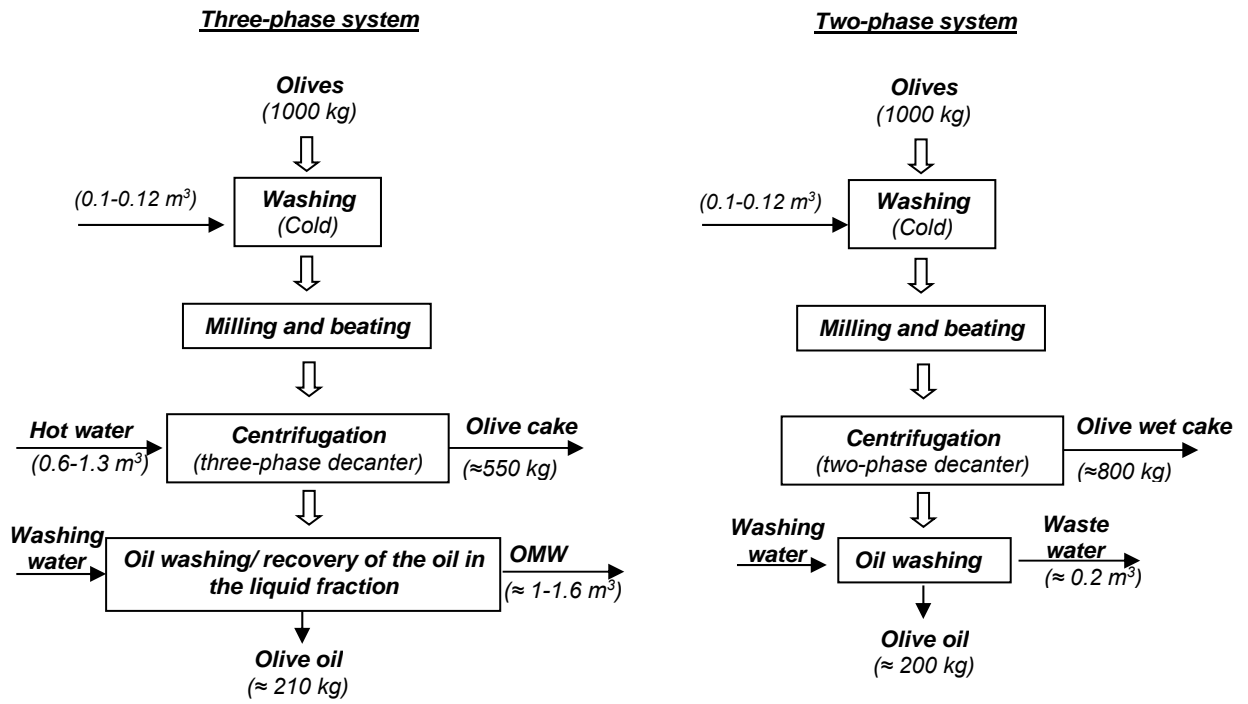


Figure 1. Three and two-phase centrifugation systems (Albuquerque *et al*, 2004).

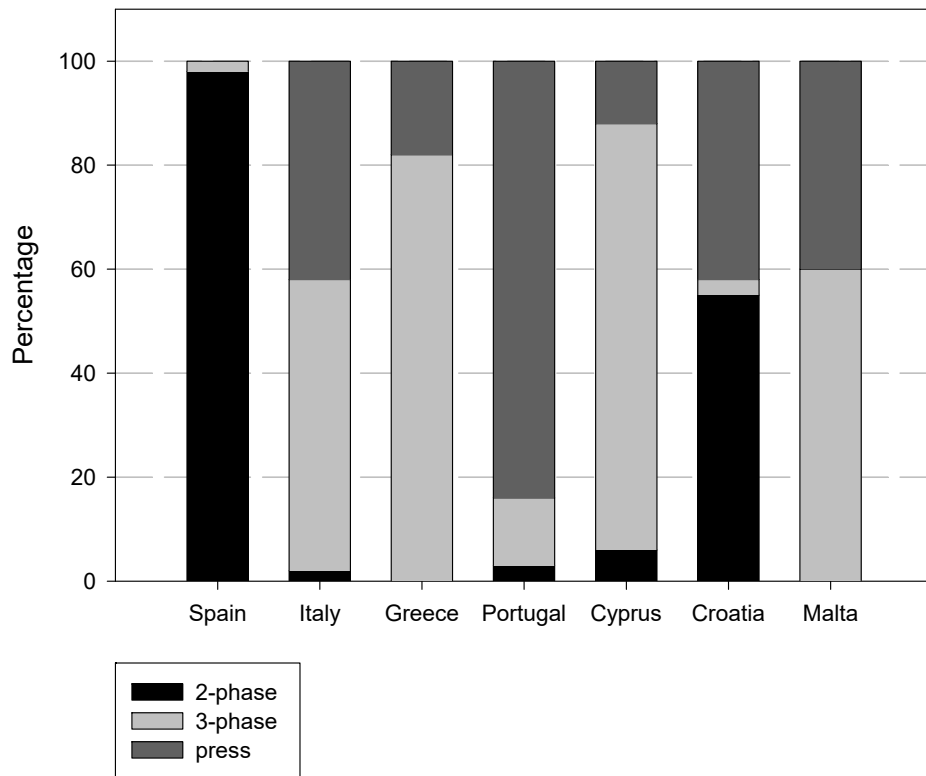


Figure 2. Technologies used by European olive oil mills. (IMPEL, 2003).

Table 1. Main chemical characteristics of olive mill wastewater (OMW) given by several authors

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
Dry matter (%)	6.35	7.1	n.d.	n.d.	7.19	6.33	n.d.	n.d.
pH	4.8	4.93	4.8	n.d.	5.17	5.00	4.2	5.0
EC (dS/m)	12.0	7.3	n.d.	10.0	5.50	n.d.	7.0	n.d.
OM (g/l)	57.4	n.d.	62.1	n.d.	46.5	57.2	n.d.	n.d.
TOC (g/l)	39.8	n.d.	n.d.	n.d.	34.2	n.d.	n.d.	n.d.
TN (g/l)	0.76	0.62	0.79	n.d.	0.63	0.86	2.1	n.d.
P ₂ O ₅ (g/l)	0.53	n.d.	n.d.	n.d.	0.31	0.61	0.7	0.7
K ₂ O (g/l)	2.37	n.d.	n.d.	2.9	4.46	n.d.	3.5	10.8
Na (g/l)	0.30	n.d.	n.d.	0.2	0.11	n.d.	n.d.	0.42
Ca (g/l)	0.27	n.d.	n.d.	0.2	0.30	n.d.	n.d.	0.64
Mg (mg/l)	44	n.d.	n.d.	92	129	n.d.	n.d.	220
Fe (mg/l)	120	n.d.	n.d.	18.3	68.5	n.d.	n.d.	120
Cu (mg/l)	6	n.d.	n.d.	2.1	1.5	n.d.	n.d.	3
Mn (mg/l)	12	n.d.	n.d.	1.5	1.1	n.d.	n.d.	6
Zn (mg/l)	12	n.d.	n.d.	2.4	4.1	n.d.	n.d.	6
d (g/cm ³)	1.048	n.d.	n.d.	n.d.	1.02	1.048	n.d.	n.d.
Lipids (g/l)	1.64	8.6	12.2	n.d.	3.1	n.d.	n.d.	n.d.
Poliphenols (g/l)	10.7	0.98	3.8	n.d.	1.6	n.d.	7.8	n.d.
Carbohydrates(g/l)	16.1	4.8	4.7	n.d.	8.79	n.d.	1.4	n.d.
COD (g/l)	93	67	103	178	n.d.	130	177	n.d.
BOD ₅ (g/l)	46	n.d.	n.d.	n.d.	n.d.	55	94	n.d.

n.d. not determined.

- (a) Vlyssides *et al.* (2004)
(b) Filidei *et al.* (2003)
(c) Aktas *et al.* (2001)
(d) Piperidou *et al.* (2000)

- (e) Paredes *et al.* (1999)
(f) Vlyssides *et al.* (1996)
(g) Saviozzi *et al.* (1991)
(h) Moreno *et al.* (1987)

Table 2. Main chemical characteristics of two-phase olive mill waste (TPOMW) given by several authors.

n.d.: not determined.

Parameters	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
Humidity (%)	61.8	64	57	64.5	65	64	49.6	71.4
pH (H ₂ O)	4.9	5.32	n.d.	5.23	5.4	5.5	6.8	5.19
EC (dS·m ⁻¹)	1.78	3.42	n.d.	5.24	n.d.	3.47	1.2	2.85
OM (%)	97.4	93.3	98.5	94.3	95.4	91.6	60.3	94.5
C _{OT} /N _T	53	47.8	59.7	49.3	29.3	42	32.2	46.6
N _T (g/kg)	10.5	11.4	10.0	11.3	18.5	13.5	11.0	9.7
P (g/kg)	n.d.	1.2	0.5	0.9	n.d.	1.4	0.3	1.5
K (g/kg)	n.d.	19.8	6.3	24.3	n.d.	15.9	29.0	17.1
Ca (g/kg)	n.d.	4.5	2.6	n.d.	n.d.	2.3	12.0	4.0
Mg (g/kg)	n.d.	1.7	n.d.	n.d.	n.d.	0.9	1.0	0.5
Na (g/kg)	n.d.	0.8	n.d.	n.d.	n.d.	n.d.	0.2	1.0
Fe (mg/kg)	n.d.	614	n.d.	526	n.d.	769	2600	1030
Cu (mg/kg)	n.d.	17	n.d.	17	n.d.	21	13	138
Mn (mg/kg)	n.d.	16	n.d.	13	n.d.	20	67	13
Zn (mg/kg)	n.d.	21	n.d.	18	n.d.	27	10	22
Lignine (%)	41.2	42.6	19.8	47.5	n.d.	46.8	n.d.	35
Hemicellulose (%)	n.d.	35.1	15.3	38.7	n.d.	n.d.	n.d.	n.d.
Cellulose (%)	n.d.	19.4	33.7	17.3	n.d.	n.d.	n.d.	n.d.
Lipids (%)	3.76	12.1	10.9	18.0	11.0	12.7	n.d.	8.6
Protein (%)	n.d.	7.2	6.7	n.d.	n.d.	n.d.	n.d.	n.d.
Carbohidrates (%)	n.d.	9.6	19.3	9.6	12.7	10.4	n.d.	n.d.
Phenols (%)	0.54	1.4	2.4	1.2	2.1	0.5	n.d.	n.d.
Pb, Cd, Cr, Hg (mg/kg)	n.d.	n.d.	n.d.	<5	n.d.	n.d.	n.d.	<1

(a) Baeta-Hall *et al.* (2005)

(b) Albuquerque *et al.* (2004)

(c) Vlyssides *et al.* (2004)

(d) Cayuela (2004)

(e) Saviozzi *et al.* (2001)

(f) Cegarra *et al.* (2000)

(g) Ordoñez *et al.* (1999)

(h) Madejón *et al.* (1998)