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# Sustainability analysis and benchmarking of olive mill wastewater treatment methods

Dimitris P. Zagklis,[a,b] Eleni C. Arvaniti,[a,b] Vagelis P. Papadakis[c] and Christakis A. Paraskeva [a,b*]

## Abstract

**A large number of publications are available in the literature regarding olive mill wastewater treatment methods. However, none of the proposed methods can be considered as a best available method in terms of its effectiveness, and its environmental and economic impact. Using a literature survey, data were collected and evaluated in order for a sustainability and benchmarking analysis to be developed. Physicochemical, biological and advanced oxidation methods were evaluated and judged in terms of their effectiveness, environmental impact and cost. Effectiveness of each method was estimated in terms of COD and phenolic compounds reduction, environmental impact in terms of $CO_2$ production, while for the economic impact the operational costs were taken into account. Finally, a procedure is suggested for selection of the most appropriate method based on user preferences (in terms of effectiveness, environmental impact and cost). The present analysis showed that the most effective processes in terms of organics reduction are membrane filtration, electrolysis, supercritical water oxidation and photo-Fenton. Lower environmental impact was found with anaerobic digestion, coagulation and lime processes, while the lowest cost category involves biocomposting and membrane filtration, thanks to the exploitation of byproducts (biocompost and phenolic compounds, respectively).**

**Keywords:** olive mill wastewater; treatment methods; sustainability; benchmarking

## INTRODUCTION

The Mediterranean countries host 95% of the global olive oil production;[1,2] this makes it a very important product for their economies. As a byproduct of the three phase olive oil production process, large quantities of olive mill wastewaters (OMWW) are produced. OMWW is a waste with very high organic content and phytotoxic characteristics, caused by the phenolic compounds responsible for the antimicrobial and antioxidant activity of olive oil. These compounds make biodegradation of the waste difficult in conventional wastewater treatment facilities (e.g. anaerobic digestion processes) that use microorganisms for the biodegradation of organic waste, as they inhibit their growth. On the other hand epidemiological studies have shown that consumption of plant phenolic compounds, in which olive oil is rich, leads to health benefits such as protection from cancer and cardiovascular diseases, because of their antioxidant activity.[3] Several methods have been proposed as possible solutions for the management of OMWW. These methods are divided into four main categories: disposal, physicochemical, biological and advanced oxidation methods. Several review papers have been published on the subject[4−8] but in this study, following a literature survey, a technique for comparison of the different methods used for OMWW treatment is presented. All the methods mentioned here have their own strengths and weaknesses; for example lime treatment is a low cost method but not so effective, whereas membrane filtration, although effective, consumes a lot of energy because of the high trans-membrane pressures required, which leads to the production of large quantities of carbon dioxide. In order to determine which method is more suitable, several aspects can be examined. In this study, a sustainability analysis was carried out, concerning the available methods for treatment of OMWW with the main characteristics examined being: treatment effectiveness in terms of COD and phenolic content reduction, $CO_2$ emissions in terms of energy consumption, and economic viability in terms of treatment cost and possible profit from byproducts produced. A comparison of existing methods was performed based on the experimental results of other researchers, after an extended literature review. Starting from an initial selection of papers, the comparison was made only for those papers that referred to treatment by only one autonomous method (physicochemical, biological or advanced oxidation technique). A second limitation was to examine only those papers that referred to the treatment of raw or diluted OMW without any pretreatment steps that could change the cost, effectiveness and $CO_2$ footprint. Effectiveness, environmental and economic impact of each method was calculated and through an evaluation

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* *Correspondence to: CA Paraskeva, Department of Chemical Engineering, University of Patras, GR 26504, Rion, Patras, Greece. Email: takisp@chemeng.upatras.gr*

a *Institute of Chemical Engineering Sciences, Foundation for Research and Technology, Hellas (FORTH/ICE-HT), Stadiou Str., Platani, GR 26504, Patras, Greece*

b *Department of Chemical Engineering, University of Patras, GR 26504, Rion, Patras, Greece*

c *Department of Environmental & Natural Resources Management, University of Western Greece, GR 30100, Agrinio, Greece*

system each method received a score from the effectiveness, environmental and economic point of view. A selection method was then proposed through a ternary diagram, depending on weights chosen for each of the aspects examined.

## AVAILABLE OLIVE MILL WASTEWATER TREATMENT METHODS

Many methods of OMWW treatment have been reported in the literature and some are in the process of commercial exploitation.[9] For the purposes of the present study of existing treatment methods they are grouped into four main categories: disposal, physicochemical, biological and advanced oxidation methods.

### Disposal methods

The combination of treatment with calcium oxide (neutralization and coagulation) and then disposal to waterproof lagoons is an accepted method.[10] The main disadvantages of this method are bad odors, growth of mosquitoes, the need for land very far from residential areas, and transfer costs. Alternatively OMWW can be transported to olive tree fields and spread with certain limitations, providing soil enrichment with nutritious compounds.[11]

### Physicochemical methods

Membrane filtration includes technology such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis, for the fractionation of compounds from liquid solutions.[1,2,12,13] Although highly efficient, membrane filtration processes require high operational pressures that lead to high energy consumption. On the other hand, there is a possible income from exploitation of the phenolic compounds in byproducts.[14] Lime treatment has been proposed[15–20] as a pre-treatment procedure for reduction of the polluting effect of OMWW and it is a less expensive method. Coagulation–flocculation is similar to lime treatment, in which different coagulants/flocculants are employed. For this process coagulants such as ferric chloride, and poly-electrolytes such as FLOCAN 23 can be used.[21] Although it has low cost and energy consumption this method is not as effective in reducing the organic content of the waste and is aimed mainly at the total suspended solids (TSS). In electro-coagulation charged particles suspended in the waste are precipitated through the imposition of an applied voltage. Electrodes are made of metals such as Al and Fe, and release metal ions in the solution creating nuclei for coagulation.[22]

### Biological methods

In aerobic digestion aerobic strains are used for biodegradation of the organic content of waste. Such strains are either aerobic bacteria or fungi.[23,24] Because of the high phenolic content of OMWW, it may have to be diluted prior to aerobic treatment for the method to be effective, as phenolic compounds inhibit the growth of microorganisms.[25] This method has a high energy demand, leading to high $CO_2$ emissions. In anaerobic digestion, bacteria are used for degradation of the organic matter. Again OMWW might have to be diluted in order not to inhibit bacterial growth, or mixed with other wastes,[26] or pretreated[27] or used in combination with physicochemical processes.[28] Because of the methane produced during the process, the energy demands of the process might be partially compensated.[29] Composting is the digestion of waste combined with a solid substrate: this substrate can be straw,[30] sesame bark,[31] olive leaves, vineyard leaves, wood chips, animal manure, etc.[32] After composting, the phenolic content of the waste is diminished and the final product is suitable for use as a fertilizer providing a possible profit.[31,32] On the other hand, due to the long duration of the process, which is around 6–7 months,[31] a significant amount of energy is required. Energy requirements in composting include spreading and compacting of solid material in layers and covering with soil each day, liquid (leachates) and/or air circulation and systems with leachates and gas collection over a long period of time.

Methods such as disposal in wetlands[33,34] and use of trickling filters[35] can also be considered as alternative methods with low operational and fixed cost but with low effectiveness. Because of limited available economic data, these methods are not evaluated in the present study.

### Advanced oxidation methods

In electrolysis, the organic content is either oxidized directly on the anode or indirectly by the oxidizing agents produced in the solution.[36] Some anodes that have been used are Pt/Ir,[37] $Ti/IrO_2$,[38,39] Pt/Ti[36] and boron-doped diamond.[40] Because of the important role that electricity plays in this method, the energy requirements are very high. Fenton oxidation uses Fenton's reagent, which consists of $H_2O_2$ and Fe(II), for the oxidation of waste through a series of reactions.[41] As it is not an electrically driven method, it has low energy consumption but the need for $H_2O_2$ increases the cost. Photo-Fenton is similar to Fenton as it uses the same reagents, with the difference that UV radiation is applied to the solution. The UV radiation accelerates the regeneration of $Fe^{2+}$, increasing the efficiency of the process[42] but also this method needs high energy consumption for the production of UV radiation. Supercritical water oxidation is the oxidation of the waste on catalysts such as $Pt/\gamma\text{-}Al_2O_3$[43] or without the presence of a catalyst,[44,45] above the critical temperature of water and at high pressure (25–35 MPa[43]). This method is very effective for reduction of the organic content but because of the high temperatures and pressures employed, the treatment cost and energy consumption are high. Ozonation uses $O_3$ as an oxidant for oxidation of the waste.[46–48] It's not so effective in reduction of the organic content but reduction of the phenolic content is quite high. The main cost and energy demand occur from production of the ozone required for the process.

## RESULTS AND DISCUSSION

### Sustainability analysis

The sustainability analysis carried out in this study is based on three main aspects. The first is the effectiveness of the method, i.e. the efficiency of waste removal in terms of the reduction of COD and phenolic content achieved by each method. COD and phenolic compound values were selected as the characteristic values of OMWW organic load despite the fact that the presence of other components of OMWW may affect the treatment processes. The second aspect is the impact that each method has in the environment. In this study this is measured by the amount of $CO_2$ emitted for every kilogram of COD removed from the organic content of OMWW. The $CO_2$ taken into account is the $CO_2$ produced during the process mainly due to energy consumption. The third aspect is the economic evaluation of each method.

#### *Effectiveness*

Data for COD and phenolic compound removal taken from the literature are presented in Fig. 1. It should be noticed here that data even for the initial COD of untreated OMWW and final COD reduction values differ and mean values and standard deviations were used for the discussion that follows. Figure 1 was constructed using the following data:

Membrane filtration includes a combination of a pretreatment method and use of ultrafiltration and nanofiltration and leads to high COD and phenolic content reduction.[49,50] According to the literature,[1,2,12,13] an average value of 97.7% ± 0.8 for the reduction of COD occurred and the phenolic content can be reduced by up to 98%.[1,2]

Lime treatment refers to the addition $Ca(OH)_2$ or CaO in tanks containing OMWW. This is one of the low cost methods available for the treatment of OMWW, but suffers from low efficiency. A mean value of COD reduction of 42.6% ± 3.3 is given in the literature[15,51] whereas the phenolic content is reduced by 72% ±8.8.[15,51]

Coagulation/flocculation is similar to lime treatment, but more efficient electrolytes and poly-electrolytes are used. The COD and phenolic content removal efficiency is similar as well, at around 45.9% ± 18.9 and 64.2% ± 11.1, respectively.[21,51,52]

Electro-coagulation affects the OMWW through the application of an electric field and the dissolution of metal ions from the electrodes, that lead to the coagulation of charged particles suspended in the waste. This method shows medium reduction of COD at an average of 51.9% ± 16.1[22,53–55] and quite high reduction of phenolic content at an average of 79% ± 17.[53,54]

Aerobic digestion is the biodegradation of wastes with the use of aerobic strains, and can effectively reduce COD and phenolic content of the OMWW by 77.2% ± 8.5 and 79% ± 16.8, respectively.[25,56]

Anaerobic digestion is the use of anaerobic bacteria for the degradation of wastes. This method reduces COD by 68% ± 24.3[27,57,58] and phenolic content by 54.5% ± 12.[57,58]

Composting refers to the production of fertilizer by the biodegradation of wastes, usually combined with solid substrates.[32] Although composting has a low mean COD reduction of about 38.2% ± 24.5,[30,31,59] it demonstrates a reduction of phenolic content as high as 83.5% ± 16.3[31,59] which makes the compost fit for exploitation as fertilizer.

Electrolysis leads to oxidation of the organic matter and shows an average COD reduction of 68.4% ± 23.6,[36–38,60] and a mean reduction of phenolic content of 98.1% ±2.7.[36,38,60]

Fenton processes utilize a mixture of ferrous ions and $H_2O_2$ for the production of hydroxyl radicals, and present reductions of COD and phenolic content by an average of 75.3% ± 7.8[41,61–63] and 50%,[62] respectively.

Photo-Fenton treatment includes the use of UV radiation for acceleration of the Fenton process. It is very effective for the reduction of both COD and phenolic content by 79.5% ± 18.4[42,64] and 88.3% ± 11.1,[64] respectively.

Supercritical water oxidation is the oxidation of dissolved organic matter in water at critical conditions and can lead to a significant reduction of COD and phenolic content by 72.5% ± 1.5,[44] and 98.1% ± 0.6,[44] respectively.

Ozonation of OMWW leads to the oxidation of its organic matter, with ozone as an oxidant. Although ozonation appears to be effective for removal of the phenolic content by 80.7% ± 1.2[48] it does not have the same effect on COD, which is reduced by only 44% ± 24.7.[48,61]

A comparison of the methods discussed above is presented in Fig. 1. As one can see, most of the methods have a significant deviation in their effectiveness. This is caused by variations in the treatment parameters used by the different researcher (i.e. different types of microorganisms used in aerobic and anaerobic digestion, or different types of electrodes used in electrolysis) and by variations in the parameters of the OMWW used in the experiments.

### *Environmental impact*

The environmental impact is measured in terms of $CO_2$ emissions and it is referred to the $CO_2$ produced due to the energy consumption during the process, with 1 kWh producing 722 $gCO_2$.[65] For this analysis, the $CO_2$ emissions are calculated per $kgCOD_{removed}$ from the organic content of the wastes after the implementation of each method. For this reason, the kg of COD removed per $m^3$ was calculated for each method, depending on the COD% reduction and the $COD_{initial}$. The following formula is used for the calculation of the final emission of $CO_2$ using the data described below.

$$\frac{gCO_2}{kgCOD_{reduced}} = 722\,\frac{gCO_2}{kWh}\,Energy\,demands\left(\frac{kWh}{m^3}\right) \Big/ \left[CODreduction\,\frac{kgCOD}{treated\,m^3}\right] \tag{1}$$

Despite the fact that in some cases there are extra $CO_2$ emissions, in the present study only $CO_2$ emissions due to energy consumption are considered, which in most cases is the dominant cause of emissions.

In membrane filtration a large amount of energy is needed. Almost 370 kW are needed for ultrafiltration followed by reverse osmosis, with a permeate filtration rate of 8 $m^3$ $h^{-1}$ (=46.25 kWh $m^{-3}$).[66] The average COD reduction is 97.7% for an average $COD_{initial}$ of 47.524 g $L^{-1}$ [1,2,12,13] thus the COD reduction per $m^3$ of treated OMWW is 46.43. As a result 0.996 kWh $kg^{-1}COD_{reduced}$ was calculated and corresponds to the production of 719.112 g of $CO_2$ $kg^{-1}COD_{reduced}$.

Lime treatment uses energy only for stirring, which leads to minimal $CO_2$ emissions. An average COD reduction of 42.6% for an average $COD_{initial}$ of 66.55 g $L^{-1}$ was reported.[15,51] The average processing time was found to be 0.283 h[15,51] and the agitation power required for every $m^3$ of waste was 0.0575 kW,[67] and thus only 0.0006 kWh $kg^{-1}COD_{reduced}$ was calculated which corresponds to the emission of 0.433 g of $CO_2$ $kg^{-1}COD_{reduced}$.

In coagulation/flocculation energy is used only for stirring. An average COD reduction of 45.9% for an average $COD_{initial}$ of 88.433 g $L^{-1}$ was reported.[21,51,52] The average process time was found to be 0.4 h.[51,52] The energy demand is similar to the lime process and is equal to 0.0006 kWh $kg^{-1}COD_{reduced}$ corresponding to 0.433 g of emitted $CO_2$ per $kgCOD_{reduced}$.

As electricity plays an important role in the electro-coagulation method, a substantial amount of energy is required, about 30 kWh $m^{-3}$.[55] An average COD reduction of 51.9% for a $COD_{initial}$ of 29.88 g $L^{-1}$ is given in the literature.[22,53–55] A lot of energy is needed (1.934 kWh $kg^{-1}$ $COD_{reduced}$) for the application of the electro-coagulation method, which corresponds to the emission of 1396.348 g $CO_2$ $kg^{-1}COD_{reduced}$.

Energy requirements in aerobic digestion have been calculated at 30 kWh $m^{-3}$.[29] Literature suggests an average COD reduction of 77.2% for $COD_{initial}$ 25.2 g $L^{-1}$.[25,56] Based on the energy requirements and the amount of COD removed with this method it is estimated that 1.542 kWh is needed per $kgCOD_{reduced}$. Thus, 1113.24 g $CO_2$ is expected to be produced per $kgCOD_{reduced}$.

Because of the production of extra energy during anaerobic digestion through methane exploitation, which is greater than the

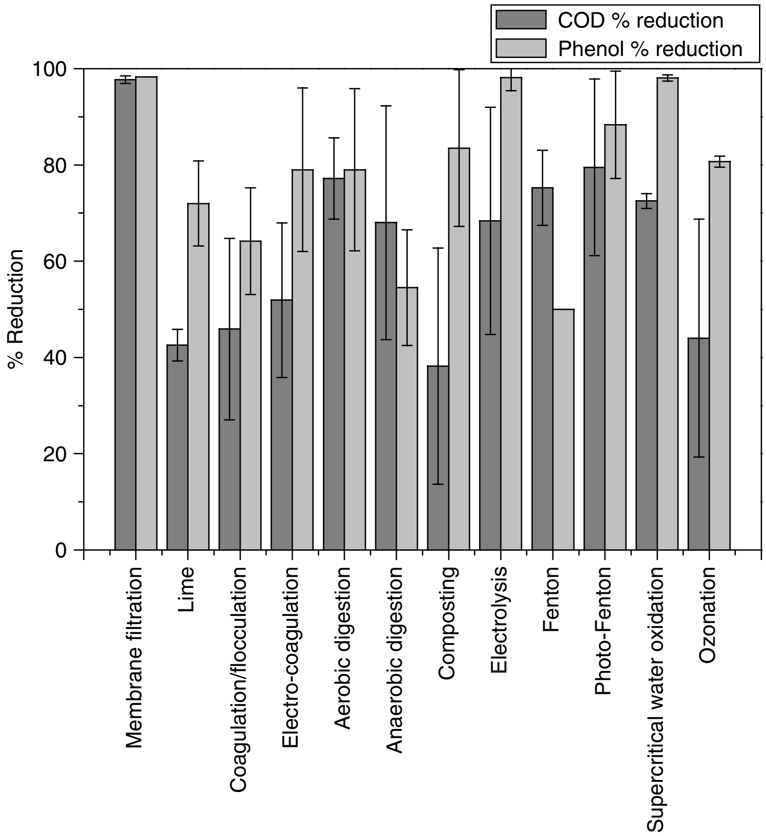

**Figure 1.** COD and phenolic content reduction of each olive mill wastewater treatment method.

energy requirements of the process, the energy requirement is negative, −39 kWh $m^{-3}$, as energy is produced.[29] An average COD reduction of 68% for initial COD 28.9 g $L^{-1}$ is reported.[27,57,58] This 'profit' in energy terms reduces the energy consumption of the entire process and 1.985 kWh $kg^{-1}COD_{reduced}$ can be saved. Thus, the balance for $CO_2$ emission is negative and 1433.17 $gCO_2$ are saved per $kgCOD_{reduced}$ using the anaerobic digestion process.

During composting, 0.02778 kWh $kg^{-1}$ treated wastes are consumed, with about half of the initial waste being OMWW and the other half being a solid substrate such as straw,[68] olive leaves and branches, animal manure, etc. As OMWW has a density of about 1 kg $L^{-1}$, 55.6 kWh $m^{-3}$ OMWW are consumed. An average COD reduction of 38.2%[30,31,59] for initial COD 98.7 g $L^{-1}$ is reported.[31,59] Thus it is estimated that 1.49 kWh are used for 1 kg of COD reduced, which corresponds to the emission of 1075.78 $gCO_2$ $kg^{-1}COD_{reduced}$.

In electrolysis energy consumption is quite significant with a mean value of 31.25 kWh $kg^{-1}COD_{reduced}$.[36–38,60] Thus, 22 562 $gCO_2$ is estimated to be emitted in the atmosphere per $kgCOD_{reduced}$.

As the main source of energy consumption for the Fenton process is agitation, the $CO_2$ emissions are minimal. An average COD reduction of 75.3% for an average $COD_{initial}$ of 5.913 g $L^{-1}$ is given in the literature.[41,61–63] The average process time is 2.5 h[41,63] and the agitation power required for every $m^3$ of waste is 0.0575 kW.[67] As a result 0.032 kWh is used per $kgCOD_{reduced}$, which corresponds to the production of only 23.104 g $CO_2$ $kg^{-1}COD_{reduced}$.

The UV radiation requirements in Photo-Fenton are about 150 kJ $L^{-1}$ or 41.7 kWh $m^{-3}$.[64] Researchers have shown an average COD reduction of 79.5% for a mean initial COD of 27 g $L^{-1}$.[42,64] The energy demand is estimated at 1.943 kWh $kg^{-1}COD_{reduced}$ and the corresponding $CO_2$ emissions are 1402.843 g per $kgCOD_{reduced}$.

Supercritical water oxidation shows an energy consumption of 455.95 kWh $h^{-1}$ for the treatment of 3.86 $m^3$ $h^{-1}$.[43] An average COD reduction of 72.5% for an average $COD_{initial}$ of 3.453 g $L^{-1}$ was reported.[44] Thus, the energy demand is very high and corresponds to 47.192 kWh $kg^{-1}COD_{reduced}$. As a consequence huge $CO_2$ emissions were calculated (34 072.624 g $CO_2$ $kg^{-1}COD_{reduced}$).

Ozonation has one of the highest energy consumptions. It is shown that 1.5 g of ozone is needed for every g of COD reduced in the waste.[46] Also 0.015 kWh are needed for every g of ozone produced.[47] As a result 22.5 kWh $kg^{-1}COD_{reduced}$ is needed, this corresponds to the production of 16 254 $gCO_2$ $kg^{-1}COD_{reduced}$.

Figure 2 illustrates the environmental impact in terms of the emissions of $CO_2$ concerning the environmental sustainability of each method. Three different diagrams are given in Fig. 2 as there were large deviations in the amount of $CO_2$ produced with each treatment method. The group with the lowest $CO_2$ emissions are the methods that use electricity just for agitation of the OMWW (coagulation–flocculation, lime and Fenton). The second group consists of two biological methods that have high $CO_2$ emissions due to the long treatment time needed (aerobic digestion and composting), two methods that use electricity as a driving force for the treatment and an advanced oxidation method that has high energy demands for the production of UV radiation. The last group with the highest $CO_2$ emissions contains advanced oxidation methods with very high energy consumption (ozonation, electrolysis, supercritical water oxidation).

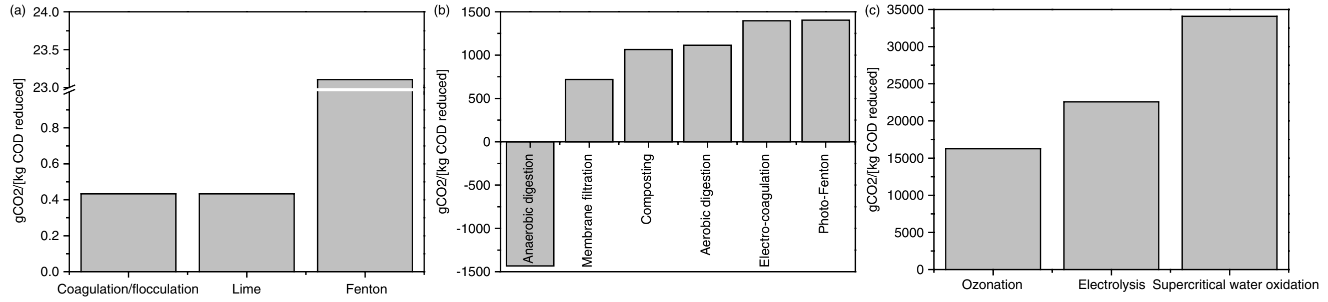

**Figure 2.** $CO_2$ emission data of olive mill wastewater treatment methods.

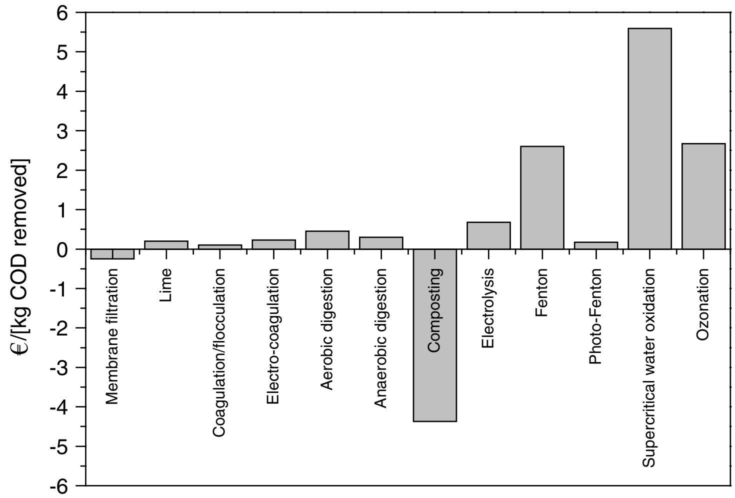

**Figure 3.** Treatment cost of olive mill wastewater treatment methods.

### *Economic*

For the economic analysis, the operational cost or profit was calculated again per kg of COD removed from the waste. The same values for the $kgCOD_{reduced}$ $m^{-3}$ that were calculated in the environmental analysis were used. In the present section two assumptions have been made: (a) the reported prices do not differ from country to country (most of them are European countries); and (b) that the costs have not changed dramatically during the last decade in the EU.

Membrane filtration: A techno-economical study[14] shows that the cost of treatment with membrane filtration can be covered by exploitation of the byproducts produced, leading to possible profit. The main profit will occur through exploitation of the phytotoxic fraction (phenolic content of the OMWW), as an ecological herbicide, but also through exploitation of the fraction rich in nutrient components as manure in fertilizers. The operational cost has been calculated at around 1 535 740€ for the treatment of 50 000 tons of waste, that is equivalent to 30.71€ per treated $m^3$ of OMWW. The possible profit for the same amount of waste has been calculated at around 250 000€ for the nutrient fraction and 1 875 000€ for the phytotoxic fraction, that is a profit of 42.5 € per treated $m^3$ of OMWW, which allows a net profit of 11.79€ per $m^3$. If this profit is calculated at a price per $kgCOD_{reduced}$ then a profit of 0.25 € $kg^{-1}COD_{reduced}$ can be obtained.

Lime is one of the low cost methods available with mean lime concentration needed for treatment at 42.5 g of lime for every litre of OMWW treated.[15,51] Lime has a price of 130€ $ton^{-1}$,[51] so the cost of 5.53 € per $m^3$ of treated OMWW or 0.2 € $kg^{-1}COD_{reduced}$ is needed.

For coagulation/flocculation, the higher cost of coagulants and flocculants used is balanced by their higher efficiency compared with lime, which leads to smaller amounts of chemicals needed for the same COD reduction, resulting in a similar cost. According to earlier reports 287 mg of coagulants per liter of treated OMWW with an average value of 3 € per kg is needed in the process. This results in 0.861 € per $m^3$ of treated OMWW. According to the calculations[52], a cost of 3.57 € is needed per $m^3$ of treated OMWW while others[21] suggest the use of 3.33 g of coagulants per liter of OMWW with an average cost of 2.5 € per kg of coagulant (8.33 € per $m^3$ of treated OMWW). Thus, a mean cost is considered as the arithmetic mean of the reported values, i.e. 0.1 € $kg^{-1}COD_{reduced}$.

The treatment cost of electro-coagulation is mainly caused by the energy consumption during the process which is around 30 kWh $m^{-3}$.[55] The price of 1 kWh is around 0.1188€,[66–69] as a result the cost is calculated at 3.564€ $m^{-3}$ or 0.23 € $kg^{-1}COD_{reduced}$.

Aerobic digestion has a treatment cost 8.78€ $m^{-3}$ according to literature,[70] equivalent to 0.45 € $kg^{-1}COD_{reduced}$.

Anaerobic digestion has a treatment cost of 10.57€ $m^{-3}$ but part of it is covered by the exploitation of the methane produced, around 4.65€ $m^{-3}$, with a final net cost of 5.92€ $m^{-3}$ or 0.3 € $kg^{-1}COD_{reduced}$.[70]

The cost of composting is around 0.0377 € $kg^{-1}$ of waste treated,[68] but only half of the treated waste is OMWW.[59] The result is 0.0754€ $kg^{-1}$ of OMWW or 0.0754€ $L^{-1}$, which is equal to 75.4 € $m^{-3}$. The income is calculated at 0.12 € $kg^{-1}$ of compost produced.[71] As half of the initial waste is OMWW,[59] the occurring income is 0.24€ $kg^{-1}$ of OMWW or 0.24€ $L^{-1}$, which equals 240€ $m^{-3}$ of OMWW. The net profit is 164.6€ $m^{-3}$ or 4.37 € $kg^{-1}COD_{reduced}$.

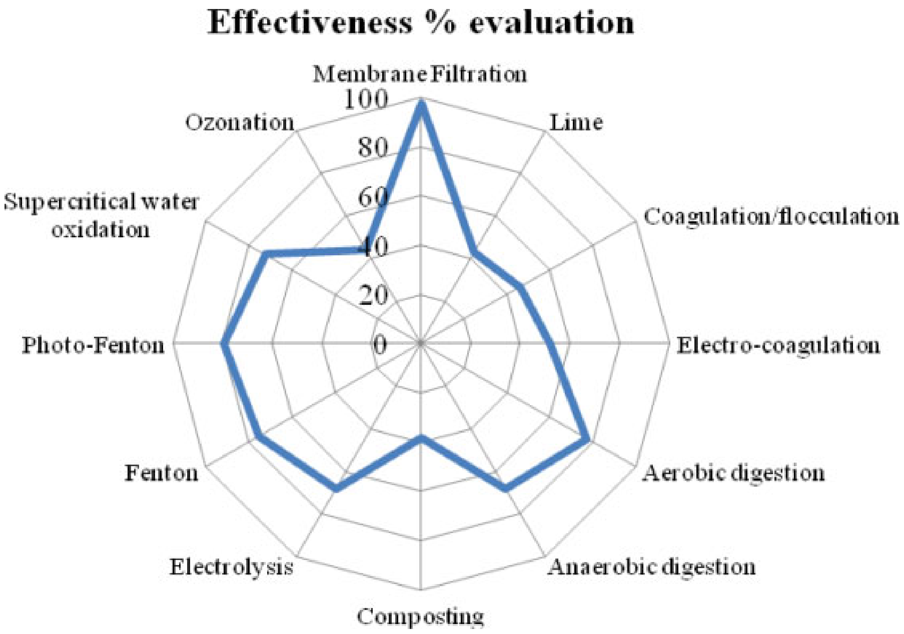

**Figure 4.** Effectiveness evaluation of olive mill wastewater treatment methods.

Electrolysis has a cost of 0.675 € $kg^{-1}$COD reduced.[60]

Fenton process has a high cost as well, because of the price of $H_2O_2$ used, which is 2.6€ $kg^{-1}COD_{reduced}$.[60] The treatment cost of photo-Fenton is 0.165 € $kg^{-1}COD_{reduced}$.[42]

Supercritical water oxidation has the highest cost of 14€ $m^{-3}$. According to the detailed economical analysis by Aki and Abraham, 1998[43] the implementation of the complex supercritical water oxidation leads to a cost of 14 € $m^{-3}$ or equivalently 5.6€ $kg^{-1}COD_{reduced}$.

Ozonation has an energy consumption of 22.5kWh $kg^{-1}COD_{reduced}$[46,47] which is the major cost of the process. With the price of 0.1188 € $kWh^{-1}$[69] the cost is calculated at 2.67 € $kg^{-1}COD_{reduced}$.

Figure 3 shows the economic data collected for the OMWW treatment methods. The two most promising treatment methods, in terms of economic viability, are composting and membrane processes, both of which appear to be profitable. The profit is derived from exploitation of the byproducts produced during each treatment.

## Benchmarking

For benchmarking the OMWW treatment methods, each method was given a score out of 100 (with 100 meaning excellent) for each of the three main aspects of the sustainability analysis described above.

### *Effectiveness*

Figure 4 shows the effectiveness evaluation of each method. The effectiveness evaluation is given by each method's COD reduction achieved. The most promising treatment method, regarding its effectiveness, turns out to be membrane filtration while anaerobic and photo-fenton processes show a value of effectiveness up to 80%. As Figure 4 shows, minimum efficiency in COD removal occurs in composting, ozonation, lime and coagulation processes.

### *Environmental impact*

The environmental evaluation presented in Fig. 5 is based on the $CO_2$ emissions of each treatment method. Supercritical water oxidation, ozonation and electrolysis have immediately been given a zero due to their high $CO_2$ emissions, compared with the rest of the methods. The remaining methods were evaluated with the following equation:

$$\text{Environmental impact} = 100 - 100 \cdot \frac{\left(\frac{gCO_2}{kgCOD_{reduced}}\right)_{method}}{\left(\frac{gCO_2}{kgCOD_{reduced}}\right)_{photo-Fenton}} \qquad (2)$$

Photo-Fenton was chosen as a base of comparison, as it has the highest emission after supercritical water oxidation, ozonation and electrolysis. As Fig. 5 shows, the methods with the highest evaluations in terms of environmental impact are the ones that are using energy only for agitation (lime, coagulation-flocculation, Fenton) and anaerobic digestion. Anaerobic digestion is considered the best in terms of environmental impact since the $CO_2$ balance is negative.

### *Economic*

In the economic evaluation presented in Fig. 6, supercritical water oxidation has been given a zero as its cost is much higher than that of the rest of the methods. The two methods that appear to be profitable have been given a score of 100. The cost of ozonation was used as a base for comparison for the rest of the methods, as it has the highest cost after supercritical water oxidation, through the following equation:

$$\text{Economic impact} = 100 - 100 \cdot \frac{\left(\frac{Cost}{kgCOD_{reduced}}\right)_{method}}{\left(\frac{Cost}{kgCOD_{reduced}}\right)_{ozonation}} \qquad (3)$$

As Fig. 6 shows, membrane filtration and composting are considered the most profitable processes. Advanced oxidation process such as ozonation, supercritical water oxidation and

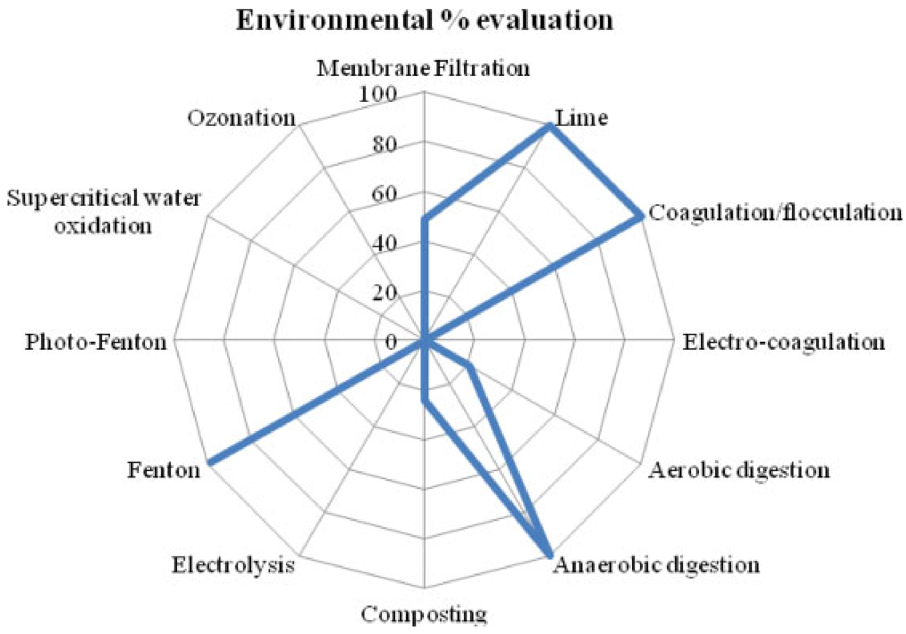

**Figure 5.** Environmental evaluation of olive mill wastewater treatment methods.

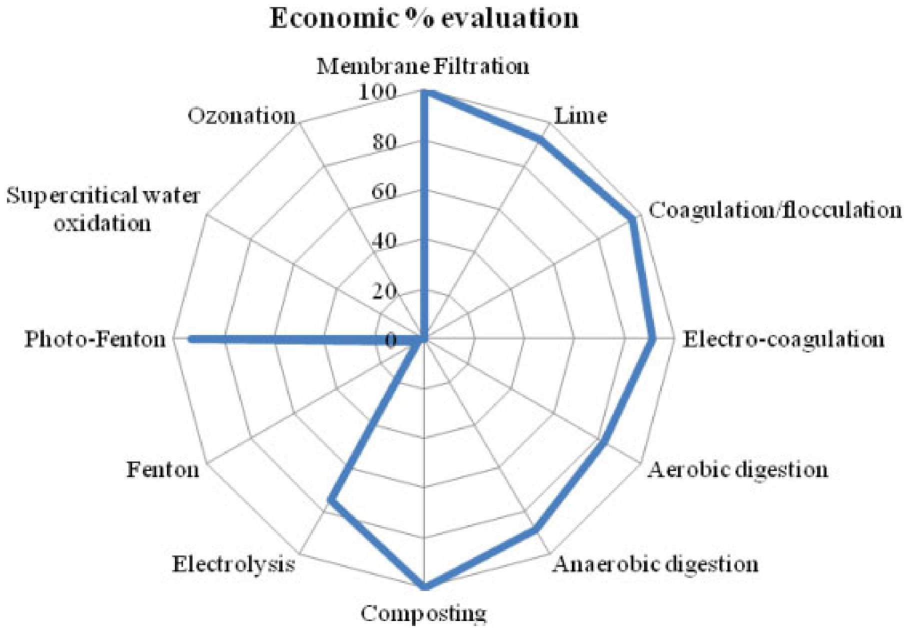

**Figure 6.** Economic evaluation of olive mill wastewater treatment methods.

Fenton are very expensive and stakeholders would never adopt them.

Final selection of an appropriate method is based on consideration of all factors that affect the process (effectiveness, environmental and economic impacts). Depending on the weights that are given to the factors above, the method that is closest to user requirements can be selected.

### Selection of the most appropriate OMWW treatment method. A ternary diagram

As the treatment of OMWW is a complicated problem, a clear answer cannot be given as to which method is the best. Before choosing the method that is considered to be the best, one must first decide the importance of each aspect presented above, effectiveness, environmental and economical. This can be depicted by three weight factors, one for each aspect. The evaluation data presented in the benchmarking part of the present work were processed and Fig. 7 was designed so that by choosing a different weight for each aspect examined, the method with the highest score can be found. For every point of the diagram that corresponds to one weight for every aspect, every method's scores (effectiveness, environmental, economic) were multiplied with their corresponding weight, then summed together to a final score. On the constructed diagram the method with the highest final score at each point is presented. As a result some methods that did not have the highest final score at any of the points of the diagram are not depicted at all. In

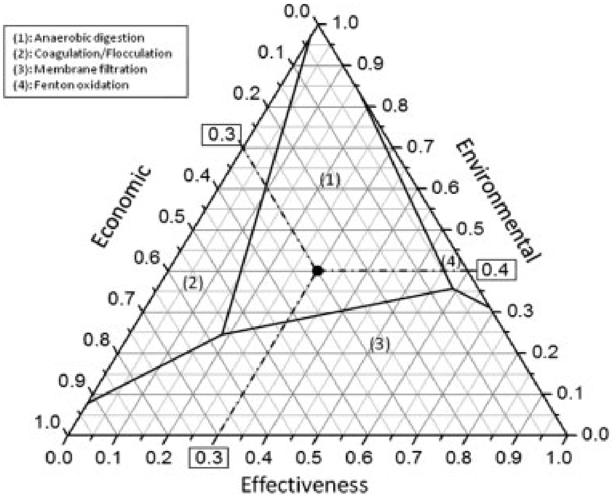

**Figure 7.** Ternary diagram for the evaluation of olive mill wastewater treatment methods.

this way four areas occurred, each one with a different optimum treatment process. Anaerobic digestion, coagulation/flocculation, membrane filtration and Fenton oxidation are the four treatment methods that presented advantages over the rest of the methods and appeared on Fig. 7, because under some conditions they were evaluated as the best available method, at bench-scale. For example, by choosing the weights 0.3 for effectiveness, 0.4 for the environment and 0.3 for the economic aspect, the optimum treatment method is anaerobic digestion (dashed lines in Fig. 7).

## CONCLUSIONS

In this study, the main treatment processes applied to OMWW were evaluated. Their effectiveness, $CO_2$ emissions and economic viability were examined and evaluated. Due to the complexity of the problem no single solution can be given, instead a method for choosing the appropriate process, according to which aspect is considered more important, was developed. The four most promising methods, based on bibliographic data, were found to be membrane filtration, coagulation/flocculation, anaerobic digestion and Fenton oxidation.

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## REFERENCES

1 Paraskeva CA, Papadakis VG, Tsarouchi E, Kanellopoulou DG and Koutsoukos PG, Membrane processing for olive mill wastewater fractionation. *Desalination* **213**:218–229 (2007).
2 Paraskeva CA, Papadakis VG, Kanellopoulou DG, Koutsoukos PG and Angelopoulos KC, Membrane filtration of olive mill wastewater and exploitation of its fractions. *Water Environ Res* **79**:421–429 (2007).
3 Yu S, Cheung KL, Li W and Kong A-N, Plant phenolic compounds: modulation of cytoprotective enzymes and Nrf2/ARE signaling. In *Plant Phenolics and Human Health*. (ed C. G. Fraga), John Wiley & Sons, Inc., Hoboken, NJ, USA, 401–426 (2009).
4 Arvanitoyannis IS, Kassaveti A and Stefanatos S, Olive oil waste treatment: a comparative and critical presentation of methods, advantages & disadvantages. *Crit Rev Food Sci Nutr* **47**:187–229 (2007).
5 Azbar N, Bayram A, Filibeli A, Muezzinoglu A, Sengul F and Ozer A, A review of waste management options in olive oil production. *Crit Rev Environ Sci Technol* **34**:209–247 (2004).
6 Mantzavinos D and Kalogerakis N, Treatment of olive mill effluents: Part I. Organic matter degradation by chemical and biological processes - an overview. *Environ Int* **31**:289–295 (2005).
7 Paraskeva P and Diamadopoulos E, Technologies for olive mill wastewater (OMW) treatment: a review. *J Chem Technol Biotechnol* **81**:1475–1485 (2006).
8 Roig A, Cayuela ML and Sánchez-Monedero MA, An overview on olive mill wastes and their valorisation methods. *Waste Manage* **26**:960–969 (2006).
9 www.lifeoleico.it/, Access date:(22/04/2012)
10 Kapellakis IE, Tsagarakis KP, Avramaki C and Angelakis AN, Olive mill wastewater management in river basins: a case study in Greece. *Agric Water Manage* **82**:354–370 (2006).
11 Chartzoulakis K, Psarras G, Moutsopoulou M and Stefanoudaki E, Application of olive mill wastewater to a Cretan olive orchard: effects on soil properties, plant performance and the environment. *Agric Ecosyst Environ* **138**:293–298 (2010).
12 Canepa P, Marignetti N, Rognoni U and Calgari S, Olive mills wastewater treatment by combined membrane processes. *Water Res* **22**:1491–1494 (1988).
13 Coskun T, Debik E and Demir NM, Treatment of olive mill wastewaters by nanofiltration and reverse osmosis membranes. *Desalination* **259**:65–70 (2010).
14 Arvaniti EC, Zagklis DP, Papadakis VG and Paraskeva CA, High-added value materials production from OMW: a technical and economical optimization. *Int J Chem Eng* 2012:7 (**2012**).
15 Aktas ES, Imre S and Ersoy L, Characterization and lime treatment of olive mill wastewater. *Water Res* **35**:2336–2340 (2001).
16 Boukhoubza F, Jail A, Korchi F, Idrissi LL, Hannache H, Duarte JC, Hassani L and Nejmeddine A, Application of lime and calcium hypochlorite in the dephenolisation and discolouration of olive mill wastewater. *J Environ Manage* **91**:124–132 (2009).
17 Lolos G, Skordilis A and Parissakis G, Polluting characteristics and lime precipitation of olive mill wastewater. *J Environ Sci Health Part A: Environ Sci Eng* **29**:1349–1356 (1994).
18 Sağlık S, Ersoy L and İmre S, Oil recovery from lime-treated wastewater of olive mills. *Eur J Lipid Sci Technol* **104**:212–215 (2002).
19 Tsonis SP, Tsola VP and Grigoropoulos SG, Systematic characterization and chemical treatment of olive oil mill wastewater. *Toxicol Environ Chem* **20**:437–457 (1989).
20 Ugurlu M and Kula I, Decolourization and removal of some organic compounds from olive mill wastewater by advanced oxidation processes and lime treatment. *Environ Sci Pollut Res* **14**:319–325 (2007).
21 Sarika R, Kalogerakis N and Mantzavinos D, Treatment of olive mill effluents: Part II. Complete removal of solids by direct flocculation with poly-electrolytes. *Environ Int* **31**:297–304 (2005).
22 Inan H, Dimoglo A, Şimşek H and Karpuzcu M, Olive oil mill wastewater treatment by means of electro-coagulation. *Sep Purif Technol* **36**:23–31 (2004).
23 McNamara CJ, Anastasiou CC, O'Flaherty V and Mitchell R, Bioremediation of olive mill wastewater. *Int Biodeterior Biodegrad* **61**:127–134 (2008).
24 Fountoulakis MS, Dokianakis SN, Kornaros ME, Aggelis GG and Lyberatos G, Removal of phenolics in olive mill wastewaters using the white-rot fungus *Pleurotus ostreatus*. *Water Res* **36**:4735–4744 (2002).
25 Yesilada O, Sik S and Sam M, Biodegradation of olive oil mill wastewaterby Coriolus versicolor and Funalia trogii:effects of agitation, initial COD concentration, inoculum size and immobilization. *World J Microbiol Biotechnol* **14**:37–42 (1998).
26 Gavala HN, Skiadas IV, Bozinis NA and Lyberatos G, Anaerobic codigestion of agricultural industries' wastewaters. *Water Sci Technol* **34**:67–75 (1996).
27 Zouari N and Ellouz R, Toxic effect of coloured olive compounds on the anaerobic digestion of olive oil mill effluent in UASB-like reactors. *J Chem Technol Biotechnol* **66**:414–420 (1996).
28 Stamatelatou K, Kopsahelis A, Blika PS, Paraskeva CA and Lyberatos G, Anaerobic digestion of olive mill wastewater in a periodic anaerobic baffled reactor (PABR) followed by further effluent purification via membrane separation technologies. *J Chem Technol Biotechnol* **84**:909–917 (2009).

29 Boari G, Brunetti A, Passino R and Rozzi A, Anaerobic digestion of olive oil mill wastewaters. *Agric Wastes* **10**:161–175 (1984).

30 Tomati U, Galli E, Fiorelli F and Pasetti L, Fertilizers from composting of olive-mill wastewaters. *Int Biodeterior Biodegrad* **38**:155–162 (1996).

31 Hachicha S, Cegarra J, Sellami F, Hachicha R, Drira N, Medhioub K and Ammar E, Elimination of polyphenols toxicity from olive mill wastewater sludge by its co-composting with sesame bark. *J Hazard Mater* **161**:1131–1139 (2009).

32 www.tirsavplus.eu/, Access date:(26/04/2012)

33 del Bubba M, Checchini L, Pifferi C, Zanieri L and Lepri L, Olive mill wastewater treatment by a pilot-scale subsurface horizontal flow (SSF-h) constructed wetland. *Annali di Chimica* **94**:875–887 (2004).

34 Yalcuk A, Pakdil NB and Turan SY, Performance evaluation on the treatment of olive mill waste water in vertical subsurface flow constructed wetlands. *Desalination* **262**:209–214 (2010).

35 Michailides M, Panagopoulos P, Akratos CS, Tekerlekopoulou AG and Vayenas DV, A full-scale system for aerobic biological treatment of olive mill wastewater. *J Chem Technol Biotechnol* **86**:888–892 (2011).

36 Israilides CJ, Vlyssides AG, Mourafeti VN and Karvouni G, Olive oil wastewater treatment with the use of an electrolysis system. *Bioresource Technol* **61**:163–170 (1997).

37 Giannis A, Kalaitzakis M and Diamadopoulos E, Electrochemical treatment of olive mill wastewater. *J Chem Technol Biotechnol* **82**:663–671 (2007).

38 Papastefanakis N, Mantzavinos D and Katsaounis A, DSA electrochemical treatment of olive mill wastewater on Ti/RuO$_2$ anode. *J Appl Electrochem* **40**:729–737 (2010).

39 Chatzisymeon E, Dimou A, Mantzavinos D and Katsaounis A, Electrochemical oxidation of model compounds and olive mill wastewater over DSA electrodes: 1. The case of Ti/IrO2 anode. *J Hazard Mater* **167**:268–274 (2009).

40 Chatzisymeon E, Xekoukoulotakis NP, Diamadopoulos E, Katsaounis A and Mantzavinos D, Boron-doped diamond anodic treatment of olive mill wastewaters: statistical analysis, kinetic modeling and biodegradability. *Water Res* **43**:3999–4009 (2009).

41 Lucas MS and Peres JA, Removal of COD from olive mill wastewater by Fenton's reagent: kinetic study. *J Hazard Mater* **168**:1253–1259 (2009).

42 Ahmed B, Limem E, Abdel-Wahab A and Nasr B, Photo-fenton treatment of actual agro-industrial wastewaters. *Ind Eng Chem Res* **50**:6673–6680 (2011).

43 Aki SNVK and Abraham MA, An economic evaluation of catalytic supercritical water oxidation: comparison with alternative waste treatment technologies. *Environ Prog* **17**:246–255 (1998).

44 Rivas FJ, Gimeno O, Portela JR, de la Ossa EM and Beltrán FJ, Supercritical water oxidation of olive oil mill wastewater. *Ind Eng Chem Res* **40**:3670–3674 (2001).

45 Chatzisymeon E, Diamadopoulos E and Mantzavinos D, Effect of key operating parameters on the non-catalytic wet oxidation of olive mill wastewaters. *Water Sci Technol* **59**:2509–2518 (2009).

46 Weichgrebe D and Vogelpohl A, A comparative study of wastewater treatment by chemical wet oxidation. *Chem Eng Process Process Intensif* **33**:199–203 (1994).

47 Katsoyiannis IA, Canonica S and von Gunten U, Efficiency and energy requirements for the transformation of organic micropollutants by ozone, O3/H2O2 and UV/H2O2. *Water Res* **45**:3811–3822 (2011).

48 Karageorgos P, Coz A, Charalabaki M, Kalogerakis N, Xekoukoulotakis NP and Mantzavinos D, Ozonation of weathered olive mill wastewaters. *J Chem Technol Biotechnol* **81**:1570–1576 (2006).

49 Turano E, Curcio S, De Paola MG, Calabrò V and Iorio G, An integrated centrifugation–ultrafiltration system in the treatment of olive mill wastewater. *J Membr Sci* **209**:519–531 (2002).

50 Garcia-Castello E, Cassano A, Criscuoli A, Conidi C and Drioli E, Recovery and concentration of polyphenols from olive mill wastewaters by integrated membrane system. *Water Res.* **44**:3883–3892 (2010).

51 Ginos A, Manios T and Mantzavinos D, Treatment of olive mill effluents by coagulation–flocculation–hydrogen peroxide oxidation and effect on phytotoxicity. *J Hazard Mater* **133**:135–142 (2006).

52 Kiril Mert B, Yonar T, Yalili Kiliç M and Kestioğlu K, Pre-treatment studies on olive oil mill effluent using physicochemical, Fenton and Fenton-like oxidations processes. *J Hazard Mater* **174**:122–128 (2010).

53 Adhoum N and Monser L, Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation. *Chem Eng Process: Process Intensif* **43**:1281–1287 (2004).

54 Khoufi S, Feki F and Sayadi S, Detoxification of olive mill wastewater by electrocoagulation and sedimentation processes. *J Hazard Mater* **142**:58–67 (2007).

55 Tezcan Ün Ü, Uğur S, Koparal AS and Bakır Öğütveren Ü, Electrocoagulation of olive mill wastewaters. *Sep Purif Technol* **52**:136–141 (2006).

56 El Hajjouji H, Fakharedine N, Ait Baddi G, Winterton P, Bailly JR, Revel JC and Hafidi M, Treatment of olive mill waste-water by aerobic biodegradation: an analytical study using gel permeation chromatography, ultraviolet–visible and Fourier transform infrared spectroscopy. *Bioresource Technol* **98**:3513–3520 (2007).

57 Bashaar Y A, Treatment of olive mill wastewater using an anaerobic sequencing batch reactor. *Desalination* **177**:157–165 (2005).

58 Sampaio MA, Gonçalves MR and Marques IP, Anaerobic digestion challenge of raw olive mill wastewater. *Bioresource Technol* **102**:10810–10818 (2011).

59 Zenjari B, El Hajjouji H, Ait Baddi G, Bailly JR, Revel JC, Nejmeddine A and Hafidi M, Eliminating toxic compounds by composting olive mill wastewater–straw mixtures. *J Hazard Mater* **138**:433–437 (2006).

60 Gotsi M, Kalogerakis N, Psillakis E, Samaras P and Mantzavinos D, Electrochemical oxidation of olive oil mill wastewaters. *Water Res* **39**:4177–4187 (2005).

61 Cañizares P, Lobato J, Paz R, Rodrigo MA and Sáez C, Advanced oxidation processes for the treatment of olive-oil mills wastewater. *Chemosphere* **67**:832–838 (2007).

62 Kallel M, Belaid C, Boussahel R, Ksibi M, Montiel A and Elleuch B, Olive mill wastewater degradation by Fenton oxidation with zero-valent iron and hydrogen peroxide. *J Hazard Mater* **163**:550–554 (2009).

63 Rivas FJ, Beltrán FJ, Gimeno O and Frades J, Treatment of olive oil mill wastewater by Fenton's reagent. *J Agric Food Chem* **49**:1873–1880 (2001).

64 Gernjak W, Maldonado MI, Malato S, Cáceres J, Krutzler T, Glaser A and Bauer R, Pilot-plant treatment of olive mill wastewater (OMW) by solar TiO2 photocatalysis and solar photo-Fenton. *Solar Energy* **77**:567–572 (2004).

65 www.iea.org/, Access date:(19/03/2012)

66 Kyriazis K and Papadakis VG, *Technoeconomical Study*. Tziolas Publications, Thessaloniki, Greece (2009).

67 Branan CR, *Rules of Thumb for Chemical Engineers - A Manual of Quick, Accurate Solutions to Everyday Process Engineering Problems*, 4th edn. Boston, Elsevier (2005).

68 Cabaraban M, Khire M and Alocilja E, Aerobic in-vessel composting versus bioreactor landfilling using life cycle inventory models. *Clean Technol Environ Policy* **10**:39–52 (2008).

69 www.energy.eu/, Access date:(22/03/2012)

70 Beccari M, Carucci G, Lanz AM, Majone M and Petrangeli Papini M, Removal of molecular weight fractions of COD and phenolic compounds in an integrated treatment of olive oil mill effluents. *Biodegradation* **13**:401–410 (2002).

71 Alfano G, Belli C, Lustrato G and Ranalli G, Pile composting of two-phase centrifuged olive husk residues: technical solutions and quality of cured compost. *Bioresource Technol* **99**:4694–4701 (2008).