OLIVE MILL WASTEWATER TREATMENT METHODS: SUSTAINABILITY AND BENCHMARKING

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Abstract: A synopsis of available techniques for the effective treatment of OMW is given in the present work. These technologies are based on biological, physicochemical and separation processes. OMW disposal methods to soil or to aqueous receptors are discussed also in the present work as alternative methods that can be affordable by stakeholders. As it is discussed in the present work there is not a unique method that can be considered as the best available technique (BAT) in terms of effectiveness, environmental impact and economic data. Based on a detailed literature survey, data were collected and compared in order a sustainability and a benchmarking analysis to be developed. Physicochemical, biological and advanced oxidation proposed methods were evaluated and judged in terms of their effectiveness, environmental impact and cost. Effectiveness of each method is estimated in terms of COD and phenolic compound reduction, environmental impact as the CO_2 production because of the use of electrical power, while for the cost both fixed and operational costs were taken into account. The present analysis showed that the most effective process are the membrane filtration, electrolysis and supercritical water oxidation, the lower environmental impacts were found in anaerobic digestion, coagulation and lime process while biocomposting and membrane filtration belong in the less expensive methods category, thanks to the exploitation of byproducts (biocompost and phenolic compounds, respectively). Finally, a procedure is suggested for the selection of the most appropriate treatment method based on the user preferences.

1. Introduction

Most of olive oil is produced in Mediterranean countries (95% percent of the global olive oil production) together with large quantities of olive mill wastewaters (OMW), which in many cases ended in aquatic receptors [1]. However, if these wastewaters are treated as byproducts then they can be exploited properly and a profit can be obtained. 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 [2]. OMW is a waste with very high organic content and phytotoxic characteristics, caused by the same phenolic compounds responsible for the antioxidant activity of olive oil. These compounds make difficult the biodegradation of the waste in conventional wastewater treatment facilities that use microorganisms for the biodegradation of the organic load of the wastes, as it inhibits their growth. Several techniques have been proposed as possible solutions for the management of olive mill wastewater. These techniques are mainly divided into four categories: Disposal, Physicochemical, Biological and Advanced Oxidation methods. Some Disposal methods are disposal to lagoons, to uncultivated or cultivated fields and controlled disposal of OMW to poplar fields. Physicochemical techniques include lime treatment, coagulation-flocculation, electro-coagulation, membrane filtration, etc. Biological treatment refers to aerobic and anaerobic digestion and composting. Finally Advanced oxidation methods are electrolysis, Fenton and photo-Fenton oxidation, supercritical water oxidation and ozonation. The methods examined in this study are physicochemical, biological and advanced oxidation methods, but a brief overview of the disposal methods available is also presented. Several review papers have been published on the subject [3-7] but in this study apart from a literature survey, a method for the comparison of the methods is presented. All the methods mentioned here have their own strengths and weaknesses, for example lime treatment is cheap but not so effective, whereas membrane filtration, although effective, consumes a lot of energy because of the high pressures required, which leads to the production of large quantities of carbon dioxide. In order to determine which technique is more suitable, several aspects can be examined. In this study, a sustainability analysis was carried out, concerning the available treatment methods of olive mill waste water (OMW) with the main examined characteristics 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 produced byproducts. After a literature review these aspects of each method were calculated and through an evaluation system each method received a different score from effectiveness, environmental and economic point of view. A selection method was then proposed through a ternary diagram, depending on weights chosen for each one of the examined aspects. There are many proposed techniques which consist of the combination of more than one of the techniques mentioned. In this study each technique was analyzed separately, with no pre-treatment.

2. Available olive mill wastewater treatment methods

There are many methods used for OMW treatment. For the purposes of the present work among the existing treatment methods the ones used in this study are categorized in four main groups: Disposal, Physicochemical, Biological and Advanced Oxidation methods. Each group consists of treatment processes which are in use today. A brief description of each technical solution as well as their advantages and disadvantages are being presented.

Disposal methods

Disposal to lagoons: The combination of treatment with calcium oxide (neutralization and coagulation) with disposal to waterproof lagoons is accepted and suggested by the law inspectors. The main disadvantages of this method are bad odors, mosquitoes and the need of land, far from residential areas. Also the transportation cost of OMW from the plants to lagoons must be covered. *Disposal to uncultivated or cultivated fields (among olive trees):* OMW is transported to olive tree fields and spread according to certain limitations (80-150 m^3/hectare/year in 3-5 dosages according to NAGREF, Chania, Greece). Researchers have shown that appropriate spreading of OMW to soil enriches it with nutritious inorganic compounds. In Portugal the waste is disposed with the regulation of 50 m^3 OMW/ hectare /year, where as in Italy 80- 100 m^3 OMW/hectare /year. In Greece this method is not yet allowed, but NAGREF (in Chania, Crete) has made an integrated proposal to the government, which is under negotiation for 150 m^3 OMW/ hectare/yr (3-4 times/year dosages). The occurring cost can be shared among members of a group of adjacent olive mill plants. A study on the environmental consequences shall be deposited to local authorities before the beginning of the operation of the process (Italy and Portugal). Authorities in other Mediterranean Countries should also decide and set rules for disposal of OMW to soil. *Control disposal of OMW to poplar fields (phytoremediation):* In this method, OMW is transported and disposed in well designed waterproofed excavated fields, where poplar trees are cultivated. There the waste is decomposed at their root system [8]. Although the operational cost is quite low (0.2 €/m^3/year) legislation problems exist, as only Italian authorities have given some limited licenses for demonstration projects.

Physicochemical methods

Membrane filtration implements membrane technology, like microfiltration, ultrafiltration, nanofiltration and reverse osmosis, for the separation of compounds from liquid solutions [1, 9-11] highly efficient, membrane filtration, especially nanofiltration and reverse osmosis, require high operational pressures which lead to high energy consumption. On the other hand, because of the fractionation of the waste, there is a possible income from the exploitation of the occurring byproducts [12]. *Lime:* This method has been proposed by many authors [13-18] as a pre-treatment procedure for the reduction of the polluting effect of OMW. Lime is cheaper than other chemicals such as ferric chloride, aluminum sulfate, magnesium sulfate, etc., which are used for pretreatment of wastewaters and can be easily purchased almost everywhere. Lime precipitation as a minimal pre-treatment procedure for the removal of organic matter content, removes suspended and colloidal matter (including pectins, phenolic compounds and mucilages and proteinecous material) as well as oil and grease. An addition of 0.5-3% CaO corresponds to a reduction of 27.6 % of the concentration of suspended solids. The optimum lime dose for flocculation of OMW is 2.5% w/v [15]. *Coagulation-flocculation* is similar to lime treatment, but instead of lime different coagulants/flocculants are employed. For this process inorganic coagulants like ferric chloride and poly-electrolytes like FLOCAN 23 can be used [19]. Although it has low cost and energy consumption this method is not as effective in reducing the organic content of the waste. For this reason, it is often used in combination with other processes, like bio-degradation (aerobic or anaerobic) and advanced oxidation methods. In *Electro-coagulation* the charged particles suspended in the waste are precipitated through the imposition of voltage. The electrodes are made out of metals like Al and Fe and release metal ions in the solution creating nuclei for coagulation [20]. This method is simple in operation and removes most of the dark color of the waste [21], but has a high energy consumption [22].

Biological methods

Aerobic digestion is the use of aerobic strains for the biodegradation of the organic content of the waste. Such strains are either aerobic bacteria or fungi [23]. Because of the high phenolic contain of OMW, it may have to be diluted prior to aerobic treatment for the method to be effective, as phenolic compounds inhibit the growth of microorganisms [24]. Because of the need for aeration, this method has a high energy demand, leading to high CO_2 emissions. In *Anaerobic digestion* anaerobic bacteria are used for the degradation of the organic matter contained in the waste. Again the OMW might have to be diluted, in order not to inhibit the bacterial growth, or pretreated [25]. Because of the methane produced during the process, the energy demands of the process might be covered without the need of energy produced from fossil fuels, preventing the emission of carbon dioxide [26]. *Composting* is the digestion of the waste, combined with a solid substrate. This substrate can be straw [27], sesame bark [28] etc. After composting, the phenolic content of the waste is diminished and the final product is suitable to be used as a fertilizer. Because of the compost produced, the treatment cost can be covered and a possible profit can occur [28]. On the other hand, due to the long duration of the process, which is around 7 months [28], a significant amount of energy is required.

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 [29]. Some anodes that have been used are Pt/Ir [30], Ti/IrO_2 [31] and Pt/Ti [29]. Because of the important role that electricity plays in this method, the energy requirements are very high. *Fenton oxidation* is the use of Fenton's reagent, which consists of H_2O_2 and Fe(II), for the oxidation of the waste through a series of reactions [32]. As it is not an electrically driven method, it has low energy consumption. On the other hand, its main disadvantage is the need of H_2O_2 that leads to a high treatment cost. *Photo-Fenton* is similar to Fenton oxidation 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 [33]. The disadvantage of this method is the high energy consumption for the production of UV radiation. *Supercritical water oxidation* is the oxidation of the waste on catalysts like $Pt/\gamma\text{-}Al_2O_3$ [34] or without the presence of a catalyst [35], above the critical temperature of water and at high pressure (25-35 MPa [34]). This method is very effective for the reduction of the organic content of the waste 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 the oxidation of the waste. It's not so effective in the reduction of the organic content but the reduction of the phenolic content is quite high. The main cost and energy demand occur from the production of the ozone required for the process.

3. Results and discussion

The sustainability and benchmarking analysis done in this study is based on three main aspects. The first aspect is the effectiveness of the method, in other words, how much does it affect the waste. In this work, this is measured by the reduction of COD and phenolic content achieved by each method. The second aspect is how much each method affects the environment. One could say that every method has a positive effect on the environment, as it removes part of the problem of the OMW, but it is important to see how efficiently this can be done. In this study this is measured by the amount of CO_2 emitted for every kg of COD removed from OMW. The CO_2 taken into account is the CO_2 produced during the process due to energy consumption. The third and final aspect is the economic evaluation of each method. Some methods exhibit a high treatment cost, while others present the opportunity of a possible profit. As the main reason that perpetuates the OMW problem is the treatment cost, this is a very important aspect that needs to be taken into consideration. The Data collected for the sustainability analysis and the benchmarking of the treatment methods is presented in Table 1.

Table 1: Data collected for OMW treatment methods for the calculation of the effectiveness of each proposed method

Method	CODinit g/lt	S.D.	COD % reduction	S.D.	Phenol % reduction	S.D.	References
Membranes	47.52	39.26	97.7	0.8	98.3	0	[9], [1], [11], [10]
Lime	66.55	36.43	42.6	3.3	72	8.8	[13], [36]
Coagulation/flocculation	88.43	26.96	45.9	18.9	64.2	11.1	[36], [37], [19]
Electrocoagulation	29.88	34.09	51.9	16.1	79	17	[20], [38], [21], [22]
Aerobic digestion	25.2	5.2	77.2	8.5	79	16.8	[39], [24]
Anaerobic digestion	28.9	34.23	68	24.3	54.5	12	[40], [25], [41]
Composting	98.7	12.3	38.2	24.5	83.5	16.3	[42], [27], [28]
Electrolysis	67.72	121.8	68.4	23.6	98.1	2.7	[29], [43], [30], [31]
Fenton	5.91	5.09	75.3	7.8	50	0	[44], [32], [45], [46]
Photo-fenton	27	17.4	79.5	18.4	88.3	11.1	[47], [33]
Supercr. water oxidation	3.45	0.52	72.5	1.5	98.1	0.6	[35]
Ozonation	3.74	4.77	44	24.7	80.7	1.2	[44], [48]

Effectiveness

Membrane filtration implies the use of different types of membranes like microfiltration, Ultrafiltration, Nanofiltration and Reverse Osmosis. The proposed method for the treatment of olive mill wastewater is the use of a prefiltration or centrifugation unit, then the use of Ultrafiltration and finally of nanofiltration and/or reverse osmosis. This method leads to a high COD and phenolic content removal. From literature, [9], [1], [11], [47], an average value of **97.7% ±0.8** for the reduction of COD, through prefiltration/centrifugation, ultrafiltration and reverse osmosis membranes occurs. Through the same treatment the phenolic content can be reduced up to **98%** [1], [11]. *Lime treatment* is the addition of calcium hydroxide $Ca(OH)_2$ or CaO in tanks containing OMW, leading to its coagulation. This is one of the less expensive methods available for the treatment of OMW, but suffers from low efficiency. Researchers have shown a mean value of COD reduction of **42.6% ±3.3** [13], [36] whereas the phenolic content is reduced by **72% ±8.8** [13], [36]. Treatment through *coagulation/flocculation* is similar to lime treatment, but lime is replaced by more efficient electrolytes and polyelectrolytes. The COD and phenolic content removal efficiency is similar as well, as it is around **45.9% ±18.9** and **64.2% ±11.1** respectively [36], [37], [19]. *Electro-coagulation* affects the OMW through the application of an electric field and the dissolution of metal ions from the electrodes, that lead to the coagulation of the charged particles suspended in the waste. This method shows a medium reduction of COD at an average of **51.9% ±16.1** [20], [38], [21], [22] and a quite high reduction of the phenolic content at an average value of **79% ±17** [38], [21]. *Aerobic digestion* is the biodegradation of wastes with the use of aerobic strains, such as aerobic bacteria and fungi. It can effectively reduce both COD and the phenolic content of the OMW by **77.2% ±8.5** and **79% ±16.8,** respectively [39], [24]. *Anaerobic digestion* is the use of anaerobic bacteria for the degradation of wastes. This method appears to reduce COD at a percentage of **68% ±24.3** [40], [25], [41] and the phenolic content by **54.5% ±12** [40], [41]. *Composting* refers to the production of fertilizer by the biodegradation of wastes, usually combined with a solid substrate, like straw. Although *composting* appears a low mean COD reduction of about 38.2% ±24.5 [42], [27], [28], it demonstrates a reduction of the phenolic content as high as **83.5% ±16.3** [42], [28], which makes the occurring compost fit for exploitation as fertilizer. *Electrolysis* implements electrodes made of metals like Ti-Pt, and the imposition of voltage. This leads to the oxidation of the organic matter, either directly at the anode surface, or indirectly, by the oxidants produced electrochemically, like chlorine, hydroxyl radicals, ozone etc [43]. This method shows an average COD reduction of **68.4% ±23.6** [29], [43],[30], [31], and a mean reduction of the phenolic content of **98.1% ±2.7** [29], [43], [31]. *Fenton* process utilizes a mixture of ferrous ions and H_2O_2 for the production of hydroxyl radicals, that cause the oxidation of the organic matter contained in the OMW. Treatment with Fenton's reagent leads to the reduction of COD and phenolic content by an average of **75.3% ±7.8** [44], [32], [45], [46] and **50%** [46], respectively. *Photo-Fenton* treatment is the use of UV radiation for the acceleration of the Fenton process. It is very effective for the reduction of both, COD and phenolic content by **79.5% ±18.4** [47], [33] and **88.3% ±11.1** [47] respectively. *Supercritical water oxidation* is the oxidation of dissolved organic matter in water at high temperatures, above the critical point, and pressures. It can lead to a significant reduction of COD and phenolic content by **72.5% ±1.5** [35], and **98.1% ±0.6** [35] respectively. *Ozonation* of OMW leads to the oxidation of its organic matter, with ozone as an oxidant. Although ozonation appears to be effective for the removal of the phenolic content by **80.7% ±1.2** [48] it doesn't have the same effect on COD, which is reduced only by **44% ±24.7** [44], [48]. The data that concerns the effectiveness of each method are presented in Figure 1.

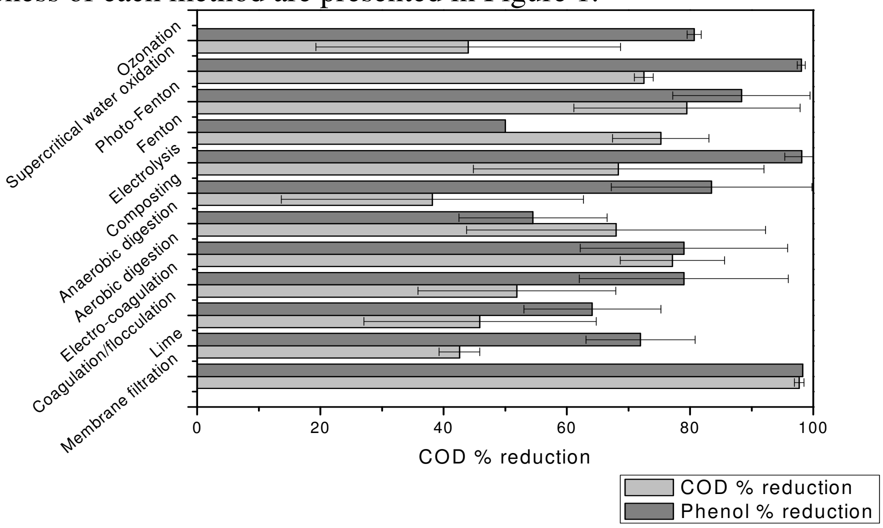

Fig. 1: COD and phenolic content reduction of each olive mill wastewater treatment method

As one can see, most of the methods have a significant deviation in their effectiveness. This is caused by the variation of treatment parameters used by every researcher (like different types of microorganisms used in aerobic and anaerobic digestion, or different types of electrodes used in electrolysis, etc) and by the variation of the parameters of the OMW used in every experiment. Nevertheless, the occurring mean values are significant for the evaluation of each method. Membrane filtration appears to be the most effective method for the removal of COD and the phenolic content, followed by electrolysis, photo-Fenton and supercritical water oxidation.

Environmental

The CO_2 emissions calculated for each method refer to the CO_2 produced due to the energy consumption during the process, with 1kWh producing 722 gCO_2 [49]. For this analysis, the CO_2 emissions are calculated per kg of COD removed from the waste with 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 $COD_{initial}$. *Membrane filtration* may achieve a high COD and phenolic content reduction, but on the other hand a large amount of energy is needed for the separation. Researchers have shown that 370kW are needed for ultrafiltration followed by reverse osmosis, with a filtration rate of 10 m^3/h [50]. The average COD reduction is 97.7% for an average initial COD of 47.524 g/lt [9], [1], [11], [10]. As a result 719 gCO_2 per $kgCOD_{reduced}$ are produced. *Lime treatment* uses energy only for stirring, which leads to minimal CO_2 emissions. Researchers have shown an average COD reduction of 42.6% for an average $COD_{initial}$ of 66.55 g/lt [13], [36]. The average processing time is found to be 0.283 h [13], [36] and the agitation power required for every m^3 of waste is 0.0575 kW [51], which leads to the production of 0.433 gCO_2 per $kgCOD_{reduced}$. *Coagulation/flocculation* has very low CO_2 emissions for the same reasons as lime treatment. Researchers have show an average COD reduction of 45.9% for an average $COD_{initial}$ of 88.433 g/lt [36], [37], [19]. The average process time is found to be 0.4h [36], [37] and the total CO_2 that is produced per kg of $COD_{reduced}$ is equal to 0.433g. As electricity plays an important role in *Electro-coagulation,* a substantial amount of energy is required, about 30 kWh/m^3 [22]. Researchers have shown an average COD reduction of 51.9% for an initial COD of 29.88 g/lt [20], [38], [21], [22]. Following these data an amount of 1390 gCO_2 per kg of $COD_{reduced}$ was calculated. In *Aerobic Digestion* CO_2 emissions have been calculated as follows: Energy requirements have been calculated at 30 kWh/m^3 [26]. Researchers have shown an average COD reduction of 77.2% for $COD_{initial}$ 25.2 g/lt [39], [24]. Thus 1113 gCO_2 per kg of $COD_{reduced}$ are produced. Because of the production of extra energy during *anaerobic digestion* through methane exploitation, which is greater than the energy requirements of the process, the value of energy requirements is negative -39 kWh/m^3 as energy is produced [26]. Researchers have shown an average COD reduction of 68% for initial COD 28.9 g/lt [40], [25], [41] and using these data, 1433 gCO_2 per $kgCOD_{reduced}$ are estimated. During *composting*, 0.02778 kWh/kg of treated wastes are consumed, with about half of the initial waste being OMW and the other half being a solid substrate like straw, etc [52]. As OMW has a density of about 1kg/lt, it occurs that 55.6 kWh/m^3 of OMW are consumed. Researchers have shown an average COD reduction of 38.2% [42], [27], [28] for initial COD 98.7 g/lt [42], [28]. The total CO_2 that is estimated here is 1075 g per $kgCOD_{reduced}$. In *electrolysis* energy consumption is quite significant with a mean value of 31.25 kWh/kg $COD_{reduced}$ [29], [43], [30], [31], so 22560 gCO_2 per $kgCOD_{reduced}$ are produced. As the main source of energy consumption for the *Fenton* process is agitation, the CO_2 emissions are minimal. Researchers have show an average COD reduction of 75.3% for an average initial COD of 5.913 g/lt [44], [32], [45], [46]. Only 23 gCO_2 per $kgCOD_{reduced}$ are produced in Fenton method. The UV radiation requirements in *Photo-Fenton* are about 150 kJ/lt or 41.7 kWh/m^3 [47]. Researchers have shown an average COD reduction of 79.5% for a mean initial COD of 27 g/lt [47], [33] and the estimated gCO_2 produced are 1400 g per $kgCOD_{reduced}$. *Supercritical water oxidation* shows an energy consumption of 455.95 kWh/h for the treatment of 3.86 m^3/h [34]. Researchers have shown an average COD reduction of 72.5% for an average initial COD of 3.453 g/lt [35]. Because of the large quantities of energy that are used here up to 34000 g CO_2 are produced per $kgCOD_{reduced}$. *Ozonation* has one of the highest energy consumptions. Researchers have shown that 1.5 g of ozone is needed for every g of COD reduced in the waste [53]. Also 0.015 kWh are needed for every g of ozone produced [54]. As a result 16245 gCO_2 are produced per $kgCOD_{reduced}$.

Figure 2 contains the information concerning the environmental sustainability of each method. Three different diagrams are given in Figure 2 as there was a big deviation in the amount of CO_2 produced with each treatment method. The group with the lowest CO_2 emissions consists of the methods that use electricity just for agitation of the OMW. 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 (membrane filtration consumes energy for the creation of trans-membrane pressure and electro-coagulation for the creation of electrical potential between the electrodes) and an advanced oxidation method that has high energy demands for the production of UV radiation. In this diagram we can also see the high amount of CO_2 emissions prevented by anaerobic treatment because of the production of methane. One argument could be that the produced methane is burnt for energy production and as a result it gives CO_2, but the same amount of CO_2 produced this way will be removed from the atmosphere by the olive trees for next year's production, if the number of cultivated olive trees remains the same. The last group with the highest CO_2 emissions contains advanced oxidation methods with very high energy consumption (ozonation, electrolysis, supercritical water oxidation).

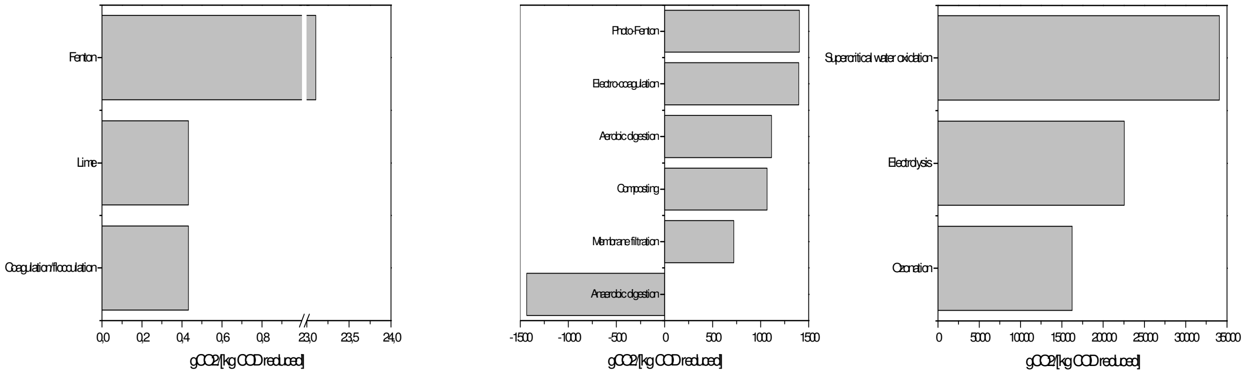

Fig. 2: CO_2 emission data of olive mill wastewater treatment methods

Economic

For the economic analysis, the operational costs or profits were calculated again per kg of COD removed from the wastes. The same values for the kg $COD_{reduced}/m^3$ that were calculated in the environmental analysis were used here (Table 1). A techno-economical study [12] shows that the occurring cost of treatment with *membrane filtration* can be covered by the exploitation of the byproducts produced, leading to a possible small profit. The profit will occur through the exploitation of the phytotoxic fraction, which contains most of the phenolic content of the OMW, as an ecological herbicide but also through the exploitation of the fraction rich in nutrient components as manure in fertilizers. The operational cost has been calculated around 1535740 € for the treatment of 50000 tons of waste. The possible profit for the same amount of waste has been calculated around 250000 € for the nutritious fraction and 1875000 € for the phytotoxic fraction. As for the net profit 0.25 € can be saved per kg of $COD_{reduced}$. *Lime* is one of the cheapest methods available with the mean lime concentration needed for treatment of the waste be 42.5 g of lime for every lt of OMW treated [13], [36]. Lime has a price of 130 €/ton [36]. As a result 0.2 € are needed per kg of $COD_{reduced}$. As for *Coagulation/flocculation*, the higher cost of coagulants and flocculants used is balanced by their higher efficiency compared to lime, which leads to smaller amounts of chemicals needed for the same COD reduction (Aktas et al., 2001, Sarika et al., 2005, [37] and only 0.1 € are needed per kg of $COD_{reduced}$. The treatment cost of *electro-coagulation* is mainly caused by the energy consumption during the process which is around 30 kWh/m^3 [22]. The price of 1 kWh is around 0.1188 € [55], and as a result, the cost is calculated at 3.564 €/m^3 or 0.23 € per kg of $COD_{reduced}$. *Aerobic digestion* has a treatment cost 8.78 €/m^3 [56]which is equal to 0.45 € per kg$COD_{reduced}$. *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 [56] that is 0.3 € per kg$COD_{reduced}$. The cost of *composting* is around 0.0377 €/kg of waste treated [52], but only half of the treated waste is OMW [42]. The result is 0.0754 €/kg of OMW or 0.0754 €/lt, which is equal to 75.4 €/m^3. The income is calculated at 0.12 €/kg of compost produced [57]. As half of the initial waste is OMW [42], the occurring income is 0.24 €/kg of OMW or 0.24 €/lt, which equals to 240 €/m^3 of OMW. The occurring net profit is 240 €/m^3-75.4 €/m^3=164.6 €/m^3 or 4.37 € per kg$COD_{reduced}$. *Electrolysi***s** has a cost of 0.675 €/[kg COD reduced] [43]. *Fenton* process has a high cost as well, because of the price of H_2O_2 used, which is 2.6 €/[kg COD reduced] [43]. The treatment cost of *photo-Fenton* is 0.165 €/[kg COD reduced] [33]. *Supercritical water oxidation* has, the highest cost of 14.08 €/m^3 [34] taking into account raw material, operational costs, etc 5.5 € are needed per kg$COD_{reduced}$. *Ozonation* has an energy consumption of 22.5 kWh/[kg COD reduced] [53], [54] which is the major cost of the process. With the price of 0.1188 €/kWh [55] the cost is calculated at 2.67 €/kg $COD_{reduced}$.

Figure 3 shows the economic data collected for the OMW treatment methods. The two most promising treatment methods, concerning the economic viability, are composting and membrane processes, both of which appear to be profitable. The occurring profit is derived by the exploitation of the byproducts produced during each treatment. From composting, the main byproduct is a fertilizer (compost), where as for the membrane filtration the two main occurring by-products are a phytotoxic fraction, suitable to be used as an ecological herbicide and a nutrient rich fraction, suitable to be used as a component in fertilizers. The rest of the treatment methods appear to have a reasonable cost, except of supercritical water oxidation, Fenton oxidation and ozonation which have significantly higher treatment costs.

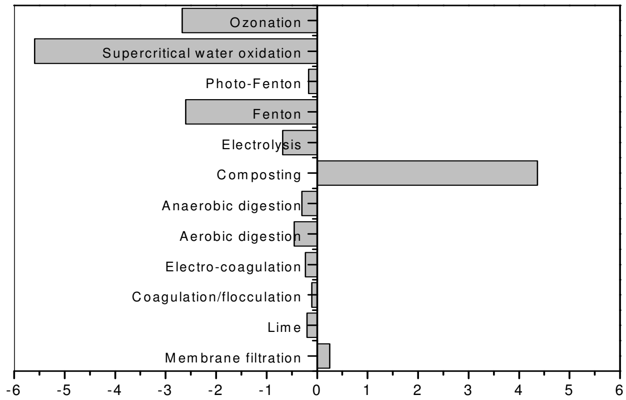

Fig. 3: Treatment cost of olive mill wastewater treatment methods

3. OMW treatment methods ternary diagram

As the treatment of OMW 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 weights, one for each aspect. The evaluation data presented in the benchmarking part of the present work were processed and figure 4 was designed in a way that by choosing a different weight for each aspect examined, the method with the highest score occurs. An example is given, by choosing the weights 0.3 for efficiency, 0.4 for the environment and 0.3 for the economic aspect, the optimum treatment method that occurs is anaerobic digestion.

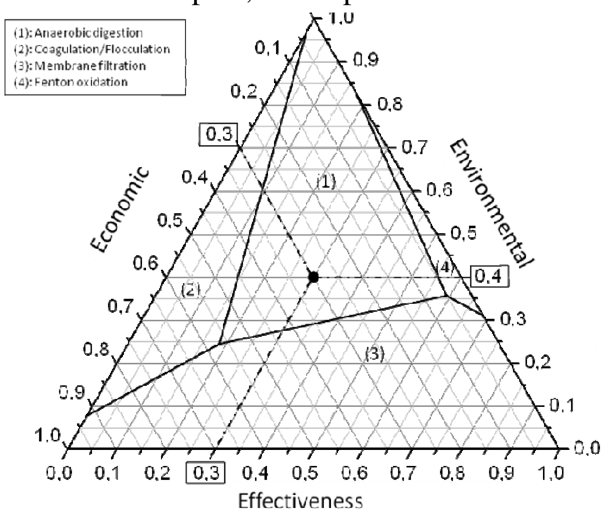

Fig. 4: Ternary diagram for the evaluation of olive mill wastewater treatment methods

4. Conclusions

Olive mill wastewater constitutes a major environmental problem for the Mediterranean countries. Each year, millions of tons of this toxic waste are produced and most of it is not properly treated causing serious damage to the environment. Many treatment methods exist but the occurring cost prevents their application. In this study, the main treatment processes of OMW were presented. Their effectiveness, CO_2 emissions and economic viability were examined as well as a way of evaluation. 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 were found to be membrane filtration, coagulation/flocculation anaerobic digestion and Fenton oxidation.

5. Acknowledgments

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