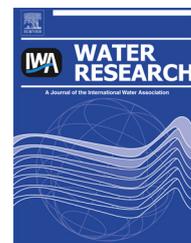


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Utilizing solar energy for the purification of olive mill wastewater using a pilot-scale photocatalytic reactor after coagulation-flocculation

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ABSTRACT

This study investigated the application of a solar-driven advanced oxidation process (solar Fenton) combined with previous coagulation/flocculation, for the treatment of olive mill wastewater (OMW) at a pilot scale. Pre-treatment by coagulation/flocculation using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (6.67 g L^{-1}) as the coagulant, and an anionic polyelectrolyte (FLOCAN 23, 0.287 g L^{-1}) as the flocculant, was performed to remove the solid content of the OMW. The solar Fenton experiments were carried out in a compound parabolic collector pilot plant, in the presence of varying doses of H_2O_2 and Fe^{2+} . The optimization of the oxidation process, using reagents at low concentrations ($[\text{Fe}^{2+}] = 0.08 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2] = 1 \text{ g L}^{-1}$), led to a high COD removal (87%), while the polyphenolic fraction, which is responsible for the biorecalcitrant and/or toxic properties of OMW, was eliminated. A kinetic study using a modified pseudo first-order kinetic model was performed in order to determine the reaction rate constants. This work evidences also the potential use of the solar Fenton process at the inherent pH of the OMW, yielding only a slightly lower COD removal (81%) compared to that obtained under acidic conditions. Moreover, the results demonstrated the capacity of the applied advanced process to reduce the initial OMW toxicity against the examined plant species (*Sorghum saccharatum*, *Lepidium sativum*, *Sinapis alba*), and the water flea *Daphnia magna*. The OMW treated samples displayed a varying toxicity profile for each type of organism and plant examined in this study, a fact that can potentially be attributed to the varying oxidation products formed during the process applied. Finally, the overall cost of solar Fenton oxidation for the treatment of 50 m^3 of OMW per day was estimated to be 2.11 € m^{-3} .

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1. Introduction

Olive oil production is one of the most important agricultural activities in the Mediterranean basin. According to

Avraamides and Fatta (2008), there are approximately 750 million productive olive trees (*Olea europea* L.) worldwide, with the countries of the Mediterranean basin concentrating 97% of the world olive oil production. Although olive oil is a product of exceptional nutritional value, its production is associated

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with several adverse effects on the environment, mainly due to the formation of high amount of OMW (Badawy et al., 2009).

The physicochemical characteristics of OMW are rather variable, depending mainly on the cultivation soil, climatic conditions, olive variety, use of pesticides and fertilizers, degree of fruit ripening, harvesting time, and extraction process (Niaounakis and Halvadakis, 2006; Kallel et al., 2009). Nevertheless, OMW is characterized by high organic load (typically 130–150 g L⁻¹ COD; 10–30 g L⁻¹ DOC; 0.5–25 g L⁻¹ phenolic compounds), high inorganic concentration, and acidic pH (Gernjak et al., 2004). According to the literature, the organic matter of OMW consists of a great variety of pollutants, including polysaccharides, sugars, phenolic compounds, tannins, polyalcohols, proteins, organic acids and lipids (El Hadrami et al., 2004; Canizares et al., 2007).

In Cyprus, olive oil production is one of the most traditional industries. According to data obtained from governmental sources, approximately 35 olive mills are registered in Cyprus, producing approximately 7500 tonnes oil per year. Water use in oil production is about four times the amount of oil produced, suggesting that Cyprus produces more than 25,000 tonnes per year of OMW (Anastasiou et al., 2011). In Cyprus, the most common practice for the management of OMW includes the use of evaporation ponds and the subsequent discharge of solids in landfills and/or on soil. While evaporation ponds offer a good way of reducing the liquid portion of the wastewater, they do not contribute in the reduction of its toxicity, while they simultaneously impart an odor problem to the areas where such waste is stored. Furthermore, evaporation results in the loss of large quantities of water, which is an important and limited resource in Cyprus. At the moment there is no European legislation regulating OMW disposal, and standards are left to be set by individual countries.

The problems associated with the OMW are mainly related to its toxic character due to the presence of phenolic compounds, which cannot be degraded by biological treatment (Martins and Quinta-Ferreira, 2011). The improper disposal of OMW into the environment, or to urban wastewater treatment plants, is prohibitive due to its potential threat to surface and groundwater, or due to its toxicity to microorganisms used in treatment plants. Despite being recognized as a hazardous residue, land disposal of OMW remains the most diffused approach along the Mediterranean basin (Justino et al., 2009). Phytotoxic effects on soil properties have been reported to occur when this waste is used directly as an organic fertilizer (Paredes et al., 2001). In addition, the acidic pH and the polyphenols' complexing abilities increase the solubility of heavy metals in the environment (Gernjak et al., 2004).

Through the years, researchers have tested a variety of technologies for OMW treatment. It is evident from the literature, that a single process cannot offer an efficient and viable solution to the problem. Conventional biological processes (aerobic or anaerobic) have shown moderate efficiencies in terms of OMW mineralization (Paraskeva and Diamadopoulos, 2006; Ouzounidou et al., 2010). Aerobic treatment of OMW by three microorganisms, namely *Geotrichum* sp., *Aspergillus* sp. and *Candida tropicalis*, led to an average reduction in terms of COD and total phenolic compounds of 52.5–62.8% and

44.3–51.7%, respectively (Fadil et al., 2003). Anaerobic processes have resulted in 60–70% of COD removal, while total phenolic compounds have been removed by 50–80% (Marques et al., 2001; El Hajjouji et al., 2008; Martinez-Garcia et al., 2009).

In addition to biological processes, various physicochemical processes such as coagulation/flocculation and membrane filtration and separation processes have also been employed for the OMW treatment. The use of direct flocculation with polyelectrolytes for the treatment of OMW showed that two polyelectrolytes, one anionic and one cationic, failed to yield separation, whereas a minimum dose of 2.3–3 g L⁻¹ was required. Nearly complete reduction of solids was observed in subsequent analysis, while COD and BOD reduction was up to 55 and 23%, respectively (Sarika et al., 2005). The pre-treatment of OMW by means of coagulation/flocculation combining various inorganic materials and organic poly-electrolytes was investigated by Ginos et al. (2006). Combining lime or ferrous sulphate with cationic poly-electrolytes led to significant solids removal, while COD and total phenolic compounds (TP) removal varied between 10–40% and 30–80%, respectively. The reduction of OMW organic content was also attempted through the use of combined methodologies (i.e. physicochemical and biological). According to Dhaouadi and Marrot (2008), the integration of biological treatment with membrane filtration for the OMW treatment led to moderate COD abatement, depending on the dilution factor and the oxygen transfer to the mixed liquor contained in the membrane bioreactor (MBR).

Within this context, the application of advanced remediation strategies is required either to fulfill legislative requirements for direct disposal into landfills or, when economically wiser, to reduce toxicity and improve biodegradability to allow a posterior inexpensive bioprocess (Hodaifa et al., 2013). Advanced oxidation processes (AOPs) are known for their capability to mineralize a wide range of organic compounds. These processes are based on the *in situ* generation of very reactive and oxidizing free radicals, principally the hydroxyl radicals (HO•). The versatility of the AOPs is enhanced by the fact that there are many ways of producing HO•. During the last several years, AOPs have been extensively studied for the OMW treatment through ozonation (Beltran-Heredia et al., 2001; Canizares et al., 2007), photo-Fenton (Gernjak et al., 2004; Rizzo et al., 2008; Nieto et al., 2011; Hodaifa et al., 2013), TiO₂ photocatalysis (Gernjak et al., 2004; Badawy et al., 2009), electrochemical oxidation (Giannis et al., 2007; Chatzisyneon et al., 2009a; Belaid et al., 2013) and wet air oxidation (Chatzisyneon et al., 2009b). Mantzavinos and Kalogerakis (2005) presented a comprehensive review on the OMW treatment by the application of various AOPs. A process of particular interest is photo-Fenton, as it can be powered by sunlight with wavelengths of $\lambda < 580$ nm, thus lowering the process operational costs (Michael et al., 2012). From the engineering point of view, simplicity in both equipment and operation has postulated photo-Fenton system as one of the most economic alternatives for treating those effluents. In the literature, sufficient information can be found with regard to the OMW treatment using the Fenton reagent. Nevertheless, all the works so far have been carried out in laboratory-scale reactors. To the best of authors' knowledge, only two studies are available on the solar Fenton process application at a pilot scale (Gernjak et al.,

2004; Hodaifa et al., 2013), focusing on the main operating conditions affecting the chemical oxidation.

Having this in mind, the current study explored the efficiency of the solar Fenton process combined with previous coagulation/flocculation pre-treatment at a pilot-scale reactor, in removing the different organic carbon fractions present in OMW (i.e. COD, DOC, total phenolic compounds). In addition, the feasibility of the oxidation process was assessed in terms of the toxicity removal using a set of bio- and phyto-assays, an evaluation never been performed previously. The toxicity of the OMW samples was assessed towards *Daphnia magna* and three plant species (*Sorghum saccharatum*, *Lepidium sativum* and *Sinapis alba*), prior to and after the photocatalytic treatment. Finally, the aim of this study was to determine the investment and operational cost of the pilot-scale photocatalytic reactor. According to the authors' knowledge, this study constitutes the first integrated approach regarding OMW treatment in terms of both OMW purification (removal of organic load and toxicity) and economic feasibility of the application of the advanced chemical treatment examined herein. This is of special interest in the context of sustainable water reuse strategies, since the proposed treatment scheme combines technologically simple and relatively inexpensive treatment processes such as iron-based coagulation and solar-driven advanced oxidation.

2. Materials and methods

2.1. Chemicals

Analytical grade iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Sigma Aldrich) and hydrogen peroxide (H_2O_2 30% w/w, Merck) were used in the solar Fenton experiments. The pH of the wastewater was adjusted by 2 N H_2SO_4 (Merck). The Fenton reaction was terminated at specific time intervals by adding manganese dioxide (MnO_2 , particle size 10 μm , reagent grade $\geq 90\%$) (Sigma Aldrich). The anionic polyelectrolyte FLOCAN 23 that was used as a flocculation agent, was manufactured by SNF Floerger and purchased from ChemFlo-Hellas. For toxicity analyses the treated solutions were neutralized by 2 N NaOH (Merck), and the residual hydrogen peroxide was removed from the treated samples with commercially available catalase solution (*Micrococcus lysodeikticus* 170000 U mL^{-1} , Fluka).

2.2. Olive mill wastewater

OMW was supplied by a three-phase olive mill located in Larnaca, Cyprus (sampling period: November–January). Samples were taken from the mid-point of storage tank, avoiding sampling from the bottom of storage tank which could alter the representativeness of the results due to settled solids. The samples were stored at 4 °C immediately after being brought to the laboratory. A quantity of OMW was vacuum filtered through 0.45 μm glass fibre filters (GF/D, Whatman, USA) and stored at –15 °C in order to avoid initial composition discrepancies. OMW samples were homogenised by stirring, prior to their physicochemical characterization and photocatalytic experiments. The OMW samples were characterized before use for a number of qualitative

characteristics as shown in Table 1. The physicochemical parameters that have been used to characterize the OMW were determined according to the Standard Methods (APHA, 1998).

2.3. Experimental setup and procedure

2.3.1. Coagulation/flocculation

The OMW pre-treatment prior to the solar Fenton process was performed in a tank specifically designed for the coagulation/flocculation procedure. The tank ($V = 90$ L) is constructed of stainless steel and it has a cone shape. The OMW pre-treatment consisted at first of coagulation with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, followed by flocculation using the anionic polyelectrolyte FLOCAN 23. Initially, the appropriate dose of coagulant was added to the OMW sample while stirring for 15 min at 120 rpm. This was followed by a transfer of a measured volume of 0.1% polyelectrolyte solution, while stirring for another 15 min at 120 rpm. Finally, the mixture was stirred for another 30 min at lower speed at 50 rpm to provide the required agglomeration. After the addition of reagents, the OMW mixture was left to rest and, as soon as separation was achieved, the supernatant was transferred through a tube to the tank of the solar compound parabolic collector (CPC) pilot plant.

2.3.2. Solar Fenton

The photocatalytic experiments were carried out in a solar CPC pilot plant comprising of six borosilicate tubes mounted on a fixed platform tilted at the local latitude (35°), operated in batch mode. The surface is constructed of resistant and highly reflecting polished aluminium. OMW flows directly from one tube to the other (meander flow) and finally to a reservoir tank. Mixing was accomplished by means of a closed circuit through the irradiated part of the reactor, and the reservoir tank by the use of a centrifugal pump. The overall volume capacity of the reactor V_T is 100 L and the total irradiated volume V_i (tubes volume) is 22.4 L. The temperature and pH in the reactor, as well as the UV solar irradiation were continuously recorded. Solar UV radiation was measured by a UV radiometer (UV_air_ABC) mounted on the platform of the CPCs.

Table 1 – Main qualitative characteristics of the OMW used in this work.

Parameter	Value ^a
pH (25 °C)	5.7 ± 0.5
Conductivity (25 °C) (mS cm^{-1})	8.56 ± 0.76
COD ^b (g L^{-1})	13.5 ± 5.1
BOD ₅ (g L^{-1})	3.17 ± 1.5
DOC (g L^{-1})	4.0 ± 0.8
TS (g L^{-1})	49.5 ± 6.5
TSS (g L^{-1})	19.5 ± 7.8
TP (g L^{-1})	3.1 ± 0.2
Total-P (g L^{-1})	0.30 ± 0.06
Total-N (g L^{-1})	0.15 ± 0.04

^a Mean value of three measurements.

^b It is noted that the OMW generated is further diluted at the olive mill and this explains the relevant low COD.

During the loading of the reactor with the chemicals, the collectors were covered to avoid any photoreaction. At the beginning, the reactor was filled with the pre-treated OMW. Here it is noted, that the pre-treated OMW before entering the tank passes through a cylindrical filter (200 μm pore size μm , \varnothing 25.4 mm, PALAPLAST, Greece) installed at the entrance of the storage tank. Then, the OMW was diluted using tap water and after homogenization by stirring (15 min), a sample was taken representing the initial COD concentration. The recirculation of the OMW solution in the reactor was chosen to be 15 min, a time duration sufficient for good mixing, according to the operative flow rate (150 L h^{-1}). The pH was then adjusted with 2 N H_2SO_4 and the appropriate volume of ferrous iron solution was added. Then, the solution was stirred for 15 min. Finally, a pre-determined dose of hydrogen peroxide was added and the collectors were uncovered.

Samples were taken periodically at specific time intervals from the sampling point of the pilot unit, and transferred in vials containing a certain quantity of MnO_2 to decompose any residual hydrogen peroxide, and prevent further reactions of the latter with organic substrates present in OMW. The samples were then filtered through 0.22 μm Millipore filters prior to further analysis.

The comparison of the experimental data deriving from different days at different times of the day and under different solar illumination conditions was performed after applying Eqn. (1) to “normalized illumination time”. This equation has been reported elsewhere (Maldonado et al., 2007; Klammerth et al., 2010).

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30} \frac{V_i}{V_T}; \quad \Delta t_n = t_n - t_{n-1} \quad (n = 1, t_n = 0 \text{ min}) \quad (1)$$

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured between t_{n-1} and t_n , and $t_{30W,n}$ is the “normalized illumination time”. In this case, time refers to a constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon).

It is important to mention that $t_{30W,n}$, calculated using the Eqn. (1), is lower than the actual experimental time (t_{exp}). This is because the Eqn. (1) includes the term V_i/V_T and the irradiated volume is significantly lower than the total volume of the treated OMW ($V_i \approx V_T/5$).

The pilot-scale experiments were performed in triplicate and mean values are quoted as results. The uncertainty quoted as the relative standard deviation (RSD) of three separate measurements, was never higher than 20%.

2.4. Analytical methods

Chemical oxygen demand (COD) was measured with Merck® Spectroquant kits, and the absorbance of the samples was measured at 445 nm using a photometer (Photolab S6). Dissolved organic carbon (DOC) was monitored by direct injection of the filtered samples (0.22 μm , Millipore) into an Aurora 1030 W TOC analyzer. Biodegradability was measured by the 5-day biochemical oxygen demand (BOD_5) test according to the standard methods protocol (APHA 5210B). Total

phenolic compounds (TP) in the liquid phase were determined colorimetrically according to the Folin-Ciocalteu method (Singleton and Rossi, 1965). A calibration curve was prepared using standard solutions of gallic acid and TP concentrations were expressed as gallic acid equivalent. The residual hydrogen peroxide remaining in the treated OMW samples was measured using the spectrophotometric method employing ammonium metavanadate ($\lambda_{\text{max}} = 450 \text{ nm}$) as described elsewhere (Oliveira et al., 2001; Nogueira et al., 2005). The presence of H_2O_2 in the treated samples was also monitored using Merckoquant® test sticks. Colour fading was monitored by measuring the absorbance of the treated OMW samples at 450 nm, which is the wavelength that corresponds to the maximum absorbance in the visible region (Chatzisyneon et al., 2008). The percentage of colour removal was calculated from the difference in absorbance values prior to and after treatment. The photometric measurements were performed using a double beam UV–Vis Jasco V-530 spectrophotometer. Colorimetric determination of total iron concentration with 1,10-phenanthroline was performed in the treated samples following the ISO 6332 (1988).

2.5. Ecotoxicity assessment

Toxicity measurements were carried out, in samples taken at various times during the photocatalytic treatment, with: (a) the Phytotestkit microbiotest (MicroBioTests Inc.), and (b) the Daphtoxkit F™ magna toxicity test. Toxicity tests were conducted according to the standard operating protocols for three plant species (*S. saccharatum*, *L. sativum*, *S. alba*), and for the crustacean *D. magna* (ISO 6341:1996), respectively. The residual hydrogen peroxide was removed from the OMW treated samples with catalase solution prior to analysis.

3. Results and discussion

3.1. Pre-treatment of OMW by coagulation/flocculation

The pre-treatment of OMW was investigated by means of coagulation/flocculation at a pilot scale. The aim of the pre-treatment was to reduce the solid fraction of OMW in order to improve the efficiency of the subsequent treatment by solar Fenton that was later on applied. The OMW pre-treatment consisted at first of coagulation with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, followed by flocculation using the anionic polyelectrolyte FLOCAN 23 (FLC 23). Here it is noted that $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and FLC 23 have been selected for use as the coagulant and flocculant agent respectively, according to previous findings of our group that demonstrated their better efficiency among a variety of coagulants and flocculants (Papaphilippou et al., 2013). The experiments were performed at constant FLC 23 concentration (0.287 g L^{-1}), whereas $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration was altered from 3 to 10 g L^{-1} (Fig. 1). The treatment of OMW with 6.67 g L^{-1} of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.287 g L^{-1} of FLC 23 led to approximately 44% of COD removal, whereas DOC and TSS were removed by 16% and 94%, respectively. At lower flocculant doses (3 g L^{-1}), the COD removal was lower (32%), whereas at 10 g L^{-1} of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, the organic content removal was similar to that obtained at 6.67 g L^{-1} of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Jaouani

et al. (2005) who studied the OMW treatment by coagulation reported the existence of an optimum coagulant concentration (i.e. $20 \text{ g L}^{-1} \text{ FeCl}_3$) at which treatment efficiency was maximized; at concentrations higher than the optimum one, separation was suppressed, and this was mainly attributed to the colloids re-stabilization.

It should be noted that the use of the specific coagulant and flocculant does not alter the acidic, inherent pH of OMW, and this is significant from a practical point of view, since solar Fenton post-oxidation would require acidic media (Papaphilippou et al., 2013).

Similar, to the above-mentioned results, other studies have revealed that the application of coagulation and flocculation processes for the OMW treatment can lead to significant reduction of TSS but moderate removal of COD. In Sarika et al. (2005), three cationic and one anionic polyelectrolytes were shown to be capable of removing TSS but did not cause any significant COD reduction. Meysami and Kasaeian (2005) added coagulants (i.e. chitosan, starch, alum and ferric chloride) to olive oil water emulsions with the aim to separate the coagulated oil droplets from suspension. Their results revealed that alum and chitosan were effective in reducing primary turbidity of the emulsions by 90%. Rizzo et al. (2008) investigated the pre-treatment of OMW by coagulation using chitosan and it was found that the optimum removal of TSS (81%) was achieved at 400 mg L^{-1} coagulant dose. The bench-scale coagulation/flocculation of OMW was also studied by Ginos et al. (2006). Coupling lime or ferrous sulphate (in the range of several g L^{-1}) with cationic polyelectrolytes (in the range of $200\text{--}300 \text{ mg L}^{-1}$) led to quantitative TSS removal, while COD and TP removal varied between $10\text{--}40\%$ and $30\text{--}80\%$, respectively. In another study on the effect of a classic coagulation/flocculation/sedimentation process on OMW treatment, using a range of lime doses from 10 to 40 g L^{-1} , revealed that 40% of COD removal was achieved (Aktas et al., 2001).

3.2. Solar Fenton oxidation

To enhance the relatively low COD removal that was recorded throughout the coagulation/flocculation experiments, the pre-treated OMW samples were further submitted to solar

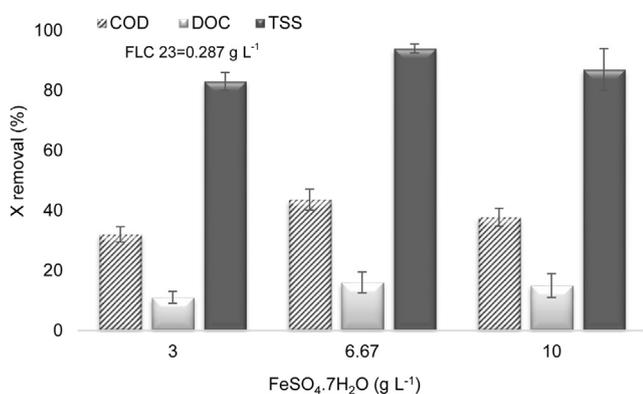


Fig. 1 – Organic content removal profiles in terms of COD, DOC and TSS during the coagulation/flocculation pre-treatment of OMW.

Fenton oxidation. One important issue of the pilot-scale study was to work with low concentration of reagents, thus lowering the operational cost significantly (mainly represented by the cost of the catalyst and the oxidizing agent). With this regard, experiments were performed to achieve optimum conditions, so as to accomplish a sufficient organic content removal for reuse of the produced water, as well as to avoid high concentration of residual reactants in the treated OMW. Here it is noted that the reagents' doses used by many studies (Gernjak et al., 2003, 2004; Badawy et al., 2009; Dogruel et al., 2009) are much higher than those used herein.

The solar Fenton experiments were carried out using pre-treated OMW that had been diluted 30 times with tap water (i.e. $[\text{COD}]_0 = 350 \text{ mg L}^{-1}$). The dilution of the OMW sample prior to photocatalytic treatment was deemed necessary for two reasons: (i) due to the difficulty in filtering high volume of OMW, and (ii) to reduce the inner filter effects in the reactor. The inner filter effects present in the OMW solution are considered as an important issue regarding the effect of the high concentration of organic compounds present in the OMW on the mineralization rate during the solar Fenton process. Inner filter effects include competitive absorption of photons by other organic compounds present in the OMW matrix (Malato et al., 2009). It should be noted that this dilution (30x) was selected after performing a series of experiments over a wide range of dilutions ($5\times\text{--}40\times$) (data not shown). It is important to mention that the dilution of OMW can be performed using treated urban wastewater, instead of tap water. Some additional experiments were performed using secondary treated urban wastewater (with negligible DOC and COD compared to that of OMW) and it was found that the process efficiency was not modified compared to that of using tap water (data not shown).

Prior to the photocatalytic treatment, photolytic experiments under direct sunlight were performed (Fig. 4), with the aim to assess whether the photolytic effect can contribute to the COD reduction. Results obtained from the photolytic experiments, showed no significant removal of the organic matter, since less than 8% of COD removal was observed after 240 min of solar irradiation ($t_{30W,n} = 54.3 \text{ min}$).

3.2.1. Effect of ferrous salt (Fe^{2+}) and hydrogen peroxide (H_2O_2) concentration

To elucidate the role of the initial Fe^{2+} and H_2O_2 concentration on the organic content removal of the OMW, a series of experiments was conducted with several combinations of catalyst ($0.02\text{--}0.1 \text{ g L}^{-1}$) and oxidant ($0.5\text{--}2.0 \text{ g L}^{-1}$), at $\text{pH} = 2.8\text{--}2.9$ and irradiation time of 240 min (t_{exp}).

Fig. 2 depicts the effect of ferrous initial concentration on the COD removal at $\text{pH} = 2.8\text{--}2.9$ as a function of $t_{30W,n}$. The original concentration of Fe^{2+} was altered from 0.02 to 0.1 g L^{-1} , while the initial concentration of H_2O_2 was kept constant ($[\text{H}_2\text{O}_2]_0 = 1 \text{ g L}^{-1}$). It is important to point out that although the residual concentration of Fe^{2+} after the coagulation/flocculation step was found to be around 80 mg L^{-1} , it was not capable of inducing Fenton reactions, probably due to the presence of Fe^{2+} complexes with organic ligands present in the wastewater. This was also confirmed by performing an additional experiment in the presence of $1 \text{ g L}^{-1} \text{ H}_2\text{O}_2$ without

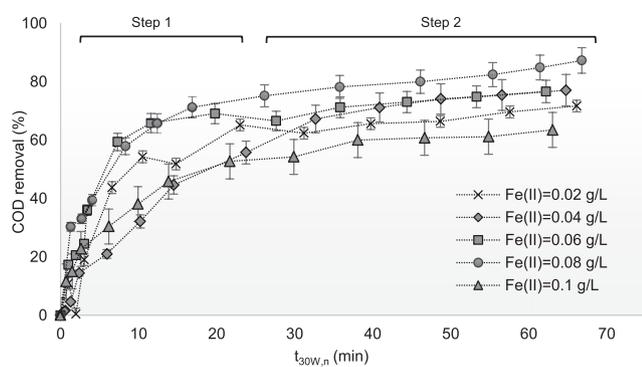


Fig. 2 – Effect of initial ferrous concentration on the COD removal of OMW. Experimental conditions: $[\text{COD}]_0 = 350 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 1.0 \text{ g L}^{-1}$; $\text{pH} = 2.8\text{--}2.9$.

adding any iron solution yielding only 18% of COD removal. Thus, a new dose of iron salt was added in the reactor.

The maximum COD removal (87.3%) was observed with Fe^{2+} concentration of 0.08 g L^{-1} within 240 min of irradiation ($t_{30W,n} = 66.8 \text{ min}$). According to Zapata et al. (2009), when the iron concentration is very low, H_2O_2 is consumed by less desirable reactions, while part of H_2O_2 is decomposed into molecular oxygen and water, without the generation of HO^\bullet . In the presence of higher iron concentrations, the process is accelerated due to the regeneration of Fe^{2+} from ferric (Fe^{3+}) iron, that results in the rapid generation of additional HO^\bullet . Nevertheless, an excess of Fe^{2+} (i.e. $[\text{Fe}^{2+}] = 0.1 \text{ g L}^{-1}$) in the system was found to result in decreased COD removal. The possible formation of an intermediate iron species (ferryl iron FeO^{2+}) could be the cause of this negative behavior, producing a possible side reaction interfering with the formation of HO^\bullet that are critical for the oxidation of organic matter (Badawy et al., 2009). In addition, too high concentrations of iron can generate dark zones in the photoreactor, because the incident ray is attenuated too strongly along the optical pathlength, reducing therefore the process efficiency (Malato et al., 2009).

It is worth noting that in the early stages of treatment (up to 20 min – step 1), COD was reduced rapidly, while in the second step (step 2), COD was slowly diminished, and then almost stabilized until the end of the treatment. This observation (called space-time effect) was also observed by Hodaifa

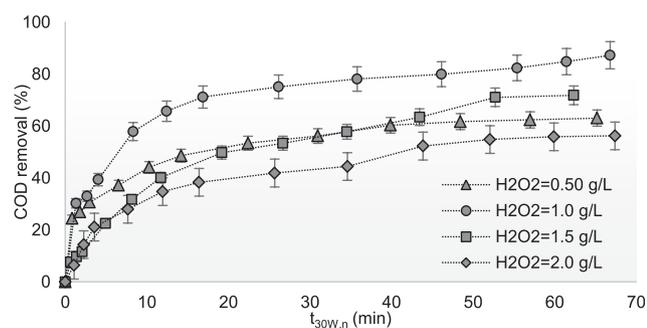


Fig. 3 – Effect of initial hydrogen peroxide concentration on the COD removal of OMW. Experimental conditions: $[\text{COD}]_0 = 350 \text{ mg L}^{-1}$; $[\text{Fe}^{2+}]_0 = 0.08 \text{ g L}^{-1}$; $\text{pH} = 2.8\text{--}2.9$.

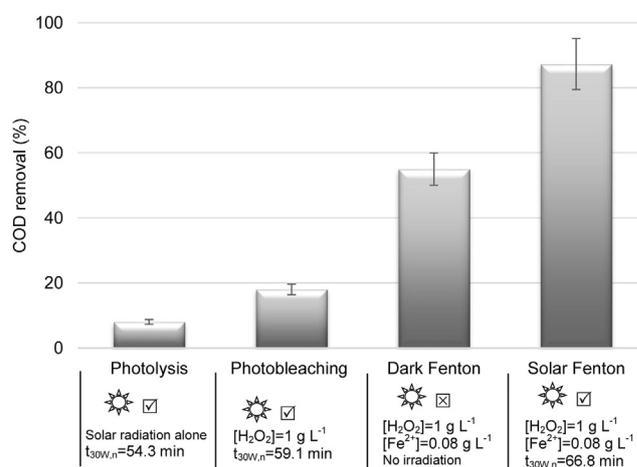


Fig. 4 – COD removal of OMW solution under different experimental conditions.

et al. (2013) during the treatment of OMW in a continuous stirred tank reactor, at a pilot scale by Fenton-like process. Similar results were also obtained by Zhang et al. (2006) in the case of landfill leachate treatment by Fenton process in a continuous stirred tank reactor.

In order to determine the effect of initial H_2O_2 concentration on the photocatalytic treatment of OMW, experiments were performed by varying the initial concentration of the H_2O_2 (between 0.5 and 2.0 g L^{-1}), while maintaining the following parameters: $\text{pH} = 2.8\text{--}2.9$, $[\text{Fe}^{2+}] = 0.08 \text{ g L}^{-1}$. Fig. 3 shows the degradation profile of COD removal at various hydrogen peroxide concentrations as a function of the $t_{30W,n}$. The results indicate that COD removal increased by increasing the concentration of peroxide from 0.5 to 1.0 g L^{-1} due to the additionally produced HO^\bullet . However, the use of excessive concentration of peroxide ($[\text{H}_2\text{O}_2] = 1.5\text{--}2.0 \text{ g L}^{-1}$), hindered the %COD removal, possibly due to the enhancement of the competition reactions, mainly the recombination of HO^\bullet and the reaction of HO^\bullet with H_2O_2 , contributing to the HO^\bullet scavenging capacity (Bautitz and Nogueira, 2007). In addition, saturation of active iron ion sites resulting from the excess dosage of H_2O_2 , could be another explanation as reported by Chen et al. (2010).

Under the specific experimental conditions, it appears that 1.0 g L^{-1} of H_2O_2 was the optimal dosage during the solar Fenton process. It is important to note that under the optimum conditions employed in this study, H_2O_2 was almost completely consumed at the end of the treatment ($[\text{H}_2\text{O}_2]_{\text{residual}} = 0.16 \text{ g L}^{-1}$), revealing that the selected $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio was appropriate and the specific oxidant consumption was high. Solar Fenton oxidation under the optimum conditions led to a remarkable colour reduction by 72%. This is in accordance with the fact that at the end of the treatment, an almost total disappearance of the phenolic compounds was achieved.

After the optimization of the solar process, further experiments were performed in the presence of 1 g L^{-1} which is the optimum H_2O_2 concentration as determined previously, aiming at evaluating the contribution of the combined action of solar radiation and H_2O_2 at acidic conditions (Fig. 4). The

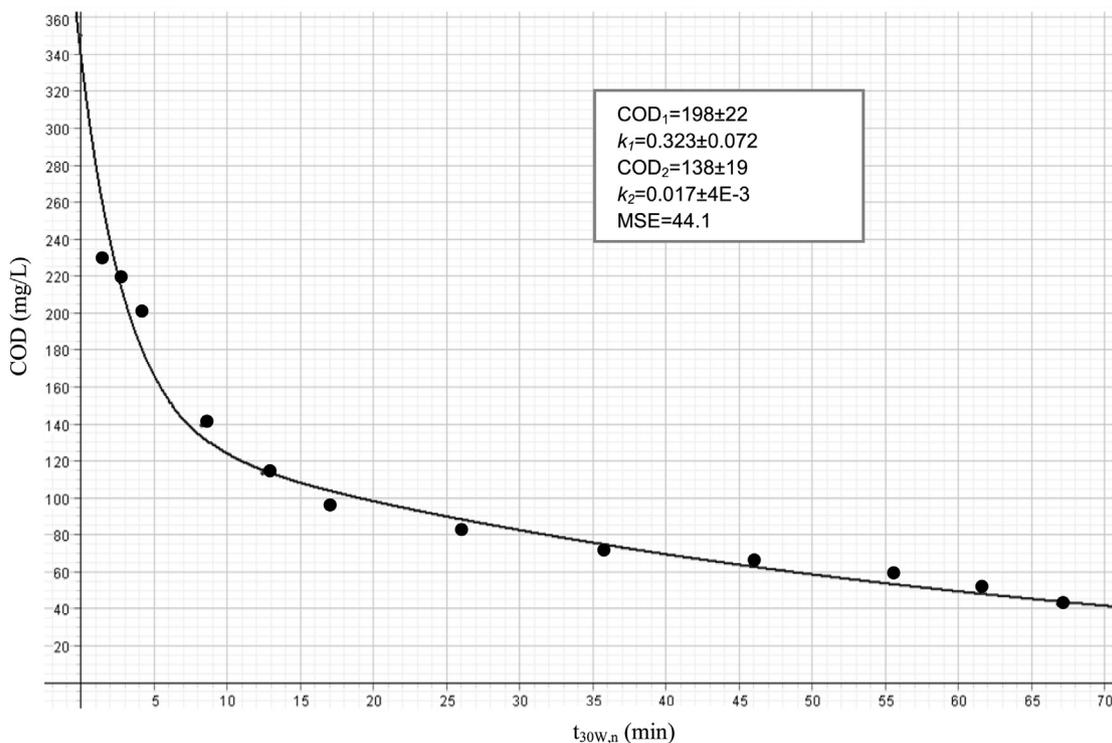


Fig. 5 – Fitting of the experimental data to the kinetic model for solar Fenton oxidation.

results showed that 18% of COD was removed within 240 min ($t_{30W,n} = 59.1$ min). This degradation can be attributed to the photochemical cleavage of H_2O_2 to yield HO^\bullet by solar light absorption (Tuhkanen, 2004). Dark Fenton experiments at the optimum reagent doses were also conducted to assess the oxidation power of the Fenton reagent in the absence of solar irradiation. The dark Fenton experiments were performed in order to investigate the efficiency of the process and thus, the possibility of the continuous operation of the plant overnight. The extent of COD removal during the dark Fenton oxidation was 55%, which was lower compared to that observed in the presence of solar irradiation, due to the lower generation of HO^\bullet .

The residual COD after the completion of the combined treatment (coagulation/flocculation + 30× dilution-solar Fenton) is approx. 44 mg L^{-1} , while the residual TSS is approx. 11 mg L^{-1} . Due to the fact that the OMW can be discharged in the environment mainly for irrigation purposes, it is important to comply with the local environmental limits. The regulations in Cyprus set maximum limits of 125 mg L^{-1} COD and 35 mg L^{-1} TSS for treated effluents that can be used for irrigation and can be discharged in water bodies (Cyprus, 2003); the combined process seems to be an effective solution for OMW treatment, that can reduce the organic load of the effluent to values below that of the Cypriot discharge limits.

3.2.2. Kinetics of solar Fenton reaction

The complexity of the OMW matrix due to its high organic content, in combination with the new chemical compounds formed as intermediates during the solar Fenton oxidation, makes it virtually impossible to carry out a detailed kinetic

study with the different individual reactions that take place during the chemical oxidation. In this study, COD values were used to carry out the kinetic study. In essence, what can be learnt by the kinetics is how fast the COD can be removed (and consequently how fast the various intermediates can be formed during oxidation), and also when the potential toxicity related to them can appear.

As previously mentioned, the evolution of organic matter in the reactor versus time, can be divided into two steps (step 1 and 2). During the first, organic matter removal progresses with higher rate (k_1), while during the second one (k_2) decreases slowly until the end of the chemical oxidation (where $k_1 \gg k_2$). The fit of the COD values versus time during the solar Fenton treatment at the optimum conditions, was performed using a two-step first-order kinetic model (Eqn. (3)) yielding low mean square error values (MSE – sum of the squares of the differences between the model predictions and the experimental data).

$$\text{COD} = \text{COD}_1 e^{-k_1 t} + \text{COD}_2 e^{-k_2 t} \quad (3)$$

In Eqn. (3), COD_1 and COD_2 correspond to the initial COD of the two independent first-order reactions and k_1 and k_2 are the apparent reaction rate constants, respectively.

The two-step first-order kinetic equation indicates the occurrence of two sequential oxidation steps during the solar Fenton process where, on a first stage, the COD is converted quickly to intermediates, which undergo further slower degradation during a second stage into final oxidation products (Martins et al., 2010). The fitting (Fig. 5) yielded $k_1 = 0.323 \pm 0.072 \text{ min}^{-1}$ and $k_2 = 0.017 \pm 4 \times 10^{-3} \text{ min}^{-1}$ indicating that the OMW decomposition during the first step of the oxidation process occurred quickly. This model

was already applied to describe OMW mineralization during wet oxidation and ozonation as described in the works of Martins et al. (2010) and Nieto et al. (2011).

3.2.3. Solar Fenton without pH adjustment

The effect of the initial pH on the organic content removal throughout the solar Fenton process was addressed. The experiments were performed at the inherent pH value (pH ≈ 5.0) of the OMW. The idea behind this approach was to avoid the wastewater acidification associated with additional cost through the consumption of reagents (H₂SO₄), and subsequent increase of the salinity of the treated water.

Table 2 compares the results derived from the solar Fenton experiments at pH = 2.8–2.9 and the original pH of OMW (pH = 5.0) in terms of COD, DOC, TSS and TP removal. From the data presented in Table 2, it is obvious that the solar Fenton process at pH = 2.8–2.9 resulted in slightly higher COD removal (COD_{removal} [COD]_{removal} = 87.3%) compared to that observed at the inherent pH value (COD_{removal} [COD]_{removal} = 80.6%) of OMW. On the other hand, TP were observed to undergo the same reduction (>99%) under both pH values examined. Under both operating pH conditions studied, mineralization in terms of DOC removal was found to be relatively low compared to the COD removal, a fact that clearly indicates that a considerable organic load remained in the treated OMW solution, which could be attributed to the presence of stable oxidation products.

The dissolved organic matter in OMW, can contribute to the formation of complexes with the ferric iron (Fe³⁺), increasing the amount of photoactive Fe³⁺ and therefore, the efficiency of the solar Fenton process (Vione et al., 2004; Moncayo-Lasso et al., 2008). The complexes of organic compounds with Fe³⁺ have the advantage of being soluble in the OMW matrix and so preventing the Fe³⁺ precipitation at the inherent pH (De la Cruz et al., 2012). It is important to note that in the case of unadjusted pH, the latter decreased reaching values close to 3 at the end of the treatment (Fig. 6), potentially due to the formation of organic acids (Radjenović et al., 2009).

3.3. Ecotoxicity evaluation

Toxicity tests using *D. magna* and three plant species (*S. saccharatum*, *L. sativum*, *S. alba*) were used as they are considered suitable to evaluate the toxicity of the treated OMW prior its disposal to water bodies and use for agricultural irrigation, respectively. The two bio-assays were conducted on OMW samples taken during the solar Fenton process (under the

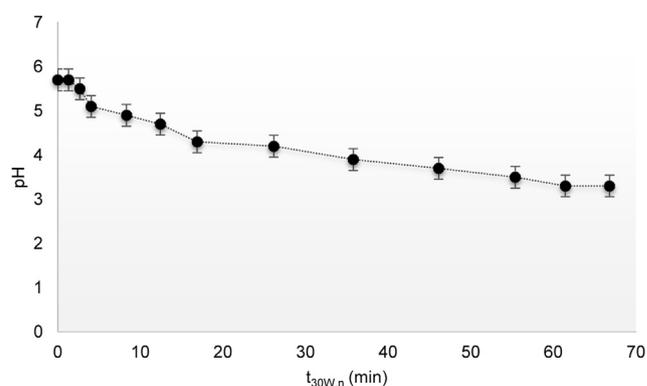


Fig. 6 – Evolution of pH during solar Fenton process. Experimental conditions: [Fe²⁺]₀ = 0.08 g L⁻¹; [H₂O₂]₀ = 1.0 g L⁻¹.

optimum experimental conditions) at various times of treatment (0–240 min). The time 0 refers to the raw diluted OMW. It should be noted that the results are presented as a function of the actual experimental time (t_{exp}) instead of the normalized illumination time (t_{30W,n}) for comparison purposes among the three plant types and the various endpoints (germination, root and shoot growth).

3.3.1. Daphnia magna toxicity test

The extent of immobilization of *D. magna* with treatment time (t_{exp}) is presented in Fig. 7. Primarily, in order to determine the toxicity of the raw diluted OMW used for the whole experimental procedure, toxicity tests were performed by exposing *D. magna* to the OMW samples. These tests showed that the immobilization of daphnids after 24 h of exposure was 45%, while after 48 h of exposure the respective value was 75%. It should be noted that the toxicity of the OMW pre-treated with coagulation/flocculation was similar to that observed for the raw diluted OMW. It is generally accepted that OMW toxicity is largely associated to the presence of phenolic compounds although other OMW constituents such as fatty acids, aldehydes, and alcohols are also known to induce toxic effects (Komilis et al., 2005). Similar toxicity levels towards *D. magna* compared to the untreated OMW solution was observed after

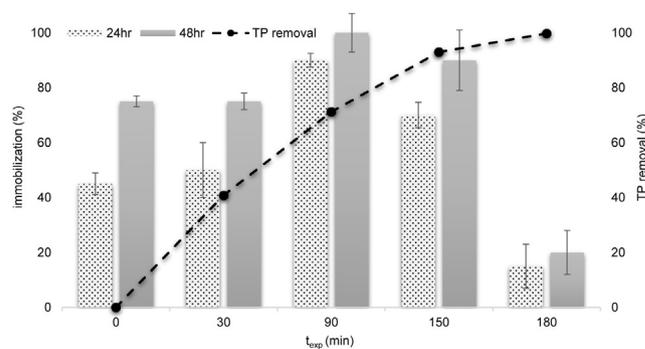


Fig. 7 – Evolution of toxicity to *D. magna* and TP removal during solar Fenton process. Experimental conditions: [Fe²⁺]₀ = 0.08 g L⁻¹; [H₂O₂]₀ = 1.0 g L⁻¹; pH = 2.8–2.9.

Table 2 – Comparison of the solar Fenton experiments performed under different pH conditions.

pH	pH = 2.8–2.9	pH = 5.0
Parameter	(%)Removal	(%)Removal
COD	87.3 ± 5.4	80.6 ± 2.4
DOC	41.7 ± 8.1	36.2 ± 3.0
TSS	73.4 ± 6.2	71.5 ± 7.3
TP	99.8 ± 2.4	99.0 ± 2.1

30 min of the photocatalytic process, although more than 60% of the original COD was removed. This trend indicates the rapid formation of toxic intermediates (probably as a consequence of the higher degradation of the COD present in solution – step 1) which may exhibit individual or/and synergistic toxic effects. The toxicity of the treated samples taken after 90 min of solar Fenton was dramatically increased to 100% after 48 h of exposure. From 90 to 150 min of irradiation, the immobilization decreased, remaining however still high at values above 70%. At this time, the oxidation products formed were presumably still present in the solution, while synergistic effects among them may also be considered. From that time onwards, a decrease in *D. magna* immobilization to 20% (48 h of exposure) was observed, which remained until the end of the treatment constant (immobilization values were lower than that of the untreated OMW), as toxic intermediates were degraded further. As shown in Fig. 7, complete degradation of the total phenolic compounds was obtained, along with a significant decrease of toxicity towards *D. magna* to values lower than 20% (immobilization). Thus, the toxicity assessment revealed that solar Fenton process is able to minimise the effluent ecological impact related with the phenolic compounds.

In general, the varying behavior of the immobilization of *D. magna* can be attributed to the concomitant generation of various oxidation products during the oxidation of the natural organic content present in the OMW matrix. Based on the available scientific literature, a contradictory behavior of OMW towards *D. magna* was observed during the application of various treatments. According to Fiorentino et al. (2004), oxidation of OMW with FeCl_3 reduced the toxicity against rotifers (*B. calyciflorus*) and *D. magna*, while a further decrease was observed by combining chemical oxidation and biological treatment. In contrast to the results presented herein, the toxicity to *D. magna* increased sharply during the electrochemical oxidation of OMW and remained quite high even after prolonged oxidation (Gotsi et al., 2005). In addition, Giannis et al. (2007) investigated the toxicity of OMW prior to and after electrochemical treatment towards *D. magna*. According to their results, the electrolytic oxidation did not reduce the toxicity of the treated wastewater, due to the formation of organochlorinated compounds, as well as other intermediate products such as spironolactone and benzoquinone and/or hydroquinone. The formation of organochlorinated compounds is attributed to the presence of NaCl (electrolyte solution), leading to the generation of active chloride intermediates during the process.

3.3.2. Phytotoxicity test

Fig. 8 illustrates the results as a percentage of the inhibition of the germination and root and shoot growth of the examined plant species after the exposure to the treated OMW solutions. The effect (%) of the OMW samples on seed germination (GI), root growth inhibition (RI) and shoot growth inhibition (SI) was calculated as described elsewhere (Michael et al., 2012).

The raw diluted OMW samples (time zero) did not cause significant inhibition on the germination for the three plant species. The negative GI values indicate the stimulating effect to the seeds by the nutrients (see Table 1) that are present in the OMW. The observed GI of the selected plant species is in

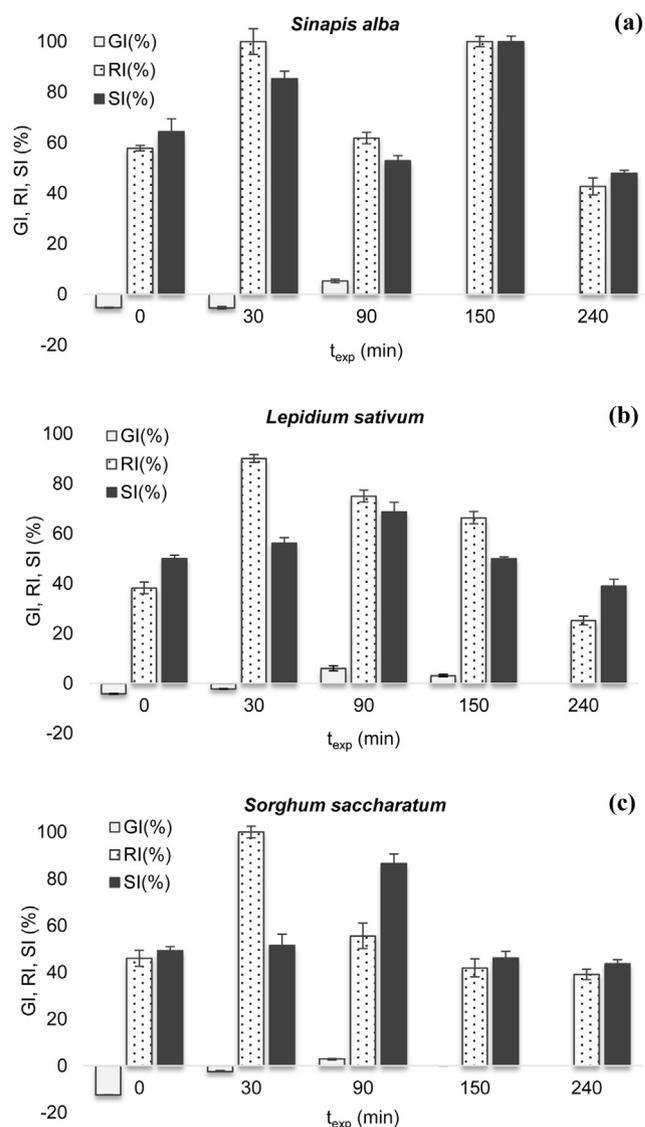


Fig. 8 – Seed germination inhibition (GI), root growth inhibition (RI) and shoot growth inhibition (SI) during solar Fenton process. Experimental conditions: $[\text{Fe}^{2+}]_0 = 0.08 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 1.0 \text{ g L}^{-1}$; pH = 2.8–2.9.

agreement with the results of Komilis et al. (2005), who showed that high dilution was necessary to remove phytotoxicity to horticultural crops (tomato and chicory seeds). It is important to highlight that no germination of seeds was observed in the presence of undiluted OMW due to its high phenolic content. When solar Fenton was applied, a negligible phytotoxic effect on seed germination was observed at 90 min ($\text{GI}_{[\text{S.alba}]} = 5.3\%$; $\text{GI}_{[\text{L.sativum}]} = 6\%$, $\text{GI}_{[\text{S.saccharatum}]} = 3\%$), while at the end of the treatment (240 min) the GI was eliminated for all the plant species.

Higher RI responses were obtained from the OMW treated samples, being strongly inhibitory for all the plant species. The RI of *S. alba* was dramatically increased from 60 to 100% after 30 min of photocatalytic treatment, implying thus the formation of transformation products that are more toxic than the original matrix. After 90 min of treatment, a decrease

in the root growth was observed indicating further oxidation of products formed at 30 min, and consequently that the formation of new intermediates was still going on. However, this increased again after 150 min of treatment indicating the formation of toxic oxidation products. This may be attributed to competitive mechanisms related to the degradation of organic compounds, the complete oxidation of organic compounds to CO₂, and the formation of toxic compounds. Finally, samples irradiated for 240 min resulted in lower toxicity, displaying a decrease in RI (42.7%) indicating the removal or further transformation of the toxic products throughout the process.

In the case of *L. sativum* and *S. saccharatum*, the root length inhibition showed approximately the same behavior. The maximum RI was recorded at 30 min ($GI_{[L.sativum]} = 90\%$, $GI_{[S.saccharatum]} = 100\%$), and from that time onwards a continuous decrease was observed yielding 25.1% and 39.2% RI for *L. sativum* and *S. saccharatum*, respectively.

The SI profile for *S. alba* (Fig. 8(a)) exhibited similarities with the RI evolution profile. However, the SI at the end of the process was higher compared to that of the RI, indicating the susceptibility of shoots compared to the roots. The highest SI for *S. alba* was observed at 150 min of treatment ($SI_{[S.alba]} = 100\%$), and it was reduced to approximately 48% at the end of the treatment. As shown in Fig. 8(b), the toxicity of the treated samples taken after 90 min of the photocatalytic process towards *L. sativum*, increased to approximately 70%, after which, a gradual decrease in SI to 39% was observed until the end of the treatment. A similar SI profile was observed for the *S. saccharatum* (Fig. 8(c)).

In general, the toxicity profile did not follow the trend of the COD removal, indicating that the phytotoxicity may be a result of the rapid formation of toxic intermediates during the oxidation treatment. In all the experiments, the inhibition of root and shoot growth was not eliminated completely; however, the toxicity of the treated samples after 240 min of solar Fenton was lower than that of the raw OMW. The remaining toxic effect can be attributed to the presence of short-chain fatty acids (typically C8–C9) formed during the process as shown by Karageorgos et al. (2006). These short-chain fatty acids, in particular nonanoic and acetic acid, are well known to be capable of inhibiting plant growth (Shiralipour et al., 1997; Andreozzi et al., 2008). Moreover, the remaining toxicity may be due to the presence of the residual organic matter (COD was removed by 87% at the end of the treatment).

Mekki et al. (2006) reported on the effects of untreated and biologically treated OMW of seed germination for tomato (*L. esculentum*), chickpea (*C. arietinum*), bean (*V. faba*), wheat (*T. durum*) and barley (*H. vulgare*), and the results showed an improvement in plant growth irrigated with treated OMW. Andreozzi et al. (2008) investigated the effect of OMW, treated by different processes (ozonation, photolysis under solar irradiation, solar modified photo-Fenton, and solar modified photo-Fenton-ozonation) on three cultivated plants, *R. sativus* L., *C. sativus* L. and *L. sativa* L. OMW treated samples during the examined treatment processes (except ozonation) did not contribute significantly to the seed germination, while after 2 h of ozonation, the OMW phytotoxicity on the three plant species was moderately reduced.

Phytotoxicity experiments using the *L. sativum* seeds were also carried out by Khoufi et al. (2009) during the application of an integrated electro-Fenton, anaerobic digestion and ultra-filtration of OMW. The results showed that the integrated process increased the OMW toxicity towards *L. sativum* (germination index up to 124% compared to 100% for control). In another study by Khoufi et al. (2006), the phytotoxicity of OMW previously treated with anaerobic digestion was significantly reduced by the application of electrocoagulation, reaching 140% germination index. The phytotoxicity behavior of the OMW after pre-treatment by coagulation/flocculation coupling various inorganic materials and organic poly-electrolytes to lettuce seeds was assessed by Ginos et al. (2006). The untreated OMW was strongly phytotoxic to lettuce seeds even after several dilutions with water; however, phytotoxicity decreased considerably following treatment with lime and cationic poly-electrolytes; this was attributed to the removal of phenols and other phytotoxic species from the liquid phase.

3.4. Economic evaluation of solar Fenton process as post-treatment of OMW

The economic evaluation presented below is based on the assumption that a cluster of olive oil mills, co-existing in the same area, is expected to produce an average of 50 m³ d⁻¹ of wastewater. The integrated treatment comprises physico-chemical pre-treatment via coagulation/flocculation and solar Fenton oxidation as post-treatment. In this study, the investment and operational cost of the post-treatment (solar Fenton) was estimated for a running period of five years. Thus, the initial investment costs and the operation and maintenance costs for five-year time were considered. The calculation was based on the assumption that the treatment plant operates on an annual basis and not only during the milling period, serving a cluster of olive mills located in the same area. An overall wastewater volume of ca. 18250 m³, generated per year at 6 olive mills in the area of the capital of Cyprus is considered. In this way, system damages due to non-use of the treatment plant is avoided, as it will be operated continuously. Since the mills already pay for the transport of their OMW to evaporation ponds, which are sometimes located even at 20 km distance from the mills, and since the mills do have storage tanks at their premises, the cost for storage and transfer of the OMW to the treatment plant is not included in our cost estimation. It should be noted, that the purchase of land is not included in the cost estimation.

Table 3 shows the total investment cost for the construction of the solar Fenton system, while in Table 4 the total operation cost for a five-year period is presented. It should be mentioned that for the calculation of the operating cost, the seasonal variations in the flow have been taken into consideration. The analysis of the operation and maintenance expenses includes the personnel salaries for maintenance and operation, the cost of electrical energy (0.25 € kWh⁻¹), and the consumption of chemicals (H₂SO₄, FeSO₄·7H₂O, H₂O₂ and NaOH) and other consumables (e.g. borosilicate glass tubes, etc.), based on 2014 values. After the solar Fenton process, NaOH can be used in order to neutralize the treated effluent for subsequent irrigation purposes.

Table 3 – Investment cost for the construction of the solar Fenton system.

Cost element	Solar Fenton system in €
Detail design € (process design, civil engineering design for infrastructure, detail engineering design for electromechanical installations)	2000
Civil works (site preparation, reinforcement, waterproof insulation, construction of services building)	2500
Supply of equipment (equipment sizing selection and cost of supply)	53850
Electromechanical installations (engineering supervision and labour)	4000
Other expenses (utilities: water and power supply, test and commissioning)	500
Total investment cost	62850

The total cost of solar Fenton process and for a five-year operation, for the treatment capacity of $50 \text{ m}^3 \text{ d}^{-1}$ OMW, is estimated to be approximately 193000 €, which corresponds to 38600 € yr^{-1} , and to 2.11 € m^{-3} .

4. Conclusions

Solar Fenton oxidation combined with previous coagulation/flocculation pre-treatment may constitute a potential solution for the purification of OMW resulting in considerable organic load removal. This study demonstrates the efficacy of solar Fenton to operate at the inherent pH of the OMW, yielding only a slightly lower organic removal. The polyphenolic fraction, which is responsible for the biorecalcitrant and/or toxic properties of OMW, can be eliminated by the chemical oxidation process. The OMW treated samples display a varying toxicity profile for each type of microorganism and plant examined in this study, which can be attributed to the oxidation products formed during the solar Fenton process applied. Interestingly, the solar oxidation process seems to be capable of achieving a reduction of the OMW final toxicity, reinforcing thus the concept of sustainable water reuse. It is also important to note that, this work clearly shows that more attention should be given to the toxicity of the OMW treated effluents. Further studies in the field are deemed necessary in order to investigate

Table 4 – Operational cost of the solar Fenton system for a five-year period.

Cost element	Solar Fenton system in €
Operation (engineering supervision, operator, technical support)	5200
Monitoring of performance (on side and lab analyses)	1000
Cost of electricity (based on 0.25 € kWh^{-1})	3500
Equipment maintenance & repairs (lubrication, maintenance, spare parts)	5000
Chemical consumption (reagents: H_2SO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2O_2 , NaOH)	115000
Total operational cost for 5 years	129700

the feasibility of irrigation of soil and crops with OMW treated by solar Fenton. Studies on chronic toxicity effects towards various plants should be further developed to evaluate the potential ecotoxicological hazard of OMW. Concluding, this is the first study according to the authors' knowledge, which is dedicated to this specific combined process.

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REFERENCES

- Aktas, E.S., Imre, S., Ersoy, L., 2001. Characterization and lime treatment of olive mill wastewater. *Water Res.* 35, 2336–2340.
- Anastasiou, C.C., Christou, P., Michael, A., Nicolaidis, D., Lambrou, T.P., 2011. Approaches to olive mill wastewater treatment and disposal in Cyprus. *J. Environ. Res.* 5, 49–58.
- Andreozzi, R., Canterino, M., Di Somma, I., Lo Giudice, R., Marotta, R., Pinto, G., Pollio, A., 2008. Effect of combined physico-chemical processes on the phytotoxicity of olive mill wastewaters. *Water Res.* 42, 1684–1692.
- APHA, 1998. Standard Methods for the Examination of Water and Wastewater, twelfth ed. American Public Health Association, Washington, DC, USA.
- Avraamides, M., Fatta, D., 2008. Resource consumption and emissions from olive oil production: a life cycle inventory case study in Cyprus. *J. Clean. Prod.* 16, 809–821.
- Badawy, M., Gohary, F.E., Ghaly, M., Ali, M., 2009. Enhancement of olive mill wastewater biodegradation by homogeneous and heterogeneous photocatalytic oxidation. *J. Hazard. Mater.* 169, 673–679.
- Bautitz, I.R., Nogueira, R.F.P., 2007. Degradation of tetracycline by photo-Fenton process-Solar irradiation and matrix effects. *J. Photochem. Photobiol. A* 187, 33–39.
- Belaid, C., Khadraoui, M., Mseddi, S., Kallel, M., Elleuch, B., Fauvarque, J.F., 2013. Electrochemical treatment of olive mill wastewater: treatment extent and effluent phenolic compounds monitoring using some uncommon analytical tools. *J. Environ. Sci.* 25, 220–230.
- Beltran-Heredia, J., Torregrosa, J., Garcia, J., Domínguez, J., Tierno, J., 2001. Degradation of olive mill wastewater by the combination of Fenton's reagent and ozonation processes with an aerobic biological treatment. *Water Sci. Technol.* 44, 103–108.
- Canizares, P., Lobato, J., Paz, R., Rodrigo, M., Sáez, C., 2007. Advanced oxidation processes for the treatment of olive-oil mills wastewater. *Chemosphere* 67, 832–838.

- Chatzisyneon, E., Stypas, E., Bousios, S., Xekoukoulotakis, N.P., Mantzavinos, D., 2008. Photocatalytic treatment of black table olive processing wastewater. *J. Hazard. Mater.* 154, 1090–1097.
- Chatzisyneon, E., Xekoukoulotakis, N.P., Diamadopoulos, E., Katsaounis, A., Mantzavinos, D., 2009a. Boron-doped diamond anodic treatment of olive mill wastewaters: statistical analysis, kinetic modeling and biodegradability. *Water Res.* 43, 3999–4009.
- Chatzisyneon, E., Diamadopoulos, E., Mantzavinos, D., 2009b. Effect of key operating parameters on the non-catalytic wet oxidation of olive mill wastewaters. *Water Sci. Technol.* 59, 2509–2518.
- Chen, Q., Wu, P., Dang, Z., Zhu, N., Li, P., Wu, J., Wang, X., 2010. Iron pillared vermiculite as a heterogeneous photo-Fenton catalyst for photocatalytic degradation of azo dye reactive brilliant orange X-GN. *Sep. Purif. Technol.* 71, 315–323.
- Cyprus Regulatory Administrative Act on the pollution of water bodies (urban wastewaters discharges), 2003/772, 2003.
- De la Cruz, N., Gimenez, J., Esplugas, S., Grandjean, D., De Alencastro, L., Pulgarin, C., 2012. Degradation of 32 emergent contaminants by UV and neutral photo-Fenton in domestic wastewater effluent previously treated by activated sludge. *Water Res.* 46, 1947–1957.
- Dhaouadi, H., Marrot, B., 2008. Olive mill wastewater treatment in a membrane bioreactor: process feasibility and performances. *Chem. Eng. J.* 145, 225–231.
- Dogrueel, S., Olmez-Hanci, T., Kartal, Z., Arslan-Alaton, I., Orhon, D., 2009. Effect of Fenton's oxidation on the particle size distribution of organic carbon in olive mill wastewater. *Water Res.* 43, 3974–3983.
- El Hadrami, A., Belaqziz, M., El Hassni, M., Hanifi, S., Abbad, A., Capasso, R., Gianfreda, L., El Hadrami, I., 2004. Physico-chemical characterization and effects of olive oil mill wastewater fertirrigation on the growth of some Mediterranean crops. *J. Agron.* 3, 247–254.
- El Hajjoui, H., Ait Baddi, G., Yaacoubi, A., Hamdi, H., Winterton, P., Revel, J., Hafidi, M., 2008. Optimisation of biodegradation conditions for the treatment of olive mill wastewater. *Bioresour. Technol.* 99, 5505–5510.
- Fadil, K., Chahlaoui, A., Ouahbi, A., Zaid, A., Borja, R., 2003. Aerobic biodegradation and detoxification of wastewaters from the olive oil industry. *Int. Biodeterior. Biodegradation* 51, 37–41.
- Fiorentino, A., Gentili, A., Isidori, M., Lavorgna, M., Parrella, A., Temussi, F., 2004. Olive oil mill wastewater treatment using a chemical and biological approach. *J. Agric. Food Chem.* 52, 5151–5154.
- Gernjak, W., Krutzler, T., Glaser, A., Malato, S., Cáceres, J., Bauer, R., Fernández-Alba, A., 2003. Photo-Fenton treatment of water containing natural phenolic pollutants. *Chemosphere* 50, 71–78.
- Gernjak, W., Maldonado, M., Malato, S., Cáceres, J., Krutzler, T., Glaser, A., Bauer, R., 2004. Pilot-plant treatment of olive mill wastewater (OMW) by solar TiO₂ photocatalysis and solar photo-Fenton. *Sol. Energy* 77, 567–572.
- Giannis, A., Kalaitzakis, M., Diamadopoulos, E., 2007. Electrochemical treatment of olive mill wastewater. *J. Chem. Technol. Biotechnol.* 82, 663–671.
- Ginos, A., Manios, T., Mantzavinos, D., 2006. Treatment of olive mill effluents by coagulation–flocculation–hydrogen peroxide oxidation and effect on phytotoxicity. *J. Hazard. Mater.* 133, 135–142.
- Gotsi, M., Kalogerakis, N., Psillakis, E., Samaras, P., Mantzavinos, D., 2005. Electrochemical oxidation of olive oil mill wastewaters. *Water Res.* 39, 4177–4187.
- Hodaifa, G., Ochando-Pulido, J., Rodriguez-Vives, S., Martinez-Ferez, A., 2013. Optimization of continuous reactor at pilot scale for olive-oil mill wastewater treatment by Fenton-like process. *Chem. Eng. J.* 202, 117–124.
- ISO 6332, 1988. Water Quality-Determination of Iron-Spectrometric Method Using 1,10-Phenanthroline.
- ISO 6341, 1996. Water Quality-Determination of the Inhibition of the Mobility of *Daphnia Magna* Straus (Cladocera, Crustacea)-Acute Toxicity Test.
- Jaouani, A., Vanthourhout, M., Penninckx, M.J., 2005. Olive oil mill wastewater purification by combination of coagulation-flocculation and biological treatments. *Environ. Technol.* 26, 633–641.
- Justino, C.I., Duarte, K., Loureiro, F., Pereira, R., Antunes, S.C., Marques, S.M., Gonçalves, F., Rocha-Santos, T.A., Freitas, A.C., 2009. Toxicity and organic content characterization of olive oil mill wastewater undergoing a sequential treatment with fungi and photo-Fenton oxidation. *J. Hazard. Mater.* 172, 1560–1572.
- Kallel, M., Belaid, C., Mechichi, T., Ksibi, M., Elleuch, B., 2009. Removal of organic load and phenolic compounds from olive mill wastewater by Fenton oxidation with zero-valent iron. *Chem. Eng. J.* 150, 391–395.
- Karageorgos, P., Coz, A., Charalabaki, M., Kalogerakis, N., Xekoukoulotakis, N.P., Mantzavinos, D., 2006. Ozonation of weathered olive mill wastewaters. *J. Chem. Technol. Biotechnol.* 81, 1570–1576.
- Khoufi, S., Aloui, F., Sayadi, S., 2006. Treatment of olive oil mill wastewater by combined process electro-Fenton reaction and anaerobic digestion. *Water Res.* 40, 2007–2016.
- Khoufi, S., Aloui, F., Sayadi, S., 2009. Pilot scale hybrid process for olive mill wastewater treatment and reuse. *Chem. Eng. Process. Process Intensif.* 48, 643–650.
- Klamerth, N., Rizzo, L., Malato, S., Maldonado, M.I., Aguera, A., Fernández-Alba, A.R., 2010. Degradation of fifteen emerging contaminants at $\mu\text{g L}^{-1}$ initial concentrations by mild solar photo-Fenton in MWTP effluents. *Water Res.* 44, 545–554.
- Komilis, D.P., Karatzas, E., Halvadakis, E., 2005. The effect of olive mill wastewater on seed germination after various pretreatment techniques. *J. Environ. Manag.* 74, 339–348.
- Malato, S., Fernández-Ibáñez, P., Maldonado, M., Blanco, J., Gernjak, W., 2009. Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. *Catal. Today* 147, 1–59.
- Maldonado, M.I., Passarinho, P.C., Oller, I., Gernjak, W., Fernández, P., Blanco, J., Malato, S., 2007. Photocatalytic degradation of EU priority substances: a comparison between TiO₂ and Fenton plus photo-Fenton in a solar pilot plant. *J. Photochem. Photobiol. A Chem.* 185, 354–363.
- Mantzavinos, D., Kalogerakis, N., 2005. Treatment of olive mill effluents: part I. Organic matter degradation by chemical and biological processes-an overview. *Environ. Int.* 31, 289–295.
- Marques, I.P., 2001. Anaerobic digestion treatment of olive mill wastewater for effluent re-use in irrigation. *Desalination* 137, 233–239.
- Martinez-Garcia, G., Johnson, A.C., Bachmann, R.T., Williams, C.J., Burgoyne, A., Edyvean, R.G., 2009. Anaerobic treatment of olive mill wastewater and piggery effluents fermented with *Candida tropicalis*. *J. Hazard. Mater.* 164, 1398–1405.
- Martins, R.C., Quinta-Ferreira, R.M., 2011. Remediation of phenolic wastewaters by advanced oxidation processes (AOPs) at ambient conditions: comparative studies. *Chem. Eng. Sci.* 66, 3243–3250.
- Martins, R.C., Lopes, R.J., Quinta-Ferreira, R.M., 2010. Lumped kinetic models for single ozonation of phenolic effluents. *Chem. Eng. J.* 165, 678–685.
- Mekki, A., Dhoub, A., Aloui, F., Sayadi, S., 2006. Olive wastewater as an ecological fertilizer. *Agron. Sustain. Dev.* 26, 61–67.
- Meyssami, B., Kasaeian, A.B., 2005. Use of coagulants in treatment of olive oil wastewater model solutions by induced air flotation. *Bioresour. Technol.* 96, 303–307.

- Michael, I., Hapeshi, E., Michael, C., Varela, A., Kyriakou, S., Manaia, C., Fatta-Kassinos, D., 2012. Solar photo-Fenton process on the abatement of antibiotics at a pilot scale: degradation kinetics, ecotoxicity and phytotoxicity assessment and removal of antibiotic resistant enterococci. *Water Res.* 46 (17), 5621–5634.
- Moncayo-Lasso, A., Pulgarin, C., Benítez, N., 2008. Degradation of DBPs' precursors in river water before and after slow sand filtration by photo-Fenton process at pH 5 in a solar CPC reactor. *Water Res.* 42, 4125–4132.
- Niaounakis, M., Halvadakis, C.P., 2006. Olive Processing Waste Management – Literature Review and Patent Survey, second ed.. In: Waste Management Elsevier, Amsterdam.
- Nieto, L.M., Hodaifa, G., Rodríguez, S., Giménez, J.A., Ochando, J., 2011. Degradation of organic matter in olive-oil mill wastewater through homogeneous Fenton-like reaction. *Chem. Eng. J.* 173, 503–510.
- Nogueira, R.F.P., Oliveira, M.C., Paterlini, W.C., 2005. Simple and fast spectrophotometric determination of H₂O₂ in photo-Fenton reactions using metavanadate. *Talanta* 66, 86–91.
- Oliveira, M.C., Nogueira, R.F.P., Neto, J.A.G., Jardim, W.F., Rohwedder, J.J.R., 2001. Sistema de injeção em fluxo espectrofotométrico par a monitorar peróxido de hidrogênio em processo de fotodegradação por reação foto-fenton. *Quim.a Nova* 24, 188–190.
- Ouzounidou, G., Zervakis, G.I., Gaitis, F., 2010. Raw and microbiologically detoxified olive mill waste and their impact on plant growth. *Terr. Aquat. Environ. Toxicol.* 4, 21–38.
- Papaphilippou, P.C., Yiannapas, C., Politi, M., Daskalaki, V.M., Michael, C., Kalogerakis, N., Mantzavinos, D., Fatta-Kassinos, D., 2013. Sequential coagulation-flocculation, solvent extraction and photo-Fenton oxidation for the valorization and treatment of olive mill effluent. *Chem. Eng. J.* 224, 82–88.
- Paraskeva, P., Diamadopoulos, E., 2006. Technologies for olive mill wastewater (OMW) treatment: a review. *J. Chem. Technol. Biotechnol.* 81, 1475–1485.
- Paredes, C., Bernal, M., Roig, A., Cegarra, J., 2001. Effects of olive mill wastewater addition in composting of agroindustrial and urban wastes. *Biodegradation* 12, 225–234.
- Radjenović, J., Sirtori, C., Petrović, M., Barceló, D., Malato, S., 2009. Solar photocatalytic degradation of persistent pharmaceuticals at pilot-scale: kinetics and characterization of major intermediate products. *Appl. Catal. B Environ.* 89, 255–264.
- Rizzo, L., Lofrano, G., Grassi, M., Belgiorno, V., 2008. Pre-treatment of olive mill wastewater by chitosan coagulation and advanced oxidation processes. *Sep. Purif. Technol.* 63, 648–653.
- Sarika, R., Kalogerakis, N., Mantzavinos, D., 2005. Treatment of olive mill effluents: part II. Complete removal of solids by direct flocculation with poly-electrolytes. *Environ. Int.* 31, 297–304.
- Shiralipour, A., McConnell, D., Smith, W., 1997. Phytotoxic effects of a short-chain fatty acid on seed germination and root length of *Cucumis sativus* cv. 'Poinset'. *Compost Sci. Util.* 5, 47–52.
- Singleton, V., Rossi, J.A., 1965. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *Am. J. Enol. Vitic.* 16, 144–158.
- Tuhkanen, T., 2004. UV/H₂O₂ processes. In: Parsons, S. (Ed.), *Advanced Oxidation Processes for Water and Wastewater Treatment*. IWA, London UK, pp. 86–109.
- Vione, D., Merlo, F., Maurino, V., Minero, C., 2004. Effect of humic acids on the Fenton degradation of phenol. *Environ. Chem. Lett.* 2, 129–133.
- Zapata, A., Velegraki, T., Sánchez-Pérez, J., Mantzavinos, D., Maldonado, M., Malato, S., 2009. Solar photo-Fenton treatment of pesticides in water: effect of iron concentration on degradation and assessment of ecotoxicity and biodegradability. *Appl. Catal. B Environ.* 88, 448–454.
- Zhang, H., Choi, H.J., Huang, C., 2006. Treatment of landfill leachate by Fenton's reagent in a continuous stirred tank reactor. *J. Hazard. Mater.* 136, 618–623.