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Sequential coagulation–flocculation, solvent extraction and photo-Fenton oxidation for the valorization and treatment of olive mill effluent

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HIGHLIGHTS

- OME was treated by coagulation–flocculation, solvent extraction and solar-Fenton.
- The solid particles were successfully removed (97%) by coagulation–flocculation.
- Solvent extraction was applied to recover a fraction (36%) of the remaining TPs.
- Solar-Fenton was able to reduce the residual COD and TP, at 73% and 87%, respectively.

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ABSTRACT

An innovative process battery comprising coagulation–flocculation, extraction of phenolic compounds and photo-Fenton post-oxidation has been developed for the valorization and treatment of olive mill effluents (OMEs). Pre-conditioning by coagulation–flocculation using $FeSO_4{\cdot}7H_2O$ as the coagulant, and an anionic polyelectrolyte (FLOCAN 23) as the flocculant was performed to remove the solid content of the effluent. The addition of 6.67 g/L of $FeSO_4{\cdot}7H_2O$ and 0.287 g/L of FLOCAN 23 led to the optimal removal of total suspended solids (TSS) (97 ± 1.3%), of Chemical Oxygen Demand (COD) (72 ± 1.5%), and of Total Phenols (TPs) (40 ± 1.3%). Solvent extraction was then applied to recover a fraction of the remaining phenolic compounds; for instance, extraction for 15 min with ethyl acetate at a solvent to sample ratio of 2:1 (v/v) led to 36% TP recovery post-coagulation–flocculation. Finally, photo-Fenton was applied as a post-treatment method; oxidation for 240 min at 0.2 g/L Fe^{2+}, 5 g/L H_2O_2 and pH = 3 reduced the remaining COD and TP by 73 ± 2.3% and 87 ± 3.1%, respectively. Toxicity assays to *Daphnia magna* as well as phytotoxicity tests to three plant species to untreated OME and oxidized samples were also performed, indicating the evolution of more biologically potent products during the oxidation.

1. Introduction

Olive oil production is an agro-industrial activity of vital economic significance for the Mediterranean countries [1]. However, the production of olive oil leads to the generation of large volumes of olive mill effluent (OME), which are difficult to be treated and managed. OME is an acidic, dark brown stream consisting of water, organic matter and minerals. Its polluting load is typically characterized by Chemical Oxygen Demand (COD) and biochemical oxygen demand (BOD_5) values up to 220 g/L and 100 g/L respectively, with the organic matter mainly comprising polyphenols, polysaccharides, sugars, proteins, nitrogenous organics, tannins and fats [2,3]. Moreover, OME has been found to be very phytotoxic and it also inhibits microbial activity because of the biocidal activity of the aromatic compounds contained. Therefore, there has been an increasing effort for the development of processes capable of purifying OME [4].

Through the years, researchers have tested a variety of technologies for OME 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 OME mineralization [5–7], i.e. aerobic treatment of OME with *Geotrichum candidum* led to 55% COD and 47% TP removal respectively [8], while anaerobic processes have resulted in 50–70% COD, and 70–80% TP removal

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Fig. 1. Schematic presentation of the treatment steps applied on the OME.

respectively [9]. In addition to biological processes, physicochemical processes such as coagulation–flocculation [10] and membrane separation [11,12] have also been employed for OME treatment. Integrating physicochemical and biological methods is conceptually advantageous as the combined process may benefit from the specific features of the individual processes [7].

During the past several years advanced oxidation processes, including ozonation [13], homogeneous ($Fe^{2+}/H_2O_2/UV$) [14], and heterogeneous ($TiO_2/H_2O_2/UV$) photocatalysis [14], electrochemical oxidation and wet air oxidation [15,16], have extensively been studied for OME treatment. In several cases, the treatment target has been the removal of inhibitory and/or toxic aromatic compounds and this has been proven to be achievable by ozonation [17] and photo-Fenton oxidation [18].

Another important aspect gaining ground is that OME contains high-value natural compounds such as polyphenols (e.g. caffeic acid, hydroxytyrosol, tyrosol, oleuropein) that exhibit potential antioxidant properties and can be used in the cosmetic, pharmaceutical and food industries [19]. It should be noted here that the market price of polyphenols is estimated at 2000 €/kg, while according to Obied et al. [20] the price of pure hydrotyrosol ranges between 800 and 1800 €/g. Up to today, several methods for polyphenols recovery have been suggested, including solvent extraction [21], adsorption onto resins [22], supercritical fluid extraction [23], and selective concentration by membrane filtration [24].

Although, numerous studies have dealt with the biological, chemical and physical treatment of OME, an integrated methodology aiming at both effluent valorization and treatment has yet to be addressed in the literature. In this respect, the aim of this work was to study the combined application of coagulation–flocculation for OME pre-conditioning, solvent extraction for the recovery of target polyphenols (i.e. tyrosol, hydroxytyrosol, oleuropein, caffeic and gallic acids), and photo-Fenton technology for OME post-mineralization. A schematic showing the processes applied within this study on OME, is provided (Fig. 1).

Firstly, the optimal coagulation–flocculation conditions were established (i.e. type and dosage of coagulant and flocculant) for the complete removal of solid particles from the effluent. Secondly, solvent extraction was tested and optimized (i.e. type and volume of solvent, extraction time) for polyphenols recovery and, finally, photo-Fenton was investigated as the final, polishing step. Phytotoxicity of OME (% germination index) was assessed in samples collected before and after photo-Fenton application, using various plants seeds. Furthermore, the acute toxicity of the OME to *Daphnia magna* was also examined.

2. Materials and methods

2.1. Chemicals

$FeSO_4{\cdot}7H_2O$ (ACS reagent, ⩾99.0%), H_2O_2 (30 wt.%, ACS reagent) and H_2SO_4 (ACS reagent, 95–98%) were purchased from Sigma–Aldrich and used without further purification. The anionic polyelectrolyte FLOCAN 23 was manufactured by SNF Floergerand purchased from ChemFlo-Hellas. It is high molecular weight poly-acrylamide with a bulk specific gravity of about 0.8, while its degree of charge varies from low to medium to high. Methanol, ethyl acetate, isopropanol, chloroform, dichloromethane and diethylether were of analytical grade and purchased from Merck. Acetonitrile and acetic acid were HPLC grade and purchased from Merck. Oleuropein, hydroxytyrosol, tyrosol, caffeic and monohydrate gallic acids with purity of 98–99% were purchased from Extrasynthese and Sigma Aldrich.

2.2. Olive mill effluent

Olive mill effluents were collected during the 2011 and 2012 production campaigns from a three-phase mill located in Nicosia, Cyprus. The samples were stored at 4 °C and shaken well before all the experiments. The main physicochemical properties of the raw OME used in this work are shown in Table 1.

2.3. Coagulation–flocculation experiments

A Jar-test apparatus (Phipps & Bird, Richmond, VA USA) with six 2 L glass beakers was employed for coagulation–flocculation experiments. Specifically, OME samples were thoroughly shaken for re-suspension of possible settled solids and then, 300 mL of the sample were transferred to the beaker. For experiments where both coagulant and flocculant were used, firstly an appropriate dosage of coagulant was added directly, while stirring for 5 min at 200 rpm; fast stirring was required to destabilize the suspension. This was followed by a transfer of a measured volume of 0.1% polyelectrolyte solution, while stirring for another 5 min at 200 rpm. Finally, the mixture was stirred for another 30 min at 90 rpm to provide the agglomeration [25]. Imhoff settling cones of 1 L capacity were used to measure the volume of the resulting liquid and solid phases following separation.

2.4. Solvent extraction

Solvent extraction was tested with either model/synthetic solutions of tyrosol, hydroxytyrosol, oleuropein, gallic and caffeic acids or actual OME. Batch equilibrium experiments were performed with four organic solvent systems, namely ethyl acetate, dichloromethane, diethylether and a 7:3 mixture of chloroform:isopropanol under different extraction periods between 0.25 and 24 h and a solvent to sample ratio of 100:50 (in mL). The initial concentration was 250 mg/L for gallic acid, caffeic acid and oleuropein, and 1000 mg/L for tyrosol; the aforementioned values are representative of the relative concentration of these compounds in real OME [22]. The flasks were sealed and placed on a magnetic stirrer at ambient temperature. Phase separation was then achieved in a separate funnel. The organic layer was evaporated to dryness at 50 °C in a water bath under vacuum. The organic residue was then reconstituted using 25 mL methanol. Having selected the best solvent in terms of separation efficiency for each individual compound, experiments were repeated with synthetic solutions containing a mixture of gallic and caffeic acids and oleuropein at a cumulative concentration of 250 mg/L in order to evaluate the effect of the organic matrix on separation yield. Finally, extraction assays were realized with the actual effluent.

Table 1
Variation in characteristics of OME.

Parameter (in g/L)	Minimum	Maximum	Average	Standard deviation
pH	5.1	5.5	5.3	0.2
COD	32.2	58.5	43.3	10.5
BOD	9.20	15.6	11.00	3.9
DOC	9.90	24.1	8.01	2.25
TS	43.3	198.0	94.3	6.5
TSS	17.6	56.7	34.05	15.49
TP	1.5	2.0	1.67	0.23
Total-Phosphorus	0.10	0.22	0.17	0.05
Total-Nitrogen	0.16	0.29	0.23	0.06

2.5. Photo-Fenton oxidation

Fenton experiments were carried out in a cylindrical Pyrex vessel of 350 mL volume at 25 °C, while radiation was provided by a solar simulator (Newport 91193) equipped with a 1000 W Xenon lamp. A radiometer (Newport 70260) was employed to determine radiation intensity at 272.3 W/m^2. The pH of the OME sample was adjusted to 3 adding a measured volume of 2 M H_2SO_4. Then, the appropriate amount of $FeSO_4{\cdot}7H_2O$ and H_2O_2 were added into the sample and the reaction mixture was stirred for 240 min. Samples (5 mL) were taken periodically from the reactor and transferred in a tube containing a certain quantity of MnO_2 to remove the residual H_2O_2. The samples were then filtered through 0.22 μm Millipore filters prior to further analysis. The residual hydrogen peroxide concentration was determined spectrophotometrically at 450 nm according to the ammonium metavanadate method [26]. The presence of H_2O_2 in the treated samples was also monitored using Merckoquent® test sticks.

2.6. Analytical methods

TS, TSS, BOD_5, total nitrogen and phosphorus were measured according to standard methods [27]. TP were determined colorimetrically according to the Folin–Ciocalteu method [28]. A calibration curve was prepared using standard solutions of gallic acid in ethanol/water; therefore, TP concentrations are expressed as gallic acid equivalent. COD was analyzed by the closed reflux colorimetric method (Merck^{R}Spectroquant kits). DOC was measured on a Shimadzu (TOC-VCPH/CPN) TOC analyzer with autosampler ASI-V. pH was recorded with a pH meter (EZDO pH/mV/Temp meter). A UV–Vis Jasco V-530 spectrophotometer was used to measure OME color. Ferric ion concentration in wastewater samples was measured by the Atomic Absorption Spectrometer, Perkin Elmer Analyst-200.

The identification and quantitation of the phenolic compounds of the OME extracts were performed using an Alliance 2690 series HPLC equipped with a UV–Vis detector. Separation was achieved on an ACE C18-R, reverse-phase column (250 mm × 4.6 mm, id 5 μm) employing a gradient elution program with two solvents (i.e. ultra pure water adjusted to pH 2.5 with acetic acid and acetonitrile). Separation was achieved on an ACE C18-R, reverse-phase column (250 mm × 4.6 mm, id 5 μm) employing a gradient elution program with two solvents, ultra pure water adjusted to pH 2.5 with acetic acid (A) and acetonitrile (B). The elution program was as follows: 0–10 min 90% A; 10–15 min 70% A; 15–17 min 66% A; 17–22 min 5% A; 22–26 min 90% A. The flow rate was 0.7 mL/min for a total running time of 26 min and the detector was set at 280 nm.

2.7. Phytotoxicity and acute toxicity assays

Phytotoxicity assays were performed using Phytotest kit microbiotest (MicroBioTests Inc.). The phytotoxicity of OME samples prior to and after photo-Fenton oxidation was assessed against three plant seeds, i.e. *Sorghum saccharatum*, *Lepidium sativum* and *Sinapis alba*. A black paper, placed on top of the test plate, was carefully irrigated with 20 mL of the respective sample. Ten seeds were then placed on top of the black paper – in one row and at equal distance to each other – of the test plate, and the plates were then located in a vertical position exposed to light for 72 h. In parallel, blank samples were also run, where seeds were irrigated with distilled water. The germination index (GI) is defined as follows:

$$\%GI = 100 \times (S_D/S_B) \times (L_D/L_B) \quad (1)$$

where S_D and S_B are the number of germinated seeds for the sample and the blank, respectively, and L_D and L_B are the average root length of seeds for the sample and the blank, respectively.

The acute toxicity of OME samples to *D. magna* was evaluated using the Daphtoxkit FTH magna. The experimental procedure for conducting this assay was based on the ISO 6341 standard protocol [29]. Tests were carried out with 5 daphnids introduced into the 100 mL test vessel at pH = 7–8, ambient temperature and dissolved oxygen concentration of at least 6 mg/L. Young *D. magna* were used in the test and exposed for 24 h and 48 h.

3. Results and discussion

The percentage of removal in all cases is calculated as function of the previous stage. Particularly, coagulation–flocculation was used as the first stage of the OME treatment to remove the high particles concentration. By this method, apart from the TSS removal, the COD and TP were also reduced, thus enhancing the quality of the effluent. Liquid–liquid extraction method was applied on pre-conditioned samples providing a further decrease of TP from the remaining concentration. At the final stage, using photo-Fenton as the post-treatment process on the pre-treated OME, the residual TP was removed up to 87%–95% after the extraction procedure. The target of the present work was to remove as much as possible the high organic load from the wastewater by combining the above processes. All the processed applied are described in detail in the sections below.

3.1. Coagulation–flocculation

A series of experiments were performed to assess the performance of coagulation–flocculation as a pre-conditioning stage to remove the solid content of OME, and the results obtained are presented in Table 2. These runs at $FeSO_4{\cdot}7H_2O$ concentrations between 3.33 g/L and 6.67 g/L and FLOCAN 23 concentrations between 0.07 g/L and 0.287 g/L. Complete (97 ± 1.3%) TSS removal was achieved combining 6.67 g/L of coagulant and 0.287 g/L of polyelectrolyte at OME's inherent pH (5.3), and this was accompanied by 72 ± 1.5% COD and 40 ± 1.3% TP removal. Decreasing coagulant dosage at 5 g/L (while keeping the flocculant concentration unchanged) resulted in 93 ± 1% TSS removal, while COD and TP removal also slightly dropped to 68 ± 2% and 30 ± 1.7%, respectively. Ginos et al., who studied OME treatment by coagulation–flocculation, reported similar TSS removal using 5 g/L of $FeSO_4{\cdot}7H_2O$ and 0.287 g/L of FLOCAN 23 although the level of COD and TP reduction was about 50% lower [30]. Discrepancies between the two studies may be attributed to different operating conditions (i.e. longer stirring times were employed in this study), as well as different OME samples tested. It should also be noted that the use of the specific coagulant and flocculant does not alter the acidic, inherent pH of OME, and this is significant from a practical point of view since photo-Fenton post-oxidation would require acidic media.

3.2. Recovery of phenolic compounds

The recovery of polyphenols from OME provides the concurrent opportunity to obtain high-value natural compounds and decrease

Table 2
Effect of coagulant and flocculant on OME treatment efficiency.

Conditions of coagulation–flocculation		% Removal		
$FeSO_4{\cdot}7H_2O$ (g/L)	FLOCAN 23 (g/L)	TSS	COD	TP
3.33	0.287	41 ± 2.5	30 ± 2.8	26 ± 5.7
5.0	0.07	29 ± 1.8	39 ± 3.0	19 ± 4.9
5.0	0.14	44 ± 1.7	48 ± 3.8	34 ± 1.5
5.0	0.287	93 ± 1.0	68 ± 2.0	20 ± 1.7
6.67	0.287	97 ± 1.3	72 ± 1.5	40 ± 1.3

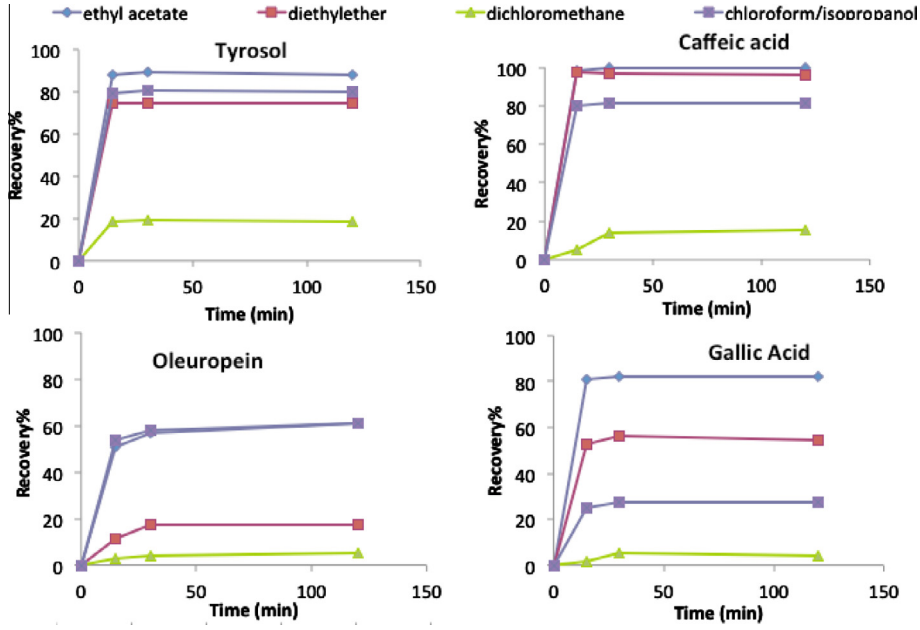

Fig. 2. Extraction recoveries of gallic acid, caffeic acid, oleuropein and tyrosol with four different solvent systems.

the toxicity of the effluent. Preliminary experiments were conducted in order to examine the effect of solvent on the rate of mass transport for each one of the selected compounds in model solutions; the respective results are shown in Fig. 2, where the recovery of each compound in single-component systems is plotted as a function of extraction time and solvent. As clearly seen, the system can reach equilibrium within 15 min for all extraction systems; it should be noted that the total extraction time was 24 h but only data for the first 120 min are shown in Fig. 2. Ethyl acetate appears to be the most efficient solvent in terms of recovery, which is 98% for caffeic acid, 89% for tyrosol, 79% for gallic acid and 68% for oleuropein.

Experiments were repeated with a mixture of gallic and caffeic acids and oleuropein at a cumulative concentration of 250 mg/L in order to test the effect of the organic matrix on separation yield. It was found (data not shown) that the matrix did not affect considerably the extraction recovery of oleuropein and caffeic acid with the respective yields being 66% and 95%. On the other hand, the matrix partially affected gallic acid recovery, which dropped from 79% to 61%. These results are promising since relatively high recoveries can be achieved; Grizis et al. reported that the absolute recovery of tyrosol and oleuropeinfrom model solutions acidified with HCl was as low as 44.5% and 9.5%, respectively with ethyl acetate [31].

Having selected ethyl acetate as the most efficient solvent, 15 min extractions were performed with OME samples that had or had not been subjected to coagulation–flocculation. It was found that the process suffered from the partial diffusion of organic solvent in the effluent, thus resulting in a COD increase of about 133%. To rectify this, anhydrous sodium sulfate was added to the OME prior to extraction at 8% w/v concentration; in this case, solvent diffusion was partly impeded leading to only about 33% COD increase in the effluent and this was also accompanied by a slight improvement of extraction recovery. Table 3 summarizes results from various OME samples; depending on the pre-conditioning step, hydroxytyrosol recovery ranges from 163 to 584 mg/L, tyrosol from 19 to 116 mg/L and TP from 1487 to 2064 mg/L. For TP, this corresponds to 33%–47% recovery (Table 4) but the respective val-

Table 3
Effect of OME pre-conditioning on extraction recovery with ethyl acetate.

Conditions of pre-conditioning	Phenolic extracts (mg/L)		
	Hydroxytyrosol	Tyrosol	TP
$FeSO_4 \cdot 7H_2O$(5 g/L) + FLOCAN 23 (0.287 g/L)	584	99	2064
$FeSO_4 \cdot 7H_2O$(6.67 g/L) + FLOCAN 23 (0.287 g/L)	260	19	1487
No pre-conditioning – Various OME samples	163–554	38–116	1670–1818

Table 4
Removal of TP during each process. Extraction was done with ethyl acetate, while photo-Fenton oxidation conditions were H_2O_2 = 5 g/L; Fe^{2+} = 0.2 g/L; pH = 3.

Conditions of pre-conditioning	TP removal (%)		
	Coagulation	Extraction	photo-Fenton
$FeSO_4 \cdot 7H_2O$ (5 g/L) + FLOCAN 23 (0.287 g/L)	20	–	71 ± 2.9
$FeSO_4 \cdot 7H_2O$ (5 g/L) + FLOCAN 23 (0.287 g/L)	20	47	95 ± 3.8
$FeSO_4 \cdot 7H_2O$ (6.67 g/L) + FLOCAN 23 (0.287 g/L)	40	–	77 ± 3.4
$FeSO_4 \cdot 7H_2O$ (6.67 g/L) + FLOCAN 23 (0.287 g/L)	40	36	87 ± 3.1
No pre-conditioning – Various OME samples	–	33–37	82 ± 4.2–91 ± 2.3

ues for hydroxytyrosol and tyrosol cannot be computed since their initial concentration in the OME was not determined due to analytical limitations. In all cases, oleuropein, caffeic and gallic acids were present in trace amounts. The results of Table 3 can be interpreted based on the removal efficiencies of coagulation–flocculation; for example, coagulation with 5 g/L $FeSO_4{\cdot}7H_2O$ results in 10% less TP removal (see section coagulation–flocculation) than with 6.67 g/L and this implies that more phenolic compounds are available for recovery. Interestingly, the extracts from the untreated OME samples show considerable variability in terms of extraction efficiency (this is more pronounced for tyrosol and hydroxytyrosol), thus highlighting the importance of the raw material. Each m^3 of OME sample could yield, upon extraction, 0.277 kg of hydroxytyrosol and 0.058 kg of tyrosol. Leonardis et al. reported comparable recoveries for extraction with ethyl acetate, i.e. up to 0.34 kg hydroxytyrosol and 0.083 kg tyrosol [32]. Agalias et al. [22] has reported a recovery of up to 0.58 kg hydroxytyrosol from 1 m^3 OME.

3.3. Photo-Fenton

3.3.1. Photo-Fenton oxidation of raw OME

To assess the ability of photo-Fenton to treat OME, preliminary experiments were performed with raw OME that had been diluted 30 times with tap water (i.e. COD_0 = 1.950 g/L). The effect of varying H_2O_2 and Fe^{2+} concentration on COD and DOC removal after 240 min of reaction at pH = 3 is shown in Fig. 3.

Increasing H_2O_2 concentration up to 5 g/L increases both COD and DOC removal up to 86 ± 2.9% and 86 ± 1%, respectively, while a further increase to 6 g/L has practically no effect. Most of the reactions occur within the first 90–120 min, as clearly seen in Fig. 4 that shows temporal profiles of COD and UV–Vis absorbance during OME photo-Fenton oxidation at 0.2 g/L Fe^{2+} and 5 g/L H_2O_2. Moreover, TP and BOD_5 removal values of 83 ± 2.6% and 94 ± 3.4% were recorded after 240 min, thus highlighting the oxidative capacity of the photo-Fenton process; this was also accompanied by 62% decolorization (Fig. 4b). This is due to the increased production of $HO^{\cdot}$ radicals compared to the dark Fenton reaction, thus increasing the oxidation rates of organic pollutants.

Although the residual concentration of Fe^{2+} after the coagulation–flocculation step was found to be around 400 mg/L, it was not capable of inducing Fenton reactions, probably due to the presence of Fe^{2+} complexes with organic ligands present in the wastewater. An increase in Fe^{2+} concentration beyond 0.2 g/L at 5 g/L H_2O_2 has a consistently detrimental effect on treatment efficiency, as seen in Fig. 3b. It is well-documented that ferrous ions in excess may scavenge radicals, thus decreasing degradation rates [33,34].

3.3.2. Effect of photo-Fenton oxidation on phytotoxicity

The effect of photo-Fenton process on phytotoxicity is illustrated in Fig. 5a. As seen, OME prior to oxidation exhibits no phytotoxicity to *L. sativum* and *S. alba* and it is only partially phytotoxic to *S. saccharatum*. Upon oxidation, phytotoxicity generally increases, thus implying the formation of transformation by-products that are more toxic than the original matrix. Fig. 5b shows the extent of immobilization of *D. magna* after 240 min of photo-Fenton oxidation at various OME concentrations. The unoxidized sample led to 40% and 85% immobilization after 24 h and 48 h

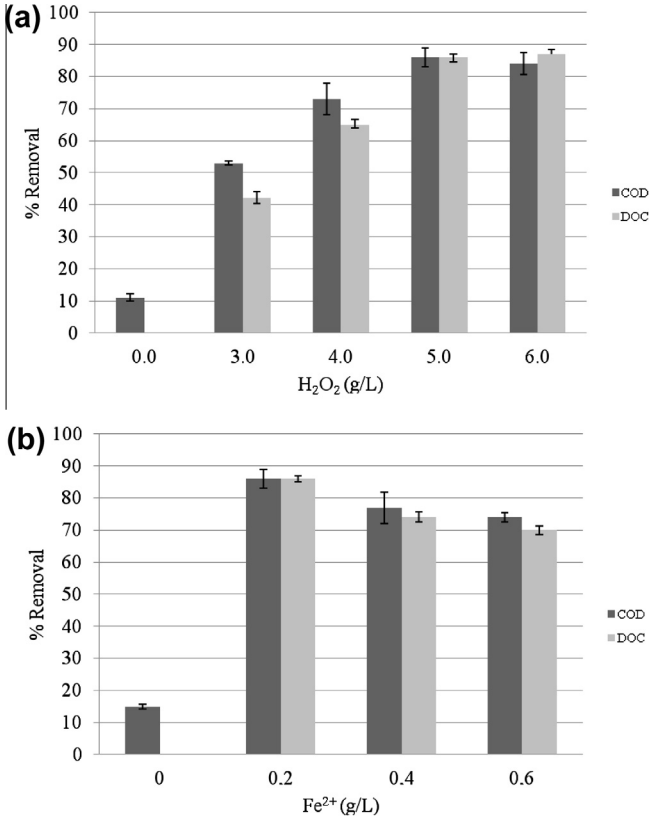

Fig. 3. Effect of (a) H_2O_2 concentration at 0.2 g/L Fe^{2+} and (b) Fe^{2+} concentration at 5 g/L H_2O_2 on COD and DOC removal of diluted, raw OME by photo-Fenton oxidation. Other conditions: COD_0 = 1950 mg/L; treatment time = 240 min; pH = 3.

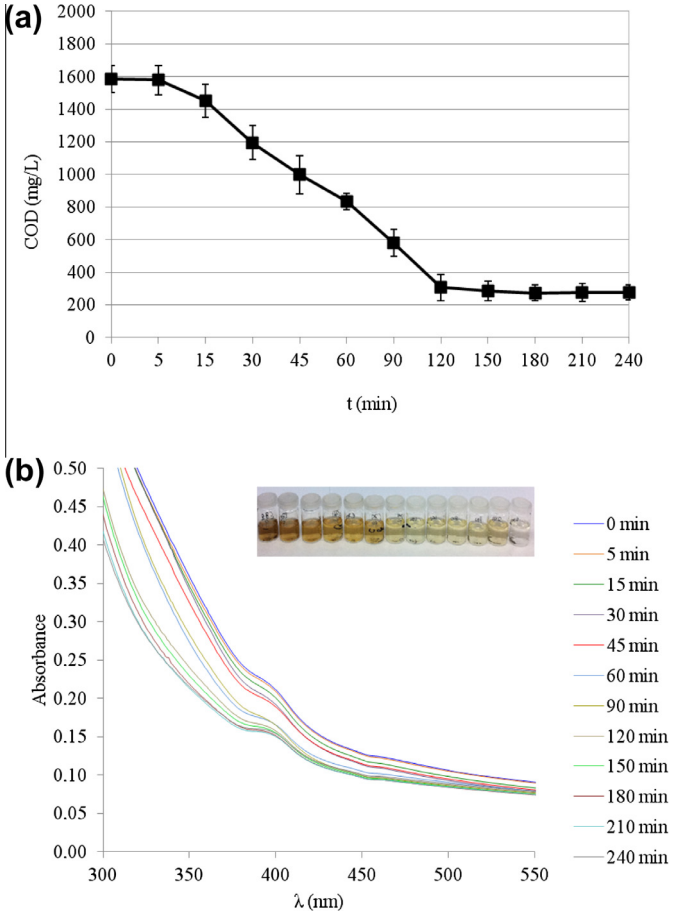

Fig. 4. Temporal profiles of (a) COD and (b) UV–Vis absorbance during photo-Fenton oxidation of diluted, raw OME. Other conditions: COD_0 = 1950 mg/L; H_2O_2 = 5 g/L; Fe^{2+} = 0.2 g/L; pH = 3. Inset graph shows changes in sample color.

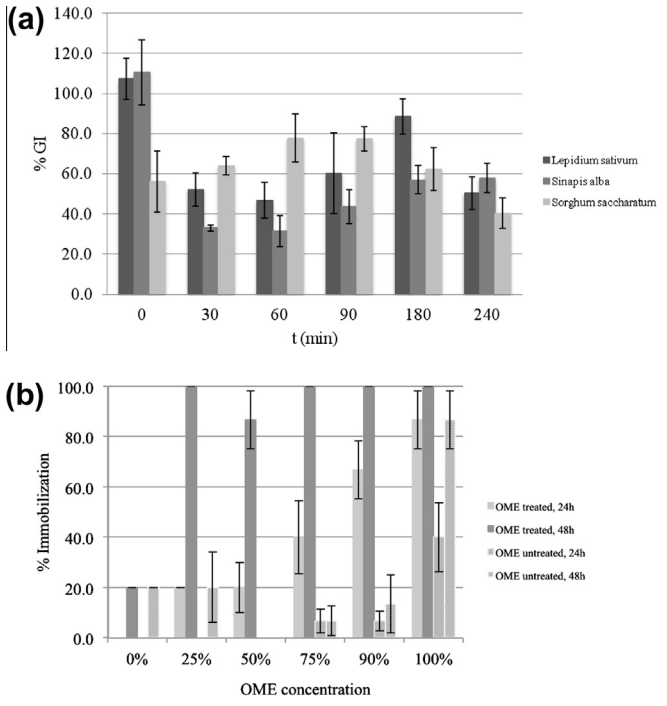

Fig. 5. (a) Evolution of phytotoxicity during photo-Fenton oxidation of diluted, raw OME. (b) Acute toxicity to *D. magna* after 240 min of photo-Fenton oxidation at various OME concentrations. Other conditions as in Fig. 4.

exposure, respectively with the corresponding values after 240 min of reaction (100% concentration) being 87% and 100%. Experiments of toxicity assays were performed in a variety of dilutions, as shown in Fig. 5b. When the toxicity of a complex mixture such as OME is studied, the concentration usually is referred to as the percentage of the diluted solution.

Comparing oxidized and unoxidized samples at different concentrations results in similar conclusions, i.e. the latter are always less toxic than the former and this is consistent with phytotoxicity data and the likely formation of persistent by-products.

3.3.3. Photo-Fenton oxidation after coagulation–flocculation

OME taken (COD_0 = 12.11 g/L, before dilution 30×) after coagulation–flocculation with 6.67 g/L of $FeSO_4{\cdot}7H_2O$ and 0.287 g/L of polyelectrolyte was subjected to photo-Fenton at 0.2 g/L Fe^{2+}, 5 g/L H_2O_2, pH = 3 and irradiation time of 240 min. Photo-Fenton post-treatment led to 85 ± 2.6% and 77 ± 3.2% removal of the remaining COD and TP, respectively, thus clearly demonstrating the positive effect of photo-Fenton treatment on the pre-conditioned OME samples. Ahmed et al. [18] recently reported that sequential OME treatment comprising sedimentation, sand filtration and photo-Fenton oxidation (0.03 g/L Fe^{2+}, 3 g/L H_2O_2 and pH = 3) led to an overall 82% COD removal, which is comparable to the results obtained in this work.

3.3.4. Photo-Fenton oxidation after coagulation–flocculation and solvent extraction

The application of photo-Fenton oxidation on OME samples that had already been pretreated by coagulation–flocculation in order to remove the solids and then valorization by solvent extraction was also investigated and representative results are summarized in Table 4. It should be noted here that the quoted removal values of each step have been computed based on the final concentrations of the previous stage. For instance, coagulation–flocculation with 6.67 g/L of $FeSO_4{\cdot}7H_2O$ and 0.287 g/L of polyelectrolyte removed 72 ± 1.5% of COD and 40 ± 1.3% of TP. Subsequent ethyl acetate extraction recovered 36% of the residual TP and the remaining stream (COD_0 = 16.11 g/L, before dilution 30x) was subjected to photo-Fenton at 0.2 g/L Fe^{2+}, 5 g/L H_2O_2 and pH = 3; this final, polishing step led to 87 ± 3.1% and 73 ± 2.3% removal of the residual TP and COD, respectively.

In conclusion, when applying coagulation–flocculation and photo-Fenton processes on OME, the TP concentration decreases from 1.67 g/L to 0.23 g/L. In the cases where, the solvent extraction was also applied, the TP concentration was reduced from 1.67 g/L to 0.083 g/L. Thus, by comparing the results in Table 4 (percentages are provided calculated using the remaining concentration of TPs at each process), it is evident that the stage of liquid–liquid extraction led to better TP removal when compared to applying coagulation–flocculation and photo-Fenton alone.

4. Conclusions

To the best of our knowledge, this is one of the few reports dealing with the integrated management of difficult agro-industrial effluents, like OME in a sustainable way. The proposed strategy combines technologically simple and relatively inexpensive treatment technologies such as iron-based coagulation and advanced oxidation driven by solar radiation with solvent extraction for effluent valorization through the recovery of high-value natural antioxidants.

Coagulation–flocculation is suggested as a pre-conditioning stage to remove the excessive concentration of solids typically found in OME. This can easily be done using ferrous salts acting as coagulants and low dosages of polyelectrolytes acting as flocculants. This step will inevitably precipitate part of OME organic matter including the polyphenolic fraction, which is responsible for the biorecalcitrant and/or toxic properties of OME. On the other hand, this very fraction possesses much sought antioxidant properties and should be recovered rather than destroyed. Solvent extraction is, therefore, proposed as a simple process to achieve this goal. In order to estimate the sustainability of the solvent extraction technique, life cycle assessment could be applied taking into account the market price of the recovered antioxidants, as well as parameters such as the type, cost and environmental compatibility of the solvent employed in the process. Post extraction, the residual stream still contains considerable concentrations of organic matter and needs to be treated prior to its final disposal. Homogeneous photocatalysis induced by solar radiation appears to be a promising technology not entailing high costs (with the possible exception of hydrogen peroxide). Further to what has been applied within the framework of this study, more research is now performed in trying to apply a statistical approach to confirm the set of optimum conditions obtained from the varied photo-Fenton experiments. More specifically, a two-level factorial experimental design is now being implemented to assess the effect of four independent variables such as, (i) hydrogen peroxide concentration, (ii) iron concentration, (iii) type of iron ions and (iv) dilution factor. It is apparent that further optimization of the work performed in this study is still possible. Overall, the proposed process battery is capable of mineralizing a strong agro-industrial effluent through well established, simple and environmentally benign unit operations.

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