Treatment of olive mill effluents by coagulation–flocculation–hydrogen peroxide oxidation and effect on phytotoxicity

Andreas Ginos [a], Thrassyvoulos Manios [b], Dionissios Mantzavinos [a,*]

[a] *Department of Environmental Engineering, Technical University of Crete, Polytechneioupolis, GR-73100 Chania, Greece*
[b] *School of Agricultural Technology, Technological and Educational Institute of Crete, GR-71500 Heraklion, Greece*

Abstract

The pre-treatment of olive mill effluents (OME) by means of coagulation–flocculation coupling various inorganic materials and organic poly-electrolytes was investigated. Tests were conducted with two different OME with chemical oxygen demand (COD) contents of 61.1 and 29.3 g/L, total suspended solids (TSS) of 36.7 and 52.7 g/L and total phenolic contents (TP) of 3.5 and 2.5 g/L, respectively. Inorganic materials such as lime, iron, magnesium and aluminum as well as four cationic and two anionic commercial poly-electrolytes were employed either alone or in various combinations and screened with respect to their efficiency in terms of TSS, TP and COD removal, the amount of sludge produced and the phytotoxicity of the resulting liquid to lettuce seeds. Coupling lime or ferrous sulphate (in the range of several g/L) with cationic poly-electrolytes (in the range of 200–300 mg/L) led to quantitative TSS removal, while COD and TP removal varied between about 10–40% and 30–80%, respectively, depending on the materials and the effluent in question; separation efficiency generally decreased with decreasing coagulant and/or flocculant concentration. To enhance organic matter degradation, iron-based coagulation was coupled with H_2O_2, thus simulating a Fenton reaction and this increased COD reduction to about 60%. The original, untreated OME 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.
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1. Introduction

Olive mill effluent (OME) management and treatment has been a major issue of environmental concern in the Mediterranean Sea area due to the unique features associated with this type of agro-industrial waste. In particular, OME are strong, seasonally generated effluents with a highly diverse organic load that reaches values as high as 220 g/L COD and also contain large amounts of suspended solids up to about 190 g/L. Amongst other organic constituents, OME contain high concentrations of phenolic compounds up to about 10 g/L that render, alongside the high organic load, OME hardly biodegradable and quite phytotoxic [1,2]. Unfortunately, dumping OME in evaporation ponds is the most common practice regarding OME treatment in Greece (the third largest olive oil-producing country in the world) and

indeed elsewhere in the Mediterranean. In some cases, lagooning is coupled with lime coagulation to remove suspended solids. Unfortunately, this practice suffers from serious drawbacks such as high cost, low efficiency and sludge-disposal problems. Interestingly and depending on the climatic conditions, OME may not evaporate by the end of the summer, thus making the pond unavailable to accept the following year's load. Moreover, fermentation processes may occur in these weathered OME, thus resulting in the formation of methane and other gases; OME can become extremely malodorous especially between late spring and summer.

Several research efforts aiming at the development of efficient technologies for the destruction of the organic matter in OME have been reported in the literature; these technologies are based on biological (anaerobic and aerobic) and advanced oxidation (such as ozonation, the Fenton's reagent, electrochemical oxidation and several others) processes as well as various combinations of them and have recently been reviewed elsewhere [1,3].

* Corresponding author. Tel.: +30 282 10 37797; fax: +30 282 10 37847.
E-mail address: mantzavi@mred.tuc.gr (D. Mantzavinos).

Given the relatively large amounts of solids typically found in OME, successful treatment may require a pre-conditioning stage to remove the suspended and colloidal fractions, which typically consist of pectins, proteins, oils and tannins. This can be done by means of separation processes such as centrifugation, filtration, clay adsorption, activated carbon adsorption and several case studies have been reported in the literature [4,5]. Coagulation with materials such as lime, alum, ferric chloride and ferrous sulphate has also been employed in OME treatment. Jaouani et al. [6] recently demonstrated a two-stage process comprising aerobic degradation followed by lime coagulation, while Beccari et al. [7] proposed a process comprising OME pre-treatment by means of lime coagulation and adsorption on bentonite followed by anaerobic digestion; they reported that pre-treatment was capable of enhancing considerably the anaerobic treatability of the original effluent. The effect of several OME pre-treatments such as lime or ammonium iron sulphate coagulation, resin adsorption and H_2O_2 oxidation on subsequent anaerobic degradability was investigated by Zouari [8] who found that the pre-treated effluent was always more readily amenable to biodegradation than the original un-treated effluent. In other studies [9], the impact of lime pre-treatment on total solids, COD and phenols removal for seventeen different OME was evaluated. Treatment of OME subject to lime or alum coagulation has also been demonstrated by Flouri et al. [10] and Lagoudianaki et al. [11].

Although coagulation with inorganic materials has, indeed, received some attention for OME treatment, it is notable that there is a lack of information concerning OME pre-conditioning by the combined use of inorganic coagulants and poly-electrolytes, a common practice in water/wastewater treatment. We recently demonstrated the feasibility of OME pre-treatment by direct flocculation (i.e. without the use of inorganic materials) with several cationic and anionic poly-electrolytes [4]; the proposed scheme gave encouraging results despite the relatively high cost of poly-electrolytes compared to lime and other inorganic materials.

The aim of this work was to study OME treatment by the combined use of coagulants and poly-electrolytes and assess the effect of operating conditions such as type and concentration of coagulant and flocculant, addition of H_2O_2 on TSS, TP and COD removal as well as on the amount of sludge produced. Moreover, the phytotoxicity of the resulting liquid phase to lettuce seeds was also evaluated and a preliminary cost analysis was conducted.

2. Experimental and analytical

2.1. Materials

OME from two olive mills (W1 and W2 for the rest of the text) located in the region of Chania, W. Crete, Greece were collected and used without any pre-treatment. The average TSS, TP and COD contents of W1 and W2 were 36.7, 3.5 and 61.1 g/L and 52.7, 2.5 and 29.3 g/L, respectively, while their average pH values were 5.3 and 5.1, respectively.

Four cationic (FO-4700-SH, FO-4490-SH, FO-4350-SHU and FO-4190-SH referred to as K1–K4, respectively, for the rest of the text) and two anionic (AN 934-SH and FLOCAN 23 referred to as A1 and A2, respectively, for the rest of the text) poly-electrolytes manufactured by SNF Floerger were provided by ChemFlo-Hellas. All of them are high molecular weight polyacrylamides with a bulk specific gravity of about 0.8, while their degree of charge varies from low to medium to high; for instance, ionicity varies from as low as 6–10% for FO-4190-SH to 30% for AN 934-SH to 70% for FO-4700-SH. In all cases, the appropriate mass of polymer was dissolved in de-ionised water to give 0.1% (w/v) feedstock solutions. This was done since addition of polymers directly in the effluent proved difficult due to their moderate solubility in water.

$Fe(Cl)_3 \cdot 6H_2O$ (Fe(III)), $FeSO_4 \cdot 7H_2O$ (Fe(II)), $MgSO_4 \cdot 7H_2O$ (Mg) and poly-aluminum chloride (Al) were supplied by Riedel, Lancaster, Merck and ChemFlo-Hellas, respectively, while lime was taken from a local supplier; all inorganic materials were used as received. Hydrogen peroxide used for Fenton oxidation experiments was supplied from Fluka as 35% (v/v) solution.

2.2. Experimental procedures

Experiments were carried out in a jar-test apparatus (Velp Scientifica) equipped with six beakers of 1 L volume. At the beginning of each experiment, the OME samples were analysed with respect to their initial TSS, dissolved COD and dissolved TP concentrations (prior to COD and TP analyses, samples were filtered through 0.45 μm disposable filters). The samples were then thoroughly shaken, for re-suspension of possible settled solids and 500 mL of the sample were transferred to the beaker. In a typical coagulation–flocculation run, the appropriate mass of coagulant was added directly to the sample while stirring for 2 min at 200 rpm; fast stirring is needed to destabilise the suspension and this was followed by the addition of a measured volume of the 0.1% poly-electrolyte solution while stirring for 15 min at 90 rpm to facilitate flocs agglomeration. In a previous study [4], we tested the effect of stirring time and speed on OME destabilisation with various poly-electrolytes and found that separation was not practically affected for stirring times between 5 and 30 min and stirring speeds between 45 and 200 rpm. The sample was then left to rest for 60 min and as soon as separation was achieved, the supernatant was analysed with respect to the concentration of TSS, COD and TP. (For those experiments where only coagulant or flocculant was added, a similar procedure was followed with intense mixing for 2 min being followed by stirring for another 15 min at reduced speed.)

For the experiments where coagulation–flocculation was coupled with H_2O_2 oxidation, two strategies for H_2O_2 addition were adopted: in most cases, the oxidant was added immediately after the addition of Fe(II) and the Fenton mixture was left to react for several hours while stirring at 90 rpm; this was followed by the addition of poly-electrolyte to complete separation. In some cases though, coagulation–flocculation with Fe(II) and the poly-electrolyte preceded H_2O_2 addition.

It should be noted that, for the runs with poly-electrolytes and/or H_2O_2, TSS, COD and TP values of the liquid after treatment were corrected for the dilution due to the addition of the flocculant or H_2O_2 solution and the adjusted volumes were used to compute the respective removals. Several experiments were duplicated to test out reproducibility; differences in results from identical experiments were typically below 5%.

2.3. Analytical techniques

TSS and COD were determined according to the procedures described elsewhere [4]. The Folin–Ciocalteau protocol, as described in detail elsewhere [12], was employed to measure the concentration of TP in the liquid phase. Changes in solution pH were measured with a GLP-21 Crison pH-meter. Imhoff settling cones of 1 L capacity were used to measure the volume of the resulting liquid and solid phases following separation.

2.4. Phytotoxicity measurement

The phytotoxic behaviour of the liquid phase to lettuce seeds was assessed for various samples (e.g. untreated OME, OME subject to coagulation–flocculation with or without H_2O_2, aqueous solutions of various coagulants and flocculants). Twenty-five lettuce seeds were placed in standard (10 cm in diameter) Petri dishes covered with three pieces of perforated paper. Seeds and paper were carefully irrigated with 5 mL of the respective sample and the dishes were then covered with tinfoil and placed in an incubator for 72 h at 21 °C. In parallel, blank samples were also run where seeds were irrigated with distilled water. For each sample, phytotoxicity was measured at three dilutions, i.e. for the original, un-diluted sample ($D = 0$), after 1:2 dilution with water ($D = 2$) and after 1:4 dilution with water ($D = 4$). Each analysis was run in six replicates and mean values of germination index are quoted as results. The germination index (GI) is defined as follows:

$$\% \, GI = 100 \times \left(\frac{S_D}{S_B}\right) \times \left(\frac{L_D}{L_B}\right)$$

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

3. Results and discussion

3.1. Screening of various coagulants

Preliminary tests were performed to assess the relative efficiency of various inorganic materials to destabilise W1. Fig. 1 shows the extent of TSS, TP and COD removal using 1000 mg/L of various coagulants with Fe(II) and Mg yielding 95% and 90% TSS removal, respectively. Reducing Fe(II) concentration from 1000 to 100 mg/L (data not shown) decreased TSS removal to 46%. On the other hand, Mg concentrations lower than 1000 mg/L failed to cause separation, while increasing progressively Mg concentration from 1000 to 2000 to 3000 and eventually to 4000 mg/L had practically no effect on TSS
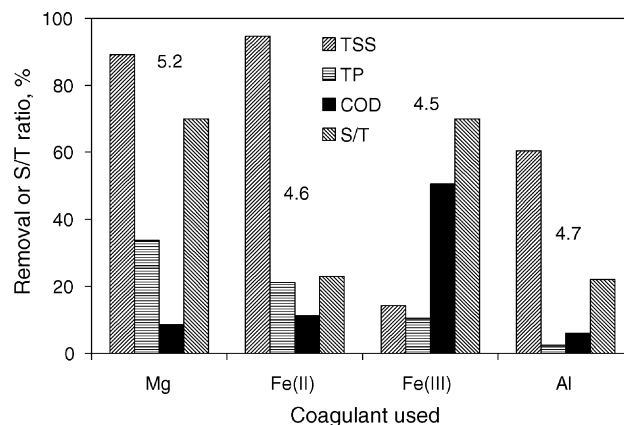

Fig. 1. Relative efficiency of various coagulants at a common concentration of 1000 mg/L for W1 treatment. Numbers next to the bars show pH values after separation. TP and COD refer to dissolved organic matter.

removal (data not shown). Fe(III) at 1000 mg/L led to about 14%, 10% and 50% TSS, TP and COD reduction, respectively; these values were reduced to 5.6%, 7% and 10%, respectively, increasing Fe(III) concentration to 2000 mg/L, while further increase to 3000 mg/L gave no separation (data not shown). Jaouani et al. [6] who studied OME treatment by Fe(III) coagulation reported the existence of an optimum coagulant concentration at which treatment efficiency was maximised; at concentrations greater than the optimum one, separation was suppressed and this was attributed to colloids being restabilised. PAC at a concentration of 1000 mg/L gave moderate TSS removal of about 60%, while COD decrease did not exceed 10%. This may be due to the low solution pH since PAC is particularly effective for pH values above neutral [13]. On the other hand, ferrous sulphate functions over a wide pH range from 3 to 13 [13,14], while ferric salts over about 4.5 [4,13].

Fig. 1 also shows the ratio (S/T) of sludge generated following separation over the total initial volume with Fe(II) and PAC resulting in only about 20% sludge volume, while Fe(III) and Mg gave considerably less concentrated sludge; one should bear in mind that minimisation of sludge production is important considering the cost implications associated with subsequent sludge treatment and disposal. It is also notable that none of these materials changed significantly the pH of the original sample, which was about 5.3 (numbers next to the bars show respective solution pH values for each material).

Lime at 1000 mg/L failed to cause separation and higher concentrations were tested as shown in Fig. 2; lime concentrations up to 40,000 mg/L led to partial OME destabilisation with TSS removal being as low as about 40%, while the pH of the resulting liquid phase increased to about 7–8. However, increasing concentration to 60,000 mg/L resulted in about 85% and 67% TSS and TP removal, respectively, with the solution pH increasing to about 11.5. An additional experiment at 60,000 mg/L lime was carried out with half the initial organic load (e.g. W1 was diluted with water) and the results are also shown in Fig. 2 (last set of data); as can be seen, TP and COD removal expectedly increased with decreasing effluent concentration. The pH range in which lime coagulation occurs may be the single most important factor
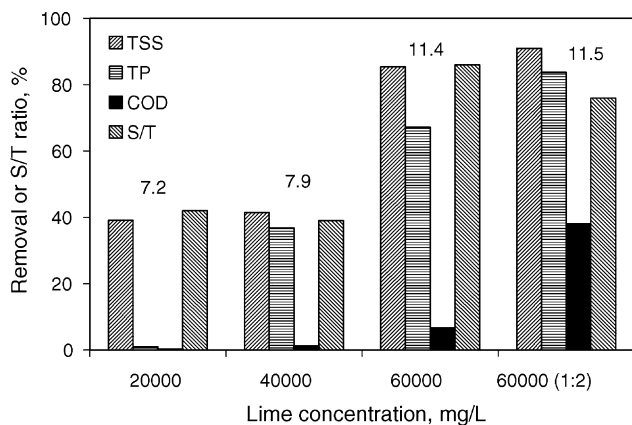
Fig. 2. Effect of lime concentration on W1 separation. Last set of bars shows data with 1:2 diluted W1. Numbers next to the bars show pH values after separation. TP and COD refer to dissolved organic matter.

affecting separation and optimal values are dependent on both lime concentration and effluent characteristics. At the conditions employed in this study, pH values between 11 and 12 resulted in successful separation and this is in accordance with the work of Jaouani et al. [6] and Aktas et al. [9] who reported that OME treatment by lime coagulation would require pH values of about 12.

From the results of Figs. 1 and 2, it appears that OME coagulation with magnesium- or iron-containing materials may be advantageous over lime since (i) the concentration needed with these materials is considerably lower than that with lime to achieve comparable removals, (ii) the change of solution pH following lime addition is far greater than that with other materials and (iii) lime generates greater volumes of sludge. In light of these observations as well as considering common wastewater treatment practices, we decided to proceed our investigations with two relatively inexpensive and readily available materials, namely lime and Fe(II). Their current bulk sales price in Greece is about €130–150 tonne^{-1} which is almost half the price of Fe(III) and PAC. Moreover, Fe(II) can be coupled with H_2O_2, thus enhancing the oxidative degradation of the organic load.

3.2. Treatment by coagulation–flocculation

The effect of coupling 5000 mg/L Fe(II) or 30,000 mg/L lime with various poly-electrolytes on OME treatment is shown in Fig. 3. In all cases, a common poly-electrolyte concentration of 287 mg/L was employed. All flocculants gave over 80% solids separation with K1 and K2 being slightly more effective than the rest in terms of both TSS removal and the quantity of sludge produced. For instance, the K1/Fe(II) pair led to 95%, 33% and 22% TSS, TP and COD removal, respectively, with the corresponding values for the K1/lime pair being 89%, 46% and 11%. On the other hand, the K2/Fe(II) pair led to 98%, 34% and 28% TSS, TP and COD removal, respectively, with the corresponding values for the K2/lime pair being 98%, 48% and 11%. Therefore, all subsequent experiments were carried out with K1 and K2.
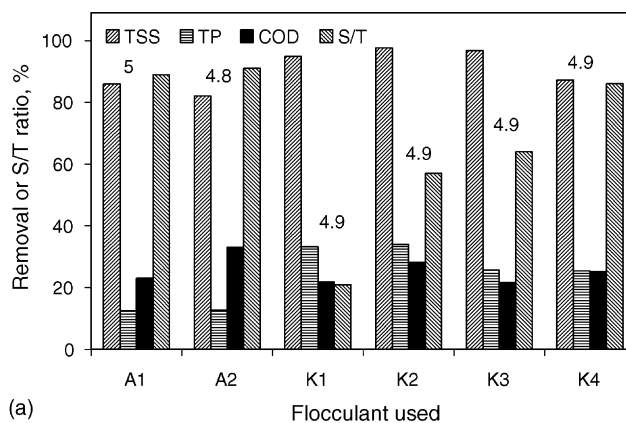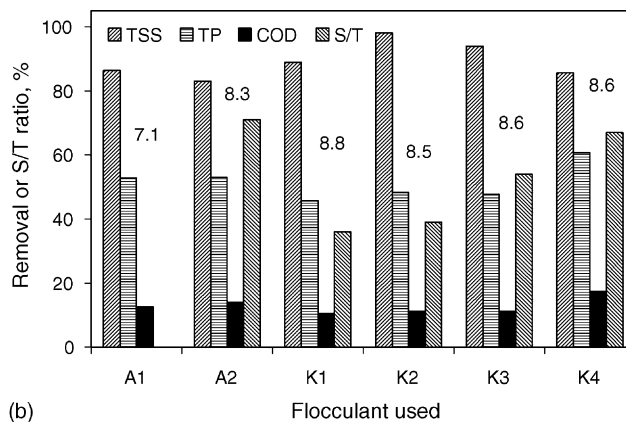
Fig. 3. Combined use of 287 mg/L poly-electrolyte with: (a) 5000 mg/L Fe(II) and (b) 30,000 mg/L lime for W1 treatment. Numbers next to the bars show pH values after separation. TP and COD refer to dissolved organic matter.

Like the experiments with coagulants alone, the combined use of Fe(II) and poly-electrolytes did not practically change the pH of the original sample, while the use of lime made the sample alkaline. Although pH is indeed a dominant factor affecting separation and should be optimised, from a practical point of view OME treatment needs to be kept as simple as possible. In view of this, the combined use of Fe(II) and poly-electrolytes, at the conditions in question, appears to be advantageous since the system (i) operates effectively at OME ambient pH (which is slightly acidic) and (ii) does not change the solution pH, thus avoiding the need for pH adjustment prior to separation and possible re-adjustment prior to subsequent treatment. For example, and in the context of coupling separation with H_2O_2 oxidation (as will be discussed in the following section), Fenton reactions in OME treatment are favoured at acidic conditions, e.g. in the pH range 3–5 [15].

The effect of changing coagulant or flocculant concentration on W1 treatment is shown in Table 1; decreasing either coagulant or flocculant concentration (at a constant flocculant or coagulant concentration, respectively) had a detrimental effect on separation. As can also be seen from Fig. 3 and Table 1, coagulation–flocculation with lime, at the conditions in question, always resulted in greater TP removal than treatment with Fe(II).

Table 1
Effect of coagulant or flocculant concentration on W1 treatment efficiency

Coagulant (mg/L)	K1 (mg/L)	TSS removal (%)	TP removal (%)	COD removal (%)
Lime: 30000	287	88.9	45.7	10.5
Lime: 30000	167	31.5	24.8	14.4
Lime: 30000	91	18.7	8.4	9.5
Lime: 30000	48	25.7	2.3	0
Lime: 50000	167	53.2	47.9	30.4
Lime: 50000	91	31.9	27.3	24.2
Lime: 50000	48	27.7	31.1	20
Fe(II): 5000	287	94.9	33.2	21.8
Fe(II): 5000	167	91.5	1.4	12.5
Fe(II): 5000	91	81.7	0	0
Fe(II): 5000	48	33.2	0	5.4

TP and COD refer to dissolved organic matter.

In further studies, the treatment of W2 with various combinations of Fe(II), lime, K1 and K2 was studied and the results are summarised in Table 2. TSS removal was quantitative regardless the type and combination of materials used. The use of coagulant had practically no effect on the extent of COD removal that could have been achieved with the respective flocculant alone but did have an impact on the extent of TP removal. Interestingly, phenol removal with Fe(II)/K1 or Fe(II)/K2 was always lower than that with K1 or K2 alone, while the opposite phenomenon occurred in the case of lime. However, in all cases the amount of sludge produced during the combined use of inorganic coagulant and poly-electrolyte was lower than that during separation with the poly-electrolyte alone; this is an important consideration regarding sludge management and disposal.

Since direct flocculation alone (i.e. without the addition of coagulants) was quite effective in terms of TSS removal, it was decided to test the relative efficiency of various poly-electrolytes and the results are shown in Fig. 4a; with the exception of anionic materials, all cationic poly-electrolytes gave sufficient separation with K1 and K2 being slightly more effective than the rest. Fig. 4b shows W2 treatment with mixtures of K1 and K2 at different K1/K2 ratios and a constant total concentration of 287 mg/L; as seen, various mixtures of K1 and K2 gave comparable results regardless the relative concentration of each material used.

Table 2
Effect of coagulant or flocculant concentration on W2 treatment efficiency

Coagulant (mg/L)	Flocculant (mg/L)	TSS removal (%)	TP removal (%)	COD removal (%)	S/T (%)
0	K1: 230	97.4	49.7	17.1	77
Fe(II): 2500	K1: 230	99.1	38.6	20.5	15
0	K2: 287	99.3	56.3	30.7	79
0	K2: 230	99.7	51	34.8	75
Fe(II): 2500	K2: 230	99.2	26.4	35.5	18
Lime: 15000	K1: 230	97.6	58.6	22.5	62
Lime: 15000	K2: 287	99.2	78.8	nd	57
Lime: 15000	K2: 230	99.1	78.6	nd	62

nd: not determined. TP and COD refer to dissolved organic matter.
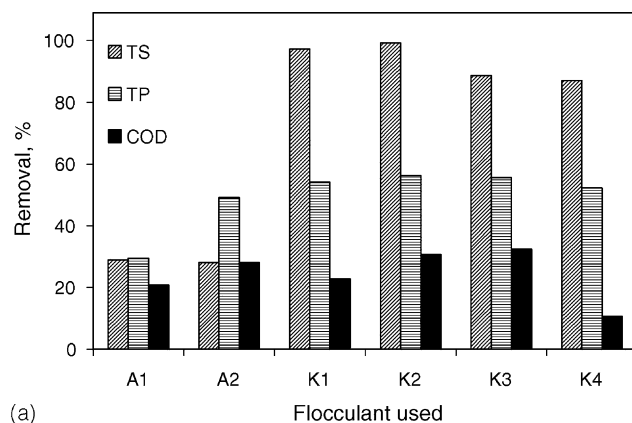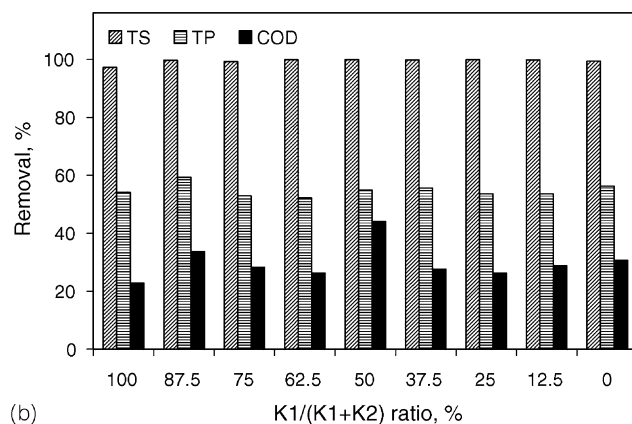
Fig. 4. Direct flocculation of W2: (a) relative efficiency of various poly-electrolytes at a common concentration of 287 mg/L and (b) flocculation with mixtures of K1 and K2 at various K1/K2 ratios at a constant total concentration of 287 mg/L. TP and COD refer to dissolved organic matter.

3.3. Coupling separation with Fenton oxidation

To enhance the relatively low COD removal that was generally recorded throughout the various coagulation–flocculation experiments, it was decided to couple Fe(II)/K1 treatment with H_2O_2 oxidation, thus simulating a Fenton-type reaction and representative results are shown in Table 3. Preliminary Fenton runs (1–4) at a constant Fe(II) concentration of 2500 mg/L and various H_2O_2 concentrations showed that, at the conditions under consideration, COD removal by oxidation reactions could reach values up to about 45% after 8 h of reaction. Rivas et al. [15] reported that Fenton oxidation of diluted OME (COD of 14.7 g/L) for 8 h with 13.9 g/L Fe(II) and 6.8 g/L H_2O_2 resulted in about 25% COD reduction with the extent of conversion depending on the concentration of both Fenton reagents as well as on solution pH. The effect of latter on efficiency was also studied by Vlyssides et al. [16]; in general, acidic conditions were found to favour OME oxidation. Beltran-Heredia et al. [17] reported that OME (initial COD of 95 g/L and pH of 4.8) oxidation for 8 h in the presence of 38 g/L Fe(II) and 15 g/L H_2O_2 led to 16% COD reduction which was doubled when the initial concentration of the Fenton reagents was also doubled.

In further runs (5–12), Fenton reagents were coupled with K1; in this series of experiments, the flocculant concentration was

Table 3
Coagulation–flocculation–H_2O_2 oxidation of W2

Run no.	Fe(II) (mg/L)	H_2O_2 (mg/L)	K1 (mg/L)	TSS removal (%)	TP removal (%)	COD removal (%)
1	2500	500	0	0	nd	30.5
2	2500	1000	0	0	nd	35.5
3	2500	5000	0	0	nd	44.7
4	2500	10000	0	0	nd	43.7
5	2500	500	230	98.7	67.1	53.9
6	2500	1000	230	98.4	72.5	55.6
7	2500	5000	230	98.3	84.9	61.4
8	2500	10000	230	98.3	82.7	53.6
9	2500	500	230	97.2	46.3	36.5
10	2500	1000	230	97.2	61.7	41
11	5000	10000	230	97.6	73.7	56.7
12	10000	10000	230	98.3	60	48.1

nd: not determined. TP and COD refer to dissolved organic matter.

kept constant at 230 mg/L since this concentration was found to be sufficient to yield complete solids separation. For all runs but 9 and 10, addition of Fe(II) was followed by H_2O_2 addition and the mixture was left to react for 8 h prior to the addition of K1. In all cases, TSS removal was quantitative. As seen from Tables 2 and 3, the oxidative degradation of phenols as well as of other organics present in W2 led to substantial enhancement of COD reduction. Increasing H_2O_2 concentration from 500 to 1000 and eventually to 5000 mg/L at 2500 mg/L Fe(II) concentration improved organic matter degradation; however, excessive amounts of oxidant (e.g. 10,000 mg/L) had no or even a slight adverse effect on performance possibly due to H_2O_2-induced radical scavenging [15]. At the end of the Fenton runs, the residual H_2O_2 concentration was measured in the order of several mg/L. Given that H_2O_2 positively interacts with the standard COD test [18], there was a concern regarding the extent of H_2O_2 contribution to the measured COD values. Therefore, standard solutions containing H_2O_2 at various concentrations up to 2500 mg/L were prepared and analysed with respect to their apparent COD content; for the range of concentrations in question, the ratio of COD to H_2O_2 concentration was found to be constant at 0.47. Therefore, for residual oxidant at, i.e. 200 mg/L the respective interference is only about 100 mg/L; this value is well below the actual COD content of the effluent. For runs 9 and 10, a different approach was followed and H_2O_2 was added in the sample following treatment with Fe(II)/K1. Comparing the results of runs 9 and 10 to those of runs 5 and 6, it is obvious that the late addition of the oxidant (i.e. after separation was completed) had a detrimental effect on TP and COD removal although solids separation remained unchanged.

3.4. Phytotoxicity

Lettuce seed germination tests were performed to assess the phytotoxicity of the original OME, the resulting liquid phase following various pre-treatments and the coagulants and flocculants used in this study and the results are summarised in Table 4. As seen, OME is strongly phytotoxic (even at 1:4 dilution) and completely hinders plant growth. It is generally accepted [2] that OME phytotoxicity is largely due to the presence of phenolic compounds although other OME constituents such as volatile fatty acids, aldehydes and alcohols are also known to be phytotoxic. Komilis et al. [2] who studied the phytotoxic properties of OME to tomato and chicory seeds before and after various pre-treatments including settling of solids, dilution, aeration and pH adjustment reported that raw OME was completely phytotoxic to both seeds and this was also the case after solids were separated from OME. They also concluded that OME dilution played a major role in reducing phytotoxicity; dilution by a factor of ten was capable of removing completely phytotoxocity to tomato seeds and nearly completely to chicory seeds.

Table 4
Phytotoxicity of original OME, treated OME, coagulant and flocculant samples at various dilutions

Sample no.	Sample type	$D = 0$	$D = 2$	$D = 4$
1	Original, untreated W2	0	0	0
2	15000 mg/L lime in water	86.1	97.5	115.5
3	2500 mg/L Fe(II) in water	22.6	24.6	35.4
4	230 mg/L K1 in water	42.2	54.7	108.2
5	230 mg/L K2 in water	20.5	68.4	108.7
6	W2 treated with 15000 mg/L lime + 230 mg/L K1	58.1	65.3	97.5
7	W2 treated with 230 mg/L K1	0	0.6	8.3
8	W2 treated with 15000 mg/L lime + 230 mg/L K2	7.6	38.6	47
9	W2 treated with 230 mg/L K2	0	0	0
10	W2 treated with 2500 mg/L Fe(II) + 10000 mg/L H_2O_2	0	0	0
11	W2 treated with 2500 mg/L Fe(II) + 10000 mg/L H_2O_2 + 230 mg/L K1	0	0	0

Table 5
Market price for bulk sales of flocculants and coagulants

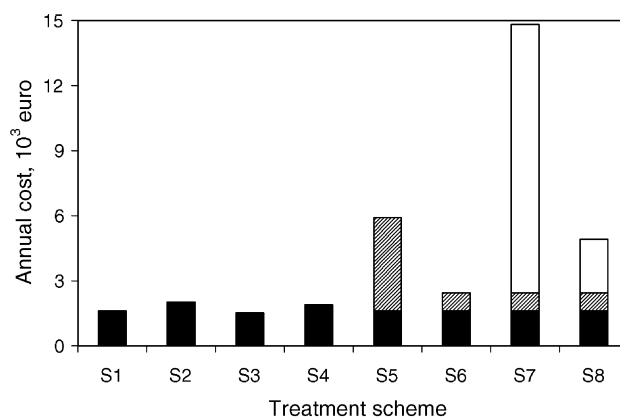| Material	€ tonne^{-1}
K1	3200
K2	3000
K3	3000
K4	3000
A1	2800
A2	2500
Lime	130
Fe(II)	150
Fe(III)	350
PAC	300

Fig. 5. Estimated annual cost of chemicals for W2 treatment. S1: K1 = 230 mg/L; S2: K1 = 287 mg/L; S3: K2 = 230 mg/L; S4 = K2 = 287 mg/L; S5: Lime = 15,000 mg/L and K1 = 230 mg/L; S6: Fe(II) = 2500 mg/L and K1 = 230 mg/L; S7: Fe(II) = 2500 mg/L, K1 = 230 mg/L, H_2O_2 = 5000 mg/L; S8: Fe(II) = 2500 mg/L, K1 = 230 mg/L, H_2O_2 = 1000 mg/L. Black bar: K1 or K2; hatched bar: Lime or Fe(II); white bar: H_2O_2.

The primary coagulants and flocculants used in this study (e.g. lime, Fe(II), K1 and K2) were only partially phytotoxic at the concentrations in question with phytotoxicity increasing with decreasing dilution (samples 2–5). The combined use of lime with K1 or K2 (samples 6 and 8, respectively) substantially reduced OME phytotoxicity. Conversely, direct flocculation with K1 or K2 (samples 7 and 9, respectively) failed to reduce the phytotoxicity of the original sample. The beneficial effect of lime may be associated with the increased extent of phenol (as well as of other phytotoxic compounds) removal as has been shown in Table 2. Davies et al. [19] recently proposed the use of sodium polyacrylate super-absorbent polymers to detoxify OME. The absorbent was capable of retaining the phenolic fraction inside the polymeric chains, thus reducing the phytotoxicity of residual liquid to pepperweed.

It should be pointed out that the pH value of liquid samples 6 and 8 was about 8, while the respective value of samples 7 and 9 was about 4.8. Given that seed germination generally depends on solution pH [2], the discrepancy in phytotoxicity levels between samples treated with and without lime might have been due to different pH values. Nonetheless, this does not seem to be the case since the phytotoxicity of K1 and K2 aqueous solutions (samples 4 and 5, respectively) was relatively low, although these solutions were nearly as acidic as samples 7 and 9 (e.g. their pH value was about 4). For those samples where an excess of H_2O_2 was used (10 and 11), the resulting toxicity was possibly due to the residual, un-reacted H_2O_2 in the mixture.

3.5. Preliminary cost estimate

A preliminary analysis was performed to evaluate the cost associated with the various materials employed in this study. For all coagulants and poly-electrolytes but lime, cost estimates were based on the current market price (bulk sales) in Greece as quoted by a major supplier (Table 5). For lime, the market price was taken from a local lime kiln. The market price for H_2O_2 (40%, v/v, solution) was quoted at €450 tonne^{-1}. On average, the maximum daily processing capacity of an olive oil mill in Crete is 22 tonnes of olives for a milling season of 100 days [20]. Given that (i) olive extraction by centrifugation typically generates about 1 m^3 of wastewaters per ton of olive processed and (ii) 97% of all mills in Crete are centrifugal, this would yield about 2200 m^3 OME per mill. For an initial TSS concentration

of 52.7 g/L (i.e. for effluent W2) and quantitative TSS removal, Fig. 5 shows the annual cost of chemicals for various treatment scenarios shown in Tables 2 and 3 and Fig. 4. The annual cost of poly-electrolytes for direct flocculation (i.e. S1–S4) would not exceed €2000; this corresponds to less than €0.02 kg^{-1} TSS removed. Inorganic materials, although far cheaper than poly-electrolytes, may introduce substantial cost depending on the dosage employed. For instance, addition of 15,000 g/L lime prior to the addition of 230 mg/L K1 (i.e. S5) would over-triple the cost of the respective direct flocculation with K1 (i.e. S1). Moreover, in the case of lime treatment the cost of chemicals may increase further should neutralisation be needed prior to e.g. biological post-treatment. For the combined separation-Fenton oxidation scheme, H_2O_2 expectedly comprises an appreciable fraction of the total cost. For example, for the optimum performance in terms of TSS, TP and COD removal recorded in this study (i.e. run 7 in Table 3 and S7 in Fig. 5), the annual cost would be as high as €15,000 with H_2O_2 comprising about 85% of the total cost. Nonetheless, a five-fold decrease in H_2O_2 dosage would result in a three-fold cost reduction without compromising process performance (i.e. run 6 in Table 3 and S8 in Fig. 5).

4. Conclusions

The treatment and safe disposal of effluents associated with olive oil manufacturing has gained significant attention over the past years due to their high polluting capacity and the strict application of legal restrictions. In view of this, intense research at international level has shown that physical, chemical and biological processes (either alone or in various combinations) can offer technically sound solutions. Unfortunately, these high-technology treatment options usually entail capital and operating costs which the owners of small- or medium-sized olive mills cannot afford (and consequently refuse) to pick up. Alternatively, OME re-use for plant irrigation is a relatively inexpensive disposal technique and may require nothing but some kind of pre-treatment to achieve phase separation.

In this work, the coagulation–flocculation of OME coupling relatively inexpensive inorganic materials with moderate concentrations of organic poly-electrolytes was investigated regarding the effect of operating conditions on solids and organic matter separation efficiency and subsequent phytotoxicity. This pre-treatment scheme was capable of separating completely the solid fraction of OME, with the resulting liquid having a reduced concentration of organics and phytotoxicity. These results are encouraging in the context of developing a low-budget technology for the effective management of OME.

Acknowledgment

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