Oxidative processes for olive mill wastewater treatment

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Abstract The present work describes an experimental study carried out in order to investigate the efficiency and feasibility of physical (lime coagulation) and advanced oxidation processes (Ozone and Fenton's process) for olive oil mill wastewater treatment. Particular attention was paid to the degradation of both organic and phenolic compounds. Lime coagulation reaches maximum removal at a pH of 12, with a TP (total polyphenols) and COD reduction of 37 and 26%, respectively. Ozone oxidation is also pH-dependent, showing the higher removal efficiency (91% for TP and 19% for COD) with an initial pH value of 12. Experimental results show a lower efficiency of Fenton's process than ozone in TP removal, reaching a maximum value of 60%. Oxidation trials carried out on gallic and p-coumaric synthetic solutions confirmed ozone and Fenton's efficiency at degrading phenolic compounds. Biological trials, both aerobic and anaerobic, highlighted a significant increase of biodegradability of treated OMW samples if compared to the untreated ones. Respirometric tests showed an increase in BOD of about 20% and anaerobic batch tests provided a methane production up to eight times higher.

Keywords Fenton's process; olive oil wastewaters; ozone; phenolic compounds

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Introduction

Olive oil extraction represents one of the most traditional agricultural industries in Italy and it still plays a role of primary importance from an economical point of view in all the Mediterranean area, which accounts, together with Aegean and Marmara regions, for approximately 95% of worldwide olive oil production (Kestioglu *et al.*, 2005). In the Mediterranean region more than 11 million tons of olives per year are produced, corresponding to 1.7 million tons of extracted oil (Beltran-Heredia *et al.*, 2000; Aktas *et al.*, 2001). Olive oil production generates different amounts of by-products, olive oil wastewaters and olive husks, depending on the extraction method. In particular, olive mill wastewater (OMW) volumes vary from 0.5–0.8 m^3 per ton of olives in conventional press extraction, to 1.2–1.7 m^3 in the recent three-phase continuous centrifugal process (Kestioglu *et al.*, 2005), reaching a world production of about 30 million m^3 per year (Dionisi *et al.*, 2005). OMWs are characterized by a high organic load (80–300 g/L of COD) and a low biodegradability, due to the acidic pH and in particular to a relevant content of phenolic and lipidic compounds, well known as toxic to bacteria (Beccari *et al.*, 1999; Gernjak *et al.*, 2004). Traditional disposal on the soil is still the most common way to discharge them (Cegarra *et al.*, 1996). The Italian law in force (L. 574/96) allows discharge of a maximum of 50 m^3/ha when OMWs come from a traditional mill and 80 m^3/ha from a continuous process. The average cost for soil disposal ranges between 10 and 15 €/m^3. During the last years, different processes for OMW treatment have been investigated. Physical and physico-chemical processes, such as centrifugation, coagulation and flocculation seem to be efficient solutions to remove the high content of

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TSS and pre-treat OMW before oxidative and biological processes. Lime coagulation is an economical and effective OMW pre-treatment, able to remove up to 50% of polyphenols and 50% of COD (Beccari *et al.*, 1999; Aktas *et al.*, 2001) and to enhance the OMW anaerobic digestion efficiency.

Advanced oxidation processes (AOPs) appear an interesting solution to reduce the phenolic content and to enhance the biological degradability (Beltran-Heredia *et al.*, 2001a; Rivas *et al.*, 2001a; Kotsou *et al.*, 2004). According to literature data, Fenton's reagents and ozone are very effective at degrading OMW total polyphenols (Andreozzi *et al.*, 1998; Kestioglu *et al.*, 2005; Bettazzi *et al.*, 2006) and are shown to be particularly effective also on phenolic synthetic solutions (Benitez *et al.*, 2005; Monteagudo *et al.*, 2005). Ozone is particularly efficient at TP removal and is highly influenced by the pH value (Benitez *et al.*, 2005; Saroj *et al.*, 2005). Fenton's reagents applied on synthetic solutions give evidence of high efficiency, with removal percentages greater than 75% for all the phenolic compounds, even the more recalcitrant ones such as p-coumaric acid (Beltran-Heredia *et al.*, 2001b; Rivas *et al.*, 2001b; Benitez *et al.*, 2005).

The present study is aimed at investigating and comparing different processes by lab oratory-scale trials, in order to find an economical and effective treatment for OMWs. In particular, we studied lime coagulation, advanced oxidation processes (ozone and Fenton's reagents) and biological treatment (in aerobic and anaerobic conditions). The efficiency of every process was assessed considering COD and total polyphenols (TP) removal. Respirometric tests and anaerobic batch trials have been carried out to evaluate the effects of the pre-treatments on the biological degradability. Aside from OMW trials, ozone and Fenton's experiments were carried out on synthetic solutions of two different phenolic compounds present in OMWs: gallic acid, commonly used for the calibration of TP colorimetric analytical method (Catalano *et al.*, 1999) and p-coumaric acid, well known for its recalcitrant nature.

Methods

All the trials were carried out on OMWs (2004/2005 olive oil campaign) supplied by one of the largest three-phase mills in Italy, located in Quarrata (Tuscany). Raw OMWs were centrifuged twice at 4000 rpm for 10 minutes in order to separate the liquid phase from the solids. All the trials were carried out on the liquid phase, whose main characteristics are summarized in Table 1.

TP content was determined by the Folin-Ciocalteau spectrophotometric method and HPLC analysis. Gallic and p-coumaric acids were used as standards to calibrate the Folin-Ciocalteau method. HPLC tests were displayed using both an UV and a mass spectrometry analysis. Both the analyses were carried out on OMW samples after filtration at 0.45 μm. As the aforementioned methods showed a good agreement, TP values reported in this work were measured by Folin-Ciocalteau method. COD, BOD, TSS and VSS were assessed according to the *Standard Methods* (2005).

In order to study the effects of oxidation on phenolic substances, synthetic solutions of two different compounds, gallic and p-coumaric acid, were used. Taking into account

Table 1 Raw and centrifuged OMW characteristics

	Raw OMW	Centrifuged OMW
pH	4.4–4.8	4.6–5.1
COD (mg/L)	262,750–301,600	48,850–72,720
TP (mg/L)	9,600–10,600	23,600–29,300
TSS (g/L)	113.5–128.4	2.19–3.02
VSS (%)	91.63–94.5	94.5–95.5

the maximum p-coumaric acid solubility and the literature data, a 300 mg/L concentration for both the synthetic solutions was chosen.

Regarding OMW lime coagulation, trials were carried out in a 1 L batch reactor comparing different lime concentrations by means of jar tests. The tested lime concentrations varied from 6.5 to 25 g/L, corresponding to sample average pH values ranging from 7.2 to 12.9. Jar tests were carried out for 10 minutes at 100 rpm, 10 minutes at 35 rpm and 2 hours of sedimentation.

Ozone treatment was applied both on OMW samples and the synthetic solutions. Trials were performed in a 400 mL batch reactor (glass Mariotte vessel) with a O_3 mass flow rate set at 7.5 mg/min. Contact time was varied from 1 to 5 hours for the OMW samples and from 1 to 2 hours for the synthetic solutions. Residual O_3 in the off gas was determined according to the *Standards Methods* by the iodometric titration (KI solution at 2% w/w). In order to evaluate the pH influence on O_3 oxidative efficiency, tests were carried out on OMW samples both at OMW initial pH value (around 4.5) and at higher pH values. Lime addition at 10–20 g/L was used to adjust the initial pH to a value of 8–12, so that coagulation and ozone combined use could be studied. The initial pH value of the synthetic solutions was set at 2, 5, 7 and 9 by adding H_2SO_4 (0.5 M) or NaOH (1 M), in order to highlight the different oxidation pathways.

Concerning Fenton's process, trials were performed in a 1 L batch reactor, monitoring pH, ORP and temperature trends by MARTINA (multiple analysis programmable titration analyser, SPES, Italy). All the experiments lasted for 24 hours. Samples were analysed before the treatment and after 2, 4 and 24 hours. OMW samples were previously centrifuged and the pH value was adjusted at around 3, using H_2SO_4 (98% w/w). For the synthetic solutions no pH adjustment was required. Epta-hydrated $FeSO_4$ (8% w/w) and H_2O_2 (35% w/w) were used as reagents for Fenton's process. Different Fe^{2+}/H_2O_2 ratios were chosen: 1/12, 1/24 and 1/60. Table 2 shows the different experimental conditions chosen for Fenton's oxidation. Considering our experimental results and the literature data, Fenton's process on phenolic synthetic solutions was performed using a 1/12 Fe^{2+}/H_2O_2 ratio and a 1/3 H_2O_2/acid ratio.

In all the experiments, oxidative efficiency was assessed measuring the COD and TP removal efficiency after filtering the treated samples at 0.45 μm. For the synthetic solutions no filtration was required. Before measuring the COD of Fenton's oxidised samples, NaOH (4 M) was added in order to increase the pH value above 11; this condition guarantees hydrogen peroxide decomposition and favours ferric ions precipitation, so that possible interferences in COD measurement are highly reduced. Before any biological tests the residual H_2O_2 in Fenton's oxidised samples was quenched by catalase addition.

The effects of the pre-treatments on the aerobic biodegradability were assessed by evaluating the ratio between the biodegradable COD fraction (BCOD) and the total COD value. In order to evaluate the BCOD fraction, both respirometric and BOD tests were used. By the subtended area in the respirograms, which represents the short-term BOD (BOD_{st}), it is possible to calculate the BCOD as $BOD_{st}/(1 - Y_H)$. The yield factor (Y_H) was calculated by measuring the filtered COD degraded during respirometric tests on OMW samples, and resulted in about 0.65 (COD/COD). Respirometric tests were carried out in a 1.5 L batch reactor, using a non-acclimated activated sludge taken from a municipal WWTP. Oxygen, temperature (fixed at 25 °C) and pH (fixed at 8) were monitored and controlled by a

Table 2 Fenton's reagents concentration

Fe^{2+} (g/L)	0.5	0.67	0.75	1.0	0.5	0.5
H_2O_2 (g/L)	6	8	9	12	12	30
Fe^{2+}/H_2O_2	1/12	1/12	1/12	1/12	1/24	1/60

biocontroller ADI 1030 Applikon. On-line pH control was ensured by $NaHCO_3$ (1 M) and CO_2 addition. The ultimate BOD (BOD_u) values were calculated by using the BOD_{20} tests. The BCOD fraction was obtained in this case as BOD_u/(0.85) (Roeleveld and van Loosdrecht, 2002). OxiTop method® was applied to determine aerobic BOD_{20}. Tests were carried out at 20 °C and a phosphate buffer solution (1 M) was added to keep the pH value around 7.2. OxiTop method® was used to assess the effects of the pre-treatments on anaerobic biodegradability. Tests lasting 60 days were performed at 35 °C, using sludge taken from a WWTP anaerobic digester, and measuring the pressure increase due to the CH_4 production.

Results and discussion

Lime coagulation

Table 3 represents the average values and the experimental results obtained with lime coagulation.

According to the literature data the removal efficiency increases as pH increases, reaching maximum at a pH of 12, which corresponds to a lime concentration of 20 g/L. Lime coagulation proved to be a suitable pre-treatment in particular for ozone oxidation, as it guarantees not only the removal efficiency reported above, but also a high TSS reduction (up to 90%).

Ozone treatment

Ozonation has been applied on centrifuged (pH 4.5) and lime pre-treated OMW samples (pH 8–12). Table 4 shows the average COD and TP removal percentages corresponding to the different initial pH values. These results refer to a contact time of 4 hours, as longer contact times did not significantly increase the ozonation efficiency.

COD removal efficiency is not greatly influenced by the pH and reaches low values (maximum percentage of 20%). On the other hand ozonation is very efficient at TP removal, reaching a maximum removal efficiency of more than 90%. According to literature data, TP degradation is greatly influenced by the initial pH value and remarkably rises to pH above 8. The optimal pH of 12 found in this study is slightly higher than the optimal value of 11 suggested by the literature data. The initial pH influences not only the final efficiency but also the reaction kinetics as shown in Figure 1.

The experimental data show that almost 2 hours are required to reach 50% of TP removal starting with a pH of 8, while only 30 minutes are necessary with an initial pH equal to 12. The iodometric titration showed that almost all the O_3 fed to the samples was consumed; after 4 hours of ozonation only a mean O_3 flow rate of 0.4 mg/min was found in the off gas.

All the removal efficiencies reported refer only to the ozonation process, lime coagulation and ozone oxidation combined use reached a removal efficiency of 34% for COD and 94% for TP. Figures 2 and 3 summarised the results obtained after 2 hours of ozonation applied on the synthetic solutions. The phenolic initial concentration was 300 mg/L

Table 3 Experimental results of lime coagulation

Lime (g/L)	pH	COD_{in} (mg/L)	COD_{out} (mg/L)	COD removal efficiency (%)	TP_{in} (mg/L)	TP_{out} (mg/L)	TP removal efficiency (%)
6.5	7.2	56,040	51,500	8.1	2,730	2,370	13.1
10	8.5	55,700	48,403	13.1	2,360	1,930	18.2
15	10.8	62,280	51,070	18.0	2,570	1,870	27.1
20	12.2	62,280	45,900	26.3	2,570	1,630	36.6
25	12.9	62,280	48,585	25.2	2,570	1,690	34.1

Table 4 Experimental results of ozone treatment

pH_{in}	COD_{in} (mg/L)	COD_{out} (mg/L)	COD removal efficiency (%)	TP_{in} (mg/L)	TP_{out} (mg/L)	TP removal efficiency (%)
4.5	56,590	51,720	8.6	2,430	1,580	38.2
8	48,500	45,590	6.0	2,170	880	59.6
10	47,900	44,980	6.1	1,620	220	86.5
12	46,900	37,760	19.5	1,590	130	91.4

both for gallic and p-coumaric acid while the initial COD values were 338 mg/L for the gallic acid solution and 560 for the p-coumaric one.

Ozone treatment applied on phenolic solutions proved to be very effective at TP removal, reaching the maximum removal percentage of about 95% at a pH of 5, both for gallic and p-coumaric acid. According to literature data p-coumaric acid ozonation is less pH-dependent, while the initial pH influence is evident for gallic acid ozonation, whose efficiency increases from less than 20% at a pH of 2 to 95.9% at a pH of 5; higher pH values did not significantly change the final degradation efficiency. Our results confirm the fact that the formation of hydroxyl radicals, which starts at a pH value equal to or higher than 5, greatly improves the efficiency obtained by the direct ozonation pathway. For both the phenolic compounds, COD reduction increases as the initial pH value increases, reaching the maximum percentage of about 60% for a pH equal to 9.

Fenton's process

Fenton's process has been applied on centrifuged OMW samples, and the average experimental results are summarised in Table 5.

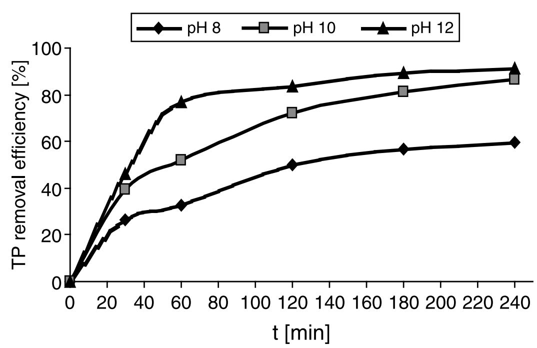

Figure 1 TP removal trends during ozonation tests carried out at initial pH values of 8, 10 and 12

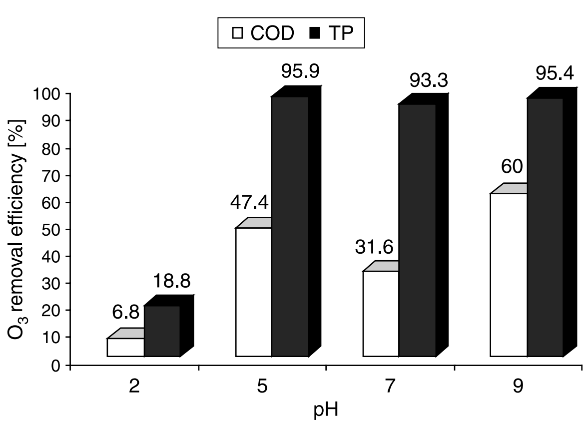

Figure 2 Gallic acid ozonation

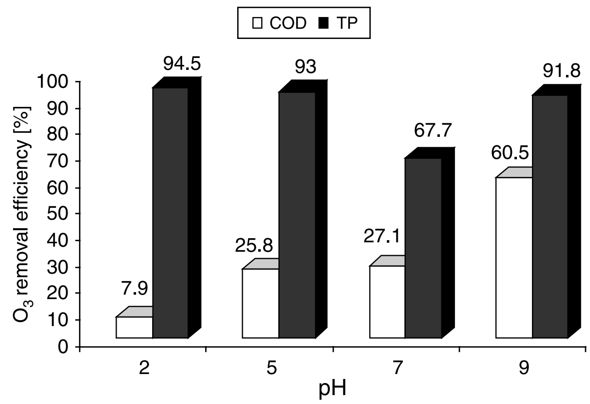

Figure 3 P-coumaric acid ozonation

Table 5 Fenton's process experimental results

Fe^{2+} (g/L)	H_2O_2 (g/L)	COD_{in} (mg/L)	COD_{out} (mg/L)	COD removal efficiency (%)	TP_{in} (mg/L)	TP_{out} (mg/L)	TP removal efficiency (%)
0.5	6	45,460	43,370	4.6	2,300	1,040	54.7
0.67	8	49,910	45,020	9.8	2,460	1,150	53.1
0.75	9	46,740	40,520	13.3	2,380	1,060	55.3
1	12	47,730	39,235	17.8	2,310	880	62.1
0.5	12	50,940	42,180	17.2	2,870	1,320	54.1
0.5	30	45,460	35,230	22.5	2,140	830	61.2

According to the data, H_2O_2 concentration influences the final removal efficiency much more than the Fe^{2+} dosage. One g/L Fe^{2+} and 12 g/L H_2O_2 proved to be the best experimental conditions. OMW maximum removal efficiency was about 62% for TP and 23% for COD. These results, according to the literature data, highlight the greater efficiency of ozone at TP degrading and the slightly higher efficacy of Fenton's process at COD removing. Fenton's process efficiency is not influenced by the way the reagents are added; experimental results showed how repeated injections, if compared to the single addition trials at the same final concentrations, only slightly increase the COD removal and have no influence on TP final degradation. Fenton's process oxidative efficacy is due to the synergic interaction of hydrogen peroxide and Fe^{2+}/Fe^{3+} ions; the addition of 12 g/L H_2O_2 to OMW samples led to a reduction of only about 30% for the TP and of about 10% for COD, much lower than the removal efficiencies obtained with the addition also of 1 g/L Fe^{2+} (about 1 and 62% for COD and TP, respectively). As regards the phenolic solutions, Table 6 summarizes the results obtained applying Fenton's process on the 300 mg/L synthetic solutions.

Fenton's process affects gallic and p-coumaric acids differently; likewise in ozone treatment, and according to previous studies, p-coumaric acid is less degradable than gallic acid, whose reduction is about twice as high. Fenton's process is less effective than ozone at degrading the phenolic compounds both in OMWs and in synthetic solutions.

Table 6 Fenton's COD and TP removal efficacy on phenolic solutions

Synthetic solutions	COD (%)	TP (%)
p-coumaric acid (300 mg/L)	19.1	35.6
Gallic acid (300 mg/L)	37.9	67.2

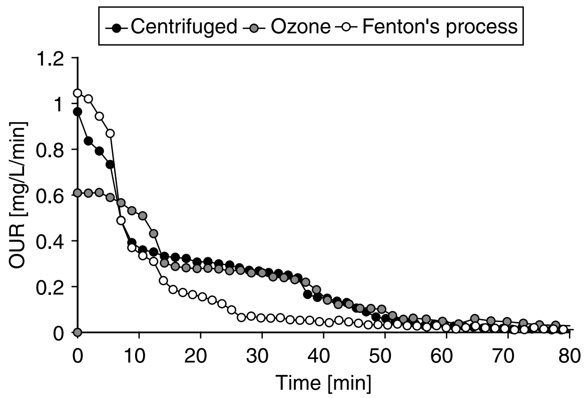

Figure 4 Respirometric tests

Aerobic and anaerobic tests

Figure 4 shows the respirometric tests obtained with injections of centrifuged, Fenton's and ozone pre-treated OMWs. BOD_{20} trends obtained with centrifuged, lime-treated, ozone and Fenton's oxidised OMW samples are reported in Figure 5. Table 7 summarises the experimental data.

BOD tests seem to underestimate the biodegradable fraction of COD if compared to respirometric results, but both methods highlight a significant increase of OMW biodegradability after the lime coagulation and in particular after both the oxidative processes (ozone and Fenton's process). For this reason, oxidative processes can constitute an effective pre-treatment before an activated sludge process (ASP).

Figure 6 shows the headspace pressure trends obtained during the 60-day anaerobic tests and Table 8 summarizes the COD fed to each vessel (COD_{in}), the volume of the produced methane (CH_{4prod}) and the ratio between the degraded COD (COD_{deg}, calculated by the methane production) and the COD_{in}.

The methane production is eight time higher in samples pre-treated with lime and oxidative processes than in the centrifuged ones. The significant increase of the anaerobic biodegradability could be due to the removal of the phenolic compounds which have

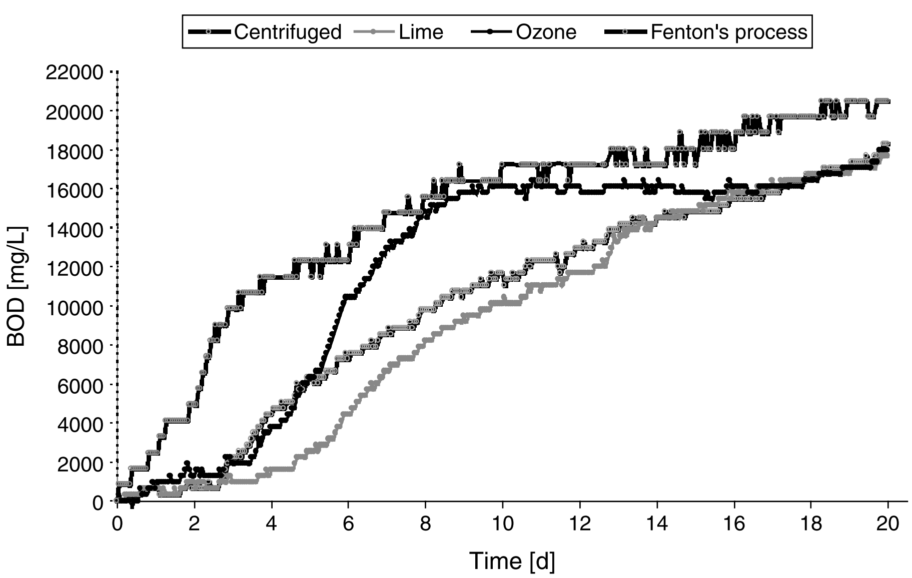

Figure 5 BOD_{20} tests

Table 7 Respirometric and BOD tests

Sample (0.45 μm filtered)	Respirometric tests			BOD tests		
	COD (mg/L)	BOD_{st} (mg/L)	BCOD/COD (%)	COD (mg/L)	BOD_u (mg/L)	BCOD/COD (%)
Centrifuged	51,250	8,879	49.5	56,900	18,060	37.3
Lime	47,900	10,812	64.6	45,900	17,446	44.7
Fenton's	41,686	11,177	76.6	40,480	20,933	60.8
Lime + O_3	39,600	10,839	78.4	37,580	19,872	62.2

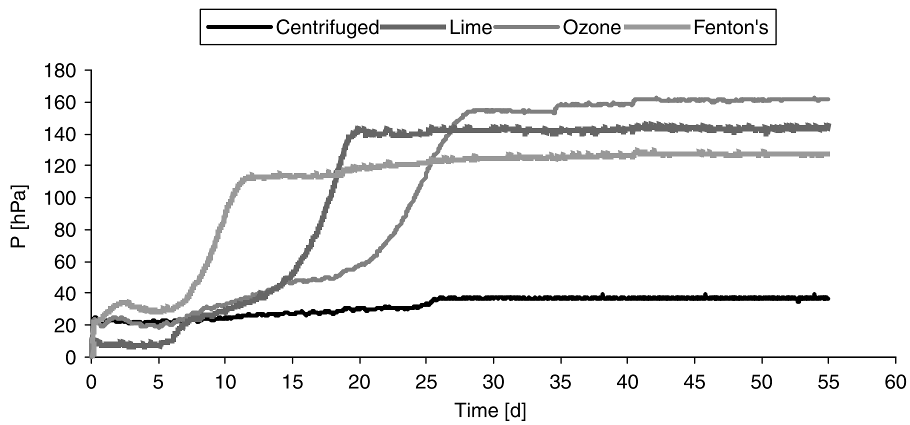

Figure 6 Pressure trends during anaerobic tests

Table 8 Anaerobic tests

Sample	COD_{in} (mg/L)	CH_{4prod} (NmL)	COD_{deg}/COD_{in} (%)
Centrifuged OMW	2,603	13.1	4.1
Lime coagulation	1,664	85.7	32.7
Ozone	1,644	88.1	34.1
Fenton's process	1,637	77.8	30.2

inhibiting and toxic effects in particular on the anaerobic bacteria (Beccari *et al.*, 1999). While the aerobic biodegradability of oxidised OMWs is much higher than of lime-treated OMWs, the methane production of oxidised and physically pre-treated samples does not differ significantly. For this reason, lime coagulation seems to be the optimal pre-treatment before anaerobic digestion.

Conclusions

According to the experimental results obtained, the following conclusions can be drawn.

- OMW ozone treatment is greatly influenced by the initial pH value. The maximum removal efficiency reaches the values of 20% for COD and 92% for TP at a pH equal to 12. TP removal efficiency of the ozone process applied on synthetic solutions reaches the maximum value of 95% at pH equal to 5 while COD maximum removal efficiency is 60% at pH of 9.
- OMW Fenton's treatment guarantees a TP removal of 60% and a COD removal of 23%. Fenton's process affects the synthetic solutions differently. Gallic acid removal efficiency at the same acid concentrations was almost twice (67%) the p-coumaric one (35%).

- Respirometric and BOD tests show the higher biodegradability of all the pre-treated OMW samples compared to one of the untreated OMW samples. Anaerobic batch tests record a methane production eight times higher in oxidised samples than in centrifuged ones.
- Oxidative processes followed by ASP, and lime coagulation process followed by anaerobic digestion, are suitable and effective treatment trains for OMW treatment.

References

Aktas, E.S., Imre, S. and Ersoy, L. (2001). Characterization and lime treatment of olive mill wastewater. *Water Res.*, **35**(9), 2336–2340.

Andreozzi, R., Longo, G., Magone, M. and Modesti, G. (1998). Integrated treatment of olive oil mill effluents (OME): study of ozonation couplet with anaerobic digestion. *Water Res.*, **32**(8), 2357–2364.

Beccari, M., Majone, M., Riccardi, C., Savarese, F. and Torrisi, L. (1999). Integrated treatment of olive oil mill effluents: effect of chemical and physical pretreatment on anaerobic treatability. *Wat. Sci. Tech.*, **40**(1), 347–355.

Beltran-Heredia, J., Torregrosa, J., Dominguez, J.R. and Garcia, J. (2000). Treatment of black-olive wastewaters by ozonation and aerobic biological degradation. *Water Res.*, **34**(14), 3515–3522.

Beltran-Heredia, J., Torregrosa, J., Dominguez, J.R. and Garcia, J. (2001a). Degradation of olive mill wastewater by the combination of Fenton's reagent and ozonation processes with an aerobic biological treatment. *Water Res.*, **44**(5), 103–108.

Beltran-Heredia, J., Torregrosa, J., Dominguez, J.R. and Peres, J.A. (2001b). Kinetic model for phenolic compound oxidation by Fenton's reagent. *Chemosphere*, **45**, 85–90.

Benitez, F.J., Real, F.J., Acero, J.L., Leal, A.I. and Garcia, C. (2005). Gallic acid degradation in aqueous solutions by UV/H_2O_2 treatment, Fenton's reagent and the photo-Fenton system. *J. Hazard. Mater.*, **126**, 31–39.

Bettazzi, E., Morelli, M., Caffaz, S., Caretti, C., Azzari, E. and Lubello, C. (2006). Olive mill wastewater treatment: an experimental study. *Wat. Sci. Tech.*, **54**(8), 17–25.

Catalano, J., Franco, I., De Nobili, M. and Leita, J. (1999). Polyphenols in olive mill waste waters and their depuration plant effluents: a comparison of the Folin-Ciocalteau and HPLC methods. *Agrochimica*, **XLIII**(5–6), 193–205.

Cegarra, J., Paredes, C., Roig, A., Paredes, C., Cegarra, J., Roig, A. and Garcia, D. (1996). Use of olive mill wastewater compost for crop production. *Int. Biodeter. Biodegrad.*, **38**, 193–203.

Dionisi, D., Carucci, G., Petrangeli Papini, M., Riccardi, C., Magone, M. and Carrasco, F. (2005). Olive oil mill effluents as a feedstock for production of biodegradable polymers. *Water Res.*, **39**(10), 2076–2084.

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

Kestioglu, K., Yonar, T. and Azbar, N. (2005). Feasibility of physico-chemical treatment and advanced oxidation processes (AOPs) as means of pretreatment of olive mill effluent (OME). *Proc. Biochem.*, **40**, 2409–2416.

Kotsou, M., Kyriacou, A., Lasaridi, K.E. and Pilidis, G. (2004). Integrated aerobic biological treatment and chemical oxidation with Fenton's reagent for the processing of green table olive wastewater. *Proc. Biochem.*, **39**, 1653–1660.

Monteagudo, J.M., Carmona, M. and Duran, A. (2005). Photo-Fenton-assisted ozonation of p-coumaric acid in aqueous solution. *Chemosphere*, **60**(8), 1103–1110.

Rivas, F.J., Beltran, F.J., Gimeno, O. and Frades, J. (2001a). Treatment of olive mill wastewater by Fenton's reagent. *J. Agric. Food Chem.*, **49**, 1873–1880.

Rivas, F.J., Beltran, F.J., Frades, J. and Buxeda, P. (2001b). Oxidation of p-hydroxybenzoic acid by Fenton's reagent. *Water Res.*, **35**(2), 387–396.

Roeleveld, P.J. and van Loosdrecht, M.C.M. (2002). Experience with guidelines for wastewater characterization in the Netherlands. *Wat. Sci. Tech.*, **45**(6), 77–87.

Saroj, D.P., Kumar, A., Bose, P., Tare, V. and Dhopavkar, Y. (2005). Mineralization of some natural refractory organic compounds by degradation and ozonation. *Water Res.*, **39**, 1921–1933.

Standard Methods for the Examination of Water and Wastewater (2005). 21st edn, American Public Health Association (APHA), American Water Works Association (AWWA) & Wat. Env. Fed (WEF), Washington DC, USA.