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Removal of organic load and phenolic compounds from olive mill wastewater by Fenton oxidation with zero-valent iron

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ABSTRACT

Pre-treatment of olive mill wastewater (OMW) by Fenton Oxidation with zero-valent iron and hydrogen peroxide was investigated to improve phenolic compounds degradation and the chemical oxygen demand (COD) removal. Experimental procedure is performed with diluted OMW with COD 19 g/L and pH 5.2. The application of zero-valent Fe/H_2O_2 procedure allows high removal efficiency of pollutants from OMW. The optimal experimental conditions were found to be continuous presence of iron metal, acidic pH (2–4) and 1 M hydrogen peroxide solution. The experimental results show that the removal of 1 g of COD need 0.06 M of H_2O_2. At pH 1, the maximum COD removal (78%) is achieved after 1 h. Therefore, with a pH value within 2 and 4 the maximum COD removal reached 92%. Phenolic compounds are identified in treated and untreated OMW by gas chromatography coupled to mass spectrometry (GC–MS). The result shows a total degradation of phenolic compounds and an increasing biodegradability of treated OMW.

1. Introduction

The annual OMW production of the Mediterranean olive-growing countries is estimated to over then 30 millions m^3 [1]. This wastewater has a high pollution potential and considerable pollution occurs as a result of seasonal OMW production. In fact, it is one of the crucial environmental issues in the Mediterranean area. Therefore it constitutes a serious problem with severe negative impact on the soil and the water quality. This effluent is characterized by a high organic load including sugars, tannins, pectin, lipids, polyphenols and polyalcohols [2–4]. The physico-chemical characteristics of OMW are rather variable, depending on climatic conditions, olive cultivars, degree of fruit maturation, storage time, and extraction process. The color of OMW varied from dark-red to black depending on its age and the extraction procedure. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD5) are as high as 140 g/L and 70 g/L, respectively. The phenolic compounds that are present in olive stone and pulp tend to be more soluble in the water phase than oil. Consequently the concentration range from 0.5 to 25 g/L in OMW [5]. This phenolic fraction is characterized by a great variety and complexity, as demonstrated by El Hadrami et al. [6] and Bianco et al. [7]. This author has identified 20 phenolic compounds in OMW by using HPLC–MS–MS. Biological processes, using selected microorganisms such as Archaea, Bacteria and fungi in aerobic or anaerobic bioreactors, have been tested to treat OMW [5]. It is well known that some components in the OMW organic fraction such as phenols and polyphenols, are phytotoxic [8–11] and resistant to biological degradation [2,12,13]. Unfortunately, dumping OMW in evaporation ponds is the most common practice in the Mediterranean region. An emerging agronomic practice in oil-producing countries involves OMW land spreading for both disposal and ferti-irrigation purposes [14]. The practice of controlled spreading on agricultural soils is normally accomplished on the basis of several technical criteria which take into account mainly soil texture, effluent volume/land surface ratio and organic load. In order to encourage this practice, it is important to develop pre-treatment of OMW that can reduce their toxicity and improve their biodegradability. In this case, advanced oxidation processes (AOPs) should be considered as a viable alternative [15,16]. Some researches on the degradation of phenolic compounds with AOPs have already been published [17,18]. They are mainly applicable to bio-refractory molecules in order to achieve the complete mineralization of the contaminants or at least the conversion of organics into less harmful or lower chain compounds [19–21]. Therefore, the classical Fenton oxidation process utilizes the reaction of aqueous iron (II) with hydrogen peroxide to generate hydroxyl radicals, according to Walling [22] and as described in Eq. (1), which can oxidize organic compound in the solution.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \qquad (1)$$

For efficient reaction, stoichiometric amount of ferrous ion and hydrogen peroxide are required and this usually means that huge

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quantities of ferric salts need to be disposed of after the reaction is complete. However, in the case of the use of zero valent iron in place of ferrous salts the following reactions occur [18].

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{2}$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \tag{3}$$

In acidic condition, the surface of the metal iron corrodes giving rise to ferrous ions and hydrogen gas (Eq. (2)). The ferric ions produced by normal Fenton reaction (Eq. (1)) can be reduced to ferrous by the zero valent iron metal surface (Eq. (3)). Therefore, the excess of ferric ions can improve the chemical coagulation of the residual COD [23].

The objective of the present work is to investigate the effectiveness of the Fenton's reagent with zero valent for an oxidative degradation of OMW and the phenolic compounds present in this effluent.

2. Materials and methods

2.1. Materials

The OMW effluent is obtained from a three-phase olive-oil plant located in Sfax (Tunisia). Based on the previous study [24], experiments were conducted, on the decanted and diluted OMW characterized by a pH 5.2, the COD is equal to19 g/L and the total polyphenol is equal to 672 mg/L. The iron metal used in this study is obtained from a metal turner. It constitutes a residual product from this activity and it is characterized by a thin and spiral form. Hydrochloric acid, sodium hydroxide and hydrogen peroxide (9.5 M) were purchased from Merck (France).

2.2. Experimental procedure

In this study, we attempt to evaluate a new method for the degradation of polyphenols in olive mill wastewater using spontaneous corrosion of iron metal sheet surfaces in the presence of hydrogen peroxide. Iron metal sheet surfaces spontaneously corrode under acidic conditions producing iron species (mainly ferrous ions) which react with hydrogen peroxide *via* the Fenton reaction. Experiments were carried out in a Floclab jar-test (Prolabo–France) equipped with six beakers (1-L capacity) and they were performed at ambient temperature (25 °C). A fixed volume of hydrogen peroxide was introduced in the reactor followed by the addition of 500 mL of OMW sample. The pH of the solution was measured by a pH-meter (Inolab WTW, Germany) and it was possibly adjusted by adding HCl (1 M) or NaOH (5 M). After the introduction of iron spires, the reactor was maintained under a continuous stirring at 200 rpm. Aqueous samples were withdrawn for analysis with adding NaOH and they were cooled in order to stop the Fenton reaction. It has been shown that hydrogen peroxide is unstable in basic solution and above pH 7 it would decompose to yield oxygen and water [25].

2.3. Analyses

Biochemical oxygen demand (BOD_5) was determined by the manometric method with a respirometer (BSB-Controlled Model OxiTop (WTW)) and the chemical oxygen demand (COD) was estimated using the method described by Knechtel [26]. Ferrous ions in aqueous solution were measured by Atomic Absorption spectrophotometer equipped with a Polarized Zeeman Z-6100 model (Hitachi, Japan). The GC–MS analyses were carried out with Hewlett-Packard 6890 Series GC, Agilent Technology equipped with a Hewlett-Packard 5973 Mass spectrometer, Agilent Technology. The separation of organic compounds was obtained by using a HP-5MS fused silica capillary column (L = 60 m, Ø = 0.25 mm, 0.25 μm film thickness, Agilent Technology). The oven temperature was programmed as follows: 100 °C hold for 2 min, raised at 5 °C/min to 290 °C (held for 20 min). Helium was used as a carrier gas at a flow rate of 1.07 mL/min. The injection was set on a splitless mode at 250 °C. The injected volume was 1.0 μL, the solvent delay was 6.00 min and the total run time was 60 min. Detection was conducted by a mass selective detector with electron impact ionization at 70 eV with 2.9 s scan time over a 50–550 a.m.u. range resolution. Mass spectra were compared to the reference compounds in Wiley 275L mass spectral library. OMW samples (20 mL) were acidified at pH 2 by HCl (1N) and four consecutive extractions with ethyl acetate (20 mL) were undergone. The organic phases were pooled and reduced to 10 ml by rotary evaporation (37 °C) and then silylated. For the silylation procedure, a mixture of pyridine (50 μL) and BSTFA (100 μL) was added and vortexed in screw cap glass tubes and it was consecutively placed in a water bath at 80 °C for 60 min. From the silylated mixture 1 μL was directly analyzed by GC–MS.

3. Results and discussion

3.1. Effect of initial H_2O_2 concentration on OMW oxidation

In order to determine the effect of initial H_2O_2 concentration on COD removal, OMW was incubated in the presence of 20 g/L of metallic iron (Fe^0) and a fixed amount of H_2O_2 ranging from 0 to 2.5 M. Results of these experiments are reported in the Fig. 1. Regarding this figure we can see that COD removal increased with H_2O_2 initial concentration and reached the maximum 92% by using 1 M of H_2O_2. From this, we can evaluate that 0.06 M of hydrogen peroxide was needed to the removal of 1 g of COD. Fig. 1 shows also that by using more than 1 M H_2O_2, the COD removal does not increase more and it is stabilized around the value of 92%. It is clear that 1 M of H_2O_2 is the optimal amount to obtain reasonable decrease in COD from olive mill wastewater. When one of the reactants (H_2O_2 or Fe^{2+}) is overdosed, both can react with the hydroxyl radicals and therefore inhibit the oxidation reaction [27,28]. It is well known that in the presence of high concentration of hydroxyl radicals the possible attack of organic compound can be reduced. This is due to the reaction of these radicals with hydrogen peroxide to produce less reactive radicals according to (Eq. (4)) [22].

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \tag{4}$$

Therefore, subsequent experiments were conducted with 0.95 M H_2O_2 concentration.

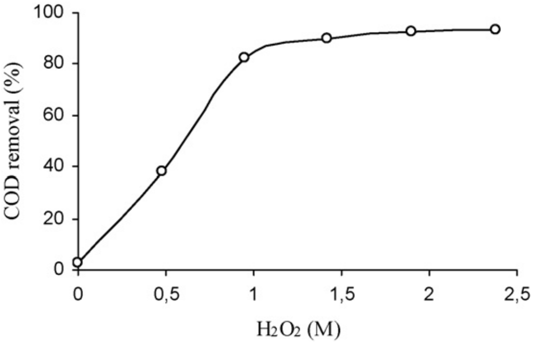

Fig. 1. Effect of H_2O_2 concentration on the COD removal efficiency during the Fenton oxidation of OMW (initial pH: 5.2, Fe^0: 20 g/L, reaction time 24 h, initial COD: 19 g/L).

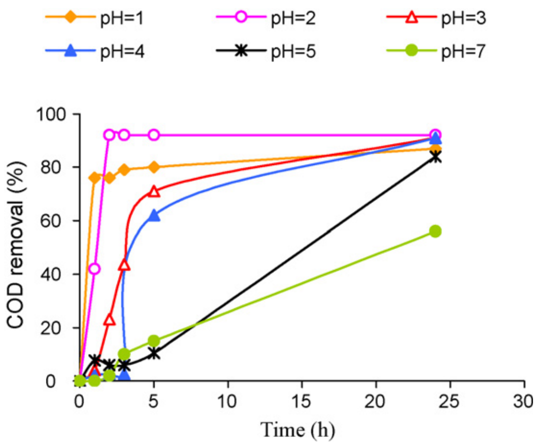

Fig. 2. Effect of initial pH on the COD removal during the Fenton oxidation of OMW (H_2O_2: 0.95 M, Fe^0: 20 g/L, initial COD: 19 g/L).

3.2. *Effect of initial pH on COD removal*

The effect of acidic and/or basic medium on the COD removal was studied by varying pH from 1 to 7. COD values obtained after the analysis of samples of treated solution under different initial pHs are shown in Fig. 2. Regarding these results, we can observe that the highest COD removal (92%) is obtained at pH 2 after 2 h of treatment. Whereas, concerning neutral pH, the COD removal does not exceed 50% after 24 h reaction time. This phenomenon is due to the low rate of Fenton's reaction at this pH value. At high pH (pH > 4), the generation of hydroxyl radicals gets slower because of the formation of the ferric-hydroxo complexes [29]. For a very acidic medium (pH < 2), the COD removal is lower than the value obtained at pH 2. In this case, Neyens and Baeyens [23] indicate that in the presence of organic substrates, in an excess of ferrous ions and at a low pH, hydroxyl radicals can add to the aromatic or heterocyclic ring and can also abstract a hydrogen atom, initiating a radical chain oxidation [22]. It can be observed that the Fenton oxidation of OMW is not able to achieve the complete removal of organic load. This might be due to the generation of high concentration of intermediate compounds (mainly carboxylic acid) that cannot be further oxidized by hydroxyl radicals and consequently are accumulated in the system. This concentration of refractory carbon seems to be a characteristic of the Fenton oxidation [16].

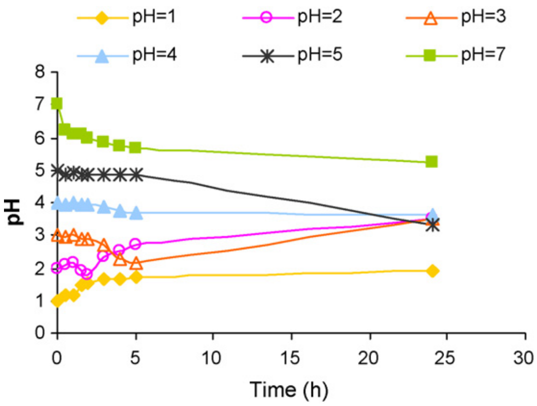

Fig. 3. Evolution of pH during the Fenton oxidation of OMW (H_2O_2: 0.95 M, Fe^0 = 20 g/L, COD: 19 g/L, time: 24 h).

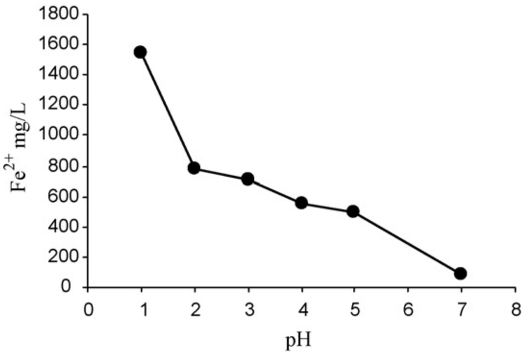

Fig. 4. The ferrous ions concentration at various initial pH after 24 h Fenton reaction of OMW (H_2O_2: 0.95 M, Fe^0 = 20 g/L, initial COD: 19 g/L).

3.3. *Evolution of pH and ferrous ions concentration during OMW oxidation*

In general, the pH end value of the treated solution after Fenton reaction is independent from the initial acidity of solution. Fig. 3 shows that in initial pH within 2 and 5, the pH increases and/or decreases to reach the pH value close to 3.5. This can be explained by the fact that OMW is transformed into organic acids with a short chain like acetic and oxalic acids. The presence of ionized form of these acids is responsible for this buffering effect in the treated solution. In the case of very acidic medium (initial pH 1), the pH end value increases to 1.9 and it is stabilized. Whereas, with initial pH 7, the pH of the solution decreases rapidly to pH 6 and it stabilizes at this value for 24 h. The Fenton oxidation is mainly determined by the availability of ferrous iron, which has a major role in the formation of hydroxyl radicals. The highest concentration of ferrous ions (1540 mg/L) is determined at pH 1 (Fig. 4). This concentration decreases with the increasing pH and reaches the value of 86 mg/L at pH 7. This result confirms that in acidic condition, the surface of the metal iron corrodes giving rise to the ferrous ions. This is in agreement with the previous study of Namkung et al. [30] and Bremner et al. [17] who find that under acidic conditions, ferrous ions are produced by corrosion that increases with a decrease in pH and an increase in hydrogen peroxide concentration. In fact, the generation of Fe (II) continues even after H_2O_2 depletes, which indicates that some of the ring-opened products and/or some organic acids or radical acids, may have roles in this regeneration process [31].

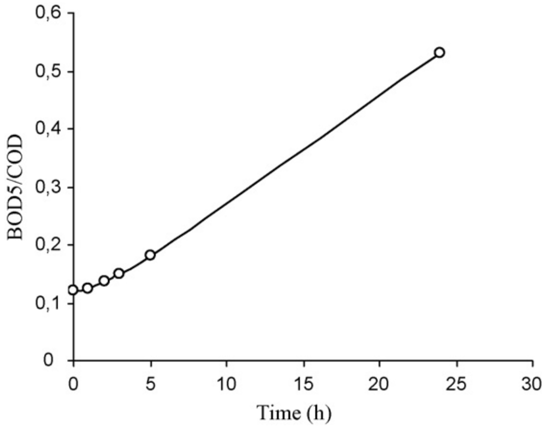

Fig. 5. Evolution of the BOD_5/COD ratio during the Fenton oxidation of OMW (H_2O_2: 0.95 M, Fe^0: 20 g/L, initial COD:19 g/L, pH 3)

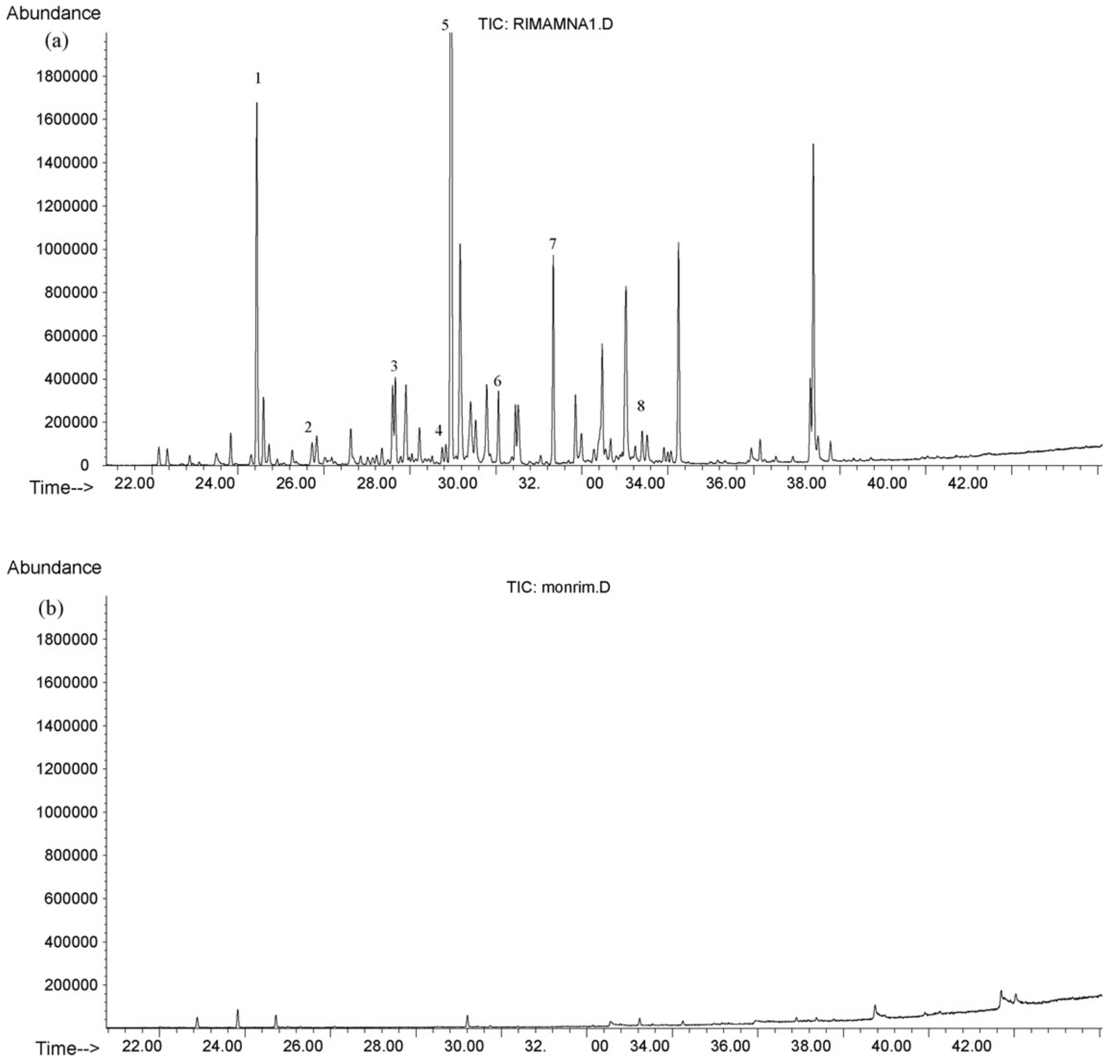

Fig. 6. GC–MS chromatograms on ethyl acetate extract from (a) crude OMW and (b) treated OMW by Fenton oxidation. The MS-identified compounds are the following: 1, tyrosol; 2, 4-hydroxybenzoic acid; 3, homovanillyl alcohol; 4, vanillic acid; 5, hydroxytyrosol; 6, protocatechuic acid; 7, 3,4-dihydroxyphenylglycol; 8, caffeic acid.

3.4. Improvement of OMW biodegradability and phenolic compounds degradation after Fenton oxidation

In this experiment, the biodegradability of treated OMW is monitored by measuring the BOD_5/COD ratio. The effluent is considered as biodegradable when the BOD_5/COD ratio is ranging from 0.4 to 0.5. Regarding BOD_5/COD ratio which is equal to 0.14, it is clear that crude OMW is toxic and not biodegradable. Fig. 5 shows the evolution of BOD_5/COD ratio during the Fenton oxidation with initial pH 3. The biodegradability of the wastewater increases after 5 h of Fenton oxidation and the BOD_5/COD ratio reaches the value of 0.22. This proves that the zero-valent Fe/H_2O_2 system is efficient to enhance the biodegradability of this toxic effluent. However, this ratio is still lower and the effluent needs more time for treatment. After 24 h of Fenton reaction, the BOD_5/COD ratio reaches the value of 0.53 which means that the wastewater is now already biodegradable.

The attenuation of the toxicity of OMW can be explained by the removal of phenolic compounds by Fenton oxidation. This is confirmed by GC–MS analysis of the treated and the untreated solutions. In fact, the two chromatograms of treated and untreated solutions are represented in Fig. 6(a) and (b). Regarding Fig. 6(a), we have identified in crude OMW eight phenolic compounds summarized in Table 1. These compounds can be divided into two groups. The major one contains hydroxytyrosol (70.93%) and thy-

Table 1
Abbreviated mass spectra of the main phenolic compounds recovered from OMW by ethyl acetate extraction.

Phenolic compound	Rate %	Retention time (min)	$M^{+\bullet}$	Main fragment of $M^{+\bullet}$ of the TMS derivatives
(1) 4-Hydroxyphenylethanol (*Tyrosol*)	16.55	24.43	282	267, 193, 179 (100%), 73
(2) 4-Hydroxybenzoic acid	1.35	25.73	282	267,223, 193, 179, 73 (100%)
(3) 4-Hydroxy-3-methoxyphenethylacohol (*Homovanillyl alcohol*)	4.25	27.65	312	297, 282, 267, 209 (100%), 193, 179
(4) 4-hydroxy-3-methoxybenzoic acid (*Vanillic acid*)	1.02	28.83	312	297 (100%), 282, 267, 253, 223, 193, 126, 73
(5) 3,4-Dihydroxyphenyl alcohol (*Hydroxytyrosol*)	70.93	28.96	370	355, 267 (100%), 193, 179, 73
(6) 3,4-Dihydroxybenzoic acid (*Protocatechuic acid*)	3.38	30.05	370	355, 311, 281, 267, 223, 193 (100%), 179, 73
(7) 3,4-Dihydroxyphenylglycol	0.55	31.32	458	443, 368, 355 (100%), 281, 147, 73
(8) 3,4-Dihydroxycinnamic acid (*Caffeic acid*)	1.93	33.39	396	396 (100%), 381, 307, 249, 219, 191, 73

rosol (16.55%). The minor one contains respectively: homovanillyl alcohol, protocatechuic acid, caffeic acid, 4-Hydroxybenzoic acid, vanillic acid and 3,4-dihydroxyphenylglycol. Similar composition from OMW was determined by DeMarco et al. [32] and Khoufi et al. [33]. By comparison, the chromatogram of Fig. 6(b) does not present any phenolic compounds. This confirms that the degradation of such products is responsible for toxicity in the OMW. Fenton oxidation has almost completely eliminated the phenolic compounds. Kang et al. [31] indicate that the availability of Fe^{2+} and his interaction with the organic intermediate, present a crucial importance to improve the decomposition performance of phenolic compounds. Therefore, the Fenton oxidation with zero-valent iron is an effective pre-treatment step to transform the organic compounds in the OMW into by-products that are more readily biodegradable and less toxic. Regarding these results, we can conclude that zero-valent Fe^{2+}/H_2O_2 system can be considered as a promising process for the degradation of polyphenols and the detoxification of olive mill wastewater.

4. Conclusion

Total phenol in the OMW is degraded and biodegradability is increased by the treatment with zero-valent Fenton oxidation. The efficiency of Fenton reaction increases with the decreasing of pH. The optimal value of pH is determined to be in the range between 2 and 4. It is estimated that the removal of 1 g of COD needs 0.06 M of H_2O_2. In this optimized condition, the maximum value of COD removal is at the level of 92%. After 24 h of Fenton reaction, the BOD_5/COD ratio reaches the value of 0.53 which indicates that the wastewater is now already biodegradable. This improvement in the biodegradability is obtained by the removal of phenolic compounds from the olive mill effluent as confirmed by GC-MS analysis of the treated OMW. This study shows that zero-valent Fe/H_2O_2 can be considered as an effective alternative solution for the treatment of OMW, and it presents different issues of possibly valorization. After Fenton oxidation, this effluent could be successfully treated by a classical biological process to achieve high quality of the effluent water. In other case, this pre-treatment can improve the land spreading and the ferti-irrigation purposes. The major advantage of Fenton process is that the reagent components are safe to handle and they are environmentally benign.

References

[1] R. Borja, E.S. Garrido, L. Martinez, R.A. Cormenzana, A. Martin, Kinetic study of anaerobic digestion of olive mill wastewater previously fermented with *Aspergillus terreus*, Process Biochem. 28 (1993) 397–404.

[2] M. Hamdi, Anaerobic digestion of olive mill wastewaters, Process Biochem. 31 (1996) 105–110.

[3] O. Yesilada, S. Sik, M. Sam, Biodegradation of olive mill wastewater by *coriolus versicolor* and *Funalia troggii*: effect of agitation, initial COD concentration, inoculum size and immobilization, World J. Microb. Biot. 14 (1998) 37–42.

[4] H. Ergüder, E. Güven, G.N. Denirer, Anaerobic treatment of olive mill wastes in batch reactors, Process Biochem. 36 (2000) 243–248.

[5] C.J. McNamara, C.C. Anastasiou, V. O'Flaherty, R. Mitchell, Bioremediation of olive mill wastewater, Int. Biodeter. Biodegr. 61 (2008) 127–134.

[6] A. El Hadrami, M. Belaqziz, M. El Hassni, S. Hanifi, A. Abbad, R. Capasso, L. Gianfreda, I. El Hadrami, Physico-chemical characterization and effects of olive oil mill wastewater fertirrigation on the growth of some Mediterranean crops, J. Agron. 3 (2004) 247–254.

[7] A. Bianco, F. Buiarelli, G. Cartoni, F. Coccioli, R. Jasionowska, P. Margherita, Analysis by liquid chromatography tandem mass spectrometry of biophenolic compounds in olives and vegetation waters. Part I, J. Sep. Sci. 26 (2003) 409–416.

[8] G. Aliotta, G. Cafiero, V. De Feo, B. Di Blasio, R. Iacovino, A. Oliva, Allelochemicals from Rue (*Ruta graveolens* L.) and olive (*Olea europea* L.) oil mill waste as potential natural pesticides, Curr. Top. Phytochem. 3 (2000) 167–177.

[9] R. Casa, A. D'Annibale, F. Pieruccetti, S.R. Stazi, G. Sermani, B. Lo Cascio, Reduction of the phenolic components in olive-mill wastewaters by an enzymatic treatment and its impact on *durum wheat* (*Triticum durum Desf.*) germinability, Chemosphere 50 (2003) 959–966.

[10] A. D'Annibale, R. Casa, F. Pieruccetti, M. Ricci, R. Marabottini, *Lentinula edodes* removes phenols from olive oil mill wastewater: impact on durum wheat (*Tritucum durum* Desf.) germinability, Chemosphere 54 (2004) 887–894.

[11] D. Quaratino, A. D'Annibale, F. Federici, C.F. Cereti, F. Rossini, M. Fenice, Enzyme and fugual treatments and a combination thereof reduce olive mill wastewater phytotoxicity on *Zea mays* L. seeds, Chemosphere 66 (2007) 1627–1633.

[12] R. Borja, J. Ala, A. Mancha, A. Martin, V. Alonso, E. Sanchez, Comparative effect of different aerobic pre-treatments on the kinetics and macroenergetic parameters of anaerobic digestion of olive mill waste water in continuous mode, Bioproc. Eng. 18 (1998) 127–134.

[13] S. Sayadi, N. Allouche, M. Jaoua, F. Aloui, Detrimental effects of high molecular mass polyphenols on olive mill wastewater biotreatment, Process Biochem. 35 (2000) 725–735.

[14] C.F. Cereti, F. Rossini, F. Federici, D. Quaratino, N. Vassilev, M. Fenice, Reuse of microbially treated olive mill wastewater as fertiliser for wheat (*Triticum durum* Desf.), Bioresour. Technol. 91 (2003) 135–140.

[15] E. Oliveros, O. Legrini, M. Hohl, T. Müller, A.M. Braun, Industrial waste water treatment: large scale development of a light-enhanced Fenton reaction, Chem. Eng. Process 36 (1997) 397–405.

[16] P. Canizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Saez, Advanced oxidation process for the treatment of olive oil mill wastewater, Chemosphere 67 (2007) 832–838.

[17] D.H. Bremner, A.E. Burgess, D. Houllemare, K.C. Namkung, Phenol degradation using hydroxyl radicals generated from zero-valent iron and hydrogen peroxide, Appl. Catal. B Environ. 63 (2006) 15–19.

[18] K.C. Namkung, A.E. Burgess, D.H. Bremner, H. Staines, Advanced Fenton processing of aqueous phenol solution: a continuous system study including sonication effects, Ultrason. Sonochem. 15 (2008) 171–176.

[19] C. Belaid, M. Kallel, M. Khadhraoui, G. Lalleve, B. Elleuch, J.F. Fauvarque, Electrochemical olive mill wastewater: removal of phenolic compounds and decolourization, J. Appl. Electrochem. 36 (2006) 1175–1182.

[20] M. Ksibi, Chemical oxidation with hydrogen peroxide for domestic wastewater treatment, Chem. Eng. J. 119 (2006) 161–165.

[21] U.T. Un, U. Altay, A.S. Koparal, U.B. Ogutveren, Complete treatment of olive mill wastewater by electrooxidation, Chem. Eng. J. 139 (2008) 445–452.

[22] C. Walling, Fenton's reagent revisited, Acc. Chem. Res. 8 (1975) 125–131.

[23] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. B98 (2003) 33–50.

[24] M. Kallel, C. Belaid, R. Boussahel, M. Ksibi, A. Montiel, B. Elleuch, Olive mill wastewater degradation by Fenton oxidation with zero-valent iron and hydrogen peroxide, J. Hazard. Mater. (2008), doi:10.1016/j.hazmat.2008.07.006.

[25] H. Tekin, O. Bilkay, S.S. Ataberk, T.H. Balta, I.H. Ceribasi, F.D. Sanin, F.B. Dilek, U. Yetis, Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater, J. Hazard. Mater. B136 (2006) 258–265.

[26] R.J. Knechtel, A more economical method for the determination of chemical oxygen demand, Water Pollut. Control (1978) 25–29.

[27] W.Z. Tang, C.P. Huang, An oxidation kinetic model of unsaturated chlorinated aliphatic compounds by Fenton's reagent, J. Environ. Sci. Health A 31 (1996) 2755–2775.

[28] W.Z. Tang, C.P. Huang, Stochiometry of Fenton's reagent in the oxidation of chlorinated aliphatic organic pollutants, Environ. Technol. 18 (1997) 13–23.

[29] W.G. Kuo, Decolorizing dye wastewater with Fenton's reagent, Water Res. 26 (1992) 881–886.

[30] K.C. Namkung, A.E. Burgess, D.H. Bremner, A Fenton-like oxidation process using corrosion of iron metal sheet surfaces in the presence of hydrogen peroxide: a batch process study using model pollutants, Environ. Technol. 26 (2005) 341–352.

[31] N. Kang, D. Lee, J. Yoon, Kinetic modeling of Fenton oxidation of phenol and monochlorophenols, Chemosphere 47 (2002) 915–924.

[32] E. De Marco, M. Savarese, A. Paduano, R. Sacchi, Characterisation and fractionation of phenolic compounds extracted from olive mill wastewaters, Food Chem. 104 (2007) 858–867.

[33] S. Khoufi, F. Aloui, S. Sayadi, Extraction of antioxidants from olive mill wastewater and electro-coagulation of exhausted fraction to reduce its toxicity on anaerobic digestion, J. Hazard. Mater. 151 (2008) 531–539.