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Removal of phenolic compounds present in olive mill wastewaters by ozonation

Olivier Chedeville ^{a,b,*}, Marie Debacq ^{a,c}, Catherine Porte ^{a,c}

^a Laboratoire de Génie des Procédés pour l'Energie, l'Environnement et la Santé (EA 21)

^b Laboratoire des Procédés Chimiques, Université d'Orléans, 16 Rue d'Issoudun - Domaine Universitaire, BP 16729, 45067 Orléans Cedex 2, France

^c Laboratoire de Chimie Industrielle Génie des Procédés, Conservatoire National des Arts et Métiers, 2 rue Conté, case courrier 302, 75003 Paris, France

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ABSTRACT

The aim of this work is to study a pre-treatment process of olive mill wastewaters based on ozonation. The efficiency of the process depends on the removal of pollutants and on ozone mass transfer performance. In order to choose an appropriate gas/liquid contactor, the rate constants of three phenolic compounds (gallic acid, p-hydroxybenzoic acid and p-coumaric acid) were determined by using competition kinetic model. These constants, obtained at pH 5, were found to be high (from 3.8×10^4 L/mol s to 2.9×10^5 L/mol s), inducing a diffusion controlled regime (Ha>3). Thus, to obtain an efficient ozonation process, gas/liquid contactor should be adapted to this regime. An ejector was chosen as gas/liquid contactor. In a first time, treatment of synthetic effluent containing the three phenolic compounds was performed to evaluate efficiency of the process. Experimental conditions were chosen to obtain a diffusion controlled regime (Ha>3). It appeared that this gas/liquid contactor permits obtaining complete and fast removal of pollutants with a very efficient ozone mass transfer (up to 90% during removal of phenolic compounds). So, this process was used to perform the ozonation treatment of olive mill wastewaters from Sfax (Tunisia). It was proved to be very efficient: up to 80% of phenolic compounds were removed and ozone mass transfer reached 95% during this oxidation.

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1. Introduction

Wastewaters resulting from olive oil production, called margines, are a serious environmental problem in Mediterranean countries, where this activity is located [1,2]. The content of olive mill wastewaters (OMW) depends on a number of parameters, such as geographic location, season, soil and weather. Generally acid (pH 4.5 to 5), they present a high organic and inorganic pollutant load [3–5]. In particular, these wastewaters contain high amounts of phenolic compounds, in concentrations varying from 6 to 20 g/L [6].

Biological degradation methods were tested to reduce pollution load of these wastewaters. Fezzani et al. [7] tested the codigestion of OMW with olive mill solid waste containing high level of nitrogen source and obtained COD removal between 16.7% and 58.4%. Ammary et al. [8] studied the treatment of OMW by using an anaerobic treatment and obtain total phenol removal of 63%. These methods were limited by the high phenolic compounds concentration of OMW. The bactericidal properties these compounds do not allow OMW to be treated in the traditional way, as they inhibit the activity of microorganisms during the biological treatment step [9,10]. A specific pre-treatment is therefore needed to remove their toxicity before they are introduced into a treatment plant. Different treatment methods have been tested (adsorption on activated carbon, ultrafiltration, and ion exchange resins) but do not present a high efficiency [11]. In contrast, ozonation and advanced oxidation processes seem to lead to interesting results [12,13]. According to Rivas et al. [14], ozonation is a suitable treatment to obtain more biodegradable effluent and permit to use a biological treatment step. Some studies showed that process based on ozone or advanced oxidation processes, much of ozone fed in is adsorbed and reacted [17]. So, ozonation process of these effluents is controlled by ozone mass transfer, and process efficiency depends on the choice of an appropriate gas/liquid contactor.

The aim of the present study is to design a pre-treatment process using ozone, which removes phenolic compounds and transfers ozone efficiently into water. Firstly, in order to determine the phenomenon limiting ozone mass transfer (reaction or diffusion) and to choose an appropriate gas/liquid contactor, the ozonation kinetics of three phenolic compounds (gallic acid, p-coumaric acid and p-hydroxybenzoic acid) were determined. Secondly, treatment of synthetic effluent containing these compounds was performed in order to evaluate process efficiency in diffusion controlled regime (Ha>3). Finally, the treatment of olive mill wastewaters from Sfax (Tunisia) was performed in the selected contactor.





^{*} Corresponding author. Laboratoire des Procédés Chimiques, Université d'Orléans, 16 Rue d'Issoudun - Domaine Universitaire, BP 16729, 45067 Orléans Cedex 2, France. Tel.: +33 238494424; fax : +33 238494425.

E-mail address: olivier.chedeville@univ-orleans.fr (O. Chedeville).

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2. Experimental

2.1. Competition kinetics model

It is admitted that ozonation is a second order reaction [18,19]. To determine the rate constants for the direct oxidation of phenolic compounds with ozone, the competition kinetics model was used [20]. In this method, a phenolic compound is introduced with a reference compound whose ozonation kinetics constant is known. In this study, the reference compound was phenol, whose ozonation kinetics rate constant was determined by Hoigné et al. [21]. To avoid radical reaction, tBuOH was used as a radical scavenger. The kinetics equations can therefore be written:

$$-\frac{\mathrm{d}[PC]}{\mathrm{d}t} = k_{03/PC} \cdot [0_3] \cdot [PC] \tag{1}$$

$$-\frac{d[phenol]}{dt} = k_{03/phenol} \cdot [O_3] \cdot [phenol]$$
⁽²⁾

where [*PC*] and [phenol] are respectively the phenolic compound and phenol concentration (mol/L), *t* the time (s), $k_{O3/PC}$ and $k_{O3/phenol}$ represent respectively the ozonation kinetics constant of the phenolic compound and the phenol (L/mol s), and [O₃] is the dissolved ozone concentration (mol/L). The ratio of Eqs. (1) and (2) gives:

$$\frac{d[PC]}{d[phenol]} = \frac{k_{O3/CP}}{k_{O3/phenol}} \cdot \frac{[PC]}{[phenol]}$$
(3)

By integrating Eq. (3), the following equation is obtained:

$$\ln\left(\frac{[PC]_{0}}{[PC]_{\infty}}\right) = \frac{k_{03/PC}}{k_{03/phenol}} \cdot \ln\left(\frac{[phenol]_{0}}{[phenol]_{\infty}}\right)$$
(4)

where $[PC]_0$ and $[phenol]_0$ are respectively phenolic compound and phenol initial concentration (mol/L) and $[PC]_{\infty}$ and $[phenol]_{\infty}$ are respectively phenolic compound and phenol concentration at the end of the reaction, while dissolved ozone was consumed (mol/L). In order to determine phenol and phenolic compound concentration at the end of the reaction, ozone has to be added in substoechiometric amount.

In this study three phenolic compounds were studied: gallic acid, p-coumaric acid and p-hydroxybenzoic acid. The ozonation kinetics of dissociating organic compounds strongly depends on pH [18,22]. For the experiments, initial pH was therefore fixed at 5, which is the average pH value of olive mill wastewaters, by adding H₂SO₄. Experiments were carried out at 20 °C. In each stirred reactor 200 mL of deionised water, 0.32 mg of phenol and phenolic compound and 10 mg of tBuOH were introduced. In these reactors, different volumes (5 to 30 mL) of ozone saturated water, were introduced. The last one was prepared in a bubble column by introducing ozone in distilled water. Ozone concentration in water was 0.75 mg/L \pm 0.01 mg/L (measured by carmin indigo method, see Section 2.3.2). After 10 min, phenol and phenolic compound concentrations were determined by HPLC. Different experiments were carried out by changing the volume of ozone saturated water (5 to 30 mL). According to Eq. (4), the ratio $\frac{k_{03/CP}}{k_{03/phenol}}$ is the slope of $\ln\left(\frac{|PC|_0}{|PC|_{w}}\right) \text{vs} \ln\left(\frac{|phenol|_0}{|phenol|_{w}}\right)$.

2.2. Ozone mass transfer

Efficiency of treatment process depends on the ozone mass transfer. So, it is very important to choose a suitable gas/liquid contactor. The Hatta number is a very important criterion giving information on the competition between the kinetics of the reaction and the diffusion inside the liquid film (Table 1). It indicates where

Table	1
Hatta	number

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Ha	Regime	Place of the reaction	G/L contactor characteristic
< 0.3	Kinetic	Bulk liquid	Liquid volume
0.3–3	Transition	Partially in film	Interfacial area and liquid volu
>3	Diffusion	Entirely in film	Interfacial area

the chemical reaction takes place (in the bulk liquid or in the film) and allows to choose the appropriate gas/liquid contactor [23]. In the case of a second order reaction the Hatta number is given by [20]:

$$Ha = \frac{\sqrt{k \cdot [A] \cdot D_{03}}}{k_{\rm L}} \tag{5}$$

where *k* is the rate constant of the reaction between ozone and compound *A* (L/mol s), [*A*] the concentration of compound *A* in the bulk liquid (mol/L), D_{O3} the diffusivity coefficient of ozone into water (m²/s) and $k_{\rm L}$ the mass transfer coefficient (m/s). If ozone reacts with two or more compounds in liquid phase, the Hatta number is expressed as:

$$Ha = \frac{\sqrt{\sum_{i} k_{i} \cdot [i] \cdot D_{03}}}{k_{\rm L}} \tag{6}$$

Where k_i is the rate constant of the reaction between ozone and compound *i* (L/mol s) and [*i*] is the concentration of compound *i* in the bulk liquid (mol/L).

2.3. Ozonation pilot

The ozonation pilot (Fig. 1) uses an ejector as gas/liquid contactor. In this contactor, water passes through a convergent, generating depressurization in the mixing chamber into which the ozone is aspired. This kind of gas/liquid contactor is recommended for a diffusion controlled regime [18]. Initially, the polluted liquid contained in a 40 L tank (Fig. 1) is first introduced into the heat exchanger, then to the ejector (Fig. 2). The temperature *T* of the liquid can be held at between 20 °C and 35 °C. The liquid flow rate *L* can be controlled between 0.5 and 1 m³/h. The two phases form an emulsion which is then fed into the mixture tube (height: 1.04 m; diameter: 20 mm), allowing a return of the liquid in the tank. The latter is surmounted by a cyclone used to separate the droplets of water from



Fig. 1. Ozonation pilot.





Fig. 3. Ozonation kinetics of phenolic compounds. pH = 5, $m_{\text{phenol}} = m_{\text{phenolic compound}} = 0.32 \text{ mg}$, $m_{\text{tBuOH}} = 10 \text{ mg}$, T = 20 °C.

2.4.4. Chemical oxygen demand

The chemical oxygen demand (COD) was measured by method 8000 of HACH with the spectrophotometer DR/2000.

the gas. This gas is fed to the ozone analyzer and to the thermal destructor.

Ozone was produced from pure oxygen in an LABO LOX ozoniser provided by the Trailigaz company. This type of apparatus guarantees an average ozone production of 16 g/h for a concentration of 5% in weight.

The hydrodynamic properties of this contactor, presented on Table 2, were determined in a previous study [24]. It was shown that this ejector presents a high gas hold up and volumetric mass transfer coefficient.

2.4. Analytical methods

2.4.1. HPLC

Phenolic compound concentration was analysed by means of high performance liquid chromatography with a UV detector (210 nm) and a hypersil C18 column (250 mm long, 4.6 mm internal diameter). Mobile phase was a mixture H_2SO_4 (4 mM):acetonitrile/80:20 at a rate of 1 mL/min.

2.4.2. Dissolved ozone

Dissolved ozone concentration was determined by using the carmin indigo method [21]. The attack of trisulfonate carmin indigo by O_3 in an acid medium leads to discoloration of the solution which was monitored by spectrophotometry at 600 nm. (spectrophotometer DR2100, HACH).

2.4.3. Total phenolic compounds concentration

Total phenolic compounds concentration was determined by using the Folin Ciocalteu method [25]. 1 mL of sample, 500μ L of Folin Ciocalteu reagent, 5 mL of distilled water and 2 mL of 10% sodium carbonate solution are introduced into a test tube. The mixture is shaken and allowed to stand for 2 h in the dark at room temperature. Absorbance was then measured by spectrophotometry at 760 nm (spectrophotometer DR2100, HACH).

Table 2

Hydrodynamic properties [24].

Volumetric mass transfer coefficient (s ⁻¹)	$k_{\rm L}$	4×10^{-5}
Gas hold up Main residence time (s)	$\frac{\varepsilon_G}{ au}$	$0.21 < \varepsilon_G < 0.32$ $0.75 < \tau < 1.15$

 $0.8{<}L\,(m^3h^{-1}){<}1;\,0.2{<}G\,(Nm^3h^{-1}){<}0.5.$

3. Results and discussion

3.1. Determination of ozonation rate constants

 $\ln\left(\frac{[CP]_0}{[CP]_t}\right)$ vs $\ln\left(\frac{[phenol]_0}{[phenol]_t}\right)$ is plotted on Fig. 3. The experimental data fit well a straight line (regression coefficient $R^2 > 0.99$). According to Eq. (4), the slope of these straight lines corresponds to the ratio of the ozonation rate constant of phenolic compound and the ozonation rate constant of phenol. The latter was estimated by Bader and Hoigné [15]: $k_{O3/phenol} = 5.10^4 L/mol s$ at pH 5. The values of the calculated rate constants of phenolic compounds are presented in Table 3.

High rate constants were obtained at pH 5 $(3.8 \times 10^4 < k_{O3/PC} (L/mol s) < 2.9 \times 10^5)$ showing that these phenolic compounds react strongly with ozone. These results are close to those obtained with other methods. Beltran et al. estimated the rate constant of ozonation of gallic acid between $0.97 \times 10^5 L/mol s$ at pH 3 and $5.1 \times 10^5 L/mol s$ at pH 7 [26]. These high rate constants associated with a high concentration of phenolic compound in margines induce a diffusion controlled regime [6]. Subsequently, an ejector, which presents adapted characteristics for this regime (high gas hold up and volumic mass transfer coefficient), should be used to transfer ozone into water during treatment of olive mill wastewater by ozonation.

3.2. Ozonation of synthetic effluent

3.2.1. Operating conditions

Process efficiency was evaluated by performing treatment of synthetic effluent prepared by introducing 1.6 g of gallic, p-coumaric and p-hydroxybenzoic acid into 40 L of water. These concentrations were chosen in order to obtain a pollution load compatible with the ozoniser capacities and a diffusion controlled regime for the ozone mass transfer (Ha>3). Indeed, in these experimental conditions, by using rate constant obtained, Ha number was estimated at 9.9 by using Eq. (6) (with $k_{\rm L} = 4 \times 10^{-5}$ m/s and $D_{\rm O3} = 1.73 \times 10^{-9}$ m²/s).

Table 3Ozonation kinetic constant of phenolic compounds - pH 5.

Phenolic compound (PC)	r^2	Slope	$k_{\rm O3/PC}$ (L/mol s)
Gallic acid	0.99	5.82	$\begin{array}{c} 2.9\!\times\!10^5 \\ 3.8\!\times\!10^4 \\ 4.8\!\times\!10^4 \end{array}$
p-Hydroxybenzoic acid	0.99	0.76	
p-Coumaric acid	0.99	0.96	

This experiment was carried out at 20 °C and the effluent was continuously recirculated at a flow rate of $0.9 \text{ m}^3/\text{h}$. Initial pH was fixed at 5 by adding H₂SO₄. The gas flow rate was $0.3 \text{ Nm}^3/\text{h}$ and the ozone concentration in the inlet gas was $C_{03,i} = 23 \text{ g/Nm}^3$. Samples were collected at suitable intervals of time. Phenolic compound concentrations were monitored by HPLC, dissolved ozone concentration was measured by the carmin indigo method and ozone mass transfer was determined by monitoring ozone concentration in the inlet gas. The efficiency of the mass transfer is given by the ozone mass transfer ratio:

$$r_{03} = \frac{(C_{03,i} - C_{03,0})}{C_{03,0}} \cdot 100 \tag{7}$$

Where $C_{O3,i}$ is the ozone concentration in the inlet gas (g/Nm³) and $C_{O3,o}$ the ozone concentration in the outlet gas (g/Nm³).

3.2.2. Results and discussion

Evolution of the phenolic compounds concentration and ozone mass transfer ratio are presented on Fig. 4. It appeared that gallic acid and p-coumaric acid were completely removed in 15 min, and phydroxybenzoic acid was removed in 20 min. During this step, ozone mass transfer was very high: it was up to 95% in the first 10 min and decrease slowly to be up to 90% after 20 min of treatment. Moreover, no dissolved ozone was detected. So, during this treatment, more than 90% of produced ozone was transferred into water and consumed to remove phenolic compounds. These results show that ejector is a very efficient gas/liquid contactor in these conditions. High ozonation kinetics constants and phenolic compound concentrations induce a diffusion controlled regime (Ha>3), and the ejector permits to obtain a very efficient ozone mass transfer which leads to a fast and complete removal of pollutants. After 20 min of treatment, it appeared that ozone mass transfer is less efficient. It corresponds to ozonation of phenolic compounds byproducts which are less reactive with ozone and do not induce a diffusion controlled regime.

3.3. Ozonation of olive mill wastewater

3.3.1. Operating conditions

Olive mill wastewaters were obtained from Sfax (Tunisia). The main characteristics of this effluent were: pH = 5, COD = 6.4 g/L, and insoluble material = 3 g/L. It is to be noted that this pollution load was lower than those usually reported in literature. In order to have a pollution load compatible with the ozoniser capacities, 6.5 L of this wastewater was mixed with 33.5 L of tap water before introduction in the ozonation pilot. The experiment was carried out at 20 °C, with a liquid flow rate L = 0.9 L/h and a gas flow rate G = 0.3 Nm³/h. Ozone concentration in the inlet gas was $C_{03,i} = 23$ g/Nm³. Samples were collected at suitable intervals of time. Total phenolic compound concentration was analysed with the Folin Ciocalteu method. Ozone mass transfer efficiency (r_{03}) was determined by monitoring the



Fig. 4. Evolution of phenolic compounds abatement and ozone mass transfer ratio (\diamond) gallic acid; (+) p-coumaric acid; (Δ) p-hydroxybenzoic acid; (\bigcirc) r₀₃. *T*=20 °C; *G*=0.3 Nm³/h; *L*=0.9 m³/h; *C*_{03,i}=23 g/Nm³.

ozone concentration in inlet and outlet gas. The Chemical Oxygen Demand (COD) of each sample was measured.

3.3.2. Results and discussion

The evolution of the total concentration of phenolic compounds (Fig. 5) shows that these compounds were eliminated at the beginning of the treatment. After 15 min, more than 65% of the phenolic compounds were removed. Then, removal of these compounds became slower. After 40 min, an abatement of about 80% was obtained. Subsequently, no evolution in the total concentration of phenolic compounds was observed.

Evolution of the COD (Fig. 5) was similar: in the first 40 min, a significant removal of COD was obtained (decrease of about 48% in COD after 40 min). After this initial period, the COD value remained constant. Other organic compounds present in margines and phenolic compounds byproducts could be responsive of this COD.

Evolution of the ozone mass transfer ratio is presented Fig. 5. It can be seen that in the first 10 min, all the ozone introduced was transferred in into the liquid ($r_{03} = 100\%$). The lack of dissolved ozone in the liquid (determined by the carmin indigo method) means that all the ozone produced was used to oxidise the pollutants present in the effluent. From 10 to 40 min, r_{03} decreased slowly. After 40 min, the ozone transfer ratio was between 50% and 75%. After this period, ozone transfer was less efficient, and after 90 min, r_{03} was about 50%, meaning that half of the ozone produced was not used for treatment.

Results show that ozonation is quite an efficient method to remove phenolic compounds from olive mill wastewaters. In spite of the presence of many other organic and inorganic compounds, phenolic compounds were significantly removed at the beginning of the treatment. In this study, abatement of up to 80% was obtained. Some phenolic compounds seem to be recalcitrant to oxidation, no further evolution being observed after 40 min. To remove them, it could be interesting to use an advanced oxidation process (O_3/H_2O_2 , O_3/UV). However, advanced oxidation processes are less selective than ozonation, and many organic compounds, including non-toxic ones, would be removed, raising the amount of ozone needed to treat these wastewaters.

Using the ejector as gas/liquid contactor resulted in a very efficient transfer of ozone into water during the first 15 min (ozone mass transfer was up to 95%). This phenomenon is due to the presence of phenolic compounds, which react strongly with ozone and induce a diffusion controlled regime. Subsequently, the decrease in ozone mass transfer efficiency is due to the removal of phenolic compounds. Results therefore show that in a very short contact time (mean residence time is about 1 s), this process can obtain very interesting



Fig. 5. Evolution of COD, total phenolic compounds removal and ozone mass transfer ratio (Δ) [*PC*]; (+) COD; (\bigcirc) r₀₃. *T*=20 °C; *G*=0.3 Nm³/h; *L*=0.9 m³/h; C_{03,i}=23 g/Nm³.

mass transfer efficiencies since target compounds are present in solution. By modifying the ozoniser capacities, it should be possible to use this process in an open circuit configuration. Results show that in this configuration, the ejector could transfer all the produced ozone in water and hence remove a high rate of phenolic compounds in a very short time.

4. Conclusions

Phenolic compounds present in olive mill wastewaters react strongly with ozone. In a first step, the ozonation kinetics constant of gallic acid, hydroxybenzoic acid and coumaric acid were determined by using competition kinetic model. The high values of these constants (from 3.8×10^4 L/mol s to 2.9×10^5 L/mol s) and the high concentration of phenolic compounds induce a diffusion controlled regime. In a second time, ozonation of a synthetic effluent containing the phenolic compounds was performed by using an ejector as gas/liquid contactor. It appeared that in a diffusion controlled regime (Ha>3), the process was very efficient: more than 90% of ozone produced was transferred into water and used to remove pollutants. So, phenolic compounds removal was fast and complete. Finally an ozonation process using an ejector as gas/liquid contactor was used to perform the treatment of olive mill wastewaters coming from Sfax (Tunisia). Positive results were obtained:

- phenolic compounds present in wastewaters were removed at the beginning of the treatment, showing that other products present in this industrial matrix do not interfere with treatment;
- abatement of phenolic compounds reached 80%;
- ozone mass transfer was very efficient since the removal of phenolic compounds: r_{03} was up to 95% during the first 15 min.

This process could be an efficient pre-treatment enabling the effluent then to be fed to a classical wastewater treatment plant.

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References

- C.A. Paraskeva, V.G. Papadakis, E. Tsarouchi, D.G. Kanellopoulou, P.G. Koutsoukos, Membrane processing for olive mill wastewater fractionation, Desalination 213 (2007) 218–229.
- [2] 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, Journal of Hazardous Materials 151 (2008) 531–539.
- [3] S. Sayadi, R. Ellouz, Screening of white rot fungi for the treatment of olive mill waste-waters, Journal of Chemical Technology & Biotechnology 57 (1993) 141–146.

- [4] H.J. Mellouli, R. Hartmann, D. Gabriels, W.M. Cornelis, The use of olive mill effluents ("margines") as soil conditioner mulch to reduce evaporation losses, Soil and Tillage Research 49 (1998) 85–91.
- [5] A. Ginos, T. Manios, D. Mantzavinos, Treatment of olive mill effluents by coagulation-flocculation-hydrogen peroxide oxidation and effect on phytotoxicity, Journal of Hazardous Materials 133 (2006) 135–142.
- [6] A.M. Amat, A. Arques, H. Beneyto, A. García, M.A. Miranda, S. Seguí, Ozonisation coupled with biological degradation for treatment of phenolic pollutants: a mechanistically based study, Chemosphere 53 (2003) 79–86.
- [7] B. Fezzani, R. Ben Cheikh, Optimisation of the mesophilic anaerobic co-digestion of olive mill wastewater with olive mill solid waste in a batch digester, Desalination 228 (2008) 159–167.
- [8] B.Y. Ammary, Treatment of olive mill wastewater using an anaerobic sequencing batch reactor, Desalination 177 (2005) 157–165.
- [9] K. Turhan, S. Uzman, Removal of phenol from water using ozone, Desalination 229 (2008) 257–263.
- [10] M. Drouiche, V. Le Mignot, H. Lounici, D. Belhocine, H. Grib, A. Pauss, N. Mameri, A compact process for the treatment of olive mill wastewater by combining OF and UV/H₂O₂ techniques, Desalination 169 (2004) 81–88.
- [11] J.M. Monteagudo, M. Carmona, A. Durán, Photo-Fenton-assisted ozonation of pcoumaric acid in aqueous solution, Chemosphere (2005) 1103–1110.
- [12] C. Vassilakis, A. Pantidou, E. Psillakis, N. Kalogerakis, D. Mantzavinos, Sonolysis of natural phenolic compounds in aqueous solutions: degradation pathways and biodegradability, Water Research 38 (2004) 3110–3118.
- [13] A.M. Amat, A. Arques, M.A. Miranda, p-Coumaric acid photodegradation with solar light, using a 2, 4, 6-triphenylpyrylium salt as photosensitizer: a comparison with other oxidation methods, Applied Catalysis B: Environmental 23 (1999) 205–214.
- [14] J. Rivas, F. Beltran, B. Acedo, O. Gimeno, Two-step wastewater treatment: sequential ozonation – aerobic digestion, Ozone Science and Engineering 22 (2000) 617–636.
- [15] F.J. Beltrán, J.F. García-Araya, J. Frades, P. Álvarez, O. Gimeno, Effects of single and combined ozonation with hydrogen peroxide or UV radiation on the chemical degradation and biodegradability of debittering table olive industrial wastewaters, Water Research 33 (1999) 723–732.
- [16] P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Sáez, Advanced oxidation processes for the treatment of olive-oil mills wastewater, Chemosphere 67 (2007) 832–838.
- [17] F.J. Beltrán, J.M. Encinar, JuanF. González, Industrial wastewater advanced oxidation. Part 2. Ozone combined with hydrogen peroxide or UV radiation, Water Research 31 (1997) 2415–2428.
- [18] J. Hoigné, H. Bader, Rate constants of reactions of ozone with organic and inorganic compounds in water—II: Dissociating organic compounds, Water Research 17 (1983) 185–194.
- [19] R.F. Dantas, S. Contreras, Sulfamethoxazole abatement by means of ozonation, Journal of Hazardous Materials 150 (2008) 790.
- [20] M. Deborde, S. Rabouan, J. Duguet, B. Legube, Kinetics of aqueous ozone-induced oxidation of some endocrine disruptors, Environmental Science and Technology 39 (2005) 6086–6092.
- [21] H. Bader, J. Hoigné, Determination of ozone in water by the indigo method, Water Research 15 (1981) 449–456.
- [22] F.J. Benitez, J. Beltran-Heredia, J.A. Peres, J.R. Dominguez, Kinetics of phydroxybenzoic acid photodecomposition and ozonation in a batch reactor, Journal of Hazardous Materials 73 (2000) 161–178.
- [23] M. Roustan, Transferts gaz liquide dans les procédés de traitement des eaux et des effluents gazeux, Tec & Doc ed, 2003.
- [24] O. Chedeville, M. Debacq, C. Porte, Récents Progrès en Génie des Procédés 92 (2005) C-5.
- [25] V.L. Singleton, J. Rossi, Colorimetry of total phenolics with phosphomolybdicphosphotungstic acid reagents, American Journal of Enology and Viticulture 16 (1965) 144–158.
- [26] F.J. Beltran, J.F. Garcia Araya, F.J. Rivas, P. Alvarez, E. Rodriguez, Kinetics of competitive ozonation of some phenolic compounds present in wastewaters from food processing industries, Ozone Science and Engineering 22 (2000) 167–183.