



ELSEVIER

Journal of Hazardous Materials B73 (2000) 161–178

**Journal of
Hazardous
Materials**

www.elsevier.nl/locate/jhazmat

Kinetics of *p*-hydroxybenzoic acid photodecomposition and ozonation in a batch reactor

F. Javier Benitez ^{a,*}, Jesus Beltran-Heredia ^a, Jose A. Peres ^b,
Joaquin R. Dominguez ^a

^a *Departamento de Ingeniería Química y Energetica, Universidad de Extremadura, 06071 Badajoz, Spain*

^b *Departamento de Química, Universidad de Tras os Montes e Alto Douro, 5001 Vila Real, Portugal*

Received 28 June 1999; received in revised form 8 October 1999; accepted 25 October 1999

Abstract

The decomposition of *p*-hydroxybenzoic acid, an important pollutant present in the wastewaters of the olive oil industry, has been carried out by a direct photolysis provided by a polychromatic UV radiation source, and by ozone. In both processes, the conversions obtained as a function of the operating variables (temperature, pH and ozone partial pressure in the ozonation process) are reported. In order to evaluate the radiation flow rate absorbed by the solutions in the photochemical process, the Line Source Spherical Emission Model is used. The application of this model to the experimental results provides the determination of the reaction quantum yields which values ranged between 8.62 and 81.43 l/einstein. In the ozonation process, the film theory allows to establish that the absorption process takes place in the fast and pseudo-first-order regime and the reaction is overall second-order, first-order with respect to both reactants, ozone and *p*-hydroxybenzoic acid. The rate constants are evaluated and vary between 0.18×10^5 and 29.9×10^5 l/mol s depending on the temperature and pH. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: *p*-Hydroxybenzoic acid degradation; Photolysis; Ozonation; Quantum yields; Rate constants

* Corresponding author. Tel.: +34-924-289384; fax: +34-924-271304; e-mail: javben@unex.es

1. Introduction

The olive oil extraction industry generates each year a great amount of wastewaters with the main contaminants being sugars, lipids, phenols and polyphenols [1]. This presents a significant contamination problem for the Mediterranean countries, particularly in some areas of Spain and Portugal, where a great number of small plants are involved in the production and refining of olive oil, and generate more than 3×10^7 m³ of olive mill wastewaters yearly [2]. Usually, the most common solutions for these effluents are the disposal into evaporation ponds, or the purification by some biological treatments such as activated sludges [3] or anaerobic digestions [4], which are used to transform these wastewaters into more biodegradable effluents before discharging into public water courses.

Specifically, most of their pollutant properties have been imputed to the phenolic compounds, because of its toxicity [5] and the inhibitor character [6] to the anaerobic digestion. As a consequence of this situation, as well as the more stringent requirements imposed by regulations to effluents released into public aqueous streams, new technologies have been developed to reduce phenolic contaminants. Among them, chemical oxidations by UV radiation [7] and ozone [8] are conducted increasingly for the reduction of organic compounds present in several wastewaters from different industrial plants.

Of the above mentioned processes, photooxidation by UV irradiation is an effective method for the removal of trace organics and bacterial substances [9], and have known significant technological applications during the last years, specifically in the treatment of ground waters and wastewaters [10], although there is little information available for the design of photoreactors.

On the other hand, ozone is one of the most powerful oxidizing reagent and has been shown to be capable of destroying several phenolic compounds effectively [11], with the advantage that oxidized products are usually less toxic than the parent compounds. As Hoigne et al. [12] pointed out, ozone can react with solutes either by direct oxidation, in which molecular ozone reacts at electron-rich sites of the organic compounds, or by an indirect pathway, whereby hydroxyl radicals resulting from the decomposition of ozone serve as the oxidants through chain reactions.

For the successful design and operation of reactors in wastewater treatments, the kinetic expressions for the photodecomposition and ozonation reactions of organic pollutants in water are needed. Therefore, a research program was designed to investigate the degradation by UV radiation and ozone separately of *p*-hydroxybenzoic acid, selected as a model of pollutant phenolic compound present in the wastewaters from the olive oil process. In this study, the degradation levels obtained are reported, the influence of the operating variables is established, and a kinetic study is performed, with the determination of the quantum yields in the photodegradation process and kinetic rate constants and reaction orders in the ozonation process.

For this purpose, in the photodecomposition process the Line Source Spherical Emission Model is used to describe the radiant energy field which will be employed in the determination of the rate of energy absorbed, parameter needed for the evaluation of the quantum yield. And for the ozonation rate constants, a model based in the film

theory is also applied to the experimental data. These kinetic parameters are the most useful quantities in the study of the reaction mechanisms of these processes, and their determination are strongly recommended for the design of reactors where those processes are carried out in wastewater treatment plants.

2. Experimental

The experiments were performed in a semi-continuous agitated glass reactor which always operated batchwise with respect to the liquid solutions. This reactor was submerged in a thermostatic bath to keep the temperature at the desired value within $\pm 0.5^\circ\text{C}$, and was equipped with a radiation source located in the axial position and a quartz sleeve which houses the lamp. This was a Heraeus TQ 150 high pressure mercury vapor lamp which emitted a polychromatic UV radiation in the range of 185–400 nm. The reactor top also had several inlets for stirring, sampling, bubbling the gas feed in the ozonation experiments, venting and measuring the temperature.

In the photochemical experiments, the reactor was charged with 350 ml of the *p*-hydroxybenzoic acid solutions (always with an initial concentration of 7.24×10^{-4} M) which were buffered at the selected pH by adding orthophosphoric acid and sodium hydroxide so that the total ionic strength in the final solution was 0.01 M. Each experiment started when the lamp was connected. In the ozonation experiments, ozone was produced from an oxygen stream in an ozone generator, and the ozone–oxygen mixture could be sent to the reactor or to a flask to analyze the ozone in the gas which was determined iodometrically [13].

In both processes and at regular times of reaction, samples were withdrawn to determine the *p*-hydroxybenzoic acid remaining concentrations in the reacting mass. These samples were analyzed by HPLC, using a Waters chromatograph with a 996 photodiode array detector and a Nova-Pak C18 Column. The detection was made at 254 nm with a mobile phase constituted by a mixture water/methanol/acetic acid (88/10/2 in volume) and with a flow rate of 1 ml/min.

Previous experiments based in the uranyl sulfate photodecomposition of oxalic acid under controlled conditions, as was proposed by Leighton and Forbes [14] and later revised by Alfano et al. [15], were conducted in order to evaluate the amount of radiation emitted by the lamp and transferred into the reactor W_L . This is a parameter needed in the determination of the radiation flow rate absorbed by the solution, as will be explained later. The value obtained for W_L in this actinometric reaction was 4.52×10^{-5} einsteins/s.

Several parameters are also later needed in the kinetic study of the ozonation: the liquid mass transfer coefficients, the interfacial areas, the diffusivities of ozone and *p*-hydroxybenzoic acid in water, and the equilibrium ozone concentrations. Values for the liquid mass transfer coefficients k_L and for the interfacial areas were determined by the chemical method described in a previous work [16]; diffusivities of ozone in water D_A were obtained from Matrosov et al. [17] while diffusivities of the *p*-hydroxybenzoic acid in aqueous solutions D_B were evaluated by means of the Wilke–Chang equation [18]. Finally, the equilibrium ozone concentrations C_A^* were calculated from data of

Henry's law constants as a function of pH and temperature provided by Sotelo et al. [19]: its values for the experiments of the present research are compiled in Table 3.

3. Results and discussion

3.1. Oxidation by direct photolysis

The photooxidation of *p*-hydroxybenzoic acid by a polychromatic UV radiation has been conducted in several experiments modifying the temperature and pH according to the values that are shown in Table 1, which also presents the conversion reached in each experiment at two selected times of photoreaction (30 and 60 min). As can be observed, the temperature has a slight direct influence on the process (see experiments P-1, P-2, P-3 and P-4), with conversions ranging between 38% and 45% at 60 min of reaction.

Regarding to the pH, its influence can be seen in Fig. 1: pH from 2 to 5, the degradation increases considerably, while at pH = 7, this increase is lower, and with very similar conversion at pH = 9. It can be explained by the reactivity of the different species present in the reacting medium: at lower pHs, the *p*-hydroxybenzoic acid mainly remains undissociated, while at higher pHs the dissociated form dominates; and as Tratnyek and Hoigne [20] pointed out, the dissociated species are more reactive than the undissociated forms.

The mechanism for photochemical reactions of organic compounds in water are usually complex, as was reported by Legrini et al. [10]. For the establishment of a simple mechanism, general considerations of the photooxidation of organics in liquid phase can be taking into account as well as similar reactions found in the literature [7,21]. With these considerations, the following mechanism can be proposed for the reaction between UV radiation and *p*-hydroxybenzoic acid. Thus in a first step, the excitation of the acid, represented by B, takes place by the absorption of one photon:



where ϕ_{Bi} is the quantum yield for the photodegradation of the *p*-hydroxybenzoic acid, and μ_{Bi} and I_i are the absorbance of the solution and the radiation intensity, respec-

Table 1
Photodegradation experiments of *p*-hydroxybenzoic acid

Experiment	<i>T</i> (°C)	pH	<i>X</i> ₃₀ (%)	<i>X</i> ₆₀ (%)	ϕ_B (l/einstein)
P-1	10	2	21	38	8.62
P-2	20	2	24	43	9.95
P-3	30	2	25	44	10.03
P-4	40	2	28	45	10.66
P-5	20	5	66	86	42.69
P-6	20	7	83	97	81.43
P-7	20	9	83	98	80.24

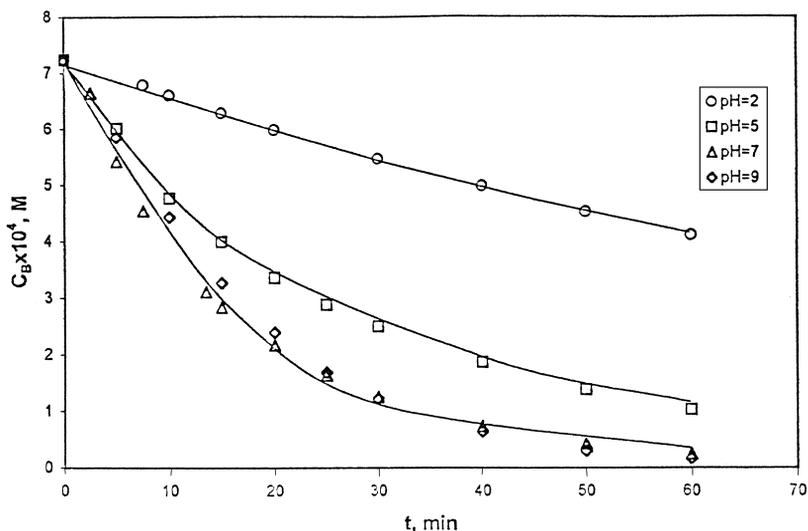
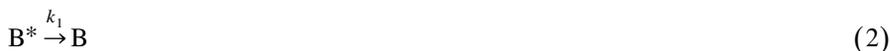


Fig. 1. Influence of pH on the photodecomposition of *p*-hydroxybenzoic acid. Experiments: P-5, P-2, P-6 and P-7.

tively, for each wavelength of the polychromatic radiation. The excited substance B^* can be later deactivated to its basic state:



or be photodecomposed to intermediates and final products:



By taking into account this group of reactions, the application of a mass balance with the assumption of the pseudo-stationary state for the activated species, leads to the kinetic equation for the photodecomposition of the solute B in each point of the reactor:

$$-r_B = -\frac{dC_B}{dt} = \sum \phi_{Bi} \left[\frac{k_2}{k_1 + k_2} \right] \mu_{Bi} I_i C_B. \quad (4)$$

By considering that the overall quantum yield for all the wavelength range of the polychromatic radiation can be defined by the expression:

$$\phi_B = \sum \phi_{Bi} \left[\frac{k_2}{k_1 + k_2} \right] \quad (5)$$

the introduction of this Eq. (5) into Eq. (4) leads to:

$$-r_B = -\frac{dC_B}{dt} = C_B \phi_B \sum \mu_{Bi} I_i. \quad (6)$$

This local reaction rate in each point of the reacting mass can be extended to the whole reactor and provides the total degradation rate:

$$-r_{BT} = -\frac{dC_B}{dt} = -\frac{1}{V} \int_V r_B dV = \frac{C_B \phi_B}{V} \sum \left[\int_V \mu_{Bi} I_i dV \right]. \tag{7}$$

In a photochemical reaction promoted by a polychromatic radiation source like the present situation, the total radiation flow rate absorbed W_{abs} is given by the general expression:

$$W_{abs} = \sum W_{abs_i} = \sum \int_V \mu_{Bi} I_i dV \tag{8}$$

where the individual contribution of the flow rate absorbed for each wavelength W_{abs_i} has been considered. By combining Eqs. (7) and (8), it is obtained:

$$-\frac{dC_B}{dt} = \frac{C_B \phi_B \sum(W_{abs_i})}{V} = \frac{C_B \phi_B W_{abs}}{V} \tag{9}$$

which can be integrated with the boundary condition:

$$t = 0, \quad C_B = C_{Bo} \tag{10}$$

and it is obtained:

$$\ln \frac{C_{Bo}}{C_B} = \frac{\phi_B}{V} \int_0^t W_{abs} dt. \tag{11}$$

According to this Eq. (11), a plot of C_B versus the integral term $\int W_{abs} dt$ in every experiment must lead to a straight line, from which slope the overall quantum yield of the reaction can be deduced. For this objective, the rate of radiation energy absorbed by the reaction medium W_{abs} must be determined previously for each reaction time. This determination is carried out by solving a radiation energy balance by means of a radiation source model which describes the distribution of radiant energy within the reactor. In this case, the Line Source Spherical Emission Model developed by Jacob and Dranoff [22] and described by Alfano et al. [23] seems to be the more suitable for the investigations conducted in this reaction medium due to the geometric characteristics of the reactor and the lamp used.

According to this model, the radiation flow rate absorbed can be expressed in the form:

$$W_{abs_i} = 2\pi\mu_i \int_0^H \int_{R_1}^{R_o} I_i(r, z) r dr dz \tag{12}$$

where $I_i(r, z)$ represents the radiation intensity for each wavelength, which is also given by:

$$I_i(r, z) = \frac{W_L P_i}{4\pi L} \int_{L_o}^{L_o+L} \frac{\exp[-\mu_i(r - R_1)c]}{r^2 + (z - 1)^2} dl \tag{13}$$

and the parameter c is:

$$c = [r^2 + (z - 1)^2]^{1/2} / r. \quad (14)$$

In these expressions, r and z are the coordinates of the general point considered, and 1 is the lamp axial coordinate; L and L_0 are the length and axial position of the lamp; R_1 and R_0 , the internal and external radii of the reactor, and H is the reactor height.

On the other hand, W_L is the total amount of radiation emitted by the lamp and transferred into the reactor, which is determined by the previous experiments based in the uranyl sulfate photodecomposition of oxalic acid already mentioned in Section 2; and P_i is the radiation fraction emitted for each wavelength (which values are provided by the manufacturer). Both parameters are related by the ratio:

$$P_i = \frac{W_i}{W_L}. \quad (15)$$

If Eq. (13) is introduced into Eq. (12), and a general parameter N_i is defined in the form:

$$N_i = \int_0^H \int_{R_1}^{R_0} \int_{L_0}^{L_0+L} \frac{\exp[-\mu_i(r - R_1)c]}{r^2 + (z - 1)^2} r d l d r d z \quad (16)$$

a reduced equation for the rate of radiation energy absorbed can be obtained:

$$W_{\text{abs}} = \sum W_{\text{abs}_i} = \frac{\sum W_i \mu_i N_i}{2L} = W_L \frac{\sum P_i \mu_i N_i}{2L}. \quad (17)$$

This equation allows to determine the total absorption flow rate W_{abs} for each time in the whole wavelength range at which *p*-hydroxybenzoic acid aqueous solutions absorb according to the following procedure: with the concentration of the organic compound in the solution determined periodically during an experiment, the absorbance μ_i was calculated for each time by means of the Lambert–Beer law:

$$\mu_i = \varepsilon_i C_B \quad (18)$$

where ε_i is the molar absorption coefficient, also experimentally determined for *p*-hydroxybenzoic acid at each wavelength. With the μ_i values, the parameter N_i was determined by Eq. (16) which is solved numerically. Once μ_i , N_i , P_i and W_L are known, Eq. (17) allows to determine W_{abs} for each photoreaction time. As an example, Table 2 shows the values obtained in the experiment P-5 conducted at 20°C and pH = 5, where it can be observed the decreasing values of W_{abs} with reaction time.

With W_{abs} , the integral term $\int W_{\text{abs}} dt$ was calculated for every C_B by fitting the experimental data (W_{abs} , t) to a polynomial expression, and by integration of the resultant function. Table 2 also depicts the values obtained in the same experiment, while similar results were deduced for other experiments.

Once the $\int W_{\text{abs}} dt$ values are known, Eq. (11) can be already used in the form described before in order to obtain the quantum yield of the reaction. Fig. 2 as an example, shows this plot for the experiments conducted varying the pH; as can be observed, points lie around straight lines, and a direct effect can be noted: when this

Table 2

Results obtained in experiment P-5 taken as example

t (min)	$C_B \times 10^4$ (mol/l)	$W_{\text{abs}} \times 10^6$ (einsteins/s)	$\int W_{\text{abs}} dt \times 10^3$ (einsteins)
0	7.24	5.54	0
5	6.02	5.43	1.64
10	4.77	5.25	3.25
15	4.00	5.07	4.80
20	3.36	4.85	6.29
25	2.89	4.63	7.71
30	2.50	4.40	9.07
40	1.87	3.88	11.55
50	1.39	3.31	13.71
60	1.03	2.75	15.53

variable increases, the slope also increases in the range 2–7, while at pH = 9, a similar slope to that of pH = 7 is obtained. Plots like those of Fig. 2 were obtained for experiments at different temperatures.

After least-square regression analysis, the ϕ_B values for the experiments depicted in Table 1 are deduced and also shown in Table 1. After regression analysis, these quantum yields can be correlated as a function of the temperature and pH in a modified Arrhenius expression:

$$\phi_B = 10607 \exp(-466.5/T) [\text{OH}^-]^{0.194} \quad (1/\text{einsteins}) \quad (19)$$

that correlates satisfactorily the results obtained.

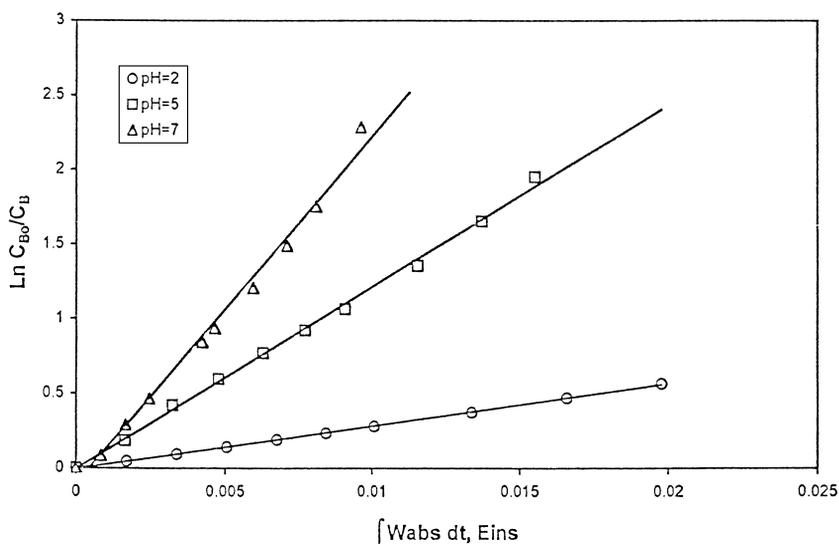


Fig. 2. Determination of the quantum yields ϕ_B in the photodecomposition of *p*-hydroxybenzoic acid when the pH is varied. Experiments: P-5, P-2, and P-6.

4. Ozonation process

Experiments of *p*-hydroxybenzoic acid degradation by ozone were carried out in the batch reactor described in Section 2, modifying the temperature (10, 20, 30 and 40°C), pH (2, 5, 7 and 9) and ozone partial pressure (between 0.10 and 0.39 kPa). Table 3 shows the values taken for all these variables in a group of experiments, as well as the conversions obtained at three selected reaction times: 5, 10 and 20 min, as a measurement of the degree of oxidation reached. As can be seen, the degradation varies widely, depending on the operating conditions.

Thus, experimental results show that ozone partial pressure have a positive effect on the phenolic acid oxidation as can be seen in Fig. 3 (experiments O-9, O-8 and O-2), which shows the remaining concentration curves versus time for different ozone partial pressures. Regarding to the influence of the temperature, Fig. 4 presents the *p*-hydroxybenzoic acid concentration with time at various temperatures (experiments O-1, O-2, O-3 and O-4): it is also observed a direct effect consisting in an increase in the degradation rate when this variable is increased. Finally, a similar positive effect on the degradation is obtained too when the pH is increased (see the conversions in experiments O-5, O-2, O-6 and O-7 of Table 3), due to the increase in the rate constant of the oxidation reactions of organic compounds when the pH increases [24].

Previous experiments were carried out at different pHs (2, 5, 7 and 9) and with several *p*-hydroxybenzoic acid/ozone initial concentration ratios, ranging between 2 and 8, in order to determine the stoichiometric ratio. This is a parameter also needed later for obtaining some kinetic data as the gas absorption rate and the instantaneous reaction factor. In that determination, the phenolic acid concentration was much higher than that of ozone in order to be consumed exclusively by its reaction with *p*-hydroxybenzoic acid, and to avoid as much as possible, the interferences of reactions between ozone and subproducts. Then the remaining *p*-hydroxybenzoic acid concentration was analyzed, and taking into account the initial concentrations of both reactants, the stoichiometric ratio was determined. The average values obtained was 2 ± 0.1 mol of ozone consumed per 1 mol of *p*-hydroxybenzoic acid reacted at all pHs and ratios of initial concentrations.

Table 3
Ozonation experiments of *p*-hydroxybenzoic acid

Experiment	<i>T</i> (°C)	pH	<i>p</i> O ₃ (kPa)	<i>C</i> _A [*] × 10 ⁵ (mol/l)	<i>X</i> ₅ (%)	<i>X</i> ₁₀ (%)	<i>X</i> ₂₀ (%)
O-1	10	5	0.32	3.84	30	51	76
O-2	20	5	0.37	2.97	37	62	86
O-3	30	5	0.36	2.70	39	71	94
O-4	40	5	0.32	2.25	53	80	97
O-5	20	2	0.36	3.74	7	15	30
O-6	20	7	0.34	3.05	60	90	100
O-7	20	9	0.39	3.27	75	98	100
O-8	20	5	0.22	2.08	26	49	77
O-9	20	5	0.10	0.90	12	21	38

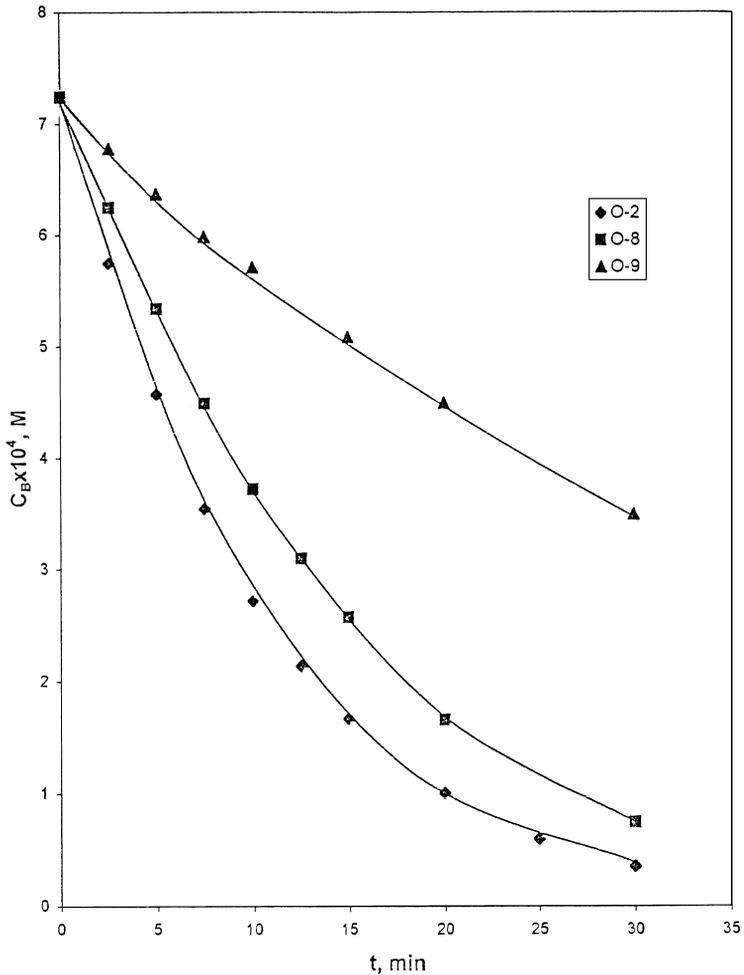


Fig. 3. Influence of ozone partial pressure in the ozonation of *p*-hydroxybenzoic acid. Experiments: O-9, O-8 and O-2.

In order to develop the kinetic study, a model based in the film theory is applied to the experimental results, which allows to determine the kinetic parameters. According to this theory [25], when a gas is absorbed into a liquid solution and reacts with the solute dissolved in the liquid with an irreversible m, n -order reaction, the gas absorption rate can be expressed by the equation:

$$N_A a = k_L a C_A^* E \quad (20)$$

where E is the reaction factor, defined as the ratio of the rate absorption in the presence of a chemical reaction to the maximum rate of physical absorption.

In the experiments of the present ozonation reaction, no free dissolved ozone was detected in the liquid solution, and it suggests that all the ozone reacts in the diffusion

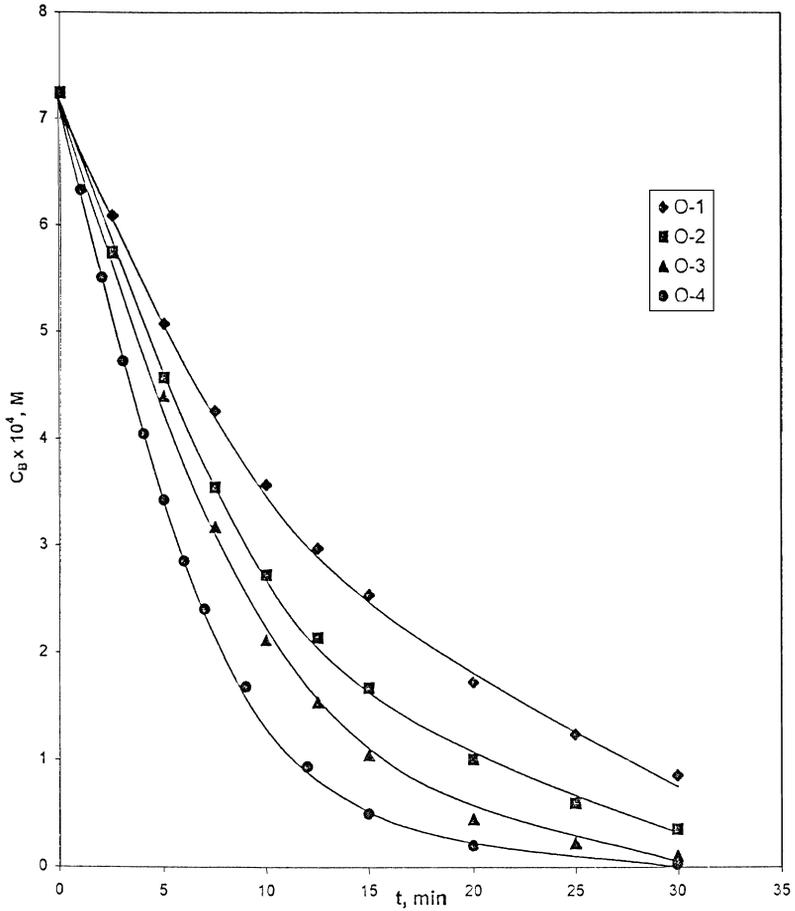


Fig. 4. Influence of temperature in the ozonation of *p*-hydroxybenzoic acid. Experiments: O-1, O-2, O-3 and O-4.

film and none diffuses unreacted into the liquid bulk. According to the film theory, this type of reactions take place in the fast kinetic regime. In addition, inside the fast regime there is a particular situation when the reaction can be considered of pseudo-*m*-order with respect to the gas being dissolved.

The film theory establishes that the mentioned pseudo-*m*-order regime of absorption is accomplished when $E = Ha$ and the following criterion is fulfilled:

$$3 < Ha < E_i/2 \quad (21)$$

where Ha is the Hatta number which indicates the relative importance of the chemical reaction compared to the mass transfer, and is defined in the form:

$$Ha = \frac{1}{k_L} \sqrt{\frac{2}{m+1} k D_A C_A^{*m-1} C_B^n} \quad (22)$$

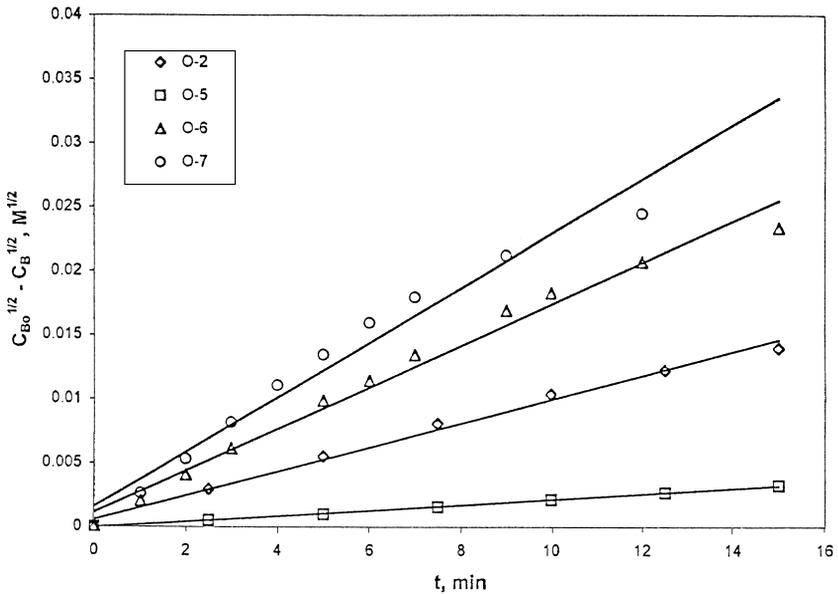


Fig. 5. Determination of k' in ozonation experiments when the pH is varied. Experiments: O-5, O-2, O-6 and O-7.

and E_i is the instantaneous reaction factor, which can be evaluated by the following equation:

$$E_i = 1 + \frac{D_B}{D_A} \frac{zC_B}{C_A^*} \tag{23}$$

In the present ozonation process, the fast and pseudo- m -order kinetic regime is initially assumed, but later it must be proved by determining the parameters Ha and E_i and verifying the condition given by Eq. (21).

On the other hand, the ozone absorption rate can be related to the p-hydroxybenzoic acid degradation rate by the expression:

$$N_A a = z \left(- \frac{dC_B}{dt} \right) \tag{24}$$

where z is the stoichiometric ratio previously evaluated. This equation holds for the first minutes of reaction in which ozone only reacts with the acid, and no other competitive reactions with intermediates formed can be expected.

With the condition $E = Ha$ and combining Eqs. (20), (22) and (24), it is obtained:

$$- \frac{dC_B}{dt} = \frac{aC_A^*}{z} \sqrt{\frac{2kD_A C_A^{*m-1} C_B^n}{m+1}} \tag{25}$$

Table 4

Rate constants for the ozonation process of *p*-hydroxybenzoic acid

Experiment	$k' \times 10^5$ (mol ^{0.5} l ^{-0.5} /s)	$k \times 10^{-5}$ (l/mol s)	Ha	E_i
O-1	1.23	2.68	4.08	18.1
O-2	1.56	5.33	5.63	23.1
O-3	1.89	7.34	5.20	25.4
O-4	2.25	11.8	5.68	30.3
O-5	0.37	0.18	3.05	18.6
O-6	2.93	17.9	10.31	22.5
O-7	4.06	29.9	13.33	21.1
O-8	1.18	6.21	6.08	32.7
O-9	0.45	4.85	5.37	74.3

If it is initially supposed a first reaction order for the *p*-hydroxybenzoic acid, that is $n = 1$, rearranging and integrating Eq. (25) with the initial condition:

$$t = 0 \quad C_B = C_{B_0} \quad (26)$$

it is obtained:

$$\sqrt{C_{B_0}} - \sqrt{C_B} = k' t \quad (27)$$

where k' is:

$$k' = \frac{aC_A^*}{2z} \sqrt{\frac{2kD_A C_A^{*m-1}}{m+1}} \quad (28)$$

According to Eq. (27), a plot of the first term versus time should lead to a straight line whose slope is k' . Thus, Fig. 5 shows as an example, this plot corresponding to the

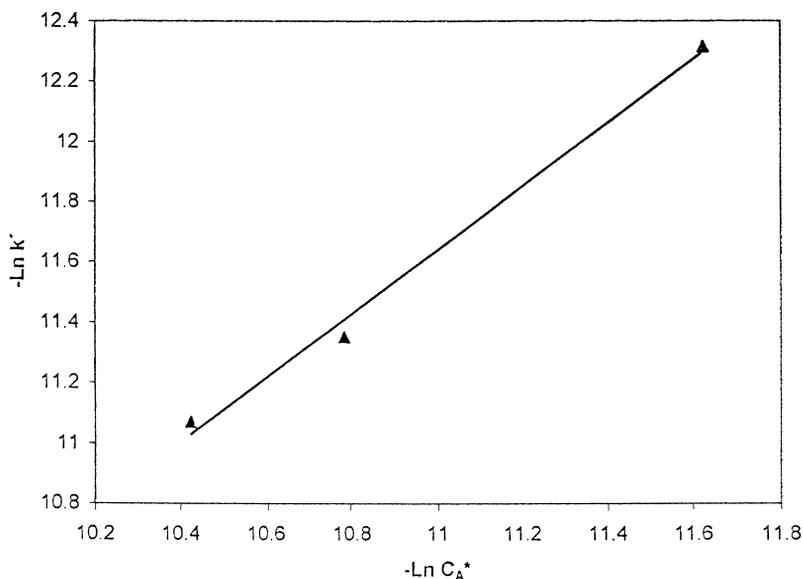


Fig. 6. Determination of m -order with respect to ozone. Experiments: O-9, O-8 and O-2.

experiments conducted modifying the pH at 20°C (experiments O-5, O-2, O-6 and O-7), where can be observed that points lie satisfactorily around straight lines, corroborating the previously supposed order for n and Eq. (27). Similar plots are obtained for the rest of the experiments by varying the temperature and the ozone partial pressure.

Table 4 shows the k' values deduced from least-square analysis: it can be observed that these slopes k' always increase with the increase of any experimental variable studied. This is due to the fact that k' depends on the ozone solubility C_A^* (which at the same time is affected by the ozone partial pressure, temperature and pH), and the rate constant k .

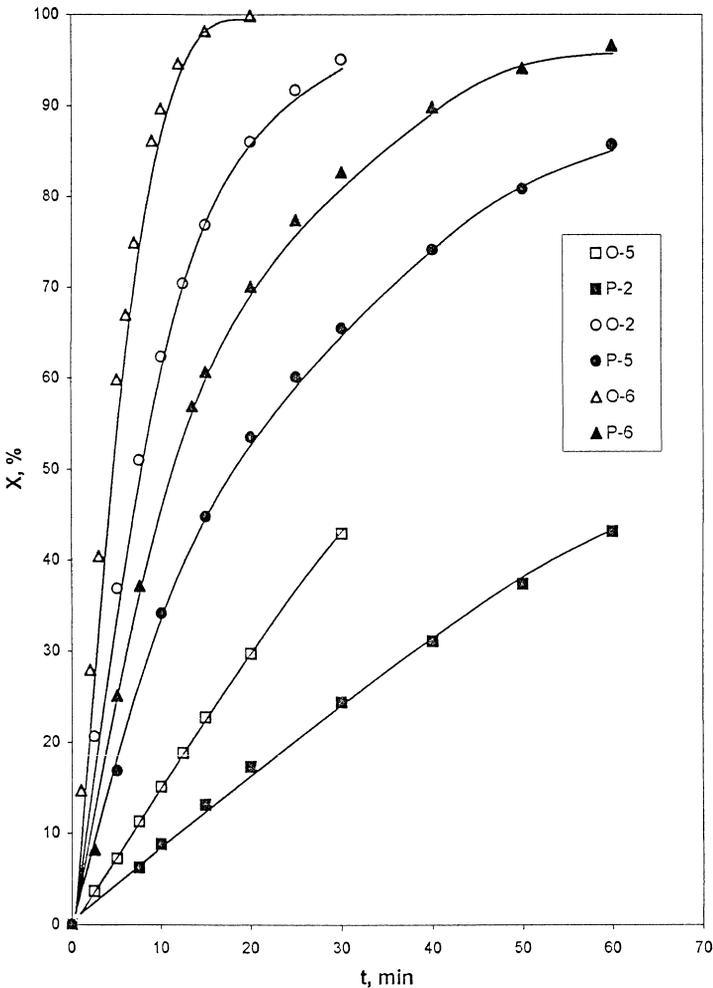


Fig. 7. Comparison of the *p*-hydroxybenzoic acid conversion by the photodegradation and ozonation processes. Experiments: O-5, P-2, O-2, P-5, O-6 and P-6.

Eq. (28) allows to determine the reaction order m for ozone. Thus, a plot of k' versus C_A^* in logarithmic coordinates for the experiments conducted at the same pH and temperature (experiments O-9, O-8 and O-2) should yield a straight line with a slope of $(m + 1)/2$. Fig. 6 shows the results and by least-square analysis a slope of 1.06 is deduced. So, an $m = 1$ order of reaction with respect to ozone can also be proposed.

Once this value is known, the rate constant k can be determined by rearranging Eq. (28) in the form:

$$k = \frac{4k'^2 z^2}{a^2 C_A^{*2} D_A} \quad (29)$$

The values obtained for k according to this expression for every experiment performed are depicted in Table 4. As they are affected by the temperature and pH, a multiple regression analysis of these values versus both variables was conducted leading to the following modified Arrhenius expression:

$$k = 3.56 \times 10^{15} \exp(-4871/T) [\text{OH}^-]^{0.306} \quad (1/\text{mol s}). \quad (30)$$

To verify that the fast and pseudo-first-order absorption kinetic regime is appropriate, the Hatta number and the instantaneous reaction factor must be calculated by means of Eqs. (22) and (23), respectively. The Ha and E_i values obtained for all the experiments at the initial times, when it can be assumed that ozone only reacts with *p*-hydroxybenzoic acid, are shown in Table 4. It can be observed that the condition (21) is fulfilled in all cases, corroborating that the absorption-reaction process is fast and pseudo-first-order with respect to ozone.

Finally, in order to compare the effectiveness of the photolysis and ozonation oxidation processes, Fig. 7 shows the *p*-hydroxybenzoic acid conversion curves for several experiments carried out at 20°C and at different pHs. It is clear that ozonation is always more effective than the photodegradation decomposition at the same pH. In addition, the positive effect of the increase in the pH for both processes, is also clear.

5. Conclusions

From the results obtained it can be concluded that the photodecomposition of *p*-hydroxybenzoic acid by a polychromatic UV radiation provides significant conversions higher than 50% at only 30 min of reaction at pH = 5 or higher, with increasing removal values when the temperature is increased. At lower pH like pH = 2, the conversion decreases, while at pH = 9, similar conversions are obtained to those at pH = 7. From a rate equation of the photodecomposition process, and with the help of an emission model which provides the radiation flow rate absorbed by the reacting medium, the quantum yields are evaluated and correlated as a function of the temperature and pH, with values in the range from 8.62 to 81.43 l/einstein.

On the other hand, *p*-hydroxybenzoic ozonation presents a direct influence of the operating variables, temperature, pH and ozone partial pressure, with increasing conversions when these variables are increased. A model based on the film theory was applied to the experimental results. This shows that the absorption process develops in the fast and pseudo-first-order kinetic regime and is accompanied by a second-order reaction

between ozone and phenolic acid. The rate constants for the reaction were evaluated and ranged between 0.18×10^5 and 29.9×10^5 l/mol s, depending on the temperature and pH. A modified Arrhenius correlation is proposed which reproduces satisfactorily the experimental results.

For the same pH, ozonation is always more effective than photodegradation. For both oxidation processes, conversion increased with pH.

Nomenclature

a	Specific interfacial area (m^{-1})
B	General organic compound, <i>p</i> -hydroxybenzoic acid in this study
C_A^*	Ozone equilibrium concentration (mol/l)
C_B	<i>p</i> -Hydroxybenzoic acid concentration (mol/l)
D_A	Ozone diffusivity in liquid phase (m^2/s)
D_B	<i>p</i> -Hydroxybenzoic acid diffusivity in liquid phase (m^2/s)
E	Reaction factor
E_i	Instantaneous reaction factor
Ha	Hatta number
I	Radiation intensity (einsteins/ m^2 s)
k	Rate constant for the direct ozone–acid reaction (l/mol s)
k'	Kinetic constant defined by Eq. (28) ($\text{mol}^{0.5/10.5}\text{s}$)
k_L	Liquid phase mass transfer coefficient (m/s)
$k_L a$	Volumetric mass transfer coefficient in liquid phase (s^{-1})
k_1	Rate constant for reaction (2)
k_2	Kinetic rate constant for reaction (3)
m	Reaction order for ozone
n	Reaction order for <i>p</i> -hydroxybenzoic acid
$N_A a$	Gas absorption rate of ozone in liquid phase (mol/l s)
P	Radiation fraction defined by Eq. (15)
$p\text{O}_3$	Ozone partial pressure (kPa)
r_B	Reaction rate for the <i>p</i> -hydroxybenzoic acid photodecomposition (mol/l s)
T	Temperature ($^\circ\text{C}$)
t	Reaction time (s)
V	Volume of reactor (l)
W_{abs}	Radiation flow rate absorbed (einsteins/s)
W_L	Radiation flow rate emitted by the lamp (einsteins/s)
X	<i>p</i> -Hydroxybenzoic acid conversion (%)
z	Stoichiometric ratio for the direct ozone– <i>p</i> -hydroxybenzoic acid reaction
<i>Greek letters</i>	
ε	Molar absorption coefficient (mol/l m)
μ	Absorbance of the solution (m^{-1})
ϕ_B	Quantum yield for the photodecomposition reaction (l/einsteins)
<i>Subscript</i>	
i	Each wavelength of the polychromatic radiation

Acknowledgements

Authors wish to thank to *CICYT* of Spain for its financial support under Project AMB97-339, and *Junta de Extremadura* for its Project IPR98A014. J.A. Peres thanks to *FCT* of Portugal for the Project PEAM/SEL/486/95 and to the *E.C.* for its support in the Project PRODEP 4/95.

References

- [1] V. Balice, C. Carrieri, O. Cera, Caratteristiche analitiche delle acque di vegetazione, *Riv. Ital. Sostanze Grasse* 67 (1990) 9–16.
- [2] J.A. Fiestas, R. Borja, Use and treatment of olive mill wastewater: current situation and prospects in Spain, *Grasas Aceites* 43 (1992) 101–106.
- [3] A. Ranalli, New biological methods for the treatment of the oil mill waste waters from industrial processing of the olive fruits, *Riv. Ital. Sostanze Grasse* 69 (1992) 267–273.
- [4] M. Hamdi, C. Festino, C. Aubart, Anaerobic digestion of olive mill wastewaters in fully mixed reactors and in fixed film reactors, *Process Biochem.* 27 (1992) 37–42.
- [5] M. Hamdi, Toxicity and biodegradability of olive mill wastewaters in batch anaerobic digestion, *Appl. Biochem. Biotechnol.* 37 (1992) 155–163.
- [6] M.D. Gonzalez, E. Moreno, J. Quevedo, A. Ramos, Studies on antibacterial activity of waste waters from olive oil mills: inhibitory activity of phenolic and fatty acids, *Chemosphere* 20 (1990) 423–432.
- [7] D.F. Ollis, E.E. Pelizzetti, N. Serpone, Photocatalyzed destruction of water contaminants, *Environ. Sci. Technol.* 25 (1991) 1523–1529.
- [8] Y.T. Wang, P.C. Pai, J.L. Latchaw, Effects of preozonation on the methanogenic toxicity of 2,5-chlorophenol, *J. Water Pollut. Control Fed.* 61 (1989) 320–326.
- [9] P.L. Yue, Modelling of kinetics and reactor for water purification by photo-oxidation, *Chem. Eng. Sci.* 48 (1993) 1–11.
- [10] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, *Chem. Rev.* 93 (1993) 671–698.
- [11] R.G. Rice, Ozone treatment of hazardous materials, *AIChE Symp. Ser.* 77 (1981) 79–107.
- [12] J. Hoigne, in: R.G. Rice, A. Netzer (Eds.), *Handbook of Ozone Technology and Applications*, Chap. 12, Vol. 1, Ann Arbor Science, Ann Arbor, MI, 1982.
- [13] I.M. Kolthoff, R. Belcher, *Volumetric Analysis*, Interscience, New York, 1957, p. 281.
- [14] W.G. Leighton, G.S. Forbes, Precision actinometry with uranyl oxalate, *J. Am. Chem. Soc.* 52 (1930) 3139–3152.
- [15] O.M. Alfano, R.L. Romero, A.C. Negro, A.E. Cassano, A cylindrical photoreactor irradiated from the bottom: III. Measurement of absolute values of the local volumetric rate of energy absorption. Experiments with polychromatic radiation, *Chem. Eng. Sci.* 41 (1986) 1163–1169.
- [16] F.J. Benítez, J. Beltran-Heredia, T. Gonzalez, Degradation of propoxur by ozone, *J. Environ. Sci. Health, Part A* 30 (1995) 365–378.
- [17] V. Matrosov, S. Kachtunov, B. Tregunov, A. Stepanov, Experimental determination of the molecular diffusion coefficient of ozone in water, *Zh. Prikl. Khim.* 49 (1976) 1070–1073.
- [18] R.C. Reid, J.M. Prausnitz, T.K. Sherwood, *The Properties of Gases and Liquids*, 3rd edn., Mc Graw-Hill, New York, 1977.
- [19] J.L. Sotelo, F.J. Beltran, F.J. Benítez, J. Beltran-Heredia, Henry's law constant for the ozone–water system, *Water Res.* 23 (1989) 1239–1246.
- [20] P.G. Tratnyek, J. Hoigne, Oxidation of substituted phenols in the environment: a QSAR analysis of rate constants for reactions with singlet oxygen, *Environ. Sci. Technol.* 25 (1991) 1596–1604.
- [21] M. Schiavello, *Photocatalysis and Environment*, Reidel, Dordrecht, Netherlands, 1988.
- [22] S.M. Jacob, J.S. Dranoff, Light intensity profiles in a perfectly mixed photoreactor, *AIChE J.* 16 (1970) 359–363.

- [23] O.M. Alfano, R.L. Romero, A.E. Cassano, Radiation field modelling in photoreactors: 1. Homogeneous media, *Chem. Eng. Sci.* 41 (1986) 421–444.
- [24] D.C.C. Yao, W.R. Haag, Rate constants for direct reactions of ozone with several drinking water contaminants, *Water Res.* 25 (1991) 761–773.
- [25] J.C. Charpentier, *Adv. Chem. Eng.* 11 (1981) 1–133, Academic Press, New York.