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Oxidation of *p*-hydroxybenzoic acid by UV radiation and by TiO_2/UV radiation: comparison and modelling of reaction kinetic

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Abstract

The phenolic compound *p*-hydroxybenzoic acid is very common in a great variety of agroindustrial wastewaters (olive oil and table olive industries, distilleries). The objective of this work was to study the photocatalytic activity of TiO_2 towards the decomposition of *p*-hydroxybenzoic acid. In order to demonstrate the greater oxidizing power of the photocatalytic system and to quantify the additional levels of degradation attained, we performed experiments on the oxidation of *p*-hydroxybenzoic acid by UV radiation alone and by the TiO_2/UV radiation combination. A kinetic model is applied for the photooxidation by UV radiation and by the TiO_2/UV system. Experimental results indicated that the kinetics for both oxidation processes can be fitted well by a pseudo-first-order kinetic model. The second oxidation process can be explained in terms of the Langmuir–Hinshelwood kinetic model. The values of the adsorption equilibrium constant, K_{pHB}, and the second order kinetic rate constant, k_c, were 0.37 ppm^{-1} and 6.99 $\mathrm{ppm\,min}^{-1}$, respectively. Finally, a comparison between the kinetic rate constants for two oxidation systems reveals that the constants for the TiO_2/UV system are clearly greater (between 220–435%) than those obtained in the direct UV photooxidation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Kinetics; Photocatalysis; *p*-Hydroxybenzoic acid; Titanium dioxide; UV radiation

1. Introduction

Industries of olive oil extraction, table olive production, and alcohol distillation from different wine fractions give rise to highly contaminant wastewaters. This is a major envi-

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ronmental problem in Mediterranean countries in general, and particularly in certain areas of Spain and Portugal where there are many small plants.

Most of these wastewaters pollutant properties have been imputed to phenolic compounds, because of their toxicity [1] and power to inhibit biological treatments [2]. As a consequence of this situation and the more stringent regulations concerning effluents released into public rivers and streams, new technologies have been developed to reduce these refractory contaminants. Among them, chemical oxidations [3,4] are increasingly used for the reduction of organic contaminants present in a variety of wastewaters from different industrial plants. However, this decomposition using single treatments may sometimes be difficult if the pollutants are present at low concentrations or if they are especially refractory to the oxidants. For such situations, it has been necessary to develop more effective processes for the destruction of the contaminants.

For example, systems based on the generation of very reactive oxidizing free radicals, especially hydroxyl radicals, have generated increasing interest due to their high oxidant power (+2.8 V). These systems are commonly termed Advanced Oxidation Processes (AOPs). The radicals are produced by combinations of ozone, hydrogen peroxide, UV radiation [5–7] and photocatalysts [8–11]. These methods can provide almost total degradation as has been reported by several authors for the decomposition of a wide variety of organic contaminants [4,12,13].

The objective was to study the decomposition of *p*-hydroxybenzoic acid in aqueous solution by UV radiation alone and by the combination titanium dioxide/UV radiation.

2. Experimental section

The experiments were carried out in a 500 ml cylindrical glass jacketed photochemical reactor, charged with 350 ml of aqueous solution of *p*-hydroxybenzoic acid (Fig. 1). The reactor was equipped with an ultraviolet lamp, located axially and held in a quartz sleeve. The radiation source was a Heraeus TQ-150 medium pressure mercury vapor lamp which emits polychromatic radiation in the range from 185 to 436 nm. A porous plate was placed at the reactor bottom below the quartz sleeve to provide some agitation through bubbling during experiments. In order to carry out all the experiments always under aerobic conditions, the dispersion was saturated by bubbling oxygen at atmospheric pressure, before starting the irradiation, during the runs also an oxygen flow rate of 40 l/h was continuously bubbled into the dispersion. Water from a thermostatic bath was circulated through the reactor jacket to ensure a constant temperature of $20 \pm 0.5^{\circ}C$ inside the reactor.

Two experimental series were carried out to study the photolytic and photocatalytic decomposition of *p*-hydroxybenzoic acid. In the direct photolytic series, the variable modified was the initial organic compound concentration, and in the photocatalytic series was also modified the photocatalyst concentration. This series was carried out using 0.5 g/l suspensions of TiO_2. Aqueous suspensions of TiO_2 containing *p*-hydroxybenzoic acid were sonicated for 15 min before illumination, to make the TiO_2 particle size uniform. During the experiments, samples were withdrawn regularly from the reactor for analysis. The quantitative determination of *p*-hydroxybenzoic acid was performed, after separation of the catalyst

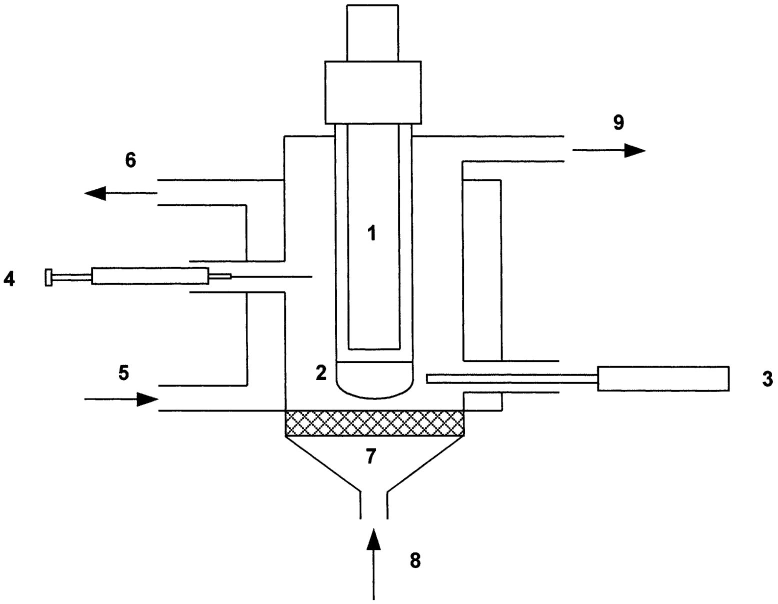

Fig. 1. Experimental photochemical reactor. 1: Medium pressure mercury vapor lamp; 2: quartz sleeve; 3: temperature measuring device; 4: sampling point; 5: cooling water flow inlet; 6: cooling water flow outlet; 7: porous plate; 8: oxygen flow inlet; 9: oxygen flow outlet.

(if it was necessary) by a 0.45 μm Millipore filter, by HPLC using a Waters chromatograph equipped with a 996 photodiode array detector and a Nova-Pack C-18 column. Detection was at 254 nm with a mobile phase composed of a methanol:water:acetic acid mixture (10:88:2 in volume) at a flow rate of 1 ml/min.

Analytical grade *p*-hydroxybenzoic acid was obtained from Sigma, titanium dioxide (Degussa P-25) from Degussa Portugal.

In order to determine the power emitted by the radiation source, several experiments were carried out with an actinometric system at the same experimental conditions. In this work, the uranyloxalate actinometry was used, which consists in the photochemical decomposition of aqueous solutions of oxalic acid in the presence of uranyl salts [14,15]. The power emitted by the lamp was deduced, its value being 3.30×10^{-5} einstein/s [16].

3. Results and discussion

3.1. Photolytic oxidation by UV radiation

Several experiments of individual *p*-hydroxybenzoic acid photodecomposition were performed. In this case the oxidizing agent is only the polychromatic UV radiation emitted by the radiation source described in the experimental section.

From an observation of the degradation curves of *p*-hydroxybenzoic acid by UV radiation, it can be deduced that the elimination of the said phenolic acid fulfils the conditions established for a first-order homogeneous reaction kinetic model. Such a simplified model has been used previously by various researches for the present system of UV radiation. By means of the present model one can carry out a simplified kinetic study of the process and calculate the first-order kinetic rate constants. The objective of its application is to be able to determine the said reaction rate constants and compare them with those obtained in other more complex oxidation systems, such as the TiO_2/UV combination. Thus, on comparing the values of the first-order constants obtained in the two processes, one will be able to compare their efficacy. Applying the above model to the simple photodegradation system, one obtains the following kinetic Eq. (1):

$$-\frac{\mathrm{d}[\mathrm{pHB}]}{\mathrm{d}t} = k_{\mathrm{UV}}[\mathrm{pHB}] \tag{1}$$

which integrated from $t = 0$ to $t = t$ becomes

$$\ln\left(\frac{[\mathrm{pHB}]_0}{[\mathrm{pHB}]}\right) = k_{\mathrm{UV}}t \tag{2}$$

According to this Eq. (2), a plot of the first term against the reaction time should be a straight line of slope k_{UV}. Photodegradation experiments using UV radiation modifying the initial *p*-hydroxybenzoic acid concentration (50, 25, 10, 5 and 2.5 ppm) are showed in Table 1. It can be seen the conversions achieved in the *p*-hydroxybenzoic acid degradation at the reference time of 5 min (X_5). The slopes, k_{UV}, clearly increase where the acid concentration decreases. This fact is attributable to the increase of the number of photons per organic molecule.

3.2. Photocatalytic oxidation over TiO_2

In the oxidation experiments with TiO_2, photoexcitation with light of an energy greater than the TiO_2 band gap promotes an electron from the valence band to the conduction band, and leaves an electronic vacancy or hole (h^+) in the valence band. Thus the act of photoexcitation generates an electron-hole pair

$$\mathrm{TiO_2} \xrightarrow{h\nu} \mathrm{TiO_2}(\mathrm{h^+} + \mathrm{e^-}) \tag{3}$$

Table 1
p-Hydroxybenzoic acid conversion (at 5 min) and pseudo-first-order kinetic rate constants in UV experiments with different initial concentration

Experiment	$[\mathrm{pHB}]_0$ (ppm)	X_5 (%)	k_{UV} (min^{-1})
U-1	50	20	0.05
U-2	25	24	0.11
U-3	10	42	0.21
U-4	5	70	0.27
U-5	2.5	72	0.28

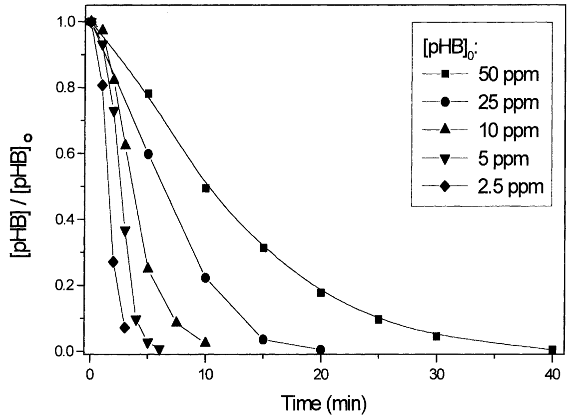

Fig. 2. Evolution of [pHB]/[pHB]0 vs. time for all the experiments where the initial concentration of *p*-hydroxybenzoic acid was varied.

In order to achieve chemically productive photocatalysis, electron-hole pair recombination must be suppressed. This can be achieved by "trapping" these species with the surface adsorbates. The photo-excited electrons are trapped by molecular oxygen

$$e^- + O_2(\text{ads.}) \rightarrow O_2^-(\text{ads.}) \quad (4)$$

The principal hole traps are adsorbed water molecules and OH^- ions [17,18] producing $OH^\bullet$ radicals

$$h^+ + H_2O(\text{ads.}) \rightarrow OH^\bullet(\text{ads.}) + H^+ \quad (5)$$

$$h^+ + OH^- \rightarrow OH^\bullet(\text{ads.}) \quad (6)$$

Fig. 2, shows a plot of [pHB]/[pHB]0 versus time for all the experiments of photocatalytic decomposition where the initial concentration of *p*-hydroxybenzoic acid was varied. The initial *p*-hydroxybenzoic acid concentration has a pronounced effect on the degradation rate, at the same illumination time the percentage of *p*-hydroxybenzoic acid decomposed is smaller if the initial *p*-hydroxybenzoic acid concentration is higher (Table 2).

Table 2
p-Hydroxybenzoic acid conversion (at 5 min) and pseudo-first-order kinetic rate constants in photocatalytic experiments with different initial concentration

Experiment	TiO_2 (ppm)	$[pHB]_0$ (ppm)	X_5 (%)	k_{obs} (min^{-1})	$1/k_{obs}$ (min)
T-1	500	50	21.8	0.13	7.63
T-2	500	25	40.2	0.27	3.65
T-3	500	10	75.1	0.46	2.16
T-4	500	5	97.2	1.16	0.86
T-5	500	2.5	100	1.20	0.82

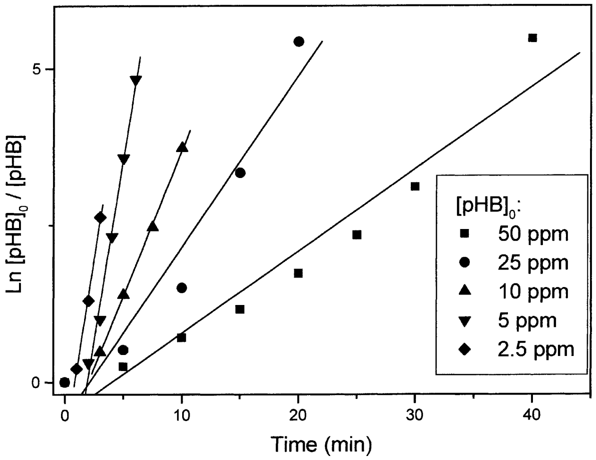

Fig. 3. Determination of the pseudo-first-order kinetic rate constant, k_{obs}.

Degradation experiments of *p*-hydroxybenzoic acid by UV radiation in the presence of TiO_2 also exhibited pseudo-first-order kinetics with respect to the concentration of the organic compound

$$-\frac{d[pHB]}{dt} = k_{obs}[pHB] \tag{7}$$

whose integration gives, for $[pHB] = [pHB]_0$ at $t = 0$:

$$\ln\left(\frac{[pHB]_0}{[pHB]}\right) = k_{obs}t \tag{8}$$

in which [pHB] is the *p*-hydroxybenzoic acid concentration at time *t*, $[pHB]_0$ is the *p*-hydroxybenzoic acid concentration at initial time, *t* the reaction time and k_{obs} the pseudo-first-order rate constant.

Fig. 3, shows a plot of $\ln([pHB]_0/[pHB])$ versus time for all the experiments with different initial concentration of phenolic acid. By applying a least square regression analysis the values of k_{obs} have been obtained. Table 2 reports the values of k_{obs} for all experiments carried out. The reaction rate proceeds according to pseudo-first-order kinetics with a kinetic constant, which decreases as the initial reactant concentration.

On the basis of all the previous considerations, a chemical kinetic model is proposed, able to explain the experimental results. The rate determining step of the catalysed reaction is considered to be the reaction between $OH^\bullet$ radicals and organic molecules over the catalyst surface.

It is well known that the titania surface possesses both acidic and basic sites. The acidic sites are associated with coordinatively unsaturated surface metal ions while the latter are associated with surface anions or anion vacancies. Two different types of surface sites are hypothesised to be involved in the adsorption processes of the reacting species. The first are able to adsorb *p*-hydroxybenzoic molecules and their degradation products. The second are able to adsorb oxygen. In this hypothesis the reaction rate for second order surface decomposition of *p*-hydroxybenzoic acid may be written in terms of Langmuir–Hinshelwood kinetics as:

$$r = k'' \Theta_{\mathrm{OH}} \Theta_{\mathrm{pHB}} \tag{9}$$

in which k'' is the surface second order rate constant, Θ_{OH} the fractional site coverage by hydroxyl radicals and Θ_{pHB} the fraction of sites covered by *p*-hydroxybenzoic acid. These two last variables can be written in the following way:

$$\Theta_{\mathrm{OH}} = \frac{K_{\mathrm{O_2}} P_{\mathrm{O_2}}}{1 + K_{\mathrm{O_2}} P_{\mathrm{O_2}}} \tag{10}$$

$$\Theta_{\mathrm{pHB}} = \frac{K_{\mathrm{pHB}}[\mathrm{pHB}]}{1 + K_{\mathrm{pHB}}[\mathrm{pHB}] + \sum_i K_i [\mathrm{I}_i]} \tag{11}$$

in which $K_{\mathrm{o_2}}$, K_{pHB} and K_i are equilibrium adsorption constants and 'I' refers to the various intermediate products of *p*-hydroxybenzoic acid degradation. Eq. (11) contains several unknown factors, but can be modified by making the following assumption:

$$K_{\mathrm{pHB}}[\mathrm{pHB}] + \sum_i K_i [\mathrm{I}_i] = K_{\mathrm{pHB}}[\mathrm{pHB}]_0 \tag{12}$$

where $[\mathrm{pHB}]_0$ is the initial concentration of *p*-hydroxybenzoic acid. The assumption is that the adsorption coefficients for all organic molecules present in the reacting mixture are effectively equal. Substitution of Eq. (12) into Eq. (11) produces the expression

$$r = k'' \frac{K_{\mathrm{O_2}} P_{\mathrm{O_2}}}{1 + K_{\mathrm{O_2}} P_{\mathrm{O_2}}} \frac{K_{\mathrm{pHB}}[\mathrm{pHB}]}{1 + K_{\mathrm{pHB}}[\mathrm{pHB}]_0} \tag{13}$$

Owing to the fact that the oxygen partial pressure remained constant for all the photocatalytic runs, the fractional site coverage by hydroxyl radicals was also constant

$$k'' \frac{K_{\mathrm{O_2}} P_{\mathrm{O_2}}}{1 + K_{\mathrm{O_2}} P_{\mathrm{O_2}}} = \text{constant} = k_{\mathrm{c}} \tag{14}$$

Eq. (13) can therefore be written as:

$$r = k_{\mathrm{c}} \frac{K_{\mathrm{pHB}}[\mathrm{pHB}]}{1 + K_{\mathrm{pHB}}[\mathrm{pHB}]_0} = k_{\mathrm{obs}}[\mathrm{pHB}] \tag{15}$$

that is a first-order kinetic equation with respect to organic concentration. The relationship between k_{obs} and $[\mathrm{pHB}]_0$ can be expressed as a linear Eq. (16).

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k_{\mathrm{c}} K_{\mathrm{pHB}}} + \frac{[\mathrm{pHB}]_0}{k_{\mathrm{c}}} \tag{16}$$

The data reported in Table 2 are plotted in Fig. 4 as $1/k_{\mathrm{obs}}$ versus $[\mathrm{pHB}]_0$. By means of a least square best fitting procedure, the values of the adsorption equilibrium constant, K_{pHB}, and the second order rate constant, k_{c}. The values were $K_{\mathrm{pHB}} = 0.37\,\mathrm{ppm}^{-1}$ and $k_{\mathrm{c}} = 6.99\,\mathrm{ppm\,min}^{-1}$.

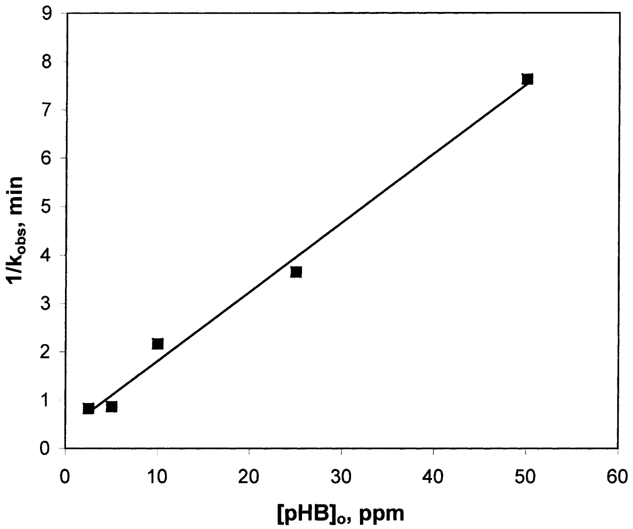

Fig. 4. Determination of the adsorption equilibrium constant, K_{pHB}, and the second order rate constant, k_{c} for the Langmuir–Hinshelwood kinetic model

Fig. 5, shows a comparison between the kinetic rate constants for two oxidation systems. As can be seen, the values of the constants for the TiO2/UV system are clearly greater than those obtained in the direct UV photooxidation. The difference clearly increase where the phenolic acid concentration decreases. This fact is attributable to the major catalytic effect because the increase of the relationship active sites per organic molecule.

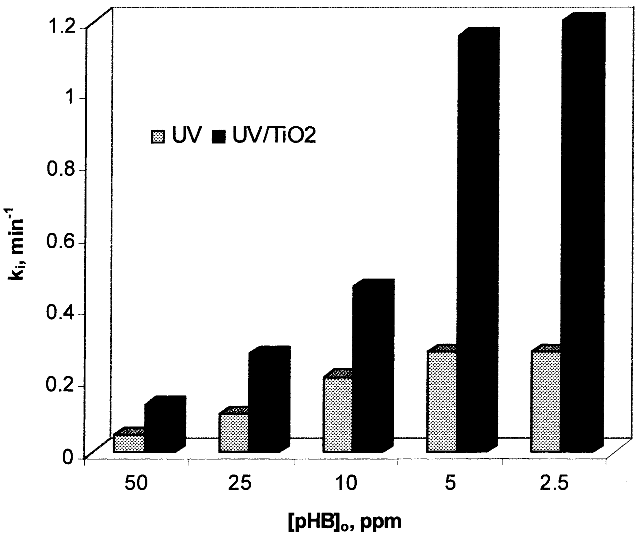

Fig. 5. Comparison between the pseudo-first-order kinetic rate constants for UV radiation and TiO_2/UV radiation processes.

4. Conclusions

The effectiveness of the photocatalytic process using TiO_2 in the degradation of *p*-hydroxybenzoic acid has been demonstrated and the kinetics of reaction has been determined. The experimental results indicated that the kinetics for both oxidation processes, UV radiation and TiO_2/UV radiation, fit well a pseudo-first-order kinetic model. The photocatalytic degradation process of *p*-hydroxybenzoic acid can be explained in terms of the Langmuir–Hinshelwood kinetic model. Experiments using various concentrations of *p*-hydroxybenzoic acid showed that the more diluted the initial solution, the faster is the *p*-hydroxybenzoic acid degradation. This fact is attributable to the increase of the relationship active sites per organic molecule. The values of the adsorption equilibrium constant, K_{pHB}, and the second order rate constant, k_c, were $0.37\,\mathrm{ppm}^{-1}$ and $6.99\,\mathrm{ppm\,min}^{-1}$, respectively.

Finally, a comparison between the kinetic rate constants for two oxidation systems reveals that the constants for the TiO_2/UV system are clearly greater (between 220–435%) than those obtained in the direct UV photooxidation.

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References

[1] N. Zouari, R. Ellouz, Toxic effect of coloured olive compounds on the anaerobic digestion of olive oil mill effluent in UASB-like reactors., J. Chem. Technol. Biotechnol. 66 (4) (1996) 414–420.

[2] R. Borja, A. Martin, R. Maestro, M. Luque, M.M. Duran, Enhancement of the anaerobic digestion of wine distillery wastewater by the removal of phenolic inhibitors, Bioresourc. Technol. 45 (2) (1993) 99–104.

[3] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, Chem. Rev. 93 (2) (1993) 671–698.

[4] R.G. Rice, Applications of ozone for industrial wastewater treatment. A review, Ozone Sci. Eng. 18 (6) (1996) 477–515.

[5] G. Ruppert, R. Bauer, G. Heisler, UV-O_3, UV-H_2O_2, UV-TiO_2 and the photo-Fenton reaction: comparison of advanced oxidation processes for wastewater treatment, Chemosphere 28 (8) (1994) 1447–1454.

[6] R. Andreozzi, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1) (1999) 51–59.

[7] F.J. Benitez, J. Beltran-Heredia, J.L. Acero, F.J. Rubio, Contribution of free radicals to chlorophenols decomposition by several advanced oxidation processes, Chemosphere 41 (8) (2000) 1271–1277.

[8] A. Mills, S.L. Hunte, An overview of semiconductor photocatalysis, J. Photochem. Photobiol. A 108 (1) (1997) 1–35.

[9] S. Malato, J. Blanco, C. Richter, B. Braun, M.I. Maldonado, Enhancement of the rate of solar photocatalytic mineralization of organic pollutants by inorganic oxidizing species, Appl. Catal. B 17 (4) (1998) 347–356.

[10] J.M. Herrmann, Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants, Catal. Today 53 (1) (1999) 115–129.

[11] M.I. Litter, Heterogeneous photocatalysis. Transition metal ions in photocatalytic systems, Appl. Catal. B 23 (2-3) (1999) 89–114.

[12] W.S. Kuo, Synergistic effects of combination of photolysis and ozonation on destruction of chlorophenols in water, Chemosphere 39 (11) (1999) 1853–1860.

[13] J. de Laat, H. Gallard, S. Ancelin, B. Legube, Comparative study of the oxidation of atrazine and acetone by H_2O_2/UV, Fe(III)/UV, Fe(III)/H_2O_2/UV and Fe(II) or Fe(III)/H_2O_2, Chemosphere 39 (15) (1999) 2693–2706.

[14] D.H. Volman, J.R. Seed, The photochemistry of uranyl oxalate, J. Am. Chem. Soc. 86 (23) (1964) 5095–5098.

[15] L.J. Heidt, G.W. Tregay, F.A. Middleton, Influence of pH upon the photolysis of uranyl oxalate actinometer system, J. Phys. Chem. 74 (9) (1970) 1876–1882.

[16] J. Beltran-Heredia, J. Torregrosa, J.R. Dominguez, J.A. Peres, Comparison of several oxidation processes for the decomposition of *p*-hydroxybenzoic acid, Chemosphere 42 (4) (2001) 351–359.

[17] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, Chem. Rev. 93 (1) (1993) 341–357.

[18] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1) (1995) 69–96.