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Kinetics of photodegradation and ozonation of pentachlorophenol

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Abstract

The oxidation of 2,3,4,5,6-pentachlorophenol (PCP) has been carried out by a photodecomposition process using a polychromatic UV irradiation, and by an ozonation process. In the photodegradation process, the pH accelerated the decomposition rate and the approximate first-order rate constants were evaluated, with values between 0.16 ± 0.005 min^{-1} at pH = 3 and 0.26 ± 0.007 min^{-1} at pH = 9. A more rigorous kinetic study led to the determination of the quantum yields of the reaction, with values of $200 \pm 7 \times 10^{-3}$ mol/Eins for pH = 3 and $22 \pm 1.1 \times 10^{-3}$ mol/Eins for pH = 9. In the ozonation process, the rate constants for the reaction between ozone and PCP were determined by means of a competition kinetics, with values in the range from 0.67×10^5 to 314×10^5 l/mol s. The specific rate constants for the un-dissociated and dissociated forms of PCP were also calculated. Finally, in both processes, the intermediate reaction products were identified, the most important being tetrachlorocatechol, tetrachlorohydroquinone and tetra-*p*-chlorobenzoquinone. Free chloride ion released, which was favored at high pHs, was also followed in both processes.

Keywords: Pentachlorophenol; UV irradiation; Quantum yield; Ozone; Rate constants; Dissociated and un-dissociated species

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1. Introduction

The presence of halogenated phenolic compounds like chlorophenols is known to cause severe pollution problems in aquatic environments. These chlorophenols are used widely in agriculture and related industries as an ingredient in pesticides, insecticides, preharvest herbicides, etc., as well as intermediates of dyes, and other industrial chemicals. However, they are highly toxic: thus, several of them have been listed among the 65 priority pollutants by the US EPA (Keith and Telliard, 1979) because they are refractory and hard to remove by conventional biological treatment processes. Therefore, it is highly recommended to conduct very effective methods for their removal from waters by degrading them, either to less harmful intermediates or to complete mineralization.

Among the degradation methods to be followed, some chemical oxidation processes have been proposed as effective technologies for the removal of such as toxic and hazardous pollutants. Thus, although at low rates, UV irradiation decomposes organic molecules by bond cleavage, and therefore it has shown significant industrial applications in the treatment of wastewaters containing harmful pollutants like organo-chlorinated compounds in general, and chlorophenols in particular (Legrini et al., 1993; Yue, 1993). In addition, several studies on the photochemical oxidation of chlorophenols can be found in the literature (Benoit-Guyod et al., 1994; Shen et al., 1995; Hugul et al., 2000).

Similarly, ozone has been found to be an effective oxidizing agent for the removal of many organic pollutants from water (Masten and Davies, 1994). It is often

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preferred over chlorination because it has a higher oxidation potential than chlorine and also because chlorination has been linked to the generation of trihalomethanes such as chloroform, methylene chloride and carbon tetrachloride. Studies on the ozonation of chlorophenols have also been reported by several authors (Kuo and Huang, 1995; Trapido et al., 1997; Ku and Wang, 2002).

Specifically 2,3,4,5,6-pentachlorophenol (PCP) has a primary end-use as a wood preservative, and therefore it can be found a contamination of PCP in surface and ground waters and soils in the vicinities of past wood-treating facilities. It is a needlelike white solid, with a solubility in water in the range of 10–20 mg/l at room temperature. Even a low concentration of 0.1 mg/l is toxic to plants, animal and the human body, because it can easily be absorbed thorough the skin. So, PCP has been included in the list of priority pollutants published by the European Union in the last directive about water policy (Directive, 2000/60/EC). As the degradation rates by some bacteria are very low and natural environmental conditions are usually unfavorable for the biological process to be activated, PCP contamination often requires chemical or physical methods for its removal or degradation. However, kinetic studies of PCP photodegradation and ozonation have rarely been reported in the literature.

Due to these considerations, the photodecomposition by UV irradiation and the oxidation by ozone of PCP was proposed to be investigated in the present research, as a continuation of preceding studies were these degradation processes where applied to other CPs like 4-CP, 2,4-DCP, 2,4,6-TCP and 2,3,4,6-TeCP (Benitez et al., 2000; Benitez et al., 2001). Thus, the first objective of this research was to report values of the degradation levels obtained in each process. Secondly, to investigate the kinetics of PCP elimination in both processes, with the determination of the quantum yield in the photodegradation reaction and the rate constant of the reaction between ozone and PCP. Finally, the specific ozonation rate constants for the deprotonated and protonated forms of PCP were also evaluated, and some intermediates and final products were identified and quantified in both processes.

2. Experimental

2.1. Chemicals

99% PCP was obtained from Fluka Chemical Co. Sodium hydroxide and phosphoric acid of analytical grade were obtained from Panreac. The intermediate products, tetrachlorohydroquinone and tetrachloro-*p*-benzoquinone were from Sigma Chemical Co., tetrachlorocatechol from Aldrich, and 2,3,5,6-tetrachlorophenol from Riedel-de-Haen, all of them with a purity of 99% and were used without further purification. Finally, 2,4,6-trichlorophenol (TCP), used in the ozonation experiments simultaneously with PCP, was also purchased from Sigma. All the solutions were prepared using ultrapure water obtained from a Mill-Q system (Millipore Co.).

2.2. Equipment

The photochemical experiments were carried out in a 500 cm^3 cylindrical glass reactor which contained a radiation lamp located in axial position and a quartz sleeve which houses the lamp. This radiation source was a Hanau TQ150 high pressure mercury vapor lamp which emitted a polychromatic radiation in the range from 185 to 436 nm. Fig. 1 shows the fraction emitted by the lamp for each wavelength (P_i) according to the data supplied by the manufacturer. As can be seen, within this wavelength range, the strongest emission fractions are in the wavelengths of 254 and 366 nm. The two main wavelengths within this range at which PCP absorbs are 254 and 313 nm, while at 366 nm its absorbance is almost negligible as it is observed in Fig. 1, which also shows the experimentally determined molar absorption coefficients (ε) of PCP solutions at different pHs. It can be seen an increase in the absorbance of PCP when the pH is increased, with great ε values at $\text{pH} = 9$.

On the other hand, the ozonation experiments were performed in the same 500 cm^3 cylindrical glass reactor. In this case, the ozone was produced in an ozone generator (Yemar, mod. HPA) from commercial oxygen, and the final mixture ozone-oxygen was introduced into the reactor through a porous gas sparger located at the bottom of the reactor. The reactor operated in semi-batch mode, with continuous feeding of ozone. The system had an inlet for the measurement of the temperature and outlets for taking samples and venting the effluent gas.

2.3. Procedures and analysis

For every experiment conducted in the photochemical degradation experiments, the reactor was filled with 350 cm^3 of an aqueous solution of PCP with the desired initial concentration. An external jacket surrounded the reactor, and a water stream was pumped from a thermostatic bath in order to maintain the temperature at the selected value of 20 °C within ±0.5 °C. The desired pH for every experiment (3, 5, 7 or 9) was adjusted by means of a phosphoric acid/NaOH buffer so that the total ionic strength in the final solution was always 0.05 M. During each experiment, samples were periodically withdrawn from the reactor for analysis of PCP and the intermediate degradation products. In the later photo-

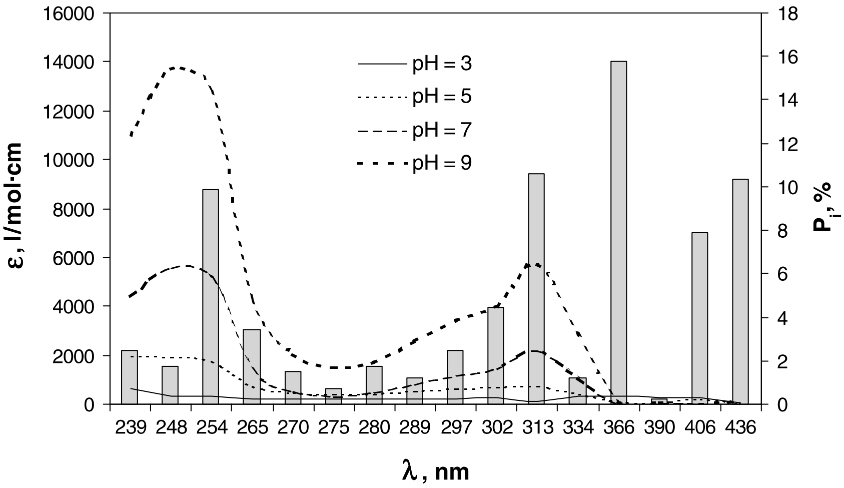

Fig. 1. Fraction of the total radiation emitted by the lamp at each wavelength (P_i) and molar absorption coefficients (ε) at different pHs.

chemical kinetic study, it will be necessary to know the radiation emitted by the lamp into the reactor. For this purpose, previous experiments based on the uranyl sulfate photodecomposition of oxalic acid (Alfano et al., 1986) were conducted, and the value obtained was 1.76×10^{-5} Eins/s. This procedure was described in detail in a former publication (Benitez et al., 1995).

In the ozonation process, simultaneous ozonation reactions of PCP and TCP were conducted in heterogeneous conditions: in every experiment, a solution containing a mixture with the desired initial concentrations of both organics was previously introduced into the reactor and the experiment started when the ozone-oxygen mixture was fed. The pH for each experiment and the temperature (always maintained constant at 20 °C) were adjusted to the desired value in the same way as in the photochemical process. Similarly, samples were retired at regular intervals in order to analyse both CPs concentrations. Further ozonation experiments of PCP alone were carried out to determine its intermediate degradation products from ozone attack.

Specifically, the stoichiometric ratio of the reaction between ozone and PCP was evaluated by conducting several experiments in homogeneous conditions: aqueous solutions of ozone and PCP of known initial concentrations were mixed in the reactor. The initial concentration of PCP was around 10 times higher than that of ozone, in order to assure immediately the total consumption of ozone by PCP. At the end of the experiment, the remaining PCP concentration was measured and the stoichiometric ratio was evaluated as is described in the Section 3.2.1.

The concentrations of PCP (and TCP in the ozonation process) as well as the rest of intermediate products were analysed by HPLC, in a Waters Chromatograph with a 996 Photodiode array detector and a Nova-Pak C18 column. The detection was performed at 300 nm, and the mobile phase was a mixture 75:25 methanol and 1% aqueous acetic acid with a 1 ml/min flow. A different mobile phase was used for the reaction samples where the intermediate degradation products were analysed. In this case, the initial conditions were 35% of methanol and 65% of aqueous acetic acid (1%) with a linear gradient to 77% of methanol within 21 min, and then 5 min isocratic with 77% of methanol. After that, the initial conditions were reached within 2 min, and the system was equilibrated for 6 min. The injection volume was 100 μl in all samples. Chloride ions were measured by potentiometry using a chloride selective electrode (Metler Toledo).

3. Results and discussion

3.1. Photodegradation of 2,3,4,5,6-pentachlorophenol

Experiments on the photodecomposition of PCP by UV irradiation were carried out at 20 °C and modifying the pH (3, 5, 7, and 9). The concentration of PCP at pH 7 and 9 was 10 ppm (equivalent to 3.75×10^{-5} M). However, the low solubility of PCP at lower pHs, induced to prepare its solution at pH 3 and 5 with an initial concentration of 5 ppm (1.875×10^{-5} M). This fact has also been pointed out by Huang et al. (2000), which reported data on the PCP solubility from pH = 1.74 to 13.2, significantly lowers than those for 2,4-DCP, 2,4,6-TCP and 2,3,4,6-TeCP. In the same way, Trapido et al. (1997) worked with PCP solutions of 4×10^{-5} M in their study on the ozonation of several CPs, when the

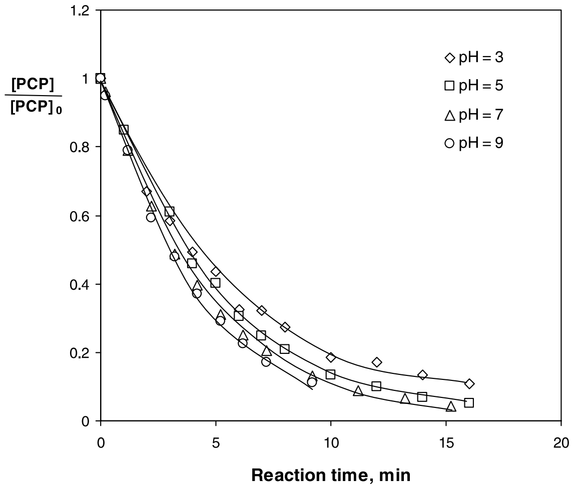

Fig. 2. Evolution of the normalized concentration of PCP at different pHs in the photochemical oxidation process.

concentrations for the remaining CPs were 1×10^{-4} and 4×10^{-4} M.

Fig. 2 shows the PCP normalized concentration curves with reaction time in these experiments: it can be observed a slightly positive influence of the pH on the process, with decreasing values of $[PCP]/[PCP]_0$ and subsequent increasing decomposition rates when the pH is increased. These results can be explained by taking into account that, for a given wavelength of the polychromatic irradiation, the absorbance of PCP increases when the pH also increases. This effect can be seen in Fig. 1, which also represents the experimentally determined molar absorption coefficients ε versus the wavelengths at different pHs. In conclusion, the pH effect on the light absorbance and on the photodecomposition rate is found to be quite similar.

3.1.1. Kinetic study

The reaction mechanism for the photodecomposition of general pollutants in aqueous solutions by UV radiation has been studied in previous works (Ollis et al., 1991; Legrini et al., 1993). Applying these reaction mechanisms to the photodegradation of PCP, a first approach can be made by assuming that the photochemical oxidation:

$$\mathrm{PCP} + h\nu \xrightarrow{\phi_i \mu_i I_i} \mathrm{PCP_{oxid}} \tag{1}$$

follows first-order kinetics. In this Eq. (1), ϕ_i, μ_i and I_i represent the quantum yield of the reaction, the absorbance of the solution and the radiation intensity respectively, for every individual wavelength of the polychromatic irradiation source used in this research.

In accordance with this model, the kinetic equation for PCP will be:

Table 1
Determination of the first-order rate constant and quantum yield for the photochemical degradation of PCP

pH	k_p, min^{-1}	ϕ/V	$\phi \times 10^3$, mol/E
3	0.16 ± 0.005	0.57 ± 0.02	200 ± 7.0
5	0.19 ± 0.004	0.32 ± 0.01	112 ± 3.5
7	0.21 ± 0.005	0.15 ± 0.005	52.5 ± 1.8
9	0.26 ± 0.007	0.06 ± 0.003	22 ± 1.1

$$\ln \frac{[\mathrm{PCP}]_0}{[\mathrm{PCP}]} = k_p t \tag{2}$$

where k_p represents the first-order rate constant.

This simplified model has been used successfully by several authors (Sundstrom et al., 1989; Shen et al., 1995). Then, a plot of $\ln [PCP]_0/[PCP]$ versus time leads to a straight line whose slope is k_p. The values deduced for the first-order rate constants are depicted in Table 1, all of them with correlation coefficients greater than 0.99. These k_p values confirm the trend previously observed for the PCP concentration curves: that is, the highest k_p corresponds to pH = 9 and the lowest to pH = 3. These findings for PCP are in agreement with the results of Shen et al. (1995), who studied the photodegradation of several CPs (2-CP, 2,4-DCP and 2,4,6-TCP) in the range of pH between 3 and 11. They also reported increasing values for the first-order rate constant when the pH was increased in every CP studied. Thus, first-order rate constants between 7.1×10^{-3} at pH = 3 and 101×10^{-3} min^{-1} at pH = 11 for 2-CP; 3.6×10^{-3} at pH = 3 and 126×10^{-3} min^{-1} at pH = 11 for 2,4-DCP, and 2.3×10^{-3} pH = 3 and 36.3×10^{-3} min^{-1} at pH = 11 for 2,4,6-TCP were reported. Although in the same range, those rate constants are lower than the values obtained in this research and presented in Table 1, probably due to the fact that they used a monochromatic radiation source (at constant wavelength of 254 nm) while the present study was conducted with a polychromatic radiation source with higher input energy.

The first-order kinetics constitutes an approximation for a more complex reaction mechanism as noted previously for other organics, like atrazine, chloroethanes and CPs (Hugul et al., 2000). In this mechanism, the overall reaction (1), between PCP and the UV radiation, can be separated into the following partial reactions:

- Activation of a PCP molecule by the absorption of one photon, leading to an excited molecule:

$$\mathrm{PCP} + h\nu \xrightarrow{\phi_i \mu_i I_i} \mathrm{PCP}^* \tag{3}$$

- Deactivation of this excited specie to its basic state:

$$\mathrm{PCP}^* \xrightarrow{k_1} \mathrm{PCP} \tag{4}$$

- Real photodecomposition of the excited PCP molecule:

$$PCP^* \xrightarrow{k_2} PCP_{oxid} \tag{5}$$

This hypothesized reaction scheme can be analyzed via steady state approximation, by setting the rate of accumulation of unstable intermediates to zero. Then, this rate equation is obtained for the photodecomposition of PCP

$$r_{PCP} = \sum \phi_i \left[\frac{k_2}{k_1 + k_2}\right] \mu_i I_i \tag{6}$$

If the overall quantum yield ϕ for all the wavelength range of the polychromatic radiation is expressed by

$$\phi = \sum \phi_i \left[\frac{k_2}{k_1 + k_2}\right] \tag{7}$$

then Eq. (6) is transformed into

$$r_{PCP} = \phi \sum (\mu_i I_i) \tag{8}$$

If this Eq. (8), which represents the reaction rate in a specific point inside the reactor, is integrated for the whole reactor, the following expression is obtained for the total photodecomposition rate

$$-\frac{d[PCP]}{dt} = \frac{1}{V} \int_v r_{PCP}\, dV = \frac{\phi}{V} \sum \left[\int_V \mu_i I_i\, dV\right] \tag{9}$$

By considering the definition of the global radiation flow rate absorbed by the solution when irradiated by a polychromatic radiation

$$W_{abs} = \sum W_{abs_i} = \sum \int_v \mu_i I_i\, dV \tag{10}$$

it is finally obtained for the overall photodecomposition rate

$$-\frac{d[PCP]}{dt} = \frac{\phi \sum (W_{abs_i})}{V} = \frac{\phi W_{abs}}{V} \tag{11}$$

which can be integrated yielding to the following final equation:

$$[PCP] = [PCP]_0 - \frac{\phi}{V} \int_0^t W_{abs}\, dt \tag{12}$$

The integral term in Eq. (12) cannot be solved analytically, because the flow rate absorbed W_{abs} varies with the reaction time, and therefore, it must be solved numerically. For this evaluation, the following procedure was conducted: firstly the values of W_{abs} at any reaction time were determined by means of the Line Source Spherical Emission Model (Alfano et al., 1986), according to the procedure described in detail in a previous research (Benitez et al., 1995). Then, with W_{abs} evaluated, each term $\int W_{abs}\, dt$ was calculated for every [PCP] by fitting the experimental data (W_{abs}, t) to a polynomial expression by least squares regression analysis, and finally, by integrating the resulting function between the initial time and the selected time of photoreaction.

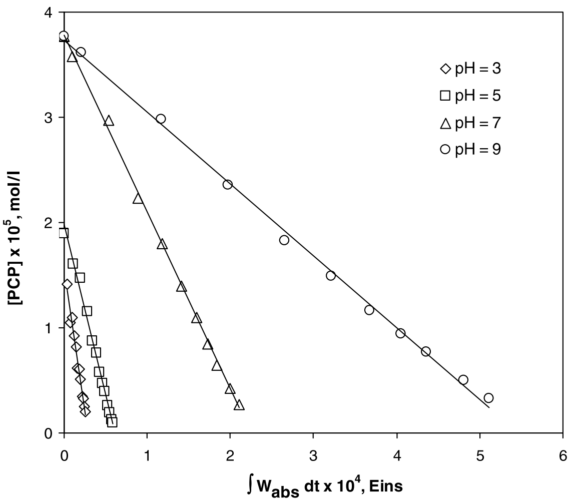

Fig. 3. Determination of the quantum yield ϕ in the photochemical oxidation of PCP.

According to Eq. (12), values of [PCP] are plotted against the corresponding term $\int W_{abs}\, dt$; and from the straight line obtained for every experiment, the intercept $[PCP]_0$ and the slope ϕ/V can be deduced. Fig. 3 shows this plot for the different PCP photodegradation experiments carried out with the variation of pH. A regression analysis provides the slope ϕ/V. The overall quantum yield ϕ of the photoreaction can then be calculated, being its values reported in Table 1. As it is observed, the quantum yield decreases when the pH is increased; that is, an opposite effect to that found for the first-order rate constant k_p, which increased with the increase in the pH.

This apparent contradiction can be explained by taking into account Eq. (9): as it is seen, the total reaction rate is dependent on the quantum yield ϕ as well as on absorbance of the solution μ_i. At the same time, the absorbance is related with the molar absorption coefficient, ε, by the expression

$$\mu_i = \varepsilon_i [PCP] \tag{13}$$

As it has been previously discussed, ε_i increases with the pH, and subsequently μ_i also increases; then, ϕ must decrease for a specific value of the rate—(d[PCP]/dt). This fact confirms the results obtained for the overall quantum yield at different pHs.

3.1.2. Reaction products

In the photochemical degradation of PCP conducted in this study, tetrachlorocatechol and tetrachlorohydroquinone have been identified, as well as important amount of another un-identified compound X_1. Both compounds were also observed by Hong et al. (2000) in the UV-irradiation of PCP, while tetrachlorohydroquinone was reported too by Mills and Hoffmann (1993) as one of the principal intermediates formed in the photocatalytic destruction of PCP in the presence of TiO_2. Jardim et al. (1997) in their study on this process, confirmed the formation of tetrachlorohydroquinone; in addition, they also detected tetrachlorobenzoquinone, although this compound has not been detected in the present study.

The first step of the PCP photodegradation mechanism must be the PCP reductive dechlorination and the formation of OH radicals, similarly to what occurs in the UV-irradiation of phenol and benzoic acid in aqueous solutions (Mills and Hoffmann, 1993). Then, the OH radicals formed in the photolysis of PCP can further attack to new molecules of PCP to give photooxidation products. Thus, tetrachlorocatechol and tetrachlorohydroquinone are produced from OH radical attack to *ortho*- and *para*-positions, respectively. In addition, free chloride ions are generated in these dechlorination steps. Besides the degradation products, polychlorinated dioxins, polychlorinated hydroxy diphenylethers and polychlorinated diphenylethers have been identified by GC-MS as minor degradation products (Hong et al., 2000).

The profiles of the species identified during the PCP (10 ppm) photodecomposition in the present study at pH 4, 5 and 7 are shown in Fig. 4. As can be observed, the formation of tetrachlorocatechol was more rapid than that of tetrachlorohydroquinone, which indicates that the addition of OH radicals at *ortho*-position is more favorable than at *para*-position. Also, it is seen that at pH 7, a very low formation of tetrachlorohydroquinone takes place and higher concentrations of tetrachlorocatechol are detected. Unfortunately, the compound X_1, which could not be identified, was the main degradation product at pH 4 and 5. This compound has been estimated using the response factor of tetrachlorocatechol and tetrachlorohydroquinone in the HPLC chromatogram. The photodegradation of tetrachlorocatechol and tetrachlorohydroquinone seems to be a rather slow process at pH 4. However, at pH 5 and specially at pH 7, these two intermediate are easily phototransformed according to the bell-shape of their concentration curves. The mass balance (sum of PCP and identified intermediate concentration) is poor, which indicates the important existence of un-identified primary degradation products such as X_1.

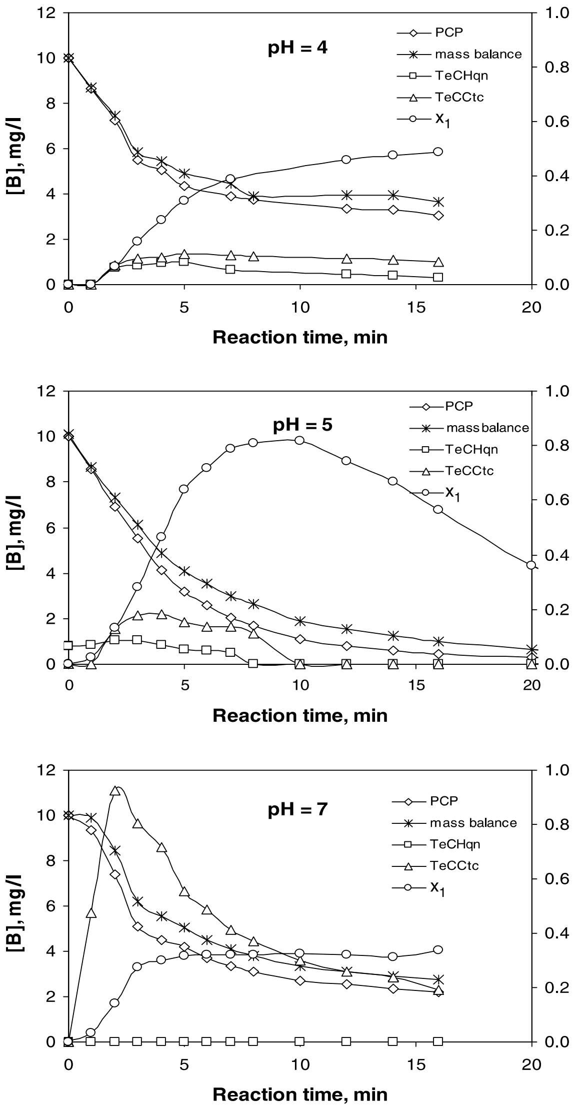

Fig. 4. Profile of the identified intermediate products during the photochemical oxidation of PCP at different pHs. [B] represents any compound; TeCHqn and TeCCtc stand for tetrachlorohydroquinone and tetrachlorocatechol respectively. PCP concentration and the mass balance are represented in the left axis, while the degradation products are in the right axis.

The evolution of the chloride ion concentration in the aqueous phase has also been measured during the experiments. The results obtained in experiments at pH 4 and 7 are shown in Fig. 5. Higher chloride ion concentration is observed at pH 7 which indicates that a dechlorination pathway is preferred at higher pH to form either dechlorinated aromatic compounds or dechlorinated aliphatic compounds. The low chloride concentration at pH 4 also indicates that the primary reaction intermediates are hardly photolyzed at acidic pH. In order to corroborate these statements, the chloride formation yield, defined as the mole of chloride formed per

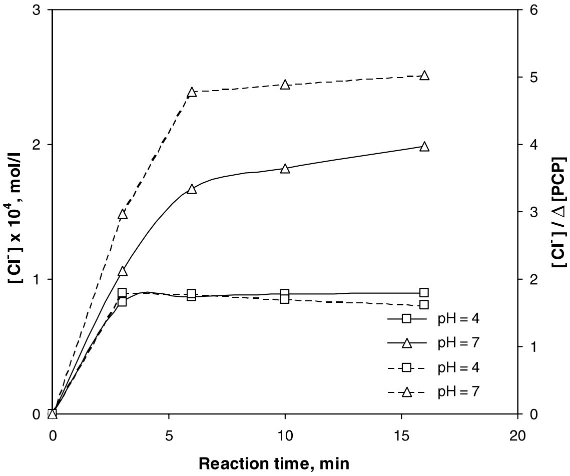

Fig. 5. Evolution of chloride ion concentration (continuous lines) and the chloride formation yield (dashed lines) during the photochemical oxidation of PCP.

mole of PCP degraded, has been calculated and included in Fig. 5. A constant chloride formation yield of 1.7 is observed at pH 4, which demonstrates that chloride is released in the first step of the PCP photolysis. However, at pH 7, the chloride yield increases continuously during the reaction time to reach a value close to 5, indicating that most of the chlorine contained in the PCP has been released as chloride ions.

In conclusion, it can be proposed that in a great extent, and specially at pH 7, the degradation preferentially occurs with the detachment of the chlorine from the benzene ring, and then most of the PCP is converted into low molecular weight acids and chloride, as well as mineralized into CO_2 and water.

3.2. Ozonation of 2,3,4,5,6-pentachlorophenol

The oxidation of PCP by ozone (with a constant ozone partial pressure in the oxygen–ozone mixture of 90 Pa) was conducted at 20 °C and by varying the pH at the same values than the photodegradation process (3, 5, 7 and 9) as well as at $pH = 2.5$. Again, and due to the low solubility of PCP in water, different initial concentrations were used: 2.85 ppm (1.03×10^{-5} M) at $pH = 2.5$, 5 ppm (1.875×10^{-5} M) at $pH = 3$, and 10 ppm (3.75×10^{-5} M) at pH 5, 7 and 9.

These experiments were carried out in the presence of *tert*-butyl alcohol, a well-known scavenger of free radicals (Staehelin and Hoigne, 1985). In the present case, these radicals can be generated from the ozone decomposition, which is accelerated rapidly by the increase in the pH, and therefore, the reactions promoted by hydroxyl radical would present an important contribution at basic solutions like those of the present research at pH 9. So, the use of *tert*-butyl alcohol assured that PCP was only degraded by a direct molecular ozone attack in alkaline solutions and the radical attack can be neglected. Some additional experiments of PCP ozonation in absence of *tert*-butyl alcohol were carried out to identify the intermediate degradation products. These experiments were performed at pH 4, 5 and 7 with initial PCP concentration of 10 ppm.

3.2.1. Kinetic study

The results of Trapido et al. (1997) in the ozonation of some CPs, as well as our previous results (Benitez et al., 2000) in the same field, revealed that the degradation rate of the direct reaction between ozone and a CP increased when the pH increased, and also when the number of substituent chlorine atoms to the aromatic ring was also increased. According to this trend, it can be expected for the ozonation of PCP very high reaction rates, which could be extremely fast at $pH = 9$.

In order to conduct the corresponding kinetic study for the reaction between ozone and PCP, a competition kinetics model proposed by Gurol and Nekouinaini (1984) which is adequate for the evaluation of high rate constants as in the present study, was applied. This model, described in detail in a previous research (Benitez et al., 2000), basically consists on the simultaneous degradation of mixtures constituted by two organic compounds, one of them act as a reference compound which degradation rate constant at the pH of work is previously known. In the present study, the reference compound was TCP, which rate constants at different pHs were evaluated before (Benitez et al., 2000), while the second organic substance is the target compound, PCP in this case, which rate constants are unknown. The competitive method also establishes that the reaction between ozone and the organics must follow second-order kinetics, and more specifically, first-order with respect to each reactant. This condition is fulfilled in the ozonation of CPs in general, as has been previously reported (Yao and Haag, 1991; Trapido et al., 1997).

According to that model, in this specific case of PCP ozonation, the disappearance rate equation will be

$$-\frac{d[PCP]}{dt} = k_i[O_3][PCP] = \frac{k_{O3i}}{z_i}[O_3][PCP] \qquad (14)$$

while the rate equation for the disappearance of the reference compound TCP is:

$$-\frac{d[TCP]}{dt} = k_R[O_3][TCP] = \frac{k_{O3R}}{z_R}[O_3][TCP] \qquad (15)$$

where k_{O3R} and k_{O3i} represent the overall ozone disappearance rate constants for the reference (TCP) and target (PCP) compounds, respectively; k_R and k_i represent the overall CP disappearance rate constants, and z_R

and z_i the stoichiometric ratios for the direct reaction between ozone and both CPs.

Regarding to the stoichiometric ratios, the value for z_R was determined in a previous research (Benitez et al., 2000), and it resulted 2 moles of ozone consumed per mol of TCP reacted. For the evaluation of z_i, previous experiments in homogeneous conditions were performed as described in Section 2. The concentration of ozone and PCP in the initial aqueous solutions and the remaining PCP concentrations in the final solutions were measured. By means of the following equation:

$$z_i = \frac{[O_3]_0}{[PCP]_0 - [PCP]} \tag{16}$$

the experimental stoichiometric ratio z_i can be calculated. Following this procedure, an experimental z_i of 1.5 moles of ozone consumed per mol of PCP reacted was obtained.

From Eqs. (14) and (15), and integrating between $t = 0$ and $t = t$, it is obtained:

$$\ln\frac{[PCP]_0}{[PCP]} = \frac{z_R k_{O3i}}{z_i k_{O3R}} \ln\frac{[TCP]_0}{[TCP]} = M \ln\frac{[TCP]_0}{[TCP]} \tag{17}$$

According to Eq. (17), Fig. 6 shows the plot of ln ($[PCP]_0/[PCP]$) against ln ($[TCP]_0/[TCP]$) corresponding to the experiments conducted at different pHs. After regression analysis, the slopes M provide the ratio between the rate constants. With the values of z_R and z_i as well as the values of k_{O3R} previously evaluated (Benitez et al., 2000) and depicted in Table 2, the rate constant k_{O3i} were deduced in every experiment conducted, being its values also reported in Table 2.

As it is seen, the obtained rate constants k_{O3i} for the reaction between ozone and PCP increase with the pH, in a similar way as it has been reported for the ozonation of other CPs (Trapido et al., 1997; Benitez et al., 2000). Unfortunately, no data has been found in the literature for this rate constant for the PCP ozonation, and therefore, no comparison can be made. Only Hoigne and Bader (1983) have proposed a value bigger than 3×10^5 l/mol s for this rate constant at pH 2.

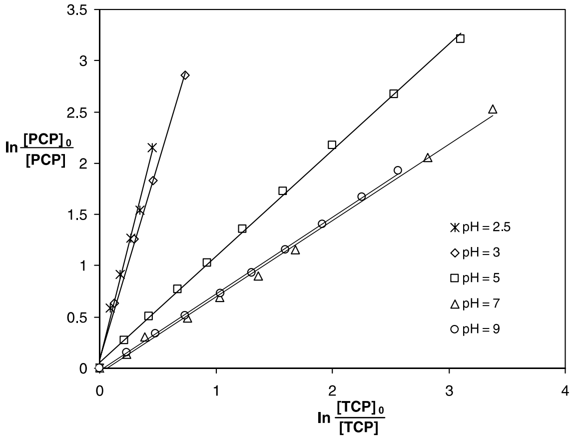

Fig. 6. Determination of the rate constant for the reaction between ozone and PCP in the ozonation process, by competition kinetics at several pHs.

Table 2
Determination of the rate constant for the ozonation of PCP

pH	$k_{O3R} \times 10^{-5}$, l/mol s	M	$k_{O3i} \times 10^{-5}$, l/mol s
2.5	0.20	4.48 ± 0.21	0.67
3	0.50	3.80 ± 0.12	1.44
5	41.3	1.03 ± 0.01	32.0
7	497	0.74 ± 0.02	278
9	559	0.75 ± 0.01	314

3.2.2. Rate constants for the un-dissociated and dissociated species

The observed increase in the rate constants, and subsequently in the reaction rate of ozone and PCP, with the increase of the pH can be explained by the acidic nature of CPs in general and PCP in particular, which pK_a is 4.7. According to this acidic nature, the pH of the solution leads to different concentration of both species, un-dissociated and dissociated. The reactivity of both species towards ozone is quite different, being the dissociated forms generally more reactive towards oxidants than the un-dissociated forms (Hoigne and Bader, 1983). Therefore, at alkaline pHs, when the dissociated species are predominant, it can be expected a higher reaction rate; on the contrary, at acidic pHs, when the un-dissociated species predominate, it can be expected lower reaction rates. These considerations are confirmed by the results obtained previously for the ozonation of other CPs (Benitez et al., 2000), and also in this research by the rate constants obtained for the reaction between ozone and PCP.

Therefore, the overall ozonation reaction rate of acidic organic substances, like CPs, can be expressed as a function of the specific ozonation rate constant of the un-dissociated and dissociated forms of the studied organic substance (PCP in this case), as follows:

$$\begin{aligned} r_{O3} &= k_{O3i}[O_3][PCP]_{tot} \\ &= k_{CP^-}[O_3][PCP^-] + k_{CP}[O_3][PCP] \end{aligned} \tag{18}$$

where k_{O3i} is the rate constant for the mentioned overall ozonation reaction based on the total concentration of PCP present.

For using Eq. (18), it is valuable to determine k_{CP^-}, the specific ozonation rate constant for the ionic form PCP^-, as well as k_{CP}, the specific ozonation rate constant for the un-dissociated form PCP. Once these specific rate constants for the ozonation of both species are known, the application of Eq. (18) provides the global reaction rate r_{O3} of the PCP ozonation reaction and the overall rate constants k_{O3i} during the treatment of natural waters and wastewaters at any pH.

For this purpose, it must be taken into account that the ratio of the dissociated form to the un-dissociated form of an acidic substance is given by the degree of dissociation (α), which is defined by the following expression:

$$\alpha = \frac{[\mathrm{PCP}^-]}{[\mathrm{PCP}^-] + [\mathrm{PCP}]} = \frac{[\mathrm{PCP}^-]}{[\mathrm{PCP}]_{\mathrm{tot}}} \tag{19}$$

At the same time, the relation between the degree of dissociation and the pH is

$$\alpha = \frac{1}{1 + \frac{[\mathrm{H}^+]}{K_a}} \tag{20}$$

From Eqs. (18) and (19) it is obtained

$$k_{O3i} = \alpha k_{CP^-} + (1 - \alpha) k_{CP} \tag{21}$$

which allows to predict the overall rate constants k_{O3i} for the ozonation of PCP at whichever pH of the water, once k_{CP^-} and k_{CP} are known.

For that determination, the procedure used was as follows: with the $pK_a = 4.7$ of PCP, and the pH values in every experiment, the values of α were calculated from Eq. (20). Then, by means of Eq. (21) applied to a couple of the previously deduced overall rate constants k_{O3i} (see Table 2), the unknown rate constants k_{CP^-} and k_{CP} are determined for PCP, the average values obtained being 9.1×10^6 and 1.0×10^4 l/mol s, respectively. These values are in the same range than those obtained in our previous research (Benitez et al., 2000) for the less substituted aromatic rings.

Finally, the determined specific rate constants k_{CP^-} and k_{CP} for PCP must be validated. For this purpose, the overall rate constants k_{O3i} in the range of pH from 2.5 to 10 were theoretically calculated by means of Eq. (21), with the values of α previously obtained from Eq. (20) at each pH. The deduced k_{O3i} values are plotted in Fig. 7 (lines) together with the experimental values (symbols) which are depicted in Table 2. It can be seen an excellent agreement between the theoretical and experimental values, which confirm the goodness of the procedure followed.

3.2.3. Reaction products

In a similar way as in the photochemical process, the main reaction products formed during the ozonation of PCP were also identified, and their evolution during the reaction at several pHs was followed. These products were: tetrachlorocatechol and tetrachlorohydroquinone again, as well as tetrachloro-*p*-benzoquinone that now was clearly identified. In addition, the un-identified compound X_1 appeared as well.

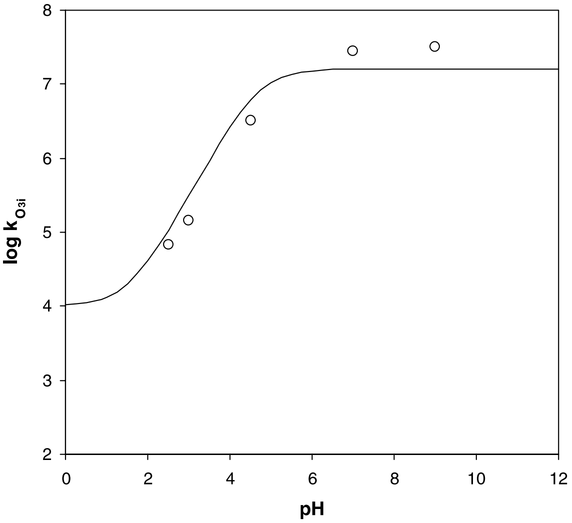

Fig. 7. Validation of the PCP specific rate constants (un-dissociated and dissociated forms) in the ozonation process, according to Eq. (21).

The formation of this kind of compounds was also reported previously by several authors. Thus, Trapido et al. (1997) identified quinones in general and chloride ions during the ozonation of several CPs, and Kuo and Huang (1995) detected chlorocatechol in the ozonation of *p*-chlorophenol. More specifically, the ozonation of PCP conducted by Hong and Zeng (2002) resulted in the generation of tetrachloro-*p*-benzoquinone and tetrachlorohydroquinone, that were further degraded by ozone into other open-ring products like ketones and acids, and finally, into oxalic acid with quantitative release of chloride ions.

Fig. 8 presents the evolution of the reaction products identified in this work at pH 4, 5 and 7. At pH 4 and 5, great amount of tetrachloro-*p*-benzoquinone was found, with a maximum value around 5 ppm at pH 5 when the initial concentration of PCP was 10 ppm. On the other hand, tetrachlorocatechol also reached a maximum value after 2–3 min of reaction, to decay later, while tetrachlorohydroquinone was still increasing after 6 min of reaction. However, at pH 7 a different behavior was observed, with higher concentrations of tetrachlorohydroquinone, and lower of tetrachlorocatechol and tetrachloro-*p*-benzoquinone. Therefore, the first degradation products from the ozone attack are tetrachloro-*p*-benzoquinone, tetrachlorocatechol and tetrachlorohydroquinone, having the un-identified compound X_1 a special importance only at pH 7. Thus, the mass balance at acid pH is higher than 80% during most of the reaction time.

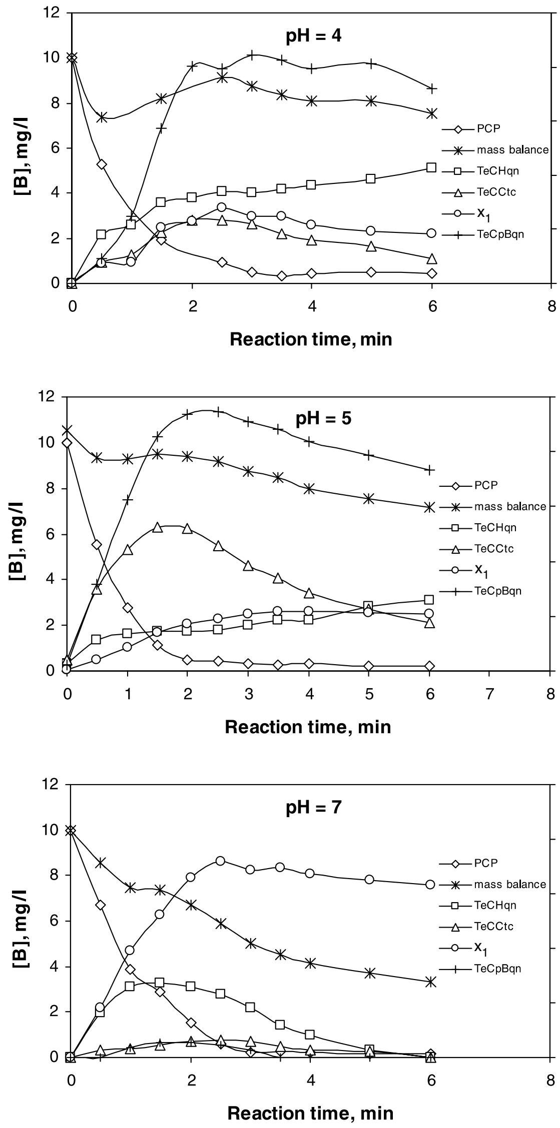

Fig. 8. Profile of the identified intermediate products during the ozonation of PCP at different pHs. [B] represents any compound; TeCHqn, TeCCtc and TeCpBqn stand for tetrachlorohydroquinone, tetrachlorocatechol and tetrachloro-*p*-benzoquinone respectively. PCP concentration and the mass balance are represented in the left axis, while the degradation products are in the right axis.

It can be also observed in Fig. 8 that at acid pH 4, tetrachloro-*p*-benzoquinone is a relatively stable compound, since its concentration does not decrease even after complete PCP elimination. However, a conversion of tetrachloro-*p*-benzoquinone into tetrachlorohydroquinone is deduced at pH 5 after complete PCP degradation, due to redox reactions between these two compounds and oxygen radicals such as superoxide radicals. When the pH is increased to 7, a fast elimination of the degradation intermediates is produced, probably due to the additional presence of OH radicals at neutral and basic pHs. A second reason for the high reactivity of intermediates at neutral or basic pH is their acid–base equilibria, since the ozone attack to the dissociated species is favored as commented before for PCP.

The most plausible reason for the formation of these products is a mechanism that considers an electrophilic ozone attack to the phenolic compound. Thus, in the first step the ozone attack tends to occur at the *ortho*- and *para*-positions, which are of higher electron density and more active compared with other positions because of the resonance donation of oxygen electrons. Consequently, the reaction of ozone attack at these positions becomes more favorable (Bailey, 1958). From the results shown in Fig. 8, ozone attack to the *para*-position is predominant in the present case to the *ortho*-position, specially at acid pHs. In these initial reactions chloride ions are released.

The intermediates later would tend to decompose upon continued ozonation. The subsequent decomposition could result in the release of chloride ion from the chlorinated aliphatic compounds, and production of oxalic acid as final product. Kim and Moon (2000) confirmed this formation of oxalic acid, and they suggested that it constitutes the final product of the PCP ozonation because it is not oxidized by ozone possibly due to the fact that it does not have any carbon–carbon double bond.

In order to check the mentioned generation of free chloride ion, its concentration was also measured in this research, being shown the results obtained in Fig. 9. As it is seen, the Cl^- concentration increased even after the PCP degradation was almost completed at pH 7 (more than 3 min of reaction), which indicates that intermediates containing chloride were continuously degraded

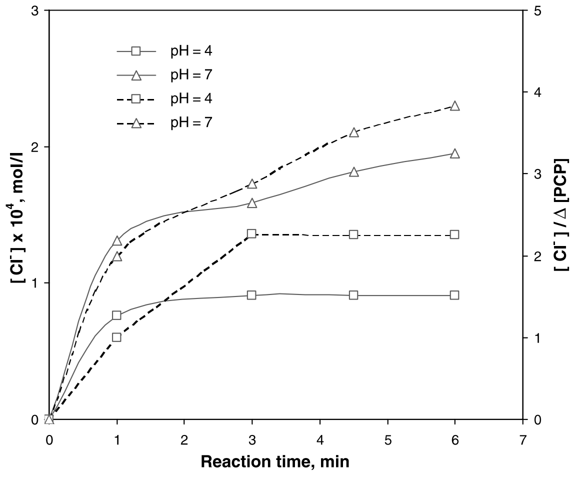

Fig. 9. Evolution of chloride ion concentration (continuous lines) and the chloride formation yield (dashed lines) during the ozonation of PCP.

in the presence of ozone and probably OH radicals, and thus a chloride formation yield of 4 was reached. However, the chloride concentration and the chloride formation yield were almost constant after complete PCP elimination at pH 4, corroborating the stability of the intermediates at this pH, as was commented above. The dechlorination of PCP took place at the same time as ring cleavage, which led to the formation of the mentioned oxalic acid. In conclusion, the ozonation of PCP yields intermediates which are probably more biodegradable prior to complete mineralization.

4. Conclusions

From the results obtained in the present study it can be concluded that in the photodegradation of PCP, increasing decomposition rates are reached when the pH is increased. In a first approximation, this process can be considered as a first-order reaction, and the values deduced for the first-order rate constants are in the range between 0.16 ± 0.005 min^{-1} (at pH 3) and 0.26 ± 0.007 min^{-1} (at pH 9). The more rigorous kinetic study leads to the determination of the overall quantum yield ϕ of the photoreaction, which values vary from $200 \pm 7 \times 10^{-3}$ mol/Eins (at pH 3) to $22 \pm 1.1 \times 10^{-3}$ mol/Eins (at pH 9). In this photochemical degradation of PCP, tetrachlorocatechol and tetrachlorohydroquinone have been identified as major intermediate products.

In the oxidation of PCP by ozone, the stoichiometric ratio was first determined, its value being 1.5 moles of ozone consumed per mol of PCP reacted. As it can be expected very high reaction rates for this process, the kinetic study for the reaction between ozone and PCP is performed by using a competition kinetics model, which is adequate for the evaluation of high rate constants. Following this model, the rate constant k_{O3i} is deduced and it increased with the pH. Values between 0.67×10^5 l/mol s (at pH 2.5) and 314×10^5 l/mol s (at pH 9) are found. In this kinetic study, the specific ozonation rate constant k_{CP^-} for the ionic form PCP$^-$, as well as the specific ozonation rate constant k_{CP} for the un-dissociated form PCP are also determined, being their values 9.1×10^6 l/mol s and 1.0×10^4 l/mol s respectively. In the ozonation process, three main intermediate products are clearly identified: tetrachlorocatechol, tetrachlorohydroquinone and tetrachloro-*p*-benzoquinone, which subsequent decompositions by ozone lead to the release of chloride ion, specially at pH 7.

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