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Estimation of $\cdot\text{OH}$ radical reaction rate constants for phenol and chlorinated phenols using UV/ H_2O_2 photo-oxidation

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Abstract

A detailed investigation on UV/ H_2O_2 photooxidation has been carried out in order to determine the kinetics of the oxidative degradation of phenol and 2- and 4-chlorophenols in dilute aqueous solutions. Effects of different process parameters, such as initial substrate and H_2O_2 concentrations, substrate to H_2O_2 ratio on the degradation kinetics of the phenolic substrates, have been studied. Degradation rates of phenol and chlorophenols are insignificantly small with ultraviolet radiation only and also with hydrogen peroxide (in the absence of UV radiation), but the synergistic effect of UV/ H_2O_2 results in a marked enhancement of the rates of degradation. A mechanistic model for UV/ H_2O_2 photooxidation has been developed. Room temperature (27°C) rate constants for the reaction of $\cdot\text{OH}$ radical (formed by absorption of photons) with the substrates have been estimated by using the model equation. The calculated rate constants are of

Abbreviations: C_S Substrate concentration at any time (g mol m^{-3}); $C_{S,0}$ Initial substrate concentration (g mol m^{-3}); f_i Fraction of radiation intensity absorbed by component i ; I_0 Radiation intensity ($\text{E m}^{-2} \text{s}^{-1}$); k Reaction rate constant obtained by using empirical correlation; k_2 $\cdot\text{OH}$ radical reaction rate constant for the reaction between substrate and $\cdot\text{OH}$ radical ($\text{g mol}^{-1} \text{s}^{-1}$); k_4 Reaction rate constant for the H_2O_2 oxidation ($\text{g mol}^{-1} \text{s}^{-1}$); k_5, k_6, k_7 Reaction rate constant of the corresponding equations; L Effective path length of UV radiation in the reactor, cm; r_{UV} Photochemical reaction rate; $r_{\text{H}_2\text{O}_2}$ Reaction rate for the degradation by H_2O_2 only; r_{R} Reaction rate between a substrate and hydroxyl ($\cdot\text{OH}$) radicals (radicalary reaction rate); R Molar concentration ratio of substrate to hydrogen peroxide; ε_i Molar extinction coefficient of component i ; ϕ_i Quantum yield of component i

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the same order of magnitude as reported for other similar aromatic compounds. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: UV/H₂O₂; Hydroxyl radical; Photo-oxidation; Rate constant; Phenolic compounds

1. Introduction

A large number of organic pollutants are discharged regularly into the natural and waste water streams from different process plants. Many of these pollutants are of hazardous or toxic nature, and sometimes refractory to degrade by using available technologies of effluent treatment. Because of their refractory nature, the chlorinated organics are receiving much attention. In particular, chlorophenols show low biodegradability and are persistent pollutants [1] posing serious problems to the environment once discharged into natural or waste waters. The toxicity of these compounds to humans and aquatic life imposes a high priority on their destruction in water. Biological treatment processes for the degradation of phenol and chlorophenols have usually proved to be inefficient due to their refractory nature. On the other hand, UV-enhanced photo-degradation using ozone and/or hydrogen peroxide as oxidant enables the destruction significantly [2].

Encouraging results using Advanced Oxidation Processes (AOPs), ozone with UV radiation, hydrogen peroxide with UV radiation, and ozone and hydrogen peroxide together with UV radiation have been reported [3], and no undesirable side-products have been detected during or after photo-oxidation. Prengle [4] visualized oxidation of organic molecules by the $\cdot\text{OH}$ radical in three steps: (i) partial oxidation of the parent species to form intermediates and small fragments, (ii) oxidation of the intermediates to form secondary intermediates and fragments, and (iii) further oxidation of fragmentary intermediates to form small and stable organic acids. Glaze and Kang [5] presented a model describing the photooxidation of water soluble hazardous organic waste with O₃/H₂O₂ system in a semibatch sparged reactor assuming $\cdot\text{OH}$ radical as the principal kinetic species responsible for the photooxidation reaction. The model predicts that the rate of substrate oxidation at a given ozone dose will increase linearly with an increase in the concentration of hydrogen peroxide. Apak and Hügül [6] reported that the photooxidation of *o*- and *m*-chlorophenol and 1,4,6-trichlorophenol by UV/H₂O₂ was pseudo first order and the rate constants increased with increasing ratio of the oxidant. Schulte et al. [7] studied photo-oxidation of chlorinated hydrocarbons like CCl₄, CHCl₃, tri- and pentachlorophenols by using H₂O₂ and a low pressure UV lamp. German and Michael [8] reported that degradation of pentachlorophenol (PCP) by H₂O₂ and UV-irradiation proceeds via $\cdot\text{OH}$ radical attack at the para position of the PCP ring to form a semiquinone radical which in turn disproportionates to yield *p*-chloranil and tetrachloro hydroquinone. Yue and Legrini [9] investigated oxidation of phenol and 4-chlorophenol by advanced oxidation process using UV/H₂O₂. They postulated that the kinetics of the photooxidation of dissolved organics are dependent on the initial concentration of the parent organic compounds. Though a number of researchers [6,9–11] worked on the degradation of chlorophenol by UV/H₂O₂, $\cdot\text{OH}$ radical

reaction rate constants based on experimental results were not estimated. The present work aims at determining the $\cdot\text{OH}$ radical reaction rate constants from the global rates. In this paper, we present results of the degradation of phenol and chlorophenols by photolysis alone, with H_2O_2 (in absence of UV radiation), and with the combination of UV radiation and H_2O_2 . On the basis of these experiments, a mathematical model has been developed and $\cdot\text{OH}$ radical reaction rate constants are estimated.

2. Experiments

The experiments were conducted in a bench-scale cylindrical Corning-glass reactor having an outer diameter of 10 cm and a height of 20 cm wrapped on with an aluminum foil. The temperature of the reactor contents was maintained at 27°C. There were provisions for insertion of pH probe, for collection of samples intermittently and for continuous stirring of the reaction mixture.

Phenol and chlorophenols of AR grade were obtained from Qualigens (India), H_2O_2 (30% w/v) of AR grade was procured from Merck (India). We used UV-dosage of 24 W/L only. All aqueous solutions of substrates were prepared in distilled water. Samples of reaction medium were withdrawn time to time from the reactor and diluted by using distilled water for analysis of substrate. Concentrations of the substrate in reaction mixtures were determined by the 4-aminoantipyrene method [12] using a Shimadzu (UV-160A) spectrophotometer. Hydrogen peroxide remaining in the reaction medium was measured by using standard ceric sulfate solution [13].

Most of the experiments were conducted twice in identical conditions. The difference in results in two consecutive experiments did not exceed more than $\pm 3\%$.

3. Results and discussion

3.1. Comparison of reaction rates

We studied the degradation of phenol and, 2- and 4-chlorophenols by using UV only, H_2O_2 only and with UV/ H_2O_2 and the conversion history by the different degradation processes are compared. Fig. 1 presents degradation of 1000 ppm 2-chlorophenol in solution. It is observed that the photolytic destructive conversion of 2-chlorophenol is much smaller compared to the oxidative conversion of the substrate by hydrogen peroxide (10 000 ppm), whereas UV/ H_2O_2 photo-oxidation results in significant degradation of 2-chlorophenol within an hour which is about 70% for a 1000 ppm aqueous solution of 2-chlorophenol. Phenol and 4-chlorophenol also show similar extent of degradation. Table 1 represents degradation of phenol, 2- and 4-chlorophenols at different time intervals using the same ratio of substrate to hydrogen peroxide. Direct photolytic conversion of substrate increases with the decrease in initial substrate concentrations, but the conversion does not exceed 11.2% in an hour even with substrate

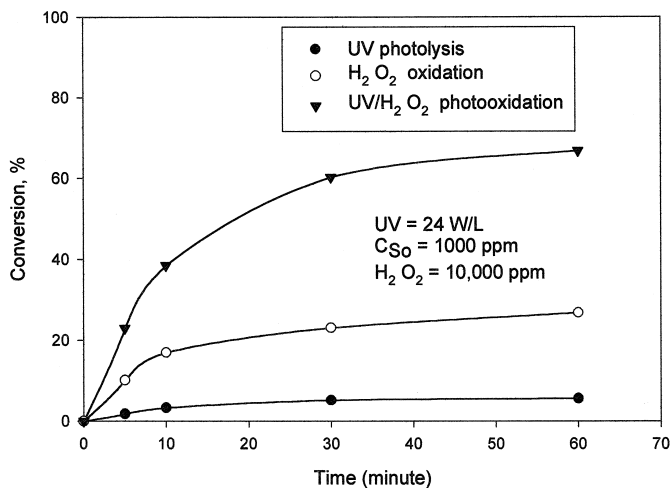


Fig. 1. Conversion-time data for degradation of *o*-chlorophenol by three different processes, e.g., UV (in absence of H₂O₂), H₂O₂ (in absence of UV radiation) and UV/H₂O₂.

concentration of 50 ppm of phenol. H₂O₂ has a standard oxidation potential (E°) of 1.77 V. In an aqueous solution, it oxidizes phenolic substrates. It is reported that in an aqueous solution, hydrogen peroxide dissociates to form HO₂⁻ anion [14] and O₂ in a chain reaction [15], which also convert substrates [15,16] to other oxygenated intermediate compounds. In the presence of UV radiation, hydrogen peroxide dissociates to form [•]OH free radicals which attack the benzene ring and undergo very rapid and effective substitution reactions to form oxygenated intermediates. A few side reactions also occur during photo-initiated homolytic fission of hydrogen peroxide. The [•]OH radical acts as an electrophilic reagent [10,11] in its attack of the aromatic ring. Sundstrom et al. [11] reported 2-chlorophenol conversion of about 85% using 25.7 ppm initial substrate concentration and hydrogen peroxide to substrate molar ratio of 7 in a UV reactor within 40 min of reaction. But, in our study, we used high initial substrate concentration (50 to 1000 ppm) and high molar ratio of hydrogen peroxide to substrate so that nearly complete mineralization to CO₂, H₂O and HCl could occur. Fig. 2 represents a comparison of the degradation kinetics of 2-chlorophenol with data of Apak and Hügül [6] using almost the same initial concentration of substrate. The degradation follows the same trend, but differs a little due to different substrate to hydrogen peroxide molar ratio (R).

Fig. 1 shows that the rates of degradation of the substrates at the initial period of the reaction are rapid but the rates slow down later on. In the initial period of the reaction, rates are higher because of the presence of high concentrations of oxidants (H₂O₂ and other species formed from H₂O₂) and the substrate. Afterwards, a number of intermediates are formed which compete with substrates to react with available oxidants. The presence of intermediates hinders the pure substrate from reaching the oxidants and vice versa.

Table 1

Conversion of phenol, 2- and 4-chlorophenols over different time intervals by using only UV, only H₂O₂ and UV/H₂O₂

Degradation process	Initial substrate (ppm)	H ₂ O ₂ (ppm)	Time (min)	Conversion (%)		
				Phenol	2-Chlorophenol	4-Chlorophenol
UV photolysis (24 W/L) (No H ₂ O ₂)	100	–	5	3.7	3.6	3.6
			15	4.0	5.8	5.4
			30	7.5	10.2	9.0
			60	9.2	13.3	12.8
	500	–	5	1.7	2.6	2.4
			15	2.6	4.0	3.2
			30	4.2	7.1	5.5
			60	4.7	7.2	6.7
	1000	–	5	1.0	2.0	1.8
			15	2.4	3.1	3.3
			30	3.2	5.6	5.2
			60	4.1	5.8	5.6
H ₂ O ₂ oxidation (No UV radiation)	100	600	5	8.3	8.6	8.5
			15	16.1	16.7	16.3
			30	20.6	21.0	20.9
			60	23.3	23.5	23.4
	500	3000	5	11.2	11.4	11.4
			15	16.2	16.8	16.7
			30	21.3	21.9	21.6
			60	24.4	25.5	25.1
	1000	6000	5	11.5	11.7	11.5
			15	17.2	17.6	17.3
			30	22.2	22.8	22.3
			60	25.5	26.6	26.0
UV/H ₂ O ₂ photooxidation (UV dosage = 24 W/L)	100	600	5	50.8	43.1	51.0
			15	82.9	67.3	72.9
			30	93.9	78.8	88.4
			60	97.5	89.4	95.3
	500	3000	5	30.2	26.7	27.1
			15	39.3	34.4	36.4
			30	63.0	51.0	53.0
			60	77.4	73.4	75.8
	1000	6000	5	29.3	17.1	18.0
			15	37.0	33.3	34.7
			30	59.0	46.0	46.8
			60	64.1	59.1	62.8

Similar dependence, as observed for concentrations of the substrate, are also observed for the pH of the reaction mixture. Immediately after addition of hydrogen peroxide, the pH of the reaction mixture drops substantially in the acidic range (Fig. 3) and remains nearly constant at that level for the remaining part of reaction. The drop in pH in the early part of reaction is probably due to the formation of oxygenated acidic reaction intermediates [6,17].

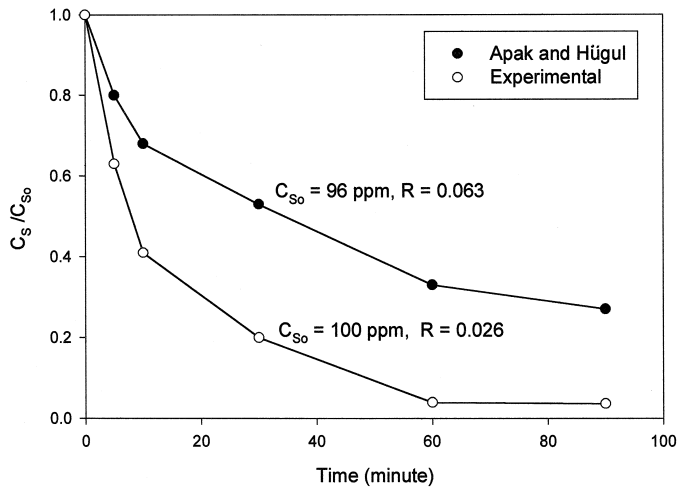


Fig. 2. Comparison of experimental results with those of Apak and Hügül [6] where initial substrate concentration is nearly the same, but H_2O_2 concentration differs.

The time-concentration data for oxidative degradation of phenol and 2- and 4-chlorophenols are presented in Fig. 4 for various initial concentrations of substrates, keeping the ratio of substrate to H_2O_2 constant. At a low concentration of the substrate, the percentage conversion is higher compared to those at higher concentrations (comparable with the results of Sundstrom et al.), whereas the rates of degradation increase almost linearly with the increase in initial concentration of substrate.

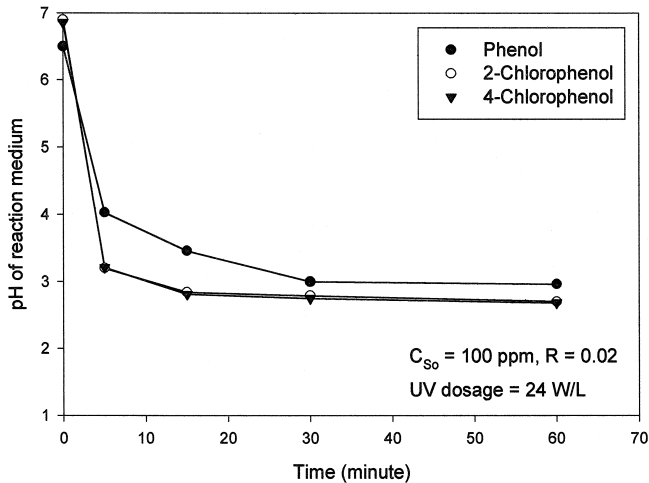


Fig. 3. pH-time profile of aqueous solutions of phenol and chlorophenols during reaction of UV/ H_2O_2 photooxidation.

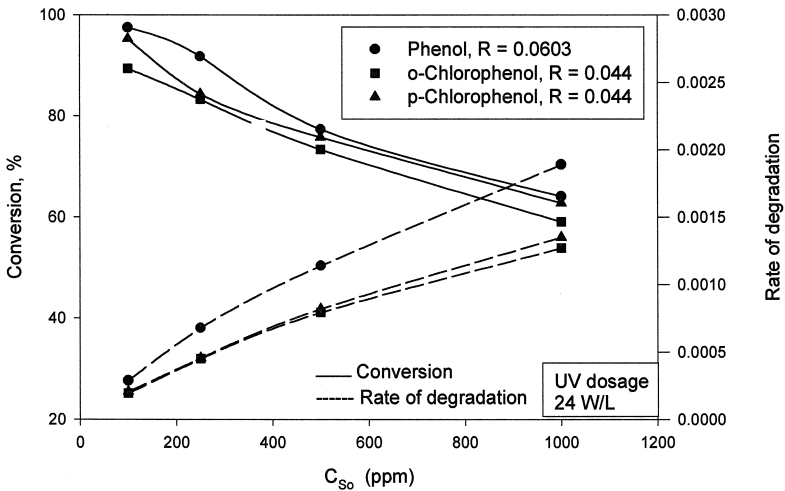


Fig. 4. Percent conversion and rates of degradation ($\text{mol}/\text{m}^3 \text{ s}$) against initial substrate concentration at constant R by UV/ H_2O_2 photooxidation.

The destruction of the substrate at several different initial H_2O_2 concentrations has been studied. It is observed that the conversion of substrate increases with an increase in the initial concentration of H_2O_2 (i.e. decreasing the substrate to H_2O_2 molar ratio, R). But a very high concentration of hydrogen peroxide retards the reaction markedly. From Fig. 5, it is observed that the substrate to H_2O_2 molar ratio R shows a maximum conversion at around $R = 0.02$, and beyond this point, conversion of the substrate decreases irrespective of whether R increases or decreases. This phenomenon could be

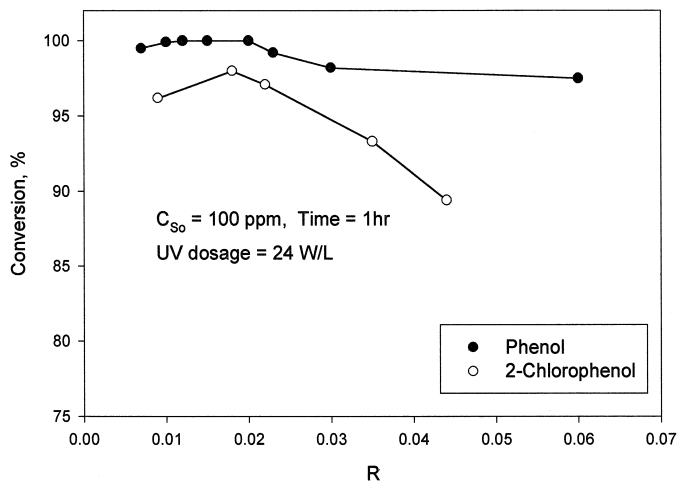


Fig. 5. Effect of substrate to H_2O_2 ratio (R) on photooxidation of phenol and *o*-chlorophenol.

explained by considering the two opposing effects of H_2O_2 in the photooxidation reaction. As the molar ratio of substrate to H_2O_2 (R) was decreased, more $\cdot OH$ radicals were available to attack the aromatic rings and the rate of reaction increased. By a large increase in H_2O_2 concentration, H_2O_2 acted as a scavenger [5,18] of highly reactive $\cdot OH$ free radicals to form oxygen and perhydroxyl radicals and thus retarded the reaction rate. The rate of decomposition of 2-chlorophenol with time was found to be a nonlinear function by Apak and Hügel [6], and they mentioned that degradation rate increased with increasing ratio of oxidant to 2-chlorophenol. However, Köpp et al. [19] reported that there should be a favorable hydrogen peroxide concentration for the effective TOC removal of organic contaminant, i.e. corresponding to the maximum degradation, an optimum hydrogen peroxide concentration exists. Thus by an increase in hydrogen peroxide concentration above the limiting value, undesirable parallel reactions of hydrogen peroxide result in a decrease in the rates of substrate destruction.

3.2. Mathematical modeling

The experimental rate equation may be written in the following form:

$$\text{Rate} = -\frac{dC_S}{dt} = kC_S^m C_{H_2O_2}^n, \quad (I)$$

where the rate constant k includes the effect of UV light intensity.

For initial rapid reaction, the values of m , n and k can be obtained from the expressions (for details, please see De et al. [20]):

$$-\ln(1 - x_S) = kC_{S_0}^{m-1} C_{H_2O_2,0}^n t,$$

and

$$-\ln(1 - x_S) = kR^{m-1} C_{H_2O_2,0}^{m+n-1} t,$$

where C_{S_0} and $C_{H_2O_2}$ are the initial concentrations of the substrate and oxidant, respectively. x_S is the fractional conversion of substrate, t is the reaction time and R is substrate to hydrogen peroxide molar ratio.

Based on these equations a log–log plot of experimental data at the initial period of

Table 2

Degradation by UV/ H_2O_2 : values of k , m and n obtained from the empirical equation and hydroxyl radical ($\cdot OH$) reaction rate constants for phenol, 2-, and 4-chlorophenol

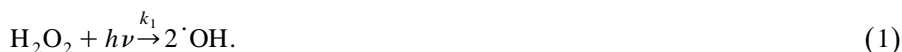
Substrate	m	n	k_2
Phenol	0.21	0.49	$(1.41 \pm 0.6) \times 10^{10}$
2-Chlorophenol	0.16	0.44	$(9.10 \pm 2.1) \times 10^9$
4-Chlorophenol	0.18	0.45	$(1.07 \pm 0.4) \times 10^{10}$

substrate degradation has yielded the values of k , m and n . These calculated values of k , m and n for phenol, 2- and 4-chlorophenols are reported in Table 2.

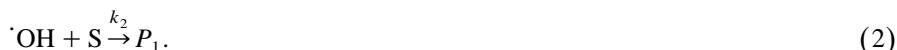
Again the rate equation may be determined by using either the integral method or the initial rate method which is usually not as accurate as the integral method. However, in the reactions of substrates with UV/H₂O₂, a number of intermediates have been produced and degraded again. This complex reaction makes the integral method approach almost impossible. In this study, we use the initial rate method for the estimation of reaction rate constants in the following manner.

3.3. Derivation of rate equation from probable mechanism of substrate / UV / H₂O₂ photooxidation

The primary and principal step for the UV/H₂O₂ degradation has been postulated as the initial attack by photon to hydrogen peroxide and the formation of hydroxyl ($\cdot\text{OH}$) free radicals [6,21,22].



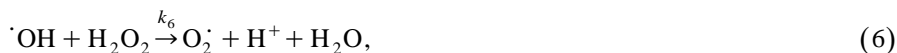
The $\cdot\text{OH}$ radicals formed then undergo radical-chain reaction with the substrate, and product(s) are formed.



During the experiments, it is observed that a small amount of the substrate is degradable by using UV-irradiation only, and by using H₂O₂ as oxidant (in absence of UV-radiation).



Other reactions involved are given below:



Here, S is the substrate (phenol, chlorophenols, etc.)

P_1 , P_2 and P_3 are the products, and P_2^* is the activated complex.

Therefore, the rate of degradation of a substrate can be written as:

$$r_T = -\frac{dC_S}{dt} = (r_{UV} + r_{\text{H}_2\text{O}_2} + r_R), \quad (8)$$

where r_T = global reaction rate for the degradation of a substrate by the enhanced oxidation process of UV/H₂O₂ reaction; r_{UV} = photochemical reaction rate; $r_{H_2O_2}$ = reaction rate for the degradation by H₂O₂ only; r_R = reaction rate between a substrate and hydroxyl (\cdot OH) radicals (radicalary reaction rate).

The photochemical reaction rate (r_{UV}) can be calculated by the expression [23,24]:

$$r_{UV} = \phi_S W_{abs,S} / V, \quad (9a)$$

where ϕ_S = quantum yield for the reaction between a substrate and UV radiation (mol/E); $W_{abs,S}$ = radiation flowrate absorbed by a substrate (E/s), where:

$$W_{abs,i} = I_0 f_i [1 - \exp(-2.3L \sum \epsilon_i C_i)], \quad (9b)$$

and

$$f_i = \frac{\epsilon_i C_i}{\sum \epsilon_i C_i}.$$

The rate of substrate degradation by H₂O₂ only can be written as:

$$r_{H_2O_2} = k_4 C_S C_{H_2O_2}. \quad (10)$$

The rate of hydroxyl radical reaction can be presented as:

$$r_R = k_2 C_S C_{OH\cdot}. \quad (11)$$

Now, the rate of formation of \cdot OH and HO₂ \cdot radicals are:

$$\begin{aligned} \frac{dC_{OH\cdot}}{dt} &= \phi_H W_{abs,H} / V + k_7 C_{HO_2\cdot} C_{H_2O_2} - k_2 C_S C_{OH\cdot} \\ &\quad - k_5 C_{OH\cdot} C_{H_2O_2} - k_6 C_{OH\cdot} C_{H_2O_2}, \end{aligned} \quad (12)$$

and

$$\frac{dC_{HO_2\cdot}}{dt} = k_5 C_{OH\cdot} C_{H_2O_2} - k_7 C_{HO_2\cdot} C_{H_2O_2}. \quad (13)$$

With steady state approximation [23–27], we may write:

$$C_{OH\cdot} = \frac{\phi_H W_{abs,H} / V}{k_2 C_S + k_6 C_{H_2O_2}}. \quad (14)$$

Therefore, the reaction rate for the radicalary reaction is:

$$r_R = k_2 C_S \frac{\phi_H W_{abs,H} / V}{k_2 C_S + k_6 C_{H_2O_2}}. \quad (15)$$

At the initial period of reaction, we can neglect the scavenging effect of H_2O_2 to OH radicals (reactions 5 and 6) and thus radicalary reaction rate becomes:

$$r_{R,o} = \phi_H W_{abs,H}/V. \quad (16)$$

Following De et al. [20], for the initial rapid reaction, we can substitute Eq. (16) as:

$$r_{R,o} = \phi_H W_{abs,H}/V = k [C_S^m C_{H_2O_2}^n]_0. \quad (17)$$

Combining Eqs. (8), (9a), (10) and (15), we can write:

$$-\frac{dC_S}{dt} = \phi_S W_{abs,S}/V + k_4 C_S C_{H_2O_2} + k_2 C_S \frac{\phi_H W_{abs,H}/V}{k_2 C_S + k_6 C_{H_2O_2}}. \quad (18)$$

From Eqs. (17) and (18), we get:

$$\left[-\frac{dC_S}{dt} - \phi_S W_{abs,S}/V - k_4 C_S C_{H_2O_2} \right] = \frac{[C_S^m C_{H_2O_2}^n]_0}{\left[\frac{1}{k} + \frac{k_6}{kk_2} \frac{C_{H_2O_2}}{C_S} \right]}. \quad (19)$$

By rearranging, we get:

$$\frac{[C_S^m C_{H_2O_2}^n]_0}{\left[-\frac{dC_S}{dt} - k_4 C_S C_{H_2O_2} + \phi_S W_{abs,S}/V \right]} = \frac{1}{k} + \frac{k_6}{kk_2} \frac{C_{H_2O_2}}{C_S}. \quad (20)$$

The global rates of substrates degradation ($-dC_S/dt$) are calculated from experi-

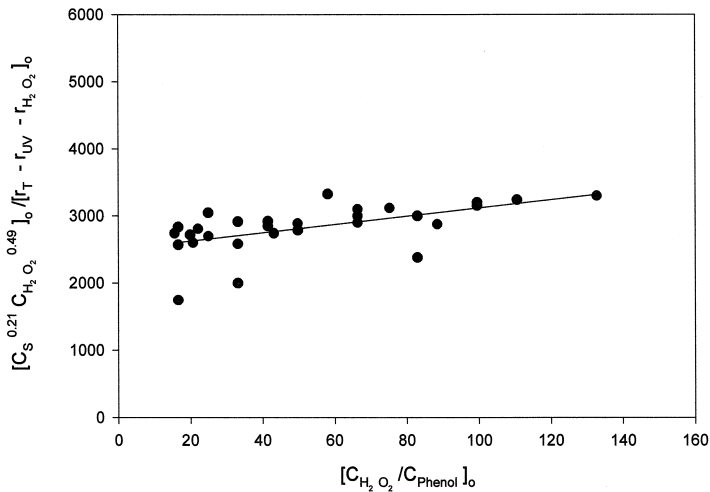


Fig. 6. Plot of Eq. (20) for phenol at the initial period of photooxidation.

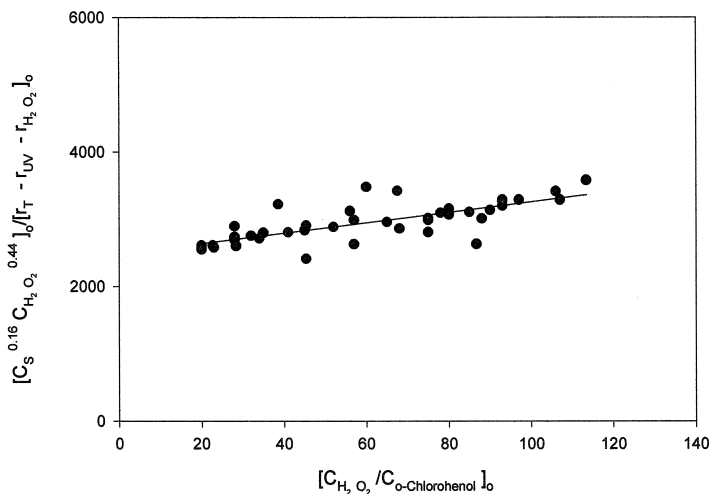


Fig. 7. Plot of Eq. (20) against initial molar ratio of H_2O_2 to *o*-chlorophenol.

mental data. The values of the rate constant k_4 for degradation of substrates using hydrogen peroxide only have been calculated by linear regression [28]. For the estimation of W_{abs} in Eq. (9b), it is assumed that only the substrate and the hydrogen peroxide present absorb radiation [29]. The radiation, (I_0), was directly measured by chemical actinometry.

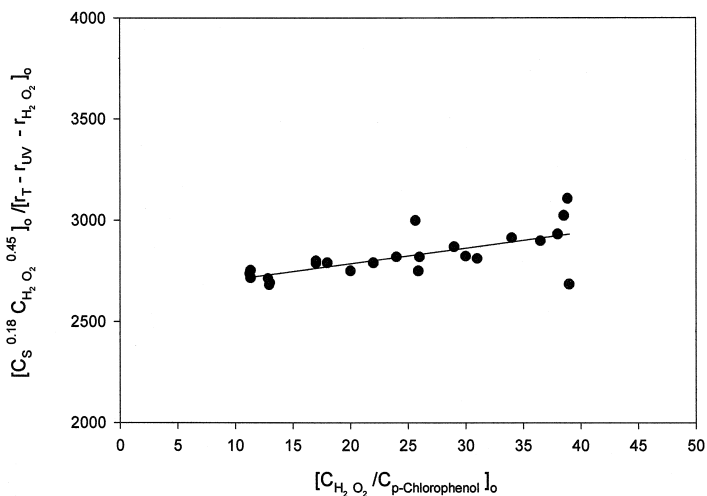


Fig. 8. Plot of left hand quantities of Eq. (20) against H_2O_2 to *p*-chlorophenol molar ratio at the initial period of photooxidation.

A plot of the left hand side of the Eq. (20) against $[C_{H_2O_2}/C_S]$ at the initial period of reaction yields the value of the slope (k_6/kk_2) and intercept ($1/k$). Plots are shown in Figs. 6–8 for phenol, *o*-chlorophenol and *p*-chlorophenol, respectively. From the intercepts and slopes of these curves, hydroxyl radical reaction rate constants for these three compounds are estimated and are listed in Table 2. The values of the rate constants are of the same order of magnitude, the values for *o*- and *p*-chlorophenols being about 25–30% less than that for phenol. The presence of chlorine atom in chlorophenols creates electron-rich atmosphere in the benzene ring because of the interaction through lone-pair, thereby making them less vulnerable to attack by \cdot OH radical as compared to phenol. Similar observations of the lower vulnerability of the chlorophenols to oxidizing radicals have been reported by Apak and Hügel [6].

The accuracy of the value of the constant k_2 is very important in context of use of the model developed in this work. We have statistical analysis of the data to determine the 95% confidence limits of the values of this rate constant. The students' *t*-test has been done taking all the data points shown in Figs. 6–8 for phenol, *o*-chlorophenol and *p*-chlorophenol, respectively. The relevant confidence limits of the values of the rate constants are reported in Table 2.

4. Conclusions

The process of the advanced oxidation technology using UV/ H_2O_2 in destroying contaminants like phenol, 2- and 4-chlorophenols present in dilute aqueous solutions has been demonstrated and the kinetics of degradation of the organics has been determined. For a given initial substrate concentration, substrate to H_2O_2 molar ratio of around 0.02 gives maximum substrate conversion. An empirical as well as a theoretical model describing the degradation kinetics has been developed. The \cdot OH radical reaction rate constants for UV/ H_2O_2 photooxidation with phenol, 2- and 4-chlorophenols have been estimated and they are typically of the order of $1 \times 10^{10} \text{ g mol}^{-1} \text{ s}^{-1}$ for the phenolic substrates studied in this work.

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