



Photocatalytic degradation of 2-chlorophenol: a study of kinetics, intermediates and biodegradability

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Abstract

The kinetics of photocatalytic (TiO_2/UV) degradation of 2-chlorophenol (2-CP), characterization of intermediates and induction of biodegradability in treated chlorophenol solutions is reported. Approximately 95% of the 2-CP is removed in approximately 2 h at pH 5 and $0.2 \text{ g TiO}_2 \text{ l}^{-1}$ when the 2-CP concentration is $\leq 100 \text{ mg l}^{-1}$; the pseudo-first-order rate constant (k) is estimated to be 0.0183 min^{-1} . GC–MS analyses detected phenol, catechol, hydroxyhydroquinone (HHQ), and chlorohydroquinone (CHQ) intermediates during the short irradiation time ($< 1 \text{ h}$); however two other higher carbon intermediates 2-hydroxy-benzaldehyde (HB) and [1,1'-biphenyl]-2,2'-diol (BPD) are found as major intermediates over longer irradiation times. The biochemical oxygen demand (BOD) of treated 2-CP solutions improved substantially. A tentative mechanistic pathway to explain formation of higher carbon intermediates is presented.

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1. Introduction

Recently, it has been demonstrated that TiO_2/UV technique can lead to effective removal of soluble organic matter [1–3] and this process can be considered as a potential alternative to conventional methods of treatment, viz. physico-chemical and biological methods. The major advantages of these photocatalytic processes include the relatively mild reaction conditions and their success in decomposing several toxic as well as refractory pollutants [4–12].

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Chlorophenols such as 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) represent important water pollutants and have been named as priority pollutants by the US EPA [13]. The stability of the C–Cl bond in halo-hydrocarbons is responsible for their toxicity and persistence in the biological environment [14,15].

The main routes of entry of 2-chlorophenol to the aquatic environment are discharges from plants manufacturing it, or from plants, those employ it as intermediate in the production of higher chlorinated phenols or phenoxy herbicides [16]. Indirect sources include discharges from paper mills as by-products of chlorine-based bleaching, as a result of disinfection of sewage and industrial wastewater with chlorine and from slow microbial breakdown of herbicides during post-application period. The compound is also used as a solvent for extracting sulfur and nitrogen compounds from coal [17].

2-Chlorophenol is very toxic and poorly biodegradable [18]. A wastewater stream containing 2-CP over 200 mg l^{-1} may not be treated effectively by direct biological methods [13].

Oxidation of 2-CP under photocatalytic [19–22], electrocatalytic [23], Fenton's oxidation [21,24] and supercritical water oxidation [25] conditions has been reported. The influence of pH, comparison of rates of direct photolysis with that of photocatalytic oxidation and formation of various intermediates has been reported [19–22]. While these reports differ insofar as the effect of pH and direct photolysis is concerned, it has also been observed that the types and distribution of intermediates is dependent on the experimental conditions. Thus, catechol and cyclopentadienic acids were reported as major intermediates in photolysis [26], whereas phenol, hydroquinone, benzoquinone, chlorohydroquinone (CHQ), hydroxyhydroquinone (HHQ) were formed under photocatalytic conditions [20].

It is reported that higher pH discourages the formation of aromatic intermediates [19]. Moreover, when organochlorine compounds undergo oxidation, they may produce other organochlorine compounds that may be more toxic than the parent compound itself [27]. This necessitates a study to examine the changes in biodegradability as a function of photocatalytic treatment time and evolution of various intermediates. This aspect of biodegradability of photocatalytically treated 2-CP solutions has not been investigated earlier. In this paper, we report the kinetics of TiO_2 -catalyzed photo-oxidation of 2-CP, identification of intermediates and assessment of biodegradability of treated 2-CP solutions.

2. Experimental

2.1. Materials

Titanium dioxide (TiO_2 , P-25) from Degussa (80:20 anatase:rutile mixed phase, surface area $55 \text{ m}^2 \text{ g}^{-1}$, non-porous) was used for all adsorption and photocatalysis experiments. 2-Chlorophenol ($\text{C}_6\text{H}_5\text{OCl}$, MW = 128.56, purity = >98.0%, density = 1.26 g ml^{-1} , solubility in water = 2.85 g per 100 ml, λ_{max} at 240 and 275 nm ($\epsilon_{275 \text{ nm}} = 2.213 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$)) was an Acros Organics product (Belgium). De-ionized water was employed for making all standard reagents and dilute solutions.

2.2. Photo-oxidation method and apparatus

In a typical dark adsorption experiment, a 100 ml sample containing $100 \text{ mg } 2\text{-CP l}^{-1}$ was mixed with 0.02 g TiO_2 and shaken for 2 h by a mechanical shaker. The initial pH of the 2-CP solutions was approximately 5.5. The pH was adjusted to 9.0 optionally, using 0.1 M NaOH . The concentration of 2-CP was varied from 50 to 500 mg l^{-1} at a fixed TiO_2 dose, i.e. 0.02 g per 100 ml and the dependence of adsorption on the concentration of 2-CP was assessed.

All photocatalytic experiments were carried out in an Immersion Well Photoreactor (Scientific Aids & Instruments Co. Ltd., Chennai). A medium pressure mercury vapor lamp (400 W, peak emission at 365 nm, $5.0 \times 10^{19} \text{ photons s}^{-1}$) was used for irradiating the test solutions. The lamp was located in a water-cooled double-walled borosilicate jacket to maintain temperature at $35 \pm 1 \text{ }^\circ\text{C}$ for all runs. An adequate flow of water through the immersion well was maintained to avoid excessive heating of the solutions. Aeration was provided through an aquarium aerator. A 400 ml solution of 2-chlorophenol was added to the reactor along with a predetermined amount of TiO_2 . The suspension was agitated by a magnetic stirrer for approximately 30 min before switching on the lamp. Test samples were withdrawn from the middle of the reactor at chosen time intervals. A silicone capillary tube fitted with syringe microfilter (13 mm, $0.22 \text{ }\mu\text{m}$ Millex[®] GV, Millipore) at one end was inserted into reactor zone through the sampling port and the required amount of sample was slowly withdrawn with the help of a syringe. Thus, liquid samples free of TiO_2 were obtained. Various concentrations of 2-chlorophenol in the range $50\text{--}500 \text{ mg l}^{-1}$ were used to evaluate the kinetics of the photodegradation reaction.

2.3. Analyses

The test samples were analyzed for changes in UV absorption as well as COD with respect to irradiation time. Prior to each analysis, the test samples were filtered through a $0.22 \text{ }\mu\text{m}$ membrane filter to remove TiO_2 particles. The clear solutions were analyzed for 2-CP concentration by monitoring at $\lambda = 275 \text{ nm}$ using Perkin-Elmer $\lambda 900$ UV-Vis Spectrophotometer. The COD tests were carried out according to Close Reflux, Colorimetric Method [28] using a Hach DR/2010 Spectrophotometer and Hach COD reactor. The estimation of chloride ion concentration as a function of irradiation time was carried out using a Dionex DX-100 Ion Chromatograph. An Ion Pac AS4A-SC Analytical Column, $1.8 \text{ mM Na}_2\text{CO}_3/1.7 \text{ mM NaHCO}_3$ eluent (flow rate of 1.2 ml min^{-1}), Anion Micro Membrane Suppressor (2 mm) were used. Double distilled water with background conductivity of $7.2 \text{ }\mu\text{S}$ was used as regenerant (flow rate, 5 ml min^{-1}).

The estimation of carbon dioxide evolved during photodegradation of 2-CP was carried out by trapping the gas in $1.2 \times 10^{-2} \text{ mol Ba(OH)}_2$ solution (three-stage serial trapping). The barium carbonate precipitate was filtered and gravimetrically determined. This estimation was corrected for background CO_2 arising from passing air into test solutions under photocatalytic conditions. For this purpose, control experiments were conducted without 2-CP under identical experimental conditions. Alternatively, the free hydroxyl concentration in the filtrate was also titrated using 0.05 N HCl . Both determinations compared well being within 5% error limit. The estimation of formaldehyde concentrations was carried

out using Nash method [29,30], according to which formaldehyde reacts with the reagent to form a colored complex, diacetyl dihydro lutidine (DDL) that exhibits absorption at 412 nm ($\epsilon = 9.1 \times 10^{-3} \text{ mg}^{-1} \text{ l cm}^{-1}$).

2.4. Biodegradability tests

The test for biodegradability of 2-CP and photo-oxidized 2-CP solutions involved the determination of biochemical oxygen demand ($\text{BOD}_5^{20^\circ\text{C}}$) as per Standard Methods [28]. For this purpose, a $100 \text{ mg } 2\text{-CP l}^{-1}$ solution was photo-oxidized as described above and test samples were collected during photo-oxidation reaction for BOD determination.

2.5. Determination of intermediates

A Varian STAR-3400 CX Gas Chromatograph coupled with a Saturn-3 Mass Spectrometer and NIST 98 Mass Spectral Library was used for detection of intermediates formed during photodegradation of 2-CP. This study was extended to the test samples collected from individual batch experiments under different irradiation times, viz. 1–5 h, using $200 \text{ mg } 2\text{-CP l}^{-1}$ and $0.20 \text{ g TiO}_2 \text{ l}^{-1}$. The intermediates were extracted into dichloromethane ($25 \text{ ml} \times 3$) using 200 ml of test sample. The extract was concentrated to 1 ml prior to its use. The chromatographic separation involved the use of a DB-5 capillary column (30 m length, 0.25 mm id, 0.25 μm film thickness), that was maintained initially at 70°C for 2 min, followed by gradual increase of temperature at a rate of $10^\circ\text{C min}^{-1}$ up to 270°C . Helium was used as the carrier gas. The analyses were performed in the electron impact (EI) mode. The ionization source temperature was kept at 240°C .

3. Results

A maximum 5% initial 2-CP concentration is reduced by adsorption on to TiO_2 at pH 5. The adsorption is improved somewhat in alkaline 2-CP solutions (pH 9), ranging between 14 and 18%.

3.1. Photocatalytic oxidation of 2-CP

The UV absorption spectra of test samples corresponding to different time intervals are shown in Fig. 1. The spectra correspond to photocatalytic degradation of 100 mg l^{-1} 2-CP solutions (pH 5.5) using $0.2 \text{ g TiO}_2 \text{ l}^{-1}$. The intensity of 275 nm band due to 2-CP showed a remarkable decrease with an increase in the irradiation period; this band being almost annihilated during first 1h. Another peak at 240 nm is also found to disappear upon prolonged irradiation.

The photocatalytic degradation of 2-CP resulted in the reduction of chemical oxygen demand, release of ring bound chlorine and evolution of carbon dioxide. The 2-CP solutions turned light yellow after 15 min irradiation. The color intensified gradually until 1–2 h passed, depending upon the initial 2-CP concentration. This color however disappeared gradually in a period of 3–4 h under photocatalytic conditions.

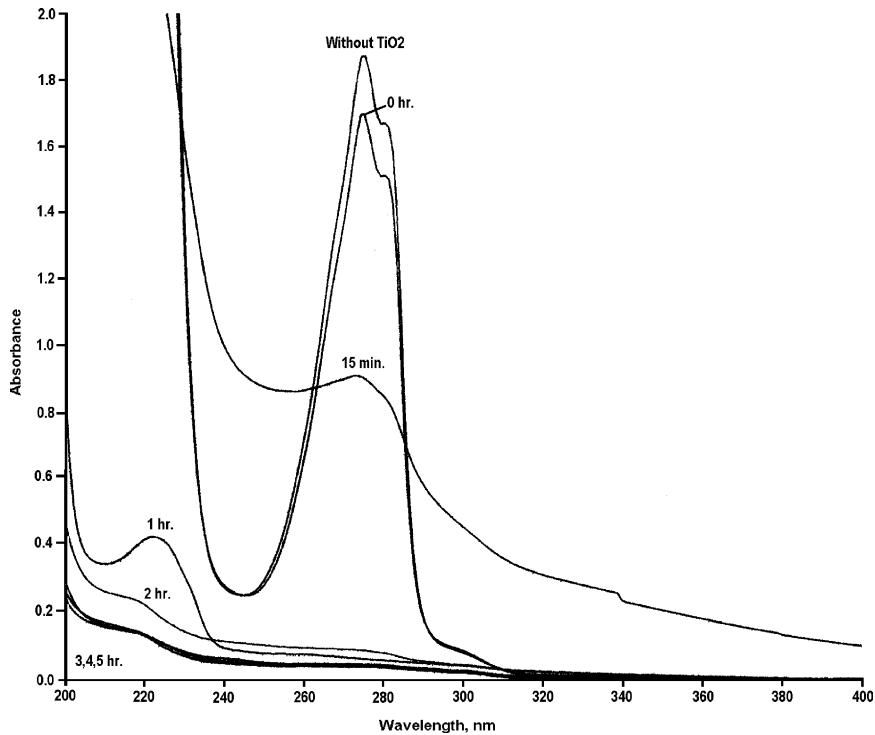


Fig. 1. UV absorption spectra of test samples depicting the degradation of 2-CP as a function of irradiation time. Initial concentration of 2-CP = 100 mg l^{-1} ; dose of TiO_2 = $0.02 \text{ g per } 100 \text{ ml}$; initial pH = 5.5.

The time course variation of COD, Cl^- and CO_2 for the case of $100 \text{ mg } 2\text{-CP l}^{-1}$ is depicted in Fig. 2. Approximately 93% COD is reduced during initial 1h at an initial rate of $2.46 \text{ mg l}^{-1} \text{ min}^{-1}$. The corresponding $\log[\text{COD}]$ versus time plot is linear ($R^2 = 0.99$), and pseudo-first-order rate constant is estimated to be 0.0183 min^{-1} .

Approximately 75% of estimated Cl^- is released during the initial 20 min., and thereafter the Cl^- concentration increased slowly and eventually reached saturation (see inset Fig. 2). The initial rate of Cl^- formation was $1.74 \text{ mg l}^{-1} \text{ min}^{-1}$ ($R^2 = 0.99$), the rate constant k derived from $\log[\text{Cl}^-]$ versus time plot assuming first-order relationship is 0.0528 min^{-1} ($R^2 = 0.97$). Thus, a total of $24 \text{ mg Cl}^- \text{ l}^{-1}$ was measured as against an estimated amount of $27.5 \text{ mg Cl}^- \text{ l}^{-1}$ in 5 h. This figure accounts for release of 87% of the expected amount of Cl^- .

The evolution of CO_2 is also faster during the initial 2 h period, but it slowed considerably after 2 h. The initial rate of evolution of CO_2 was estimated to be $6.48 \times 10^{-5} \text{ M min}^{-1}$ ($R^2 = 0.96$), while the pseudo-first-order rate constant, as derived from $\log[\text{CO}_2]$ versus time plot, is $5.07 \times 10^{-6} \text{ M min}^{-1}$ ($R^2 = 0.88$). Thus, a total of $9.41 \times 10^{-3} \text{ M CO}_2$ is evolved during 5h as against an expected amount of $1.15 \times 10^{-2} \text{ M CO}_2$, accounting for 80.5% of theoretical estimate. Of the foregoing amount, approximately 45% ($5.27 \times 10^{-3} \text{ M CO}_2$) is evolved during first 1 h.

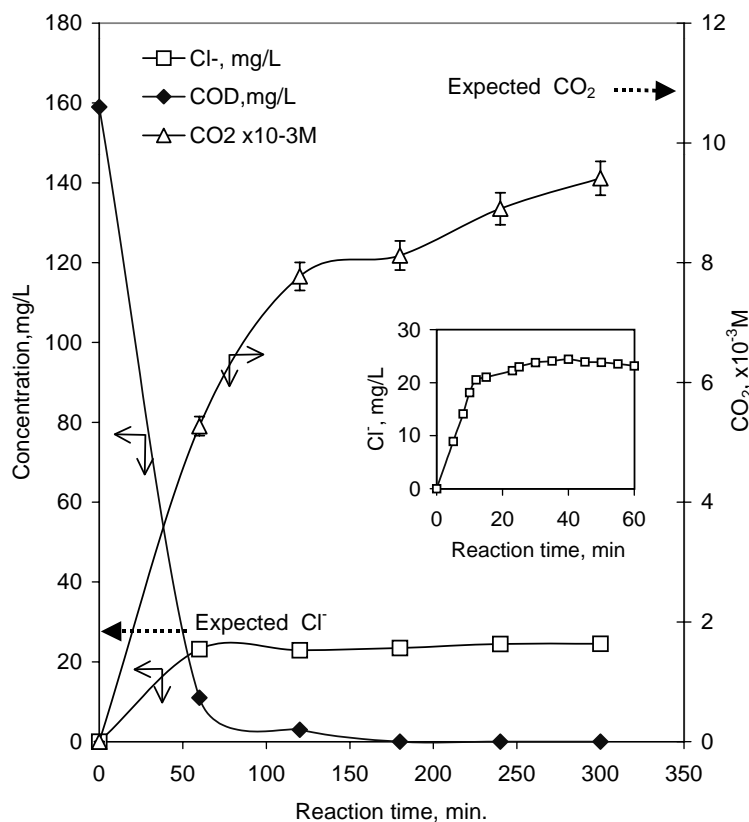


Fig. 2. Time variation of COD, Cl^- and CO_2 during photocatalytic degradation of 2-CP. Initial concentration of 2-CP = 100 mg l^{-1} ; dose of TiO_2 = $0.02 \text{ g per } 100 \text{ ml}$; initial pH = 5.5. Inset, release of chloride ions during first hour of photodegradation of 2-CP.

Formaldehyde is also formed in substantial amounts. Approximately $5.5 \text{ mg HCHO l}^{-1}$ was detected at 15 min. and this amount gradually increased to 12.84 mg l^{-1} at 1 h. Thereafter a significant decline in HCHO concentration was noticed, measuring only 2.25 mg l^{-1} at 2h and 0.71 mg l^{-1} at 3 h.

Since the 400 W medium pressure Hg lamp used in this study has intense arcs predominantly radiating at 365 nm with smaller amounts in the UV region at 265, 303, 334 nm apart from significant radiation in visible region and since 2-CP has λ_{max} at 275 nm, contribution from direct photolysis of 2-CP to the observed reaction rates in the presence of TiO_2 had to be assessed. The variation of COD (initial 2-CP concentration = 100 mg l^{-1}) as a function of time of irradiation was monitored under both direct photolytic and photocatalytic conditions. The corresponding rate constants have been derived using first hour data from $\log[\text{COD}_t/\text{COD}_0]$ versus time plots. It is found that 2-CP undergoes significant direct photolysis. The $k_{\text{direct}} = 9.7 \times 10^{-3} \text{ min}^{-1}$, while $k_{\text{TiO}_2/\text{UV}} = 18.3 \times 10^{-3} \text{ min}^{-1}$. The rate constant doubled in the presence of TiO_2 .

3.2. Effect of pH

Both 2-CP and TiO₂ surfaces undergo pH dependent changes, viz. phenoxide ion formation via deprotonation of phenolic–OH and transformation of (Ti–OH₂)_{surface} and (Ti–OH)_{surface} into (Ti–O[–])_{surface}. Hence, the photocatalytic degradation of 2-CP was carried out at pH 3, 7 and 11 in order to evaluate the effect of pH. The rate of removal of COD was 1.74, 1.83 and 1.93 mg l^{–1} min^{–1} at pH 3, 7 and 11, respectively. There is no significant change in the rate of reaction in the examined pH range.

3.3. Effect of 2-CP concentration

The change in COD as a function of irradiation time and its dependence on the initial concentration of 2-CP is shown in Fig. 3. Approximately 98% of the initial COD is reduced during 4 h at 2-CP concentration <200 mg l^{–1}. In contrast, only 80–83% of initial COD

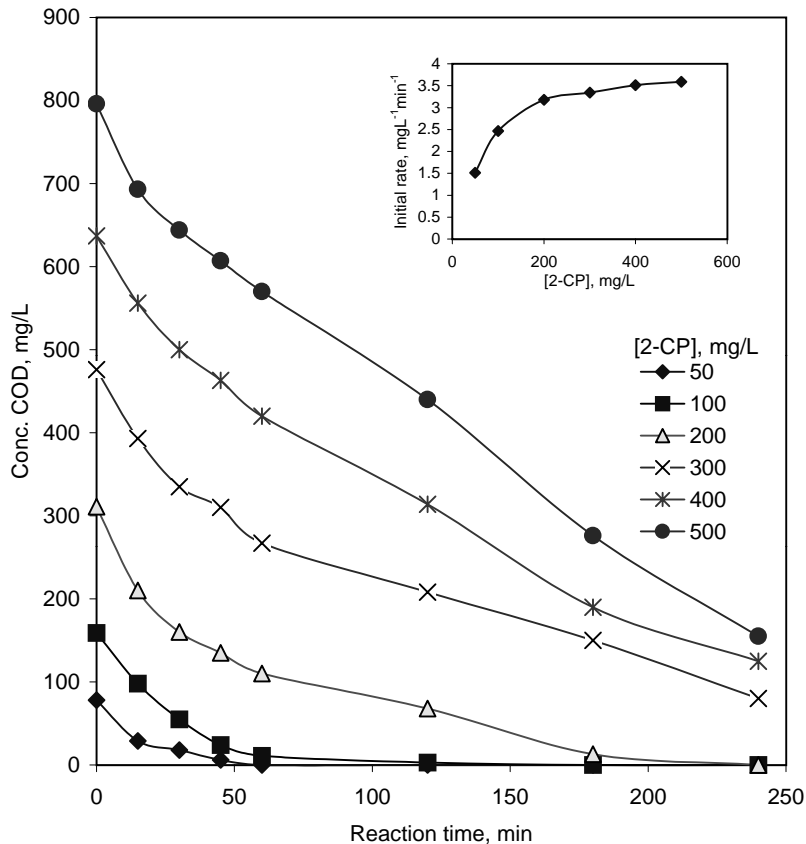


Fig. 3. Change in chemical oxygen demand as a function of irradiation time at various initial concentrations of 2-CP. Inset, dependence of initial rates of 2-CP degradation on the initial concentrations of 2-CP. Dose of TiO₂ = 0.02 g per 100 ml; initial pH = 5.5.

is reduced in the same time at 2-CP concentration $\geq 300 \text{ mg l}^{-1}$. The initial reaction rates were deduced from the first 1 h sections of the plots in Fig. 3.

The concentration dependence of rates is shown in the inset in Fig. 3. The rate increased gradually up to $100 \text{ mg 2-CP l}^{-1}$, but thereafter it became concentration independent. If the rates obey the Langmuir–Hinshelwood relationship, rate (r_0) = $kKC_0/(1 + KC_0)$, where k is the rate constant, K is the adsorption constant of 2-CP on TiO_2 from water and C_0 is the initial 2-CP concentration, the plot of r_0^{-1} as a function of C_0^{-1} should yield a straight line. This hypothesis was verified through the double reciprocal plot shown in Fig. 4. The linearity of this plot indicates that the degradation of 2-CP follows a first-order rate law. The least squares analysis of the plot revealed the values of $k = 4.484 \text{ min}^{-1}$ (expressed as mg COD l^{-1}) or 2.81 min^{-1} (expressed as mg 2-CP l^{-1} ; this is equal to $22.0 \mu\text{M}$) and $K = 0.016771 \text{ mg}^{-1}$. The low adsorption constant supports the view that 2-CP is poorly adsorbed over TiO_2 .

3.4. Identification of reaction intermediates

The test solutions turned light yellow and the color intensified during the first hour. The color disappeared slowly between 2 and 3 h and eventually the solutions became colorless.

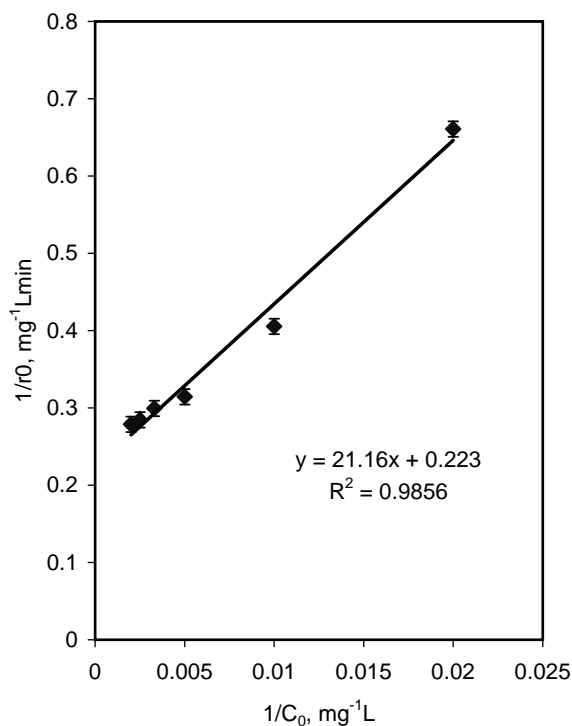


Fig. 4. Langmuir–Hinshelwood plot depicting linear relationship between reciprocal of initial rates ($1/r_0$) and reciprocal of initial 2-CP concentration ($1/C_0$). Dose of $\text{TiO}_2 = 0.02 \text{ g per } 100 \text{ ml}$; initial $\text{pH} = 5.5$.

The GC–MS analysis of samples revealed the presence of phenol, catechol, hydroxyhydroquinone, chlorohydroquinone, 2-hydroxy benzaldehyde (HB) and [1,1'-biphenyl]-2,2'-diol (BPD). Some of these intermediates have been previously reported during photocatalytic oxidation of 2-CP [20,22]. The latter two intermediates (HB and BPD) are new and contain one and six more carbons compared to 2-chlorophenol. Both these compounds were absent in the initial 2-CP solution.

The higher carbon intermediates (HB and BPD) are observed at retention times 4.20 and 11.99 min, respectively. The identification of these two intermediates is based on the following evidence.

3.4.1. 2-Hydroxy benzaldehyde (MW = 122)

The mass fragmentation spectrum of HB is displayed in Fig. 5(a). The molecular ion peak is observed at m/z 122. The other important characteristic mass fragmentation peaks are: a peak at m/z 104 due to loss of –OH group, a peak at m/z 93 due to loss of –CHO group and a peak at m/z 76 due to loss of –OH and –CHO groups simultaneously. The molecular ion peak at m/z 122 along with the above referred fragmentation peaks confirms the presence of 2-hydroxy benzaldehyde intermediate.

3.4.2. [1,1'-Biphenyl]-2,2'-diol (BPD, MW = 186)

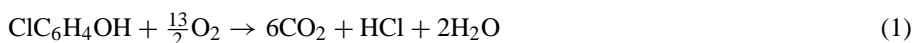
The mass fragmentation spectrum of BPD is displayed in Fig. 5(b). The molecular ion peak appeared at m/z 186. The other characteristic fragmentation peaks are: a peak at m/z 169 due to loss of one –OH; a peak at m/z 92 due to breaking of the C–C bond joining the two phenyl rings and a peak at m/z 77 due to the loss of a hydroxyl group from the phenol fragmentation product. The molecular ion peak at m/z 186 along with the above referred fragmentation peaks confirms the presence of [1,1'-biphenyl]-2,2'-diol intermediate. There are some other peaks (e.g. at m/z 157 and 121, etc.) whose origin could not be traced. At present, it is hypothesized that this compound is co-eluted with some other unknown compound.

The intermediates phenol, catechol, HHQ and CHQ disappeared during the first hour under the experimental conditions employed. A trace amount of 2-CP is present in all test samples, even after long irradiation time. The higher carbon intermediates persist a little longer, i.e. up to 3 h. BPD was found to disappear faster (1.5–2 h) than 2-hydroxy benzaldehyde (3 h) under photocatalytic conditions.

4. Discussion

4.1. Kinetics and affect of pH

The photocatalytic degradation of 2-CP resulted in reduction of COD, release of ring bound chlorine and evolution of CO₂. Based on this analyses, the overall reaction can be represented by Eq. (1).



The degradation of 2-CP is found to be pseudo-first-order in its concentration, the rate constant (k) being 2.81 min⁻¹ and $K = 0.01677$ l mg⁻¹. A rate constant value in the range

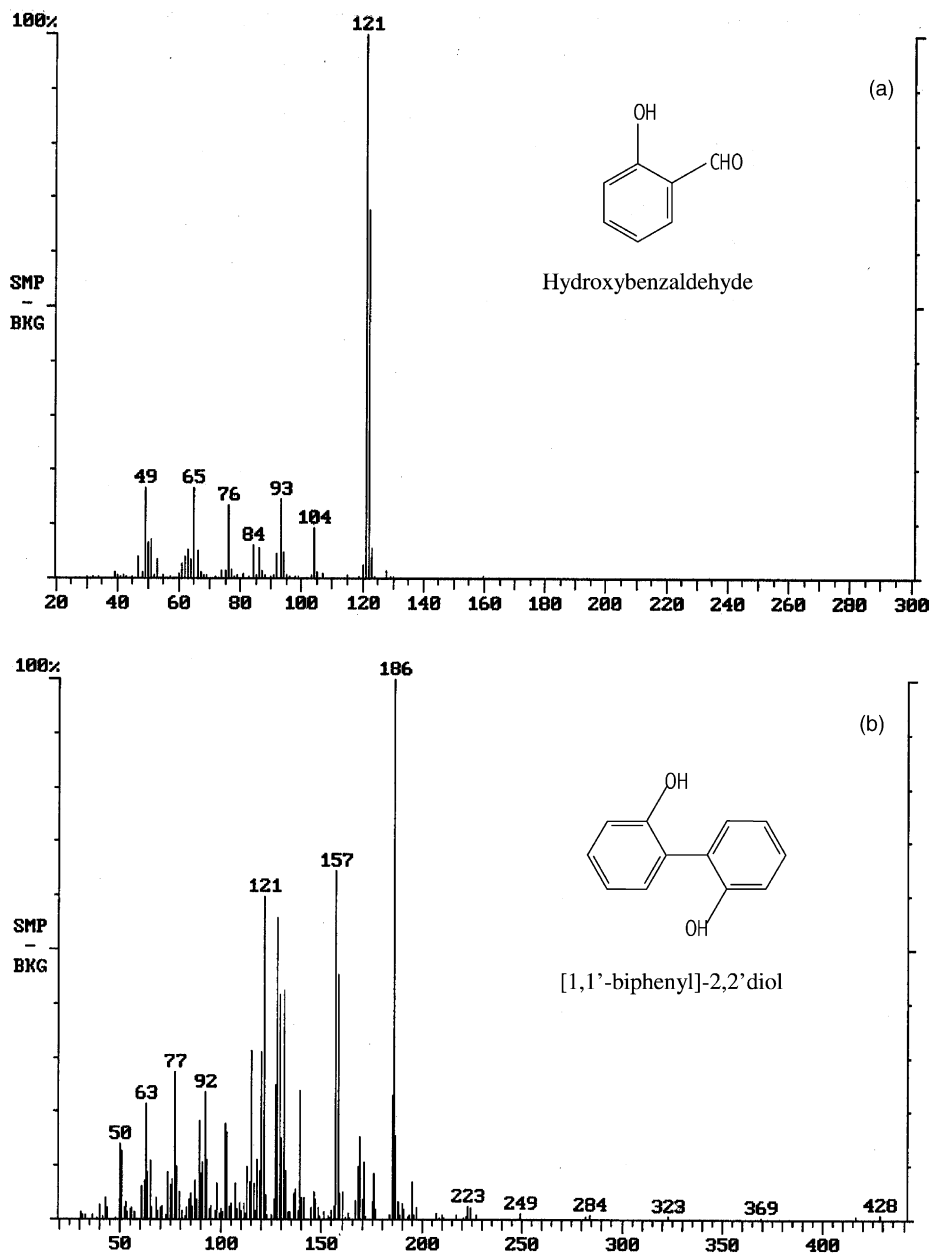


Fig. 5. Mass fragmentation spectrum obtained from (a) 2-hydroxy benzaldehyde and (b) [1,1'-biphenyl]-2,2'-diol.

0.01–0.05 min⁻¹ has been reported [19–22] for 2-CP photodegradation depending upon prevailing conditions such as type and dose of catalyst, power output and lamp intensity and pH. In this study, a 400 W medium pressure Hg lamp with a peak emission at 365 nm (5.0×10^{19} photons s⁻¹) was used. In addition, a 0.2 g TiO₂ l⁻¹ dose was used. The TiO₂ dose is lower than the 1–4 g TiO₂ l⁻¹ utilized in many other studies [19,20]. The high photon emission rate of the lamp and absence of light penetration problem that is usually encountered in reactors that use higher TiO₂ dose, could be viewed as responsible for higher rate constant found in this study.

The adsorption constant *K* is low. This result suggests that the binding force between TiO₂ surface and 2-CP is weak. Our studies also revealed that a change in pH in the range 3–11 did not exert any dramatic change in the rate of photodegradation of 2-CP. This result is in agreement with the findings of Oliveira et al. [20] who examined 2-CP degradation in the pH range 2.0–12.0. They reported no pronounced changes in the rate of degradation in the pH range of 3.5–9.0. It may be noted that this pH range is important for any practical applications, and invariance of reaction rates in this range is indeed desirable.

Concerning the photodegradation of 2-CP using 1.0 g TiO₂ l⁻¹ at pH 2.5 and 12.5, Doong et al. [21] have reported a seven-fold increase in rate constant at pH 12.5, *k* being 0.0364 min⁻¹. On the other hand, Ku et al. [19] found *k* to decrease by 5–6 times at higher pH (11.0). It appears that further investigations to understand the surface sorption and kinetics of oxidation of 2-CP vis-à-vis the changes in the surface characteristics at such high pH are needed.

4.2. Mechanism of formation of higher carbon intermediates

A possible mechanistic pathway illustrating the formation of higher carbon intermediates is given in Fig. 6. In the first step, 2-CP molecule undergoes homolytic cleavage of aryl–Cl bond giving rise to radical I and a chloride radical (Cl•). Since the aryl–Cl bond energy is 97 kcal mol⁻¹ that corresponds to 294 nm light, and because the medium pressure Hg lamp predominantly radiates at 365 nm with smaller amounts in the UV region at 265, 303 and 334 nm, the aryl–Cl bond may have polarized in the excited state and its cleavage may have occurred. Alternatively, the dechlorination of 2-CP may result through its interaction with trapped electrons on the semiconductor surface releasing radical I and chloride ions [31].

In a second step, radical I may dimerize to yield [1,1'-biphenyl]-2,2'-diol or combine with formyl radical produced in-situ to give 2-hydroxybenzaldehyde. The observation that formaldehyde is formed during the photocatalytic degradation of 2-CP supports this hypothesis. The formation of such higher carbon intermediates lends support for involvement of radicals, e.g. radical I. This result suggests that abstraction of ring bound chlorine and ensuing free radical reactions such as dimerization and substitution may also take place during photocatalytic degradation of 2-CP. Hydroxyl radicals are known to attack preferentially the aromatic moiety due to their electrophilic nature [32]. This condition leads to formation of hydroxylated products such as catechol, chlorohydroquinone and hydroxyhydroquinone. It appears that these hydroxylated products form and degrade rapidly initially as it could be inferred from evolution of CO₂ and formation of HCHO in substantial quantities during first hour. This reaction could have been partially favored by high intensity and high wattage

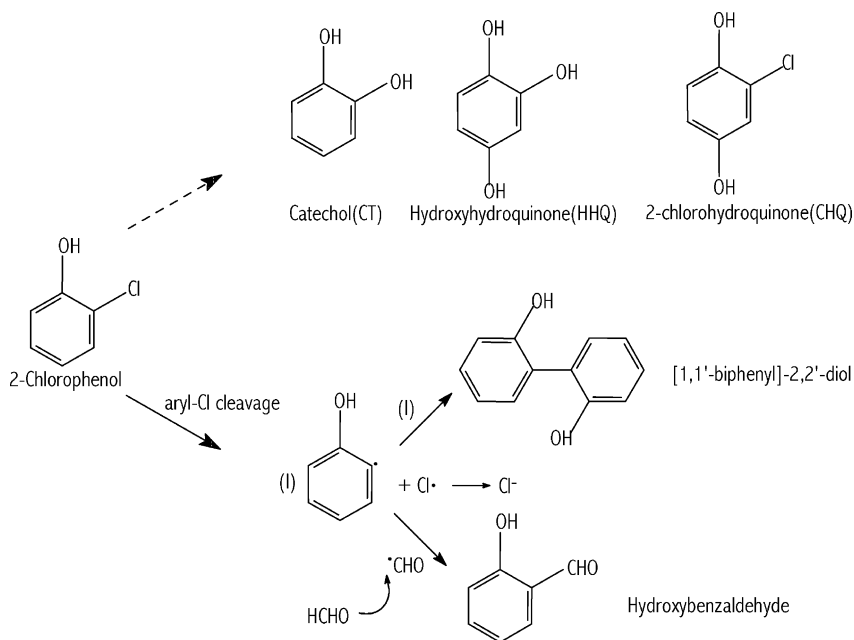


Fig. 6. Mechanism of formation of higher carbon intermediates.

medium pressure Hg lamp with a peak emission at 365 nm (5.0×10^{19} photons s^{-1}) used in this study.

4.3. Biodegradability of treated 2-CP solutions

The changes in BOD are presented as a function of percent COD removed (Fig. 7). The intermediates that prevailed in different percentage COD regimes are also shown in this figure. The initial 2-CP solution as well as samples from which approximately 65% of the COD is removed exerted no BOD implying toxicity to microorganisms. Some amount of 2-CP and prevalence of some chloro intermediates, e.g. chlorohydroquinone present in these samples may be responsible for this toxicity. The sample from which 85% COD had been removed gives the first positive test for BOD. In the percentage COD regime between 85 and 98% (45 min and 1–5 h samples) yielded a BOD in the range 8–25 $mg\ l^{-1}$. The BOD reaches a maximum when 97% of the COD is removed (3 h) and then decreases gradually in the fourth and fifth hour samples as the biodegradable intermediates are also further oxidized. This result suggests that adequately treated 2-CP solutions are biodegradable in contrast to untreated 2-CP solutions.

Our data indicated that the aryl–Cl bond undergoes cleavage very quickly under photocatalytic conditions with the release of inorganic Cl^{-} . This implies that toxicity of 2-CP is considerably reduced through photocatalytic treatment. This finding, along with the formation of hydroxylated intermediates that may be easily biodegraded, is the reason for enhancement of biodegradability.

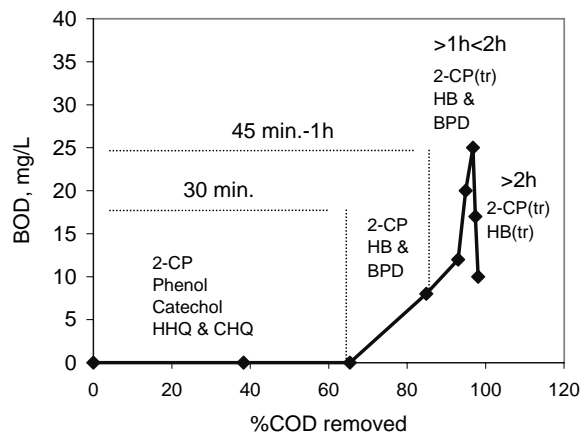


Fig. 7. Change in BOD as a function of percent COD removed. Initial concentration of 2-CP = 100 mg l^{-1} ; dose of $\text{TiO}_2 = 0.02 \text{ g}$ per 100 ml. The evolution of various intermediates at different times of irradiation is also indicated; (tr) implies trace quantity.

5. Conclusions

The TiO_2 -catalyzed oxidation of 2-CP proceeds according to pseudo-first-order kinetics conforming to the Langmuir–Hinshelwood model. A high degree of C–Cl bond cleavage and high oxidation yield (80%) can be achieved during the first hour of the photo-oxidative treatment. Apart from many hydroxy compounds, some higher carbon intermediates are also formed through free radical dimerization and substitution reactions during oxidation of 2-CP. Several of these intermediates appear to be more biodegradable than 2-CP, resulting in enhanced biodegradability of photocatalytically treated 2-CP solutions. The photocatalytic oxidation technique could be useful as a pretreatment technique for reducing toxicity of toxic/hazardous wastewaters by improving biodegradability.

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