



Photocatalytic Degradation of 2,4-dichlorophenol in Irradiated Aqueous ZnO Suspension

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Abstract

This paper focuses on the destruction of aqueous 2,4-dichlorophenol in ZnO suspension irradiated by low wattage UV light at 299 K. The operating variables studied include initial 2,4-dichlorophenol concentration, photocatalyst doses and pH. At 1.5 g l⁻¹ feed concentration of ZnO and 50 mg l⁻¹ initial 2,4-dichlorophenol level, a complete degradation was achieved in 180 min. The decomposition kinetics with respect to 2,4-dichlorophenol approximates pseudo zero-order with rate constant peaking at 0.38 mg l⁻¹ min⁻¹. High performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS) detected benzoquinone, 2-chlorohydroquinone, 4-chlorophenol, 3,5-dichlorocatechol, hydroquinone, 4-hydroxybenzaldehyde and phenol during the ZnO-assisted photodegradation of 2,4-dichlorophenol among which some pathway products are disclosed for the first time. The reaction mechanism accounting for the degradation pathway intermediates is proposed. Inorganic anion additives such as S₂O₈²⁻, SO₄²⁻, Cl⁻ and HPO₄²⁻ manifested inhibition against 2,4-dichlorophenol removal.

Keywords: 2,4-dichlorophenol, Intermediate, Photocatalysis, Anion, ZnO

1. Introduction

Chlorophenols are well-known environmental pollutants owing to their high potential of phytotoxicity and zootoxicity. In particular, 2,4-dichlorophenol (DCP) has been listed by US EPA as a priority pollutant the community has right to know (US EPA/OSHA, 2000; US EPA, 2006). As feedstock in the production of 2,4-dichlorophenoxyacetic acid, DCP may be released to the environment through uncontrolled use or improper waste management (CDC, 2000). In aquatic environment DCP would derive from biotic and abiotic degradation of higher chlorophenols and various phenoxyherbicides (Krijgsheld, 1986 and van der Gen; Brillas *et al.*, 2000). Since chlorophenols have greater sorption potential than desorption (Krijgsheld and van der Gen, 1986) they would persist in the aquatic environment for longer periods of time. Unfortunately, the widespread occurrence of DCP in open waters has been reported in several countries (Abdullah and Nainggolan, 1991; Gao *et al.*, 2008; Chiron *et al.*, 2007; Wegman and van Den Broek, 1983). Waters polluted by such resistant contaminants must be addressed by reliable treatment technologies.

Heterogeneous photocatalytic oxidation has received overwhelming interest as potential efficient method to degrade recalcitrant environmental contaminants (Saien and Soleymani, 2009; Pelizzetti *et al.*, 1990; Tariq *et al.*, 2007). A wide range of chloroaromatics have been eliminated by this process utilising mainly TiO₂ and ZnO as semiconductor photocatalyst (Djebbar and Sehili, 1998; Konstantinou *et al.*, 2001; Bahnmann *et al.*, 2007; Gaya *et al.*, 2009; Meng *et al.*, 2002). We are prompted to report our investigation of the photocatalytic degradation of DCP over ZnO photocatalyst for the following reasons. First, our results have shown that the photodegradation of DCP on ZnO suspension is more efficient than the operation on other photocatalyst particles. Previously, the removal of DCP (49 mg l⁻¹) by UV-irradiated TiO₂ particles (1.4 g l⁻¹) consumed 240 to 300 min ((Ku and Hsieh, 1992). Bayarri *et al.* (2005) reported only 90 % degradation of DCP (125 mg l⁻¹) over TiO₂ suspension (0.5 g l⁻¹) irradiated by 125 W UV lamp. Similarly, at least 480 min was required for the total removal of DCP (82 mg l⁻¹) over CdS (5 g l⁻¹) (Tang and Huang,

1995). Secondly, despite the coexistence of inorganic anions such as Cl^- and SO_4^{2-} in waters, their effect on photocatalytic degradation of DCP has not been investigated. Finally, the intermediates of photocatalytic DCP degradation have not been entirely elucidated. Previous work by Sehili *et al.* (1991) obtained some intermediates of the photo-oxidation of DCP on ZnO and explained the role of oxidising species in the process. An attempt to identify more degradation intermediates of DCP by GC-MS did not succeed (Jardim *et al.*, 1997). Herein, we report our investigation of the effect of operating variable such as catalyst dose, initial concentration and pH on the ZnO-assisted photocatalytic degradation of DCP using low wattage UV supply. The study also re-investigates the reaction pathway and discloses new stable intermediates.

2. Material and Method

2.1 Chemicals

2,4-dichlorophenol (98 % purity) was obtained from Merck-Schuchard and its stock solutions of 200 mg l^{-1} were prepared in deionised distilled water taken from Sartorius Arium 611 (background conductivity $5.5 \times 10^{-6} \text{ S m}^{-1}$) by stirring overnight. All solvents used in analyses were HPLC grade. Other chemicals used were at least 99 % pure and therefore no further purification was done. These chemicals include 4-hydroxybenzaldehyde from ACROS Organics, hydroquinone from Ajax Chemicals, phenol from Merck, benzoquinone from ACROS Organics, resorcinol from Aldrich, catechol from BDH, Na_2HPO_4 from Fischer Chemicals, $\text{Na}_2\text{S}_2\text{O}_8$ from BDH, NaCl from Prolabo R.P.

2.2 Photocatalyst characterisation

Commercial ZnO supplied by Merck, was used for all adsorption and photocatalytic experiments. The band gap of ZnO powder was characterised by diffuse reflectance spectrometry using Lambda 35 UV/Vis/NIR (Perkin Elmer). Particle size was determined by photon correlation spectroscopy using Sympatec Nanophox facility. Surface area was determined by static Brunauer-Emmet-Teller method using Thermo Finnigan Sorptomatic 1990 Series analyser.

2.3 Apparatus and Procedure

All photoexperiments were carried out in a cylindrical immersion well photoreactor. Illumination was provided by 6W UV lamp supplied by New York Spectronics. The light source has maximum intensity at 365 nm. Mass gradient was eliminated by stirring solution at speed of 195 rpm using magnetic bar. Air was bubbled from the lower part of the apparatus by a specular draft tube hung vertically from the top of the reactor. Other features of the reactor have been described previously (Gaya *et al.*, 2009). The apparatus was maintained at controlled temperature of 299 K by circulating water in and out of the outer jacket.

Usually, 1000 ml DCP synthetic solution containing desired analytical amounts of 2,4-DCP and ZnO photocatalyst was added to the photoreactor. Immediately air was bubbled at fixed flow rate of 2 l min^{-1} and the mixture was equilibrated for 5 min in the dark. Subsequently, the solution was irradiated for 300 min. Samples were taken at 0 min, 30 min, 60 min, 90 min, 120 min, 180 min, 240 min and 300 min. Each sample was passed through $0.45 \mu\text{m}$ cellulose nitrate membrane filter. The reaction progress was followed by spectrophotometrically measuring the concentration of DCP in the catalyst free test samples in quartz cuvettes having 1 cm light path. The correlation coefficient of the DCP calibration curve was 0.9999. Shimadzu model UV-1650 PC UV-Vis spectrophotometer was employed for these measurements and the percentage of the initial DCP degraded per unit irradiation time was calculated by Eq.(1).

$$\text{DCP (\% min}^{-1}\text{)} = (C_0 - C_t) \times 100 / C_0 \times t \quad (1)$$

Where C_0 (mg l^{-1}) is the initial concentration of DCP and C_t (mg l^{-1}) is the concentration of DCP at irradiation time t (min).

To evaluate the removal of chlorophenols by the backgrounds of the photocatalytic route, direct photolysis and ZnO dark adsorption were investigated at optimum substrate concentration. To test for photolytic effect, homogeneous DCP solution was irradiated for 300 min. A stream of air was continuously bubbled through the solution. In the dark adsorption test, the absorbance of DCP solution containing ZnO suspension was monitored in the absence of light for 300 min. The content of the reactor was constantly aerated and stirred thoroughly in both experiments. For both processes samples were taken and analysed by UV-Vis spectrometry as specified above.

2.4 Analysis

The degradation of DCP was followed by analysing test samples using Waters HPLC, equipped with Waters 600 controller and Waters 2487 dual λ absorbance detector. Reverse phase Ascentis- C_{18} column ($25 \text{ cm} \times 4.6 \text{ mm} \times 5 \mu\text{m}$) was utilised for the HPLC. Mobile phase was ternary mixture of acetonitrile, acetic acid and water delivered in the ratio 69:1:30 (v/v). The mobile phase flow rate was fixed at 1 ml min^{-1} . Runtime was 20 min. The detection wavelength was 284 nm. In conjunction with the HPLC, Shimadzu's GCMS-QP5050A was used for structural elucidation of photoproducts. Photoproducts were extracted three times from 25 ml catalyst free test samples by liquid-liquid extraction method using diethyl ether. The extract was dried with anhydrous Na_2SO_4 and concentrated under nitrogen stream. Separation was carried out in a 30 m length BPX-5 capillary column (0.25 mm i.d and $0.25 \mu\text{m}$ film thickness).

The capillary column was maintained at 70 °C for 2 min followed by temperature increase at the rate of 10 °C min⁻¹ up to 310 °C. The injector and detector temperatures were 250°C and 320°C respectively. The carrier gas was helium, run at the rate of 1.2 ml min⁻¹. Analytical data on degradation species were interpreted by mass spectra library.

3. Results and Discussion

3.1 Material Characterisation

Band gap (E_g) was calculated from the minimum absorption wavelength (410 nm) of the ZnO powder using the simplified form of energy-wavelength relationship, E_g (eV) = 1240/ λ (Feng *et al.*, 2009). The band gap of the ZnO powder was 3.02 eV. The static BET surface area of ZnO was 3.3 m² g⁻¹. Fig. 1 shows the average observed particle size distribution for 3 replicate measurements. It would be observed that graphing cumulative distribution and distribution density on 2y-axes reveals a partial peak doubling in the particle size distribution possibly resulting from deaggregation. The particle sizes of ZnO were distributed in the range of 0.4 – 0.5 μ m with higher densities around 0.5 μ m.

DCP exhibits a single wavelength maximum at 284 nm. This detection wavelength was used for both UV-Vis spectrometry and for HPLC analysis. Fig. 2 shows the changes in the absorption spectrum of DCP with degradation time at optimum initial experimental conditions. The figure demonstrates the typical changes in absorption peak during the degradation of irradiated DCP with time. The annihilation of the molecular peak with illumination time illustrates the disappearance of DCP from the solution.

3.2 Effect of DCP concentration

Substrate level is one of the defining factors of the guarantee for effective transformation of a pollutant. The effect of concentration was studied at 10 to 100 mg l⁻¹ DCP levels in presence of 1 g ZnO photocatalyst. Initially, the photoremoval of DCP increased concomitantly with ZnO concentration due to more occupation of catalyst sites by the substrate and its subsequent photodecomposition. The photocatalytic removal of DCP under this experimental condition was highest at initial substrate concentration of 50 mg l⁻¹ (Fig. 3). As this concentration is exceeded, the photocatalytic removal of DCP decreases owing to excess unadsorbed DCP which reduced photonic efficiency. Hence, 50 mg l⁻¹ was considered to be the optimum substrate concentration for this study.

3.3 Effect of catalyst mass

The effect of catalyst mass was investigated in the range of 0.5 g to 2 g at the 50 mg l⁻¹ initial DCP concentration (Fig. 4). As seen from the figure, there is increase in DCP removal between the photocatalyst concentration of 0.5 g l⁻¹ and 1.5 g l⁻¹ which could be attributed to the increasing availability of photocatalyst sites. Above 1.5 g l⁻¹ ZnO concentration, the photocatalytic removal rate decreased due to light scattering by excess solid particles leading to poor light utilisation. The optimum catalyst concentration (1.5 g l⁻¹) obtained in this study corresponds nearly to that reported for TiO₂ mediated degradation of DCP (1.4 g l⁻¹) [19].

3.4 Photodecomposition kinetics

Investigating the throughput of a photoprocess is one of the major facets of photocatalytic study (Brahmia *et al.*, 2004). We observed consistence of the DCP decomposition with pseudo zero-order kinetic scheme which may be simply described by Eq.(2).

$$C_t = -kt + C_0 \quad (2)$$

Where the C_t and C_0 are as defined above and k is the pseudo zero-order rate constant expressed in mg l⁻¹ min⁻¹. For DCP degradation scheme k was 0.38 mg l⁻¹ min⁻¹ (Fig. 5). DCP was totally removed in 180 min which suggests the premise that ZnO is more photoactive for the removal of DCP compared to other semiconductor photocatalysts mentioned supra. Though reasonable, the fit quality in Fig. 5 was affected by the slow decomposition of DCP in the short irradiation time span specifically in the first 30 min of irradiation. Fig. 6 shows the traditional pattern of DCP decomposition with irradiation time. The slower rate in the short irradiation period may be attributed to the formation of reactive intermediates which assumes the rate limiting role. A supporting fact for the slow removal rate in the short irradiation time can be obtained from the work of Ku and Hsieh (1992) where no evolution of CO₂ was observed during first one hour of DCP degradation on TiO₂ particles.

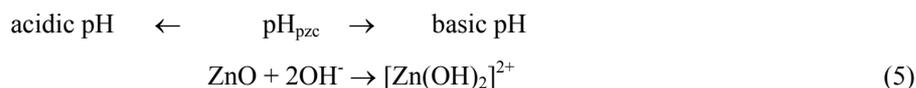
3.5 Control experiments

Although photocatalytic reactions occur in the adsorbed phase, the possibility of parallel removal of contaminant molecules partly by irradiation or adsorption may not be ruled out. Fig. 7 shows the observed effect of photolysis of 50 mg l⁻¹ DCP, and the adsorption of the same amount on 1.5 g ZnO in the dark. From the figure there seem to be modest removal by adsorption (ca. 10 %) and loss by photolysis (ca. 19 %) of DCP. The fluctuation in the amount of DCP in the figure over different intervals of time reflects the instability of photolysed DCP owing to volatilisation or due to incongruous adsorption of DCP. Previously, the adsorption of DCP (5-6 %) on TiO₂ has been reported by Fabbri *et al.*

(2006). Similarly, the photolytic removal of DCP has been reported earlier though it was negligible compared to the removal by TiO₂ photocatalysis (Ku and Hsieh, 1992). Nevertheless, during the photocatalytic process less effect of photolysis may be felt since most of the reactions of the hydroxyl radical in presence of semiconductor photocatalyst will occur at the adsorbed phase (Turchi and Ollis, 1990).

3.6 pH Effects

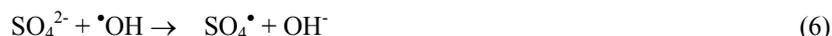
pH of solution is an essential variable in photocatalytic reaction since it governs the surface charge properties of the semiconductor photocatalyst (Haque and Muneer, 2007). The effect of pH was studied at pH 6, 7, 9 and 10. These pH values bracketed both the pK_a of DCP (7.9) and the point of zero charge (pzc) of ZnO (9) (Krijgsheld and van der Gen, 1986; Kosmulski, 2006). The degradation of DCP was hampered at pH 6. This may be due to the less degradability of molecular DCP on the surface of ZnO at this low pH. However, there is maximum DCP removal at pH 7 (Fig. 8). The DCP removal rate decreased upon increase in pH up to 10 which is probably due to the preclusion of adsorption of chlorophenoxide on the surface of ZnO by electrostatic repulsion. There are two likely reasons for the formation of these anions. First, there is shift in the dissociation equilibrium of DCP in favour of chlorophenoxide (Eq.(3)) as the pK_a of DCP is exceeded. Secondly, the deprotonation of ZnO surface above its pzc (Eq.(4)) will favour the formation of ZnO⁻. On the other hand, the decrease in reaction rate at exceedingly high pH may partly be attributed to the alkaline dissolution of ZnO shown in Eq.(5). However, this may be ruled out since the photodissolution of 1.5 g ZnO in 50 mg l⁻¹ DCP solution at pH 7 was only 0.033 % out of which dark dissolution accounted for 0.014 %.



3.7 Effect of anion additives

The effect of presence of inorganic anion additives on DCP photoremoval rate was studied at 0.4 mg l⁻¹ anion level and pH 7. Inorganic anions investigated include HPO₄²⁻, SO₄²⁻, Cl⁻ and S₂O₈²⁻ all used as Na salts. Fig. 9 shows a comparison of DCP removal in presence of added anions. The figure shows inhibition of DCP removal rate in the order SO₄²⁻ < Cl⁻ < HPO₄²⁻. Our observation is supported by the finding of several workers. Doong *et al.* (2001) has observed inhibition of the photodegradation of monochlorophenol by HPO₄²⁻ on titanium dioxide surface. Similarly, in photodefluorination of pentafluorobenzoic acid, the reaction rate was reduced by both HPO₄²⁻ and SO₄²⁻ and accordingly, the former demonstrated the highest inhibition (Ravichandran *et al.*, 2007). The mechanism of rate inhibition by HPO₄²⁻ has not been clear but the blockage of the active sites of the semiconductor particles has recently been suggested (Gaya *et al.*, 2009). The reduction in removal rate in presence of Cl⁻ and SO₄²⁻ has been attributed to the scavenging of hydroxyl radical by these anions as shown in Eq. (6) and (7) (Djebbar and Sehili, 1998). Even though SO₄^{•-} formed in the process is strongly oxidising (reduction potential E_o = 2.4) (Bao and Baker, 1996; Alipázquez *et al.*, 2005) it is less reactive than hydroxyl radical (E_o = 2.7) (Patnaik, 2004, Sawyer *et al.*, 1995).

On the other hand, S₂O₈²⁻ did not influence the DCP degradation rate even at much higher concentrations (2.0 mg l⁻¹ and 4.0 mg l⁻¹) despite the possibility of formation of 2 moles of SO₄^{•-} from 1 mole of S₂O₈²⁻. Probably the reason why removal rate remained uninfluenced in presence of S₂O₈²⁻ is the self-recombination SO₄^{•-} to regenerate S₂O₈²⁻ as shown by Eq. (8) (Criquet and Leitner, 2009).



reaction rate constant, $k_{\text{Cl}^-} = 4.3 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$



$$k = 1.6 \text{ to } 8.1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$$

3.8 Mineralisation, intermediates and mechanism

The beauty of photocatalytic oxidation on photocatalysts is that only mineral products are formed at the end of the process. In the photocatalytic removal of DCP CO_2 , H_2O and Cl^- are the final products (Ormad *et al.*, 2001). In this study, the mineralisation of DCP has been confirmed by HPLC. The application of HPLC to study mineralisation has been demonstrated previously (Neppolian *et al.*, 2002). Herein, it offered the advantage of allowing the progression of DCP and its intermediates of degradation to be monitored by following their retention peaks. Selected HPLC chromatograms depicting typical retention peaks of pathway products detected after 60, 90 and 180 min of irradiation are shown in Fig. 10. The resolution of HPLC peaks observed in this report is similar to that recorded by Sehili *et al.* (1991). All retention peaks were below detection limit at 180 min which is an indication of mineralisation. Fig. 11 demonstrates the depletion of DCP with time measured by both HPLC and UV-Vis spectrophotometry. The total removal of DCP within 180 min was confirmed by both techniques.

The degradation of DCP progressed through the formation of several partial products as shown in Table 1. Chromatographic peaks eluted at 8.425, 11.058 and 11.708 during GC-MS analysis were identified as DCP, 2-chlorohydroquinone and 3,5-dichlorocatechol by mass spectra library. HPLC peaks appeared at 3.238, 3.899, 1.887, 2.773, 3.393 and 4.669 which were identified as benzoquinone, 4-chlorophenol, hydroquinone, 4-hydroxybenzaldehyde, phenol and DCP using authentic standards. The various retention times (t_R) of these standard peaks (Table 1). Chlorohydroquinone and 3,5-dichlorocatechol were reported earlier by Sehili *et al.* (1991). Phenol was reported in TiO_2 photodegradation (Matafonova *et al.*, 2008). Other intermediates were observed for the first time in ZnO-assisted transformation of DCP. 4-hydroxybenzaldehyde has not been reported elsewhere even in DCP degradation by other advanced oxidation processes. Incidentally, Rao *et al.* (Rao *et al.*, 2003) detected 2-hydroxybenzaldehyde in the photolysis of 2-chlorophenol which supports our identification of its structural isomer 4-hydroxybenzaldehyde from DCP.

The ability of semiconductor photocatalysts to remove pollutants is based on the active oxidising species they form as they are irradiated. Hole is produced as a result of photoinduced charge separation which may then cause the formation of hydroxyl radical by direct hole transfer reaction with $\cdot\text{OH}$. Hydrogen peroxide may be generated via chain reactions involving conduction band electron. A summary of the steps in DCP degradation on photoactivated ZnO is illustrated on Fig. 12. Even though hole and hydrogen peroxide may aid the degradation of chlorophenols in ZnO dispersion, experimental evidences have proved the main oxidant to be hydroxyl radical (Minero *et al.*, 2000; Hoffmann *et al.*, 1994). Tentatively therefore, we propose the mechanistic pathways in Fig. 13 to account for the photoproducts of DCP degradation encountered in this study based on hydroxyl radical intervention. The cleavage of substituent $-\text{Cl}$ group has been shown to be the first process in the photocatalytic destruction of chlorophenols (Durand and Brown, 1995; Boule *et al.*, 1982). Thus, 4-chlorophenol can be produced by the cleavage of ortho-Cl of DCP ring shown by Eq.(9). It has been demonstrated previously that the hydroxylation of 4-chlorophenol may result in the formation of hydroquinone through transient ring adduct (Eq.(10)) (Lipczynska-Kochany *et al.*, 1991). 4-chlorophenol homolysis at Cl-ring would form hydroxyphenyl radical (Eq.(11)) which could either yield 4-hydroxybenzaldehyde via radical formylation (Eq.(12)) or by reaction with radical hydrogen addition to form phenol (Eq.(13)). Ortho-hydroxylation of DCP can result in the formation of 3,5-dichlorocatechol (Eq.(14)) whereas hydroxylation-dechlorination at para-position would yield 2-chlorohydroquinone (Eq.(15)). Hydroquinone could also be formed by the hydroxylation of phenol (Eq.(16)). Further oxidation of hydroquinone yields benzoquinone (Eq.(17)). Some of the intermediates of the ZnO photocatalysis of DCP such as benzoquinone, 4-chlorophenol, hydroquinone and phenol are reported for the first time in the photodegradation of DCP vis-à-vis ZnO. Since the mechanism of destruction of these lower chlorophenols until mineralisation has been dealt with previously (Theurich *et al.*, 1996) limited details are provided here. It is believed that quinones such as benzoquinone and hydroxybenzoquinone are formed at the brink of ring opening which are finally transformed to CO_2 and H_2O .

4. Conclusion

The photocatalytic degradation of DCP in presence of ZnO was studied and primary process parameters such as catalyst concentration, DCP concentration and pH were recommended to be 1.5 g l^{-1} , 50 mg l^{-1} and pH 7 respectively for the process. Under these experimental conditions, mineralisation of DCP was achieved in 180 min and the global rate could satisfactorily fit to the integrated equation of the pseudo-zero order. Degradation intermediates such as include benzoquinone, 2-chlorohydroquinone, 4-chlorophenol, 3,5-dichlorocatechol, hydroquinone, 4-hydroxybenzaldehyde and phenol were detected during the course of DCP degradation.

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Table 1. List of degradation products resolved either by HPLC or GC-MS. Initial conditions: DCP = 50 mg l⁻¹; ZnO = 1.5 g l⁻¹; pH 7

Degradation Product	HPLC		GC-MS	
	<i>t_R</i> (min)		<i>t_R</i> (min)	[M ⁺] (m/z)
	Experiment	Standard		
benzoquinone	3.238	3.203	-	-
2-chlorohydroquinone	-	-	11.058	144
4-chlorophenol	3.899	4.191	-	-
hydroquinone	1.887	1.841	-	-
4-hydroxybenzaldehyde	2.773	2.754	-	-
Phenol	3.393	3.477	-	-
3,5-dichlorocatechol	-	-	11.708	178
	-	-		
2,4-dichlorophenol	4.669	4.191	8.425	162

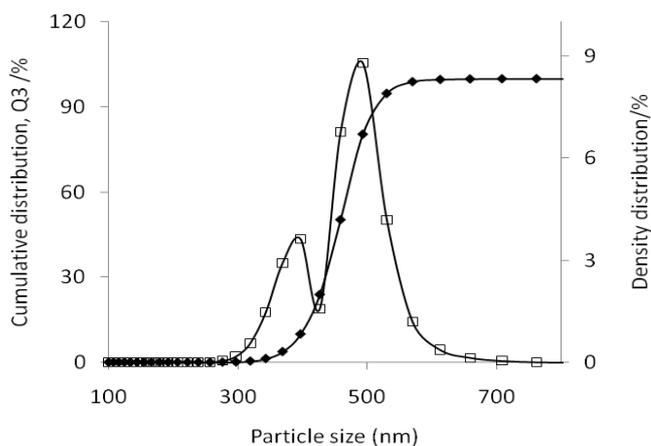


Figure 1. Particle size distribution graph for the commercial ZnO (Merck) used in the study.

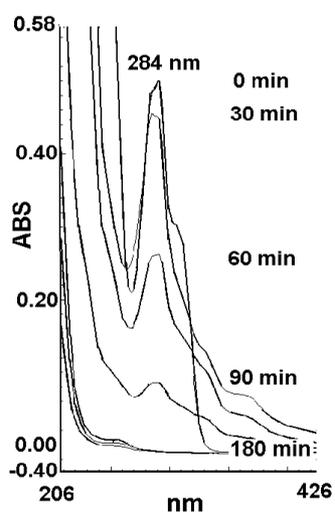


Figure 2. Spectral changes on photocatalytic DCP degradation

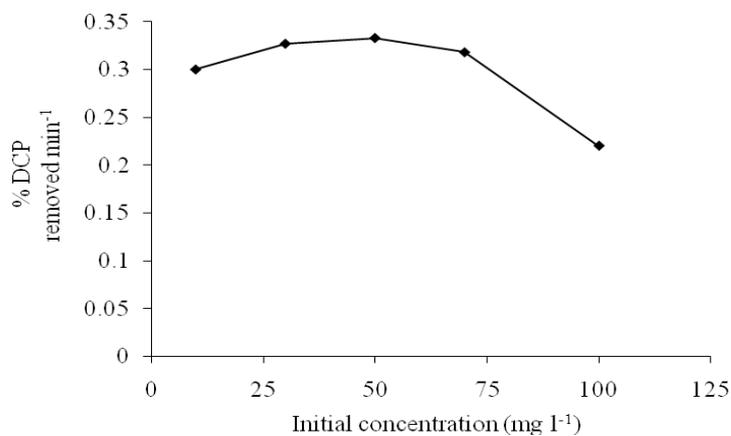


Figure 3. Observed effect of concentration on DCP photoremoval rate at photocatalyst concentration = 1 g l⁻¹

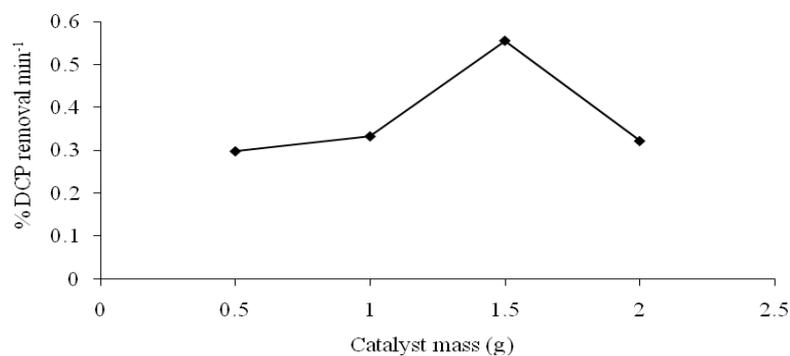


Figure 4. Influence of catalyst mass on DCP removal at 50 mg l⁻¹ DCP levels

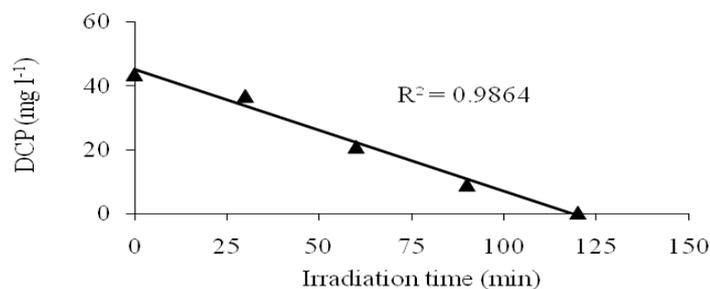


Figure 5. The pseudo zero order plot of DCP in the medium irradiation time. Initial pH = 7; Initial DCP concentration = 50 mg l⁻¹; catalyst concentration = 1.5 g l⁻¹

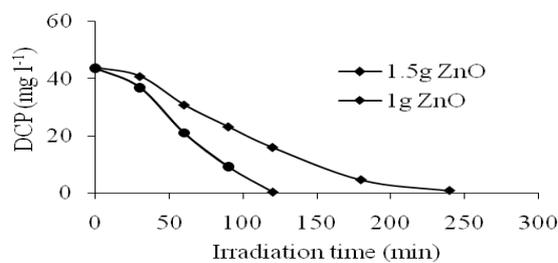


Figure 6. DCP decomposition course at 50 mg l⁻¹ levels in presence of 1 and 1.5 g l⁻¹ ZnO doses

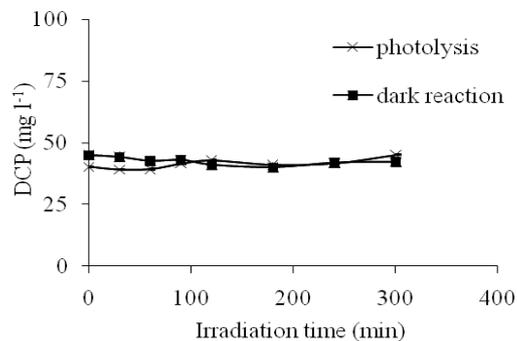


Figure 7. Observed effect of adsorption and photolysis on DCP removal. Initial pH = 7; Initial DCP concentration = 50 mg l⁻¹; catalyst concentration = 1.5 g l⁻¹

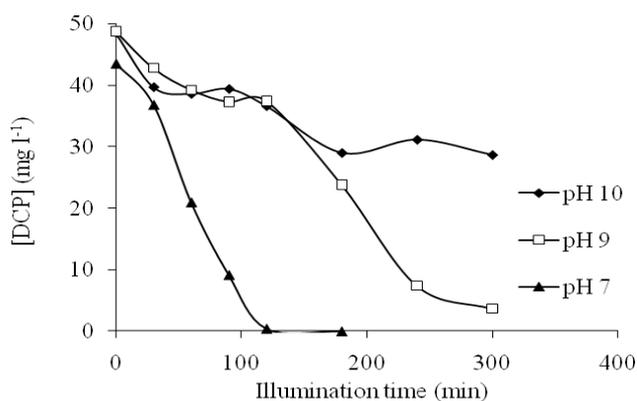


Figure 8. Influence of pH on DCP removal. Initial DCP concentration = 50 mg l⁻¹; catalyst concentration = 1.5 g l⁻¹

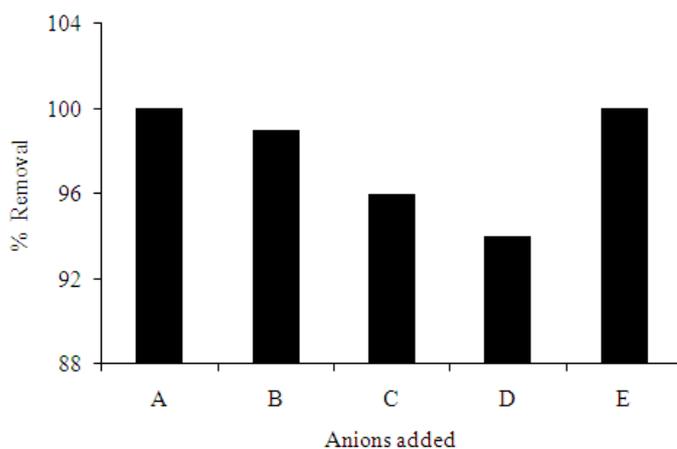


Figure 9. The influence of inorganic anions on photocatalytic removal. Initial conditions: DCP concentration = 50 mg l⁻¹; catalyst concentration = 1.5 g l⁻¹, ca. pH = 7. A = S₂O₈²⁻, B = SO₄²⁻, C = Cl⁻, D = HPO₄²⁻, E = No anion added

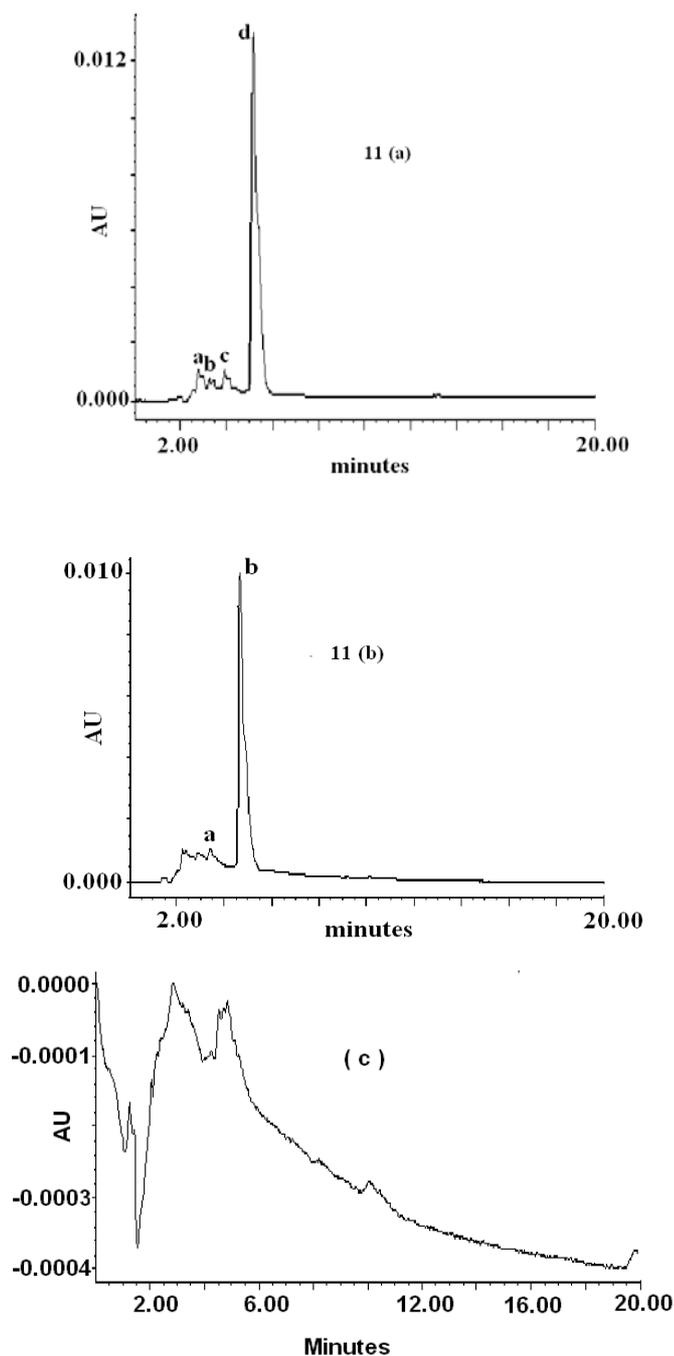


Figure 10. HPLC chromatograms showing peaks of pathway intermediates I) 60 min of irradiation: a) 4-hydroxybenzaldehyde b) benzoquinone c) 4-chlorophenol d) DCP; II) 90 min of irradiation a) phenol b) DCP; III) No compound detected at 180 min. Initial conditions: DCP = 50 mg l⁻¹; ZnO = 1.5 g l⁻¹; pH 7

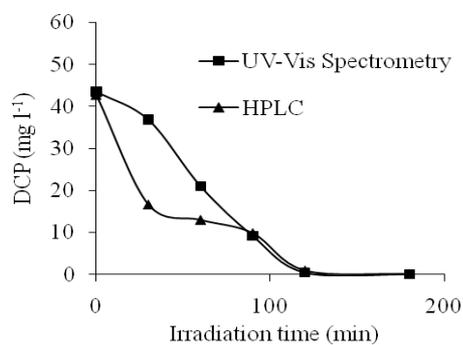


Figure 11. Mineralisation course plot of DCP recorded on UV-Vis spectrophotometer and on HPLC. Initial conditions: DCP = 50 mg l⁻¹; ZnO = 1.5 g l⁻¹; pH 7

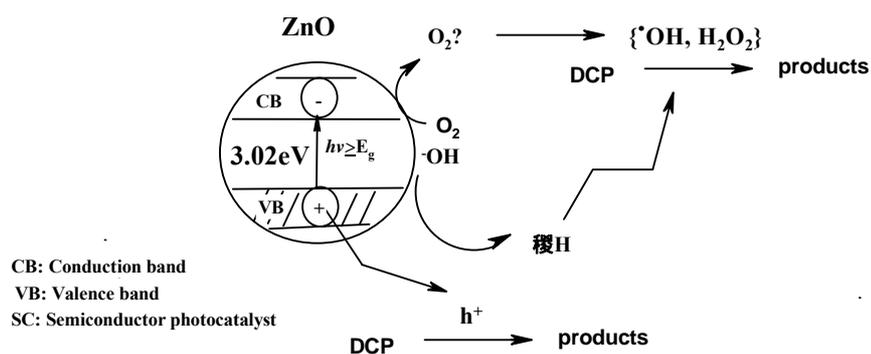


Figure 12. Schematic of the processes involved in DCP decomposition over ZnO

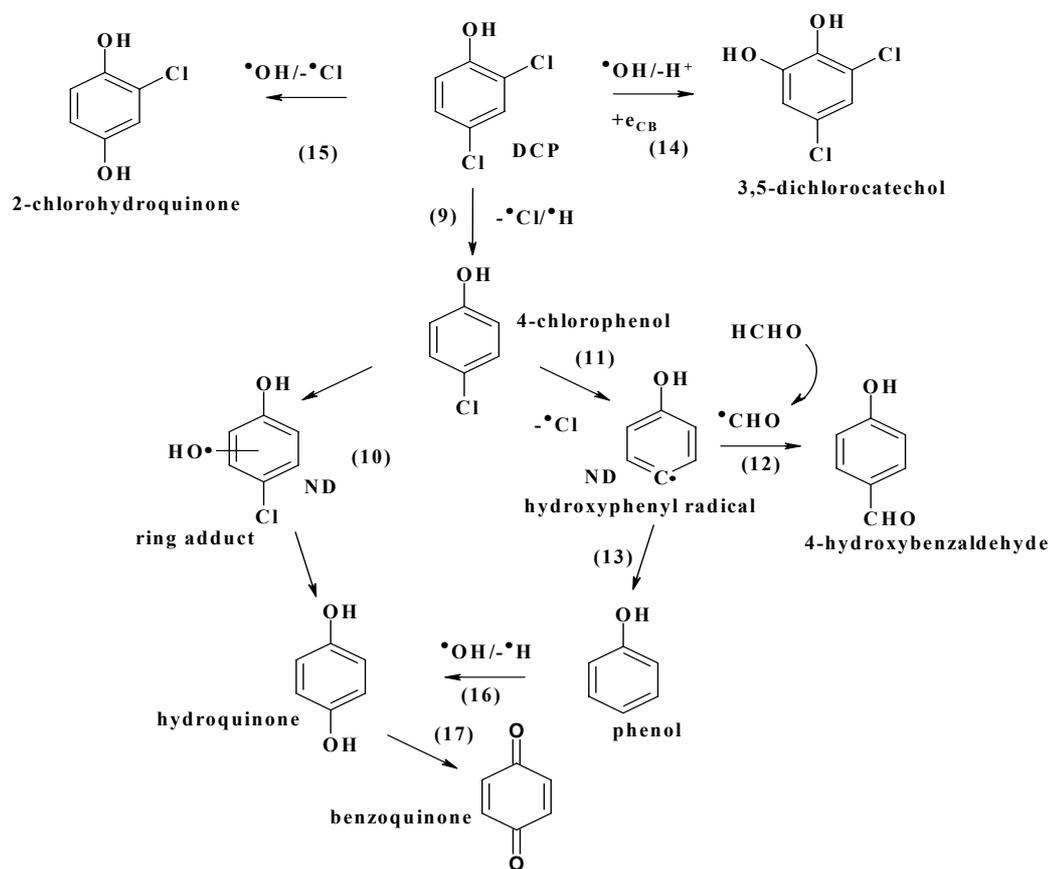


Figure 13. Reaction scheme proposed to account for the formation of degradation intermediates of DCP on illuminated aqueous ZnO