

# Photodegradation of *m*-cresol by Zinc Oxide under Visible-light Irradiation

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## Abstract

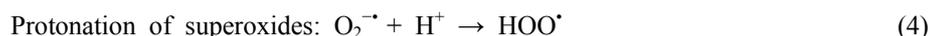
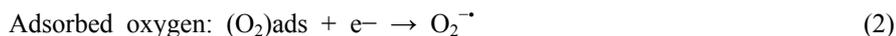
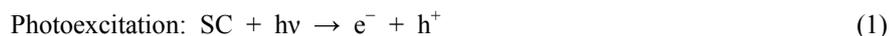
The photodegradation of *m*-cresol was carried out under visible light (46% sunlight) by ZnO as photocatalyst. To measure the efficiency of photodegradation, the different variables studied included amount of photocatalyst, concentration of *m*-cresol and pH. The maximum amount of photocatalyst and concentration of *m*-cresol was 1.5 g/L and 25 ppm respectively. The photodegradation was favorable in the pH 6-9 range. The detected intermediates were 2-methyl-1,4-benzodiol, 2-methyl-*para*-benzoquinone, 3,5-dihydroxytoluene and 2,5-dihydroxy-benzaldehyde. TOC studies show that 78% of total organic carbon is removed from solution during irradiation time. This study indicates the great potential of ZnO to remove aqueous *m*-cresol under visible-light irradiation which is part of sunlight.

**Keywords:** Photodegradation, *m*-cresol, Photoexcited, ZnO, Photocatalyst, Photochemistry

## 1. Introduction

Environmental pollution and particularly water pollution on a global scale have drawn scientists' attention to the vital need for environmentally clean and friendly chemical processes. *m*-cresol is widely used in manufacturing products such as cresol-based Resin, herbicides, pharmaceuticals and surfactants (Shivaraman, *et al.*, 2000).

Waste water from these industries contains a high concentration of *m*-cresol. *M*-cresol has been listed as the priority pollutant in the USA-EPA list (Callahan, *et al.*, 1979). Water solubility of *m*-cresol is above 24 g/l at 25 °C (Cooper, 1912). Therefore, *m*-cresol can be a significant threat to surface water, groundwater sources, or generally the environment (Kavitha, *et al.*, 2005; Pardeshi, *et al.*, 2008). The effective removal of *m*-cresol is currently both an environmental and economic problem (Flox, *et al.*, 2007; Guyer, 1998). Photocatalysis is the field of current interest given its application in disinfecting drinking water and wastewater (Hoffmann, *et al.*, 1995; Marci, *et al.*, 2003). Photocatalytic reaction is initiated when a photoexcited electron is promoted from the filled valence band of a semiconductor photocatalyst (Abou-Helal, *et al.* 2002) to the empty conduction band as the absorbed photon energy,  $h\nu$ , equals or exceeds the band gap of the photocatalyst. The hole pair ( $e^-h^+$ ) is generated at the surface of the photoexcited photocatalyst as shown below (Gaya, *et al.*, 2008)



The hydroxyl ( $\cdot\text{OH}$ ) radical is a powerful oxidant for degrading non selective organic compounds (Glaze, 1987; Peiró, *et al.*, 2001). The most frequently used photocatalysts are  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{CdS}$ , and  $\text{SnO}_2$  (Brezova, *et al.*, 1994; Maldotti, *et al.*, 2002). Among these  $\text{ZnO}$  removed several environmental contaminants under UV irradiation (Akyol, *et al.*, 2004; Daneshvar, *et al.*, 2007; Kansal, *et al.*, 2008; Sharma, *et al.*, 1995). The great advantage of  $\text{ZnO}$  is its ability to absorb larger fractions of the solar spectrum than the other photocatalysts, removing many organic contaminants in aqueous solution under visible irradiation (Dindar, *et al.*, 2001; Pardeshi, *et al.*, 2008; Sakthivel, *et al.*, 2003). This work looks at the photodegradation of *m*-cresol by  $\text{ZnO}$  (photocatalyst) under UV irradiation. The effects of variables including *m*-cresol concentration, photocatalyst loading and pH on photodegradation were studied. In addition, the mineralisation and photoproducts were investigated by total organic carbon (TOC) measurement (Heiland, *et al.*, 1959) and Waters-Acquity ultra high pressure liquid chromatography (UPLC).

## 2. Materials and methods

$\text{ZnO}$  (99%, MERCK), *m*-cresol (99%, Merck),  $\text{NaOH}$  (99%, Merck),  $\text{H}_2\text{SO}_4$  (95%-97%) and other required chemicals were of reagent grade, obtained from Merck and were used without further purification. Various concentrations of *m*-cresol solution were prepared using deionized water. Photodegradation of *m*-cresol was performed in a batch photoreactors (Fig. 1). To increase solution fluidization and access oxygen for eq. (2), air was blown into the reaction solution using an air pump at a flow rate of  $10 \text{ m}^3/\text{h}$ . Blowing cooled air into the solution eliminated the lamp's heat effect and kept the temperature at around 25 °C. Magnetic stirring at 200 rpm was applied to mix the solution during the reaction. The photoreactor is located in an aluminum-sealed tube to enhance the radiation by reflection and used a Philips lamp (23 watt) as light source. Throughout the experiment, the appropriate concentration of *m*-cresol solution was contacted with an appropriate amount of photocatalyst in the photoreactors. At specific time intervals, samples were withdrawn from the bulk solution, and filtered through  $0.45 \mu\text{m}$  PTFE filters. The concentration of *m*-cresol and residue organic carbon was measured using UV - visible spectrophotometer (shimadzu, uv-1650 pc), TOC-VCSN analyzer, respectively. The used UPLC was fitted with an Acquity BEH phenyl  $\text{C}_{18}$  column ( $10 \text{ cm} \times 2.1 \text{ mm} \times 1.7 \mu\text{m}$ ) and the detector wavelength was 277 nm. The gradient elution method was applied over a 3-minute run time. The mobile phase was acetonitrile (35%)-water (65%), while a photodiode array (PDA) spectrometer operated at fixed detection wavelength for each experiment was used as a detector. In additional, The intermediates were identified by GC-MS using a Hewlett-Packard 5890 Series II gas chromatograph fitted with an Elite-5MS  $0.25 \text{ mm}$  ( $30 \text{ m} \times 0.25 \text{ mm}$  (i.d.), column, and a Hewlett-Packard 5989 A mass spectrophotometer operating in EI mode at 70 eV. (The temperature ramp for this column was 40 °C for 1 min,  $10 \text{ }^\circ\text{C min}^{-1}$  up to 240 °C and hold time 1 min). Photoproducts were extracted three times from 20 mL catalyst free test samples by liquid-liquid extraction method using dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). The extract was dried with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under nitrogen stream. The percentage of photodegradation was calculated as follows:

$$\text{Photodegradation\%} = 100[(C_0 - C_t)/C_0] \quad (9)$$

Where  $C_0$  = initial concentration of *m*-cresol,  $C_t$  = concentration of *m*-cresol after photoirradiation. All photocatalytic degradation experiments were carried out in duplicate. Photodegradation of *m*-cresol was investigated in the absence of photocatalyst and at normal pH (7.63). Results showed only 5% of *m*-cresol was photolysed in the absence of photocatalyst in present visible-light irradiation. Therefore, *m*-cresol is relatively stable under visible light irradiation. The concentration of *m*-cresol was determined in the presence of photocatalyst in the dark. The removed *m*-cresol was 5%. The decreasing in *m*-cresol suggests it is adsorbed on the photocatalyst surface (Fox, *et al.*, 1993).

### 3. Results and discussion

#### 3.1 Effect of photocatalyst loading

A series of experiments were carried out by varying the amount of ZnO (0.5 to 3.0 g/L) to establish the effect of photocatalyst loading and to avoid unnecessary excess photocatalyst. The percent of photodegraded *m*-cresol (%) vs. irradiation time was plotted in Fig. 2. The maximum % was carried out in 1.5 g/L of photocatalyst. This may be due to the fact that increasing the amount of photocatalyst increases the number of effective sites and consequently leads to enhanced production of  $\cdot\text{OH}$  radicals. Moreover, the number of *m*-cresol molecules adsorbed was increased owing to an increase in the number of photocatalyst particles, which causes increasing photodegradation (Fox, *et al.*, 1993). When the amount of photocatalyst was enhanced beyond optimum, however, photodegradation was not increased. The decreased efficiency beyond the optimum photocatalyst loading may be attributed to the screening effect of excess photocatalyst particles in the solution (Pardeshi, *et al.*, 2008). Furthermore, agglomeration and sedimentation of photocatalyst particles is also possible (Konstantinou, *et al.*, 2004). In such a condition, a part of the photocatalyst surface probably becomes unavailable for photon absorption and *m*-cresol adsorption, thus bringing little stimulation to the photocatalytic reaction.

#### 3.2 Effect of *m*-cresol concentration

The photocatalytic degradation of various *m*-cresol concentrations, 25-100 ppm, was studied (Fig. 3). With an increase in concentration of *m*-cresol, photodegradation% was decreased. As observed the concentration of 25 ppm completely and the sample of 50 ppm more than 58% were degraded however, with an increase in concentration of *m*-cresol, photodegradation% was decreased. At a high *m*-cresol concentration, the presumption is that active sites are covered by *m*-cresol and its intermediates that can cause reduced generation of  $e^-h^+$ , which reduces photodegradation efficiency (Konstantinou, *et al.*, 2004). The other possibility is that as the initial *m*-cresol concentration increases but the mass of photocatalyst, the intensity of light and illumination time are constant, then the  $\cdot\text{OH}$  and  $\text{O}_2^{2-}$  species formed on the surface of photocatalyst are constant, so that the relative ratio of the  $\cdot\text{OH}$  and  $\text{O}_2^{2-}$  for attacking *m*-cresol decreases and the % photodegradation decreases (Lathasree, *et al.*, 2004). Another factor which may be responsible for the reduction in photocatalytic degradation rate is the competition between adsorbed *m*-cresol and  $\text{H}_2\text{O}$  molecules for photodegraded  $h^+$  (Gaya, *et al.*, 2008).

#### 3.3 Photodecomposition kinetics

The rate of the photodegradation vs *m*-cresol concentration exhibits a quadratic behaviour which has optimum values at 50 ppm (Fig.4). The rate is a nonlinear function of *m*-cresol concentration ( $C_{m\text{-cresol}}$ ). The reason for this behavior may be related to the probability interaction between *m*-cresol and ZnO surface. At very low cresols concentration, the probability of interaction between *m*-cresol molecules and surface of ZnO decrease. Hence, photodegradation rate decreases. The probability of interaction between substrates molecules and oxidizing species is increased by increasing *m*-cresol concentration, leading to an enhancement in the degradation rate (Al-Ekabi, *et al.*, 1986; Hatipoglu, *et al.*, 2004; Konstantinou, *et al.*, 2004). Therefore according to Langmuir-Hinshelwood modeling (Melián, *et al.*, 2007) the suggested model is:

$$(-r) = \frac{k_{\text{cresol}} C_{\text{cresol}}}{[1 + k_{\text{cresol}} C_{\text{cresol}}]^2} \quad (10)$$

Where, the estimated value of  $k_{\text{cresol}}$  ( $\text{mgL}^{-1}\text{min}^{-1}\text{ppm}^{-1}$ ) and  $K_{\text{cresol}}$  ( $\text{ppm}^{-1}$ ) were 0.0139 and 0.33 with R-squared value 0.98 respectively. Similar results were reported for photodegradation kinetics of aqueous sodium oxalate, sodium dodecyl sulphate and 4-nitrophenol solution using  $\text{TiO}_2$  photocatalyst (Bangun, *et al.*, 1998; Lea, *et al.*, 1998, 2001, Hudaya, *et al.*, 2009)

### 3.4 Effect of pH

pH of solution is an essential variable in photocatalytic reaction since it governs the surface charge properties of the semiconductor photocatalyst (Haque, *et al.*, 2007). The effect of pH on the photodegradation% of *m*-cresol was studied (Fig. 5). The optimum condition was used as in the previous experiment. As observed the amount of *m*-cresol photodegraded gradually increased with increasing pH from pH 6 to 9. Most organic compounds are removed on or near the surface of photocatalyst; therefore the activity of photocatalyst seriously depends on adsorption of amount of pollutant over photocatalysis (Abou-Helal, *et al.*, 2002; Anandan, *et al.*, 2007). Increasing photodegradation% may be due to the increase in adsorption of *m*-cresol on the photocatalyst surface. Increasing adsorption may be due to a decline of the electrostatic repulsive forces and increased interaction between photocatalyst surface ( $\text{pH}_{\text{zpc}} = 9$ ) (Kosmulski, 2006) and *m*-cresol because with increasing pH the number of positive species (*m*-cresol- $\text{H}^+$ ) decreases. It has also been reported that in alkaline solution (pH 8-9),  $\cdot\text{OH}$  is easier to generate by oxidizing more  $\text{OH}^-$  available on the photocatalyst surface (Konstantinou, *et al.*, 2004). Thus, the photodegradation% is expected to increase with increasing pH due to an increase in available  $\cdot\text{OH}$  for the reaction. However, photodegradation% decreased at pH 10. This can be attributed to a reduction in the amount of *m*-cresol adsorbed on the catalyst surface at pH 10. It should also be noted that  $\cdot\text{OH}$  radicals are rapidly scavenged in high concentrations of hydroxyl ions and they have insufficient opportunity to react with the substrates (Davis, *et al.*, 1989). Hence, a drastic drop in the amount of *m*-cresol photodegraded by photocatalyst was observed at pH 10.

### 3.5 Mineralisation

To confirm previous proposed *m*-cresol degradation pathway in the presence of hydroxyl radicals (Flox, *et al.*, 2007; Wang, *et al.*, 1998a), determination of the some photoproducts of *m*-cresol photodegradation was carried out by UPLC and GC-MS that show many peaks. It may be due to the detection of other intermediates such as carboxylic acids (Flox, *et al.*, 2007). Fig. 6 demonstrates the depletion of *m*-cresol with time measured by both HPLC (Fig. 7) and UV-Vis spectrophotometry. The total removal of *m*-cresol during irradiation time was confirmed by both techniques.

The degradation of *m*-cresol progressed through the formation of several intermediate as shown in Table 1. Chromatographic peaks eluted at 7.97, 7.57, 11.75 and 11.12 min during GC-MS analysis were identified as *m*-cresol, 2,5-dihydroxy-benzaldehyde, 2-methyl-*para*-benzoquinone and 2-methyl-1,4-benzodiol by mass spectra library (Fig. 8). UPLC peaks appeared at Retention time 4.041, 2.23 and 2.37 min which were identified *m*-cresol, 2,5-dihydroxy-benzaldehyde, and 3,5-hydroxytoluene using authentic standards (Table 1). All the intermediates were reported earlier by GC-MS (K.-H. Wang, *et al.*, 1998b)

The ability of semiconductor photocatalysts to remove pollutants is based on the active oxidizing species ( $\text{HO}\cdot$ ,  $\text{O}_2\cdot^-$ ,  $\text{H}_2\text{O}_2$  and  $\text{h}^+$ ) they form as they are irradiated (Eq.1-8). 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  $\text{OH}^-$  and  $\text{H}_2\text{O}$ . Hydrogen peroxide may be generated via chain reactions involving conduction band electron. Even though hole and hydrogen peroxide may aid the degradation of *m*-cresol on ZnO dispersion, experimental evidences have proved the main oxidant to be hydroxyl radical (Gaya, *et al.*, 2010; Minero, *et al.*, 2000). Therefore, we propose the mechanistic pathways in Fig. 9 to account for the photoproducts of *m*-cresol degradation encountered in this study based on hydroxyl radical intervention. Thus, 2-methyl-1,4-benzodiol, 2-methyl-*para*-benzoquinone, 3,5-dihydroxytoluene and 2,5-dihydroxy-benzaldehyde can be produced by Eq.(11, 12, 14 and 16) respectively. The mechanism of *m*-cresol degradation in presence of hydroxyl radical until mineralisation has been reported (Flox, *et al.*, 2007). It is believed that quinones such as 2-methyl-*para*-benzoquinone are the brink of ring opening. Thereafter carboxylic acids are formed. The chain of carboxylic acids is decreased with increasing irradiation time as last carboxylic acid is oxalic acid ( $\text{HOOC-COOH}$ ) which is easily transformed to  $\text{CO}_2$   $\text{H}_2\text{O}$  with taking two hydroxyl radicals.

Mineralisation is the main aim of photodegradation of *m*-cresol, followed by measuring the TOC (Heiland, *et al.* 1959) and total inorganic carbon (TIC). As Fig. 10 shows, the amount of TOC was steadily decreased with increasing irradiation time, which indicates the decline of *m*-cresol and its intermediates when irradiation time is increased. On the other hand, the TIC curve shows that the amount of total inorganic carbon was generated in the first hour of reaction and was constant thereafter. This is most likely due to some organic carbon converting to inorganic carbon, for example, carbonate ions and after a few minutes TIC remained constant. According of the results, it can be concluded that 78% organic carbon is removed from *m*-cresol solution as  $\text{CO}_2$ . The residual TOC value (22%) indicates the presence of other photo products such as carboxylic acids at the end of the reaction.

### 3.6 Reusability

The reusability of photocatalyst was investigated in order to establish the stability of the ZnO. While studying reuse of photocatalyst, all parameters including irradiation time, pH, *m*-cresol concentration, amount of photocatalyst and irradiation time were kept constant. The photocatalysis mixture was filtered, and washed five times with deionized water and then dried at 96 °C in oven. Recovered photocatalyst was then reused five times as in the previous degradation process. Results show (Fig. 11) no significant reduction in photocatalytic performance in photodegrading *m*-cresol, thus this indicates the stability of ZnO as a photocatalyst.

### 4. Conclusion

The photodegradation of *m*-cresol was carried out by ZnO under visible light irradiation. The different variables studied included the amount of photocatalyst, concentration of *m*-cresol and pH impact on the efficiency of photodegradation. Under optimum conditions, the amount of photocatalyst and concentration of *m*-cresol were 1.5 g/L, 25ppm. Results show that *m*-cresol photodegradation was favorable in the range pH 6-9. The detected intermediates were 2-methyl-1,4-benzodiol, 2-methyl-*para*-benzoquinone, 3,5-dihydroxytoluene and 2,5-dihydroxy-benzaldehyde. TOC studies shows that 78% of total organic carbon was removed from the solution during irradiation time. Reusability shows no significant reduction in photocatalytic performance in the photodegradation of *m*-cresol. This study indicates the great potential of ZnO to remove aqueous *m*-cresol under visible-light irradiation which is part of sunlight.

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Table 1. List of degradation products resolved either by UPLC or GC-MS. Initial conditions: *m*-cresol = 25 mg/L; ZnO = 1.5 g/L; pH 7.63; during 6 h

Degradation Products	UPLC		GC-MS
	Retention time (min)		Retention time (min)
	Experiment	standard	
2,5-dihydroxy-benzaldehyde	2.23	2.235	7.57
3,5-dihydroxytoluene	2.37	2.342	×
2-methyl- <i>para</i> -benzoquinone	×	×	11.75
2-methyl-1,4-benzodiol	×	×	11.117
<i>m</i> -cresol	4.041	4.041	7.97

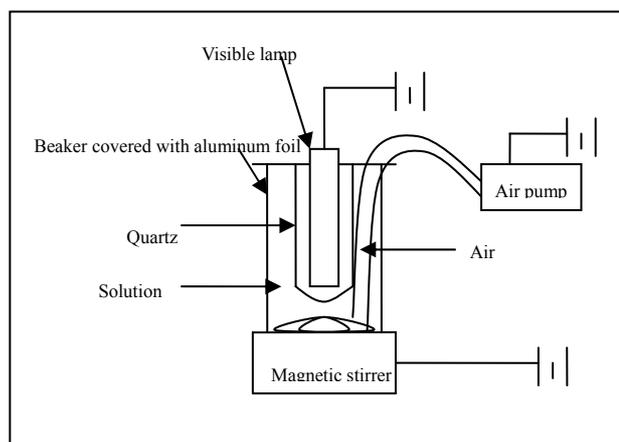


Figure 1. Schematic diagram of batch visible photoreactor

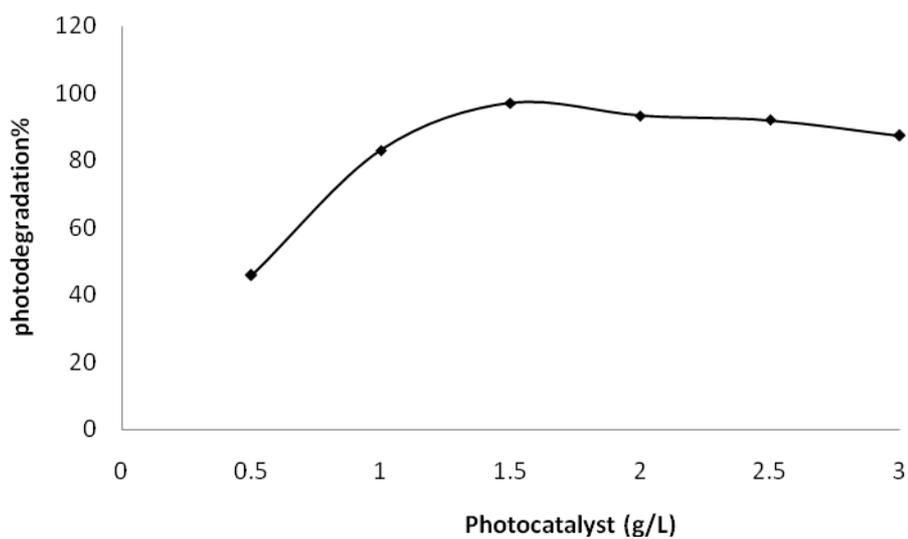


Figure 2. Effect of photocatalyst loading on photodegradation of *m*-cresol under visible irradiation, initial condition: *m*-cresols concentration = 25 mg/L and pH = 7.63, during 6 h.

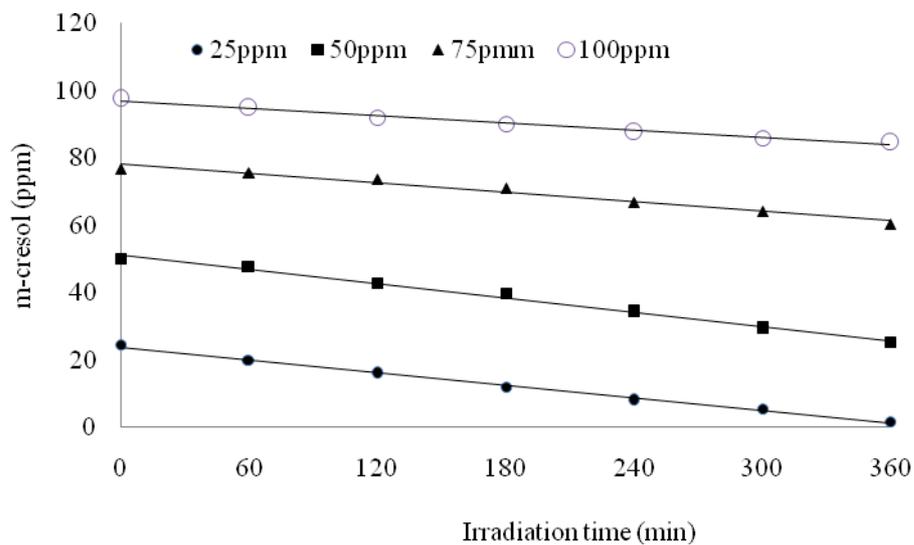


Figure 3. Effect of *m*-cresol concentration on photodegradation efficiency under visible light irradiation; Initial catalyst concentration = 1.5 g/L, pH = 7.63

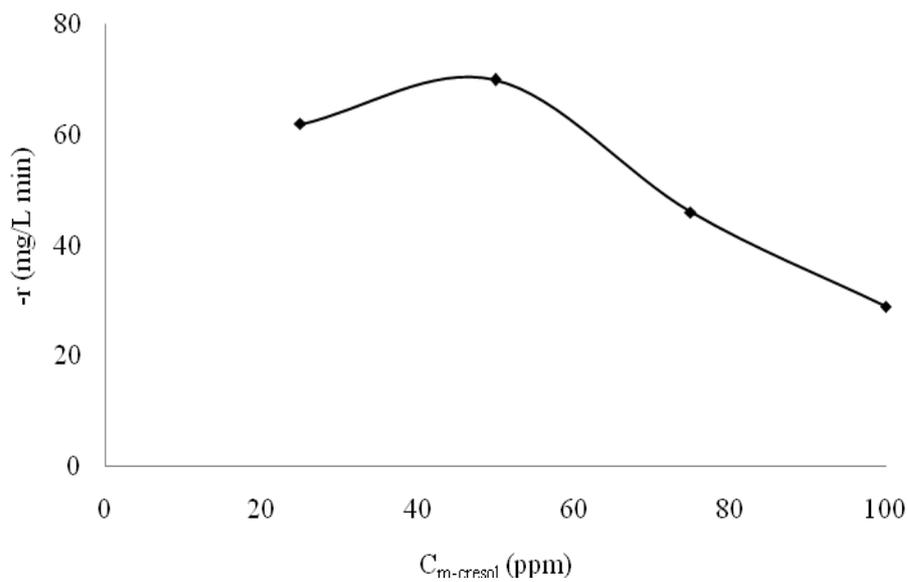


Figure 4. Rate constants ( $r$ ) of photodegradation of different *m*-cresol concentration under visible-light irradiation. Initial condition: ZnO = 1.5 g/L, pH = 7.63, at 25 °C (Derived from Fig. 3)

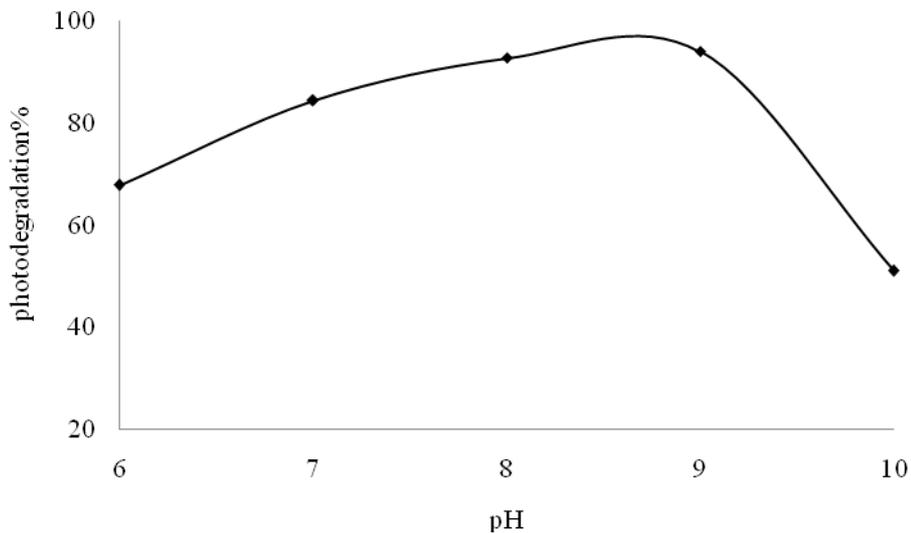


Figure 5. Photodegradation of *m*-cresol at variation initial pH under visible irradiation, initial condition, *m*-cresol concentrations = 25 mg/L, photocatalyst = 1.5 g/L, during 6 h.

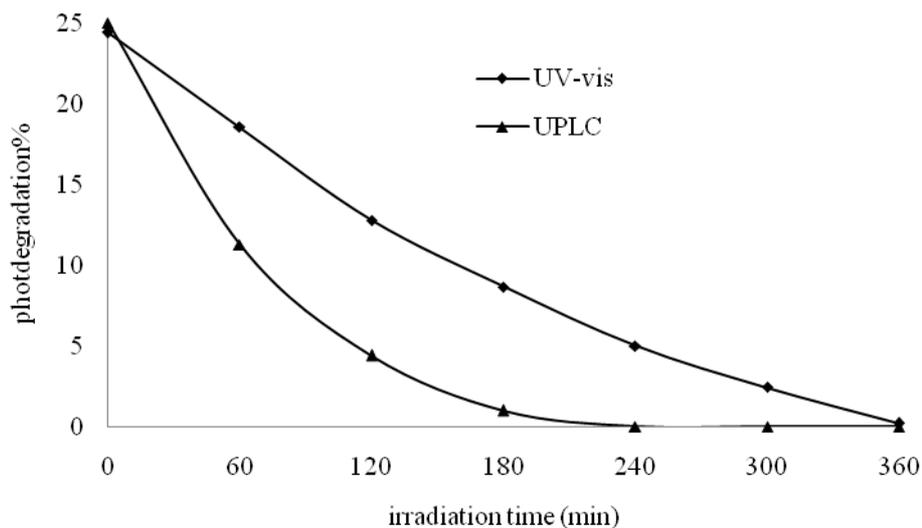


Figure 6. Mineralisation course plot of *m*-cresol recorded on UV-Vis spectrophotometer and on UPLC. Initial conditions: *m*-cresol = 25 mg/L; ZnO = 1.5 g/L; pH 7.63

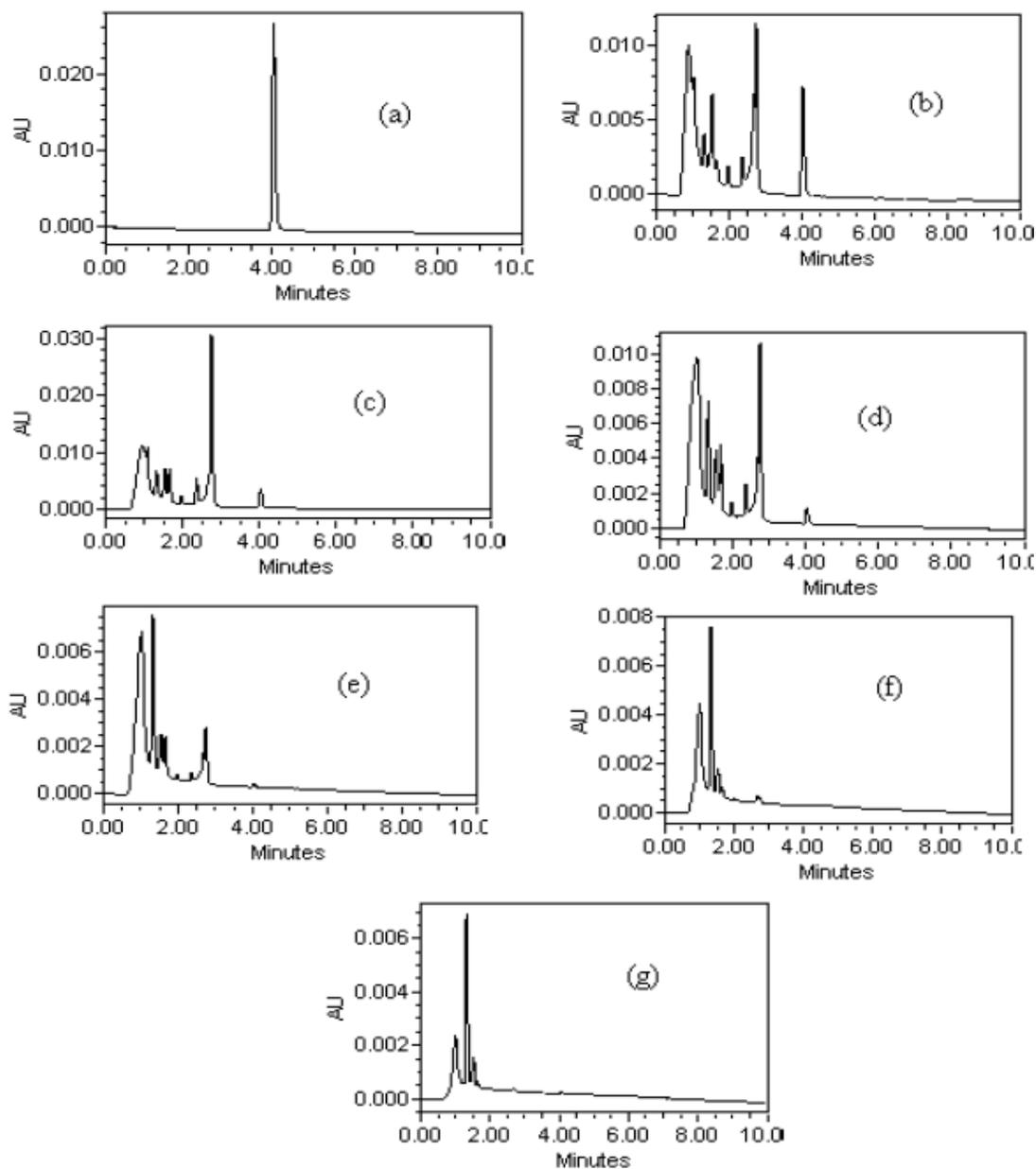


Figure 7. *m*-cresol UPLC chromatograms depicting eluted peaks at different reaction times (a) 0 min (b) 60 min (c) 120 min (d) 180 min (e) 240 min (f) 300 min (g) 360 min, under visible light irradiation. Initial condition: *m*-cresol concentration = 25 mg/L; amount of ZnO = 1.5 g/L; and pH 7.63.

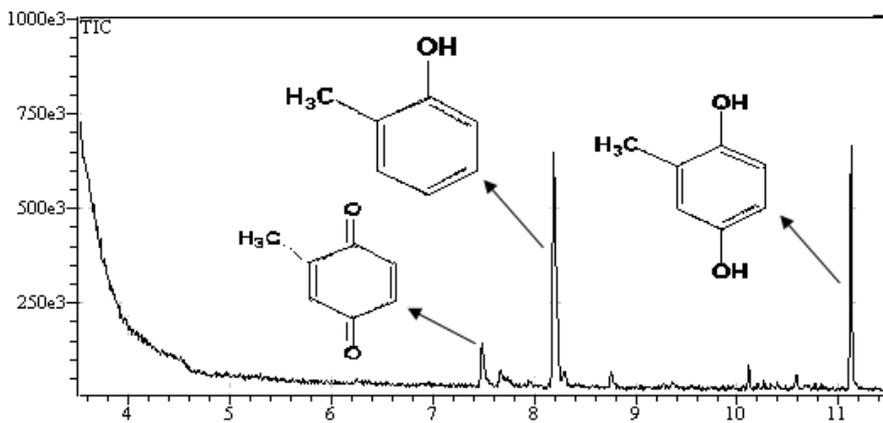


Figure 8. GC-MS spectra of the possible intermediate products formed, during photodegradation of *m*-cresol using ZnO under visible light irradiation at 120 min irradiation time

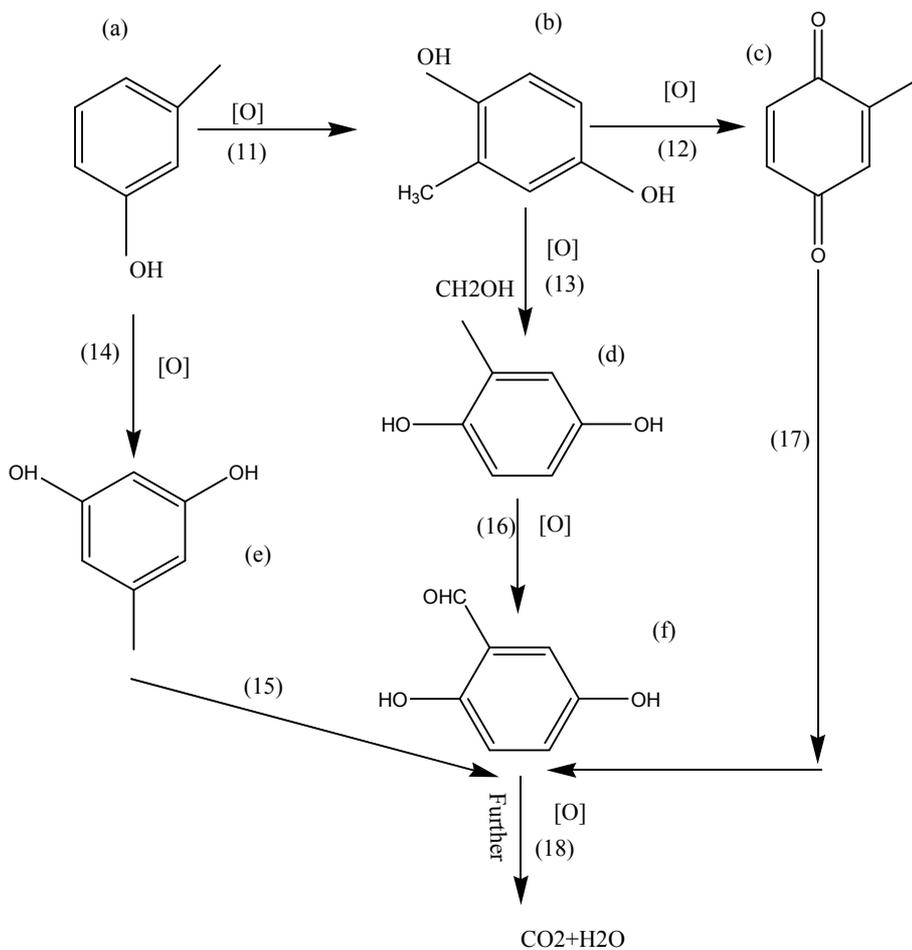


Figure 9. Reaction scheme proposed to account for the formation of degradation intermediates of *m*-cresol on illuminated aqueous ZnO. (a) *m*-cresol, (b) 2-methyl-1,4-benzodiol. (c) 2-methyl-*para*-benzoquinone, (d) undetected, (e) 3,5-dihydroxytoluene and (f) 2,5-dihydroxy-benzaldehyde, [O] = HO•, O<sub>2</sub><sup>•-</sup>, H<sub>2</sub>O<sub>2</sub> and h<sup>+</sup>

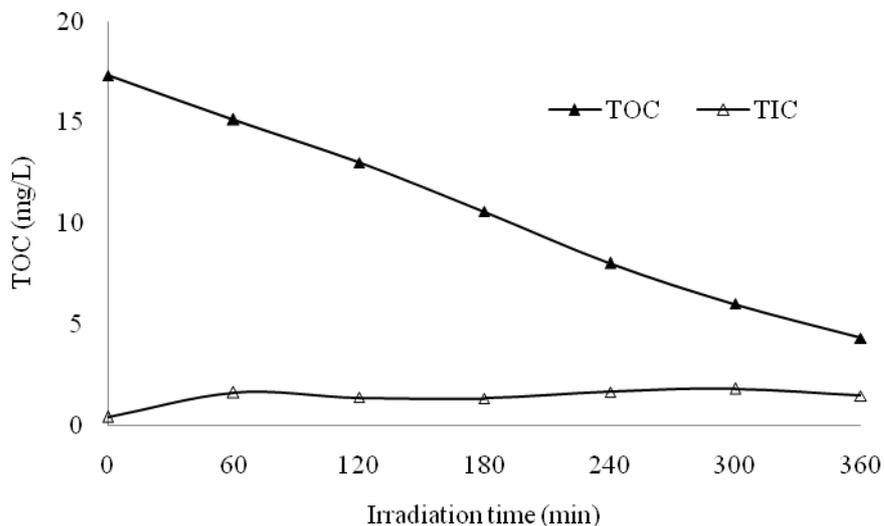


Figure 10. The amount of TOC and TIC during photodegradation of *m*-cresol under visible light irradiation, initial condition; *m*-cresol concentration = 25 mg/L, ZnO = 1.5 g/L and pH = 7.63

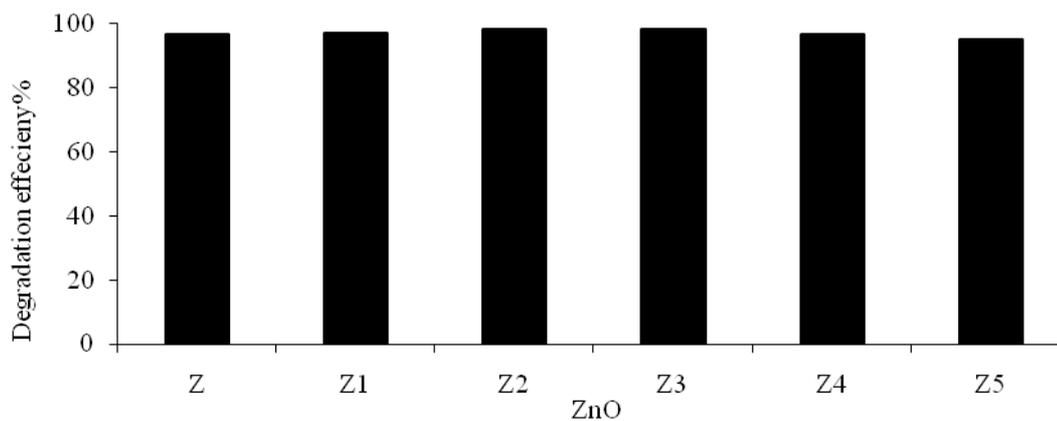


Figure 11. Reusability of ZnO in photodegrading *m*-cresol solution under visible irradiation. Z is fresh ZnO cycle and Z1, Z2, Z3, Z4 and Z5 are reused ZnO cycle. Initial condition; Concentration of cresols = 25 mg/L, ZnO concentration = 1.5 g/L, pH = 7.63, irradiation time = 6 h.