

Photodegradation of *o*-cresol by ZnO under UV irradiation

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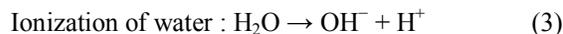
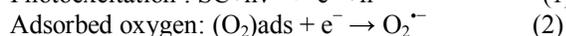
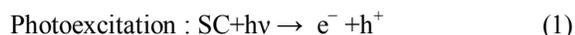
Abstract: The effective removal of *o*-cresol is currently both an environmental problem. This paper shows how degradation of *o*-cresol was carried out, in the presence of UV; by ZnO as photocatalyst. To measure the efficiency of photodegradation, the different variables studied included amount of photocatalyst, concentration of *o*-cresol and pH. The results showed photodegradation was favorable in the pH 6-9 range with amount of photocatalyst 2.5g/L, and *o*-cresol concentration 100ppm. The detected intermediates were 2-methylresorcinol, 2,5-hydroxybenzaldehyde and salicylaldehyde. TOC studies show that 94% of total organic carbon is removed from solution during irradiation time. This study indicates the great potential of ZnO to remove aqueous *o*-cresol under UV irradiation.

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1. Introduction

Environmental organic pollution on a global scale have drawn scientists' attention to the vital need for environmentally clean and friendly chemical processes. Phenolic compounds such as *o*-cresol are 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 *o*-cresol (Chang et al., 1995). *o*-cresol has been listed as the priority pollutant in the USA-EPA list (Callahan et al., 1979). Water solubility of *o*-cresol is above 24 at 25°C (Cooper, 1912). Therefore, *o*-cresol can be a significant threat to the environment (Kavitha et al., 2005; Pardeshi et al., 2008). Therefore the effective removal of *o*-cresol is currently 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 because they are plentiful, inexpensive, and environmentally friendly (Hoffmann et al., 1995; Marci et al., 2003; Rajeshwar et al., 1995). Photocatalytic reaction is initiated when a photoexcited electron is promoted from the filled valence band of a semiconductor photocatalyst (SC) to the empty conduction band as the absorbed photon energy, $h\nu$, equals or exceeds the band gap of the photocatalyst. The electron-hole pair (e^-h^+) is generated at the surface of the photoexcited photocatalyst as shown below (Gaya et al., 2008)



The hydroxyl ($\text{OH} \cdot$) radical is a powerful and non selective oxidant for degrading organic compounds (Litter, 1999; Glaze, 1987; Peiró, 2001). ZnO is one of the most frequently used photocatalysts (Brezova et al., 1994; Maldotti et al., 2002) that removed several environmental contaminants under UV irradiation (Akyol et al., 2004; Daneshvar et al., 2007; Kansal et al., 2008; Sharma et al., 1995). Although, our previous work shows photodegradation of *m*-cresol by ZnO under visible-light irradiation (Abdollahi et al., 2011) However, no study has been conducted on aquatic *o*-cresol photodegradation using ZnO under UV irradiation. This work looks at the photodegradation of *o*-cresol by ZnO under UV irradiation. The effects of variables including *o*-cresol concentration, photocatalyst loading and pH on photodegradation efficiency were studied. In addition, the mineralisation and photoproducts were investigated by TOC measurement and Waters-Acquity ultra high pressure liquid chromatography (UPLC).

2. Material and Methods

ZnO (99%, Merck), *o*-cresol (99%, Merck), NaOH (99% Merck), H_2SO_4 (95%-97%) and other required chemicals were of reagent grade, obtained from Merck and were used without further purification. Various concentrations of *o*-cresol

solution were prepared using deionized water. Photodegradation of *o*-cresol was performed in binary batch photoreactors (Fig.1). To make the produced gas volatile (maybe CO₂), and increase solution fluidization and access oxygen for eq. (Haddad et al.), air was blown into the reaction solution using an air pump at a flow rate of 10m³/h. the blowing cooled air into the solution eliminated the lamp's heat effect and kept the temperature at around 25 °C. Magnetic stirring at 196 rpm was applied to make the suspension solution during the reaction. As showed in Fig.1, an UV-A lamp (6 watt) were used as light source for UV reactor. Throughout the experiment, the appropriate concentration of *o*-cresol solution was contacted with an appropriate amount of photocatalyst in the photoreactor. At specific time intervals, samples were withdrawn from the bulk solution, and filtered through 0.45µm PTFE filters. The concentration of *o*-cresol and residue organic carbon was measured using UV - visible spectrophotometer (shimadzu, uv-1650pc), TOC-VCSN analyzer, respectively. The used UPLC was fitted with an Acquity BEH phenyl C₁₈ column (10 cm × 2.1 mm × 1.7 µm) and the detector wavelength was 271nm. The gradient elution method was applied over a 3-minute run time. The mobile phase was acetonitrile (65%)-water (35%), while a photodiode array (PDA) spectrometer operated at fixed detection wavelength for each experiment was used as a detector. The percentage degradation was calculated as follows:

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

Where C₀=initial concentration of *o*-cresol, C=concentration of *o*-cresol after photoirradiation. All photocatalytic degradation experiments were carried out in duplicate. Photodegradation of *o*-cresol was investigated in the absence of photocatalyst and at normal pH (7.37) as a background. Results show only 4.2% (2.4 mg/L) of *o*-cresol was photolysed in the absence of photocatalyst in present of UV irradiation. Therefore, *o*-cresol is relatively stable under visible light irradiation. The concentration of *o*-cresol was determined in the presence of photocatalyst in the dark. The removed amount of *o*-cresol was 7.51% (3.7mg/L) to 2.5 g/L of ZnO. The decreasing in *o*-cresol suggests it is adsorbed on the photocatalyst surface (Fox et al., 1993).

3. Results and discussion

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

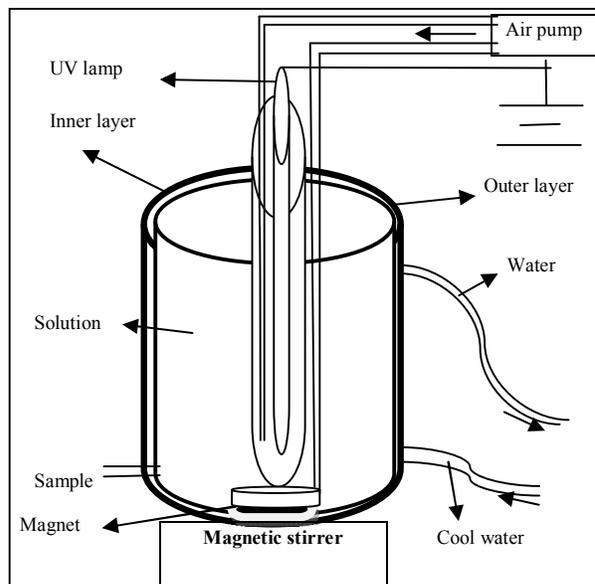


Fig.1. Schematic diagram of binary batch UV photoreactor

avoid unnecessary excess photocatalyst. The percent of photodegraded *o*-cresol (photodegradation%) vs. irradiation time was plotted in Fig. 2. The maximum photodegradation% was carried out in 2.5g/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 ·OH radicals. Moreover, the number of *o*-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 decrease in the photodegradation efficiency beyond the optimum photocatalyst loading can be attributed to increase of turbidity of the solution that reduces the light penetration through the solution known as light screening effect (Neppolian et al., 2002; 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 *o*-cresol adsorption, thus bringing little stimulation to the photocatalytic reaction.

Effect of *o*-cresol concentration

The photocatalytic degradation of various *o*-cresol concentrations, 50-250ppm, was studied (Fig. 3). With an increase in concentration of *o*-cresol, photodegradation% was decreased. Table As observed the concentration of 100ppm completely and the sample of 150ppm more than 57% were

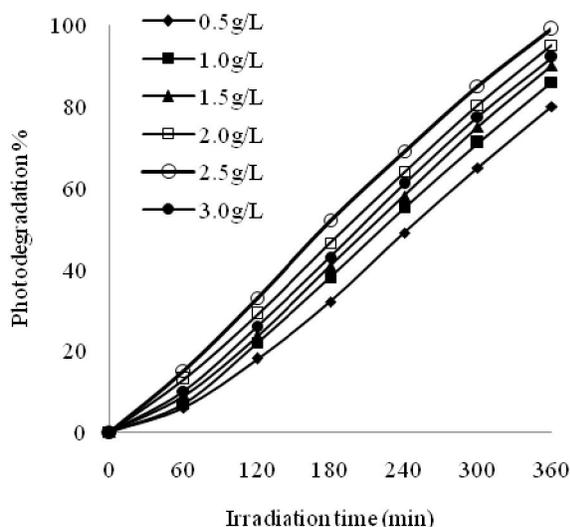


Fig.2 Effect of photocatalyst loading on photodegradation of *o*-cresol under UV irradiation, initial condition: *o*-cresols concentration = 100ppm, pH = 7.37

degraded however, with an increase in concentration of *o*-cresol, photodegradation% was decreased. At a high *o*-cresol concentration, the presumption is that active sites are covered by *o*-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 *o*-cresol concentration increases but the mass of photocatalyst, the intensity of light and illumination time are constant, then the $\bullet OH$ and O_2^{2-} species formed on the surface of photocatalyst are constant, so that the relative ratio of the $\bullet OH$ and O_2^{2-} for attacking *o*-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 *o*-cresol and H_2O molecules for photodegraded h^+ (Gaya et al., 2008). Hence, the optimum *o*-cresol concentration for photodegradation is confirmed to be 100 ppm.

Effect of pH

The effect of pH on the photodegradation of *o*-cresol was studied (Fig.4). The optimum condition was used as in the previous experiment. As observed the amount of *o*-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

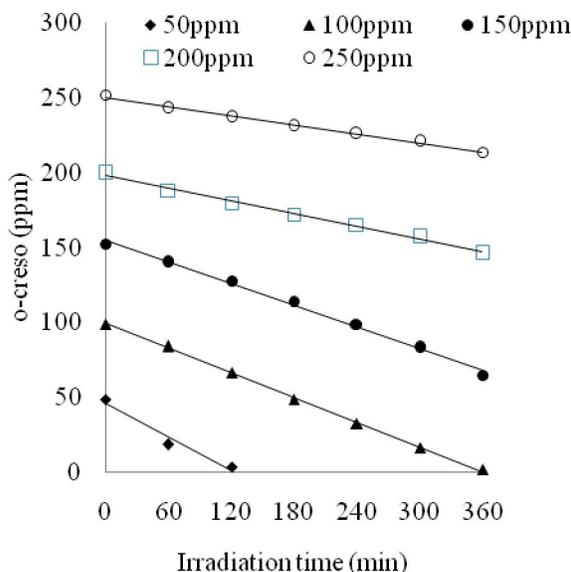


Fig. 3 Effect of *o*-cresol concentration on photodegradation under UV irradiation, initial condition: photocatalyst concentration = 2.5 g/L, and pH = 7.37

due to the increase in adsorption of *o*-cresol on the photocatalyst surface. Increasing adsorption may be due to a decline of the electrostatic repulsive forces and increased interaction between photocatalyst surface ($pH_{zpc} = 9$) (Kosmulski, 2006) and *o*-cresol because with increasing pH the number of positive species (*o*-cresol- H^+) decreases. It has also been reported that in alkaline solution (pH 8-9), $\bullet OH$ is easier to generate by oxidizing more 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 $\bullet OH$ for the reaction. However, photodegradation% decreased at pH 10. This can be attributed to a reduction in the amount of *o*-cresol adsorbed on the catalyst surface at pH 10. It should also be noted that $\bullet OH$ 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 *o*-cresol photodegraded by photocatalyst was observed at pH 10.

Mineralisation

Mineralisation is the main aim of photodegradation of *o*-cresol, followed by measuring the total organic carbon and total inorganic carbon (TIC). Fig. 5 shows the TOC and TIC values of *o*-cresol under UV irradiation. The amount of TOC was steadily decreased with increasing irradiation time, which indicates the decline of *o*-cresol intermediates when irradiation time is increased.

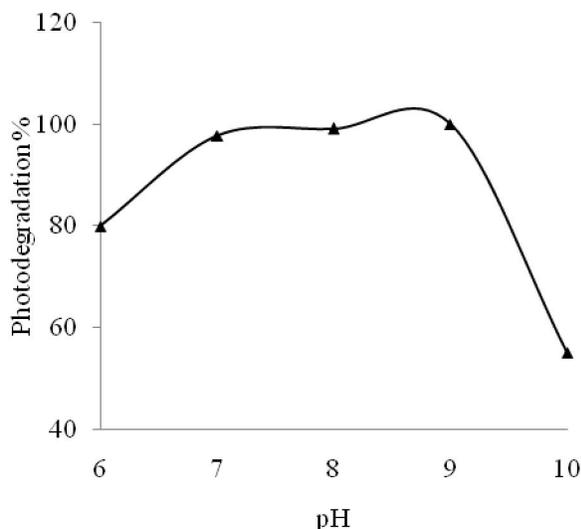


Fig.4. Photodegradation of o-cresol at variation initial pH under UV irradiation, initial condition, o-cresol concentrations = 100ppm, photocatalyst = 2.5g/L, during 6h.

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 94% organic carbon is removed from o-cresol solution.

To confirm previous proposed pathway degradation of o-cresol in the presence of $\bullet\text{OH}$ radicals (Flox et al., 2007), determination of the some photoproducts of o-cresol photodegradation was carried out by UPLC. The chromatograms show many peaks. It may be due to the detection of carboxylic acids and other aromatic intermediates (Flox et al., 2007). Detected intermediates are 2-methylresorcinol, 2,5-hydroxybenzaldehyde and salicylaldehyde with retention time (R_t)=1.989, R_t =2.230 and 4.380 min at 60 to 120 min of irradiation time (Fig. 6).

Reusability

The reusability of photocatalyst was investigated in order to establish the stability of the o-cresol. While studying reuse of photocatalyst, all parameters including irradiation time, pH, o-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.7) no significant reduction in photocatalytic performance in photodegrading o-

cresol, thus this indicates the stability of ZnO as a photocatalyst.

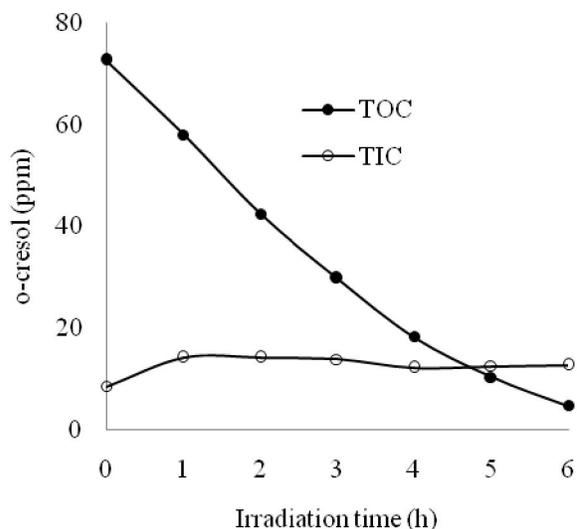


Fig.5 the amount of TOC and TIC during photodegradation of o-cresol under UV irradiation, initial condition; o-cresol concentration = 100 ppm, ZnO = 2.5g/L and pH = 7.37

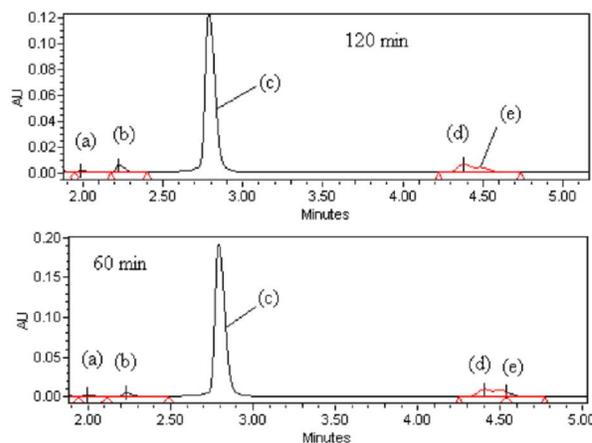
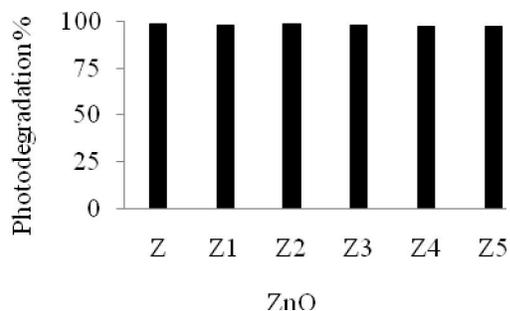


Fig. 6 selected UPLC chromatograms of o-cresol under UV irradiation that shows (a) 2-methylresorcinol, (b) 2,5-hydroxybenzaldehyde and (c) unknown (d) salicylaldehyde as intermediates and (e) o-cresol. Concentration of o-cresol= 50ppm at 60min



and 120min

Fig.7 Reusability of ZnO in photodegrading *o*-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 *o*-cresols = 100ppm, ZnO concentration = 2.5g/L, pH = 7.37, irradiation time = 6 h.

4. Conclusion

The photodegradation of *o*-cresol was carried out by ZnO under irradiation. The different variables studied included the amount of photocatalyst, concentration of *o*-cresol and pH impact on the efficiency of photodegradation. Under optimum conditions, the amount of photocatalyst and concentration of *o*-cresol were 2.5g/L and 100ppm, 25ppm. *O*-cresol photodegradation was favorable in the range pH 6-9. TOC studies shows that 94% of total organic carbon is removed from the solution during irradiation time. The detected intermediates are 2-methylresorcinol, 2,5-hydroxybenzaldehyde and salicylaldehyde. Reusability shows no significant reduction in photocatalytic performance in the photodegradation of *o*-cresol. This study indicates the great potential of ZnO to remove aqueous *o*-cresol under UV irradiation.

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