Photodegradation of *p*-cresol by Zinc Oxide under Visible Light

Yadollah Abdollahi[a*], Abdul Halim Abdullah[a,b]
Zulkarnain Zainal,[a,b], , Nor Azah Yusof[b]

[a]Advanced Materials and Nanotechnology Laboratory
Institute of Advanced Technology
Universiti Putra Malaysia
43400 Serdang, Selangor D.E., Malaysia

[b]Department of Chemistry
Faculty of Science, Universiti Putra Malaysia
43400 UPM Serdang, Selangor, Malaysia

Abstract

The degradation of p-cresol was carried out under visible light (46% sunlight) by zinc oxide as photocatalyst. To measure the efficiency of photodegradation, the different variables studied included amount of photocatalyst, concentration of p-cresol and pH. The maximum amount of photocatalyst and removed p-cresol was 1.5g/L and 25ppm respectively. The photodegradation was favorable in the pH 7-9 range. In optimum condition, total organic carbon (TOC) studies show that 94% of total organic carbon is removed from solution during irradiation time. As a result zinc oxide can remove p-cresol from wastewater under visible light irradiation, and being more economic than UV light could be applied on an industrial scale.

Keywords: Photodegradation, *p-c*resol, visible-light, ZnO, photocatalyst, zinc oxide

1. *Introduction*

Phenolic compounds such as *p*-cresol (PC) 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 PC because of water solubility above 24.4 g/L at 25°C (Cooper, 1912). On the other hand, PC has been listed as the priority pollutant in the priority pollutant in the USA-EPA list (Callahan et al., 1979). Therefore, PC can be a significant threat to the environment (Pardeshi et al., 2008). The effective removal of PC is currently both an environmental and economic problem (Flox et al., 2007). Photocatalysis is the field of current interest given its application in disinfecting drinking water and wastewater (Marcì et al., 2003). 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, *hv*, 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)

Photoexcitation : $SC+h\nu \rightarrow e^- + h^+$ (1)
Adsorbed oxygen: $(O_2)ads + e \rightarrow - O_2^{-\bullet}$ (2)
Ionization of water : $H_2O \rightarrow OH^- + H^+$ (3)
Protonation of superoxides : $O_2^{-\bullet} + H^+ \rightarrow HOO^\bullet$ (4)
$HOO^\bullet + e^- \rightarrow HO_2^-$ (5)
$HOO^- + H^+ \rightarrow H_2O_2$ (6)
$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet$ (7)
$H_2O + h^+ \rightarrow H^+ + OH^\bullet$ (8)

The hydroxyl radical ($^\bullet OH$) is a powerful oxidant for degrading non selective organic compounds (Peiró et al., 2001). The most frequently used photocatalysts are TiO_2, ZnO, ZrO_2, CdS, and SnO_2 (Maldotti et al., 2002). Among these ZnO removed several environmental contaminants under UV irradiation (Kansal et al., 2008). While the great advantage of ZnO is its ability to absorb larger fractions of the solar spectrum than the other photocatalysts (Sakthivel et al., 2003) and removed many organic contaminants in aqueous solution under visible irradiation (Dindar et al., 2001; Pardeshi et al., 2008). More recently our previous work shows successfully phototdegradation of *m*-cresol by ZnO under visible-light irradiation (Abdollahi et al., 2011). However, no study has been conducted on aquatic PC photodegradation using ZnO under visible-light irradiation.

This work looks at the photodegradation of PC by ZnO under visible light irradiation. The effects of variables including PC concentration, photocatalyst loading and pH on photodegradation were studied. In addition, the mineralisation and photoproducts were investigated by TOC measurement and Waters-Acquity ultra high pressure liquid chromatography (UPLC).

2. Materials and Methods

ZnO (99%, Merck), *p*-cresol (99.5%, Fluka), 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 PC solution were prepared using deionized water. Photocatalytic degradation of PC was performed in a batch photoreactor, which was designed in a column of 14.5-cm height and 11.5-cm diameter (Fig.1). To make the produced gas volatile (maybe CO_2), and 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 $10m^3/h$. the blowing cooled air into the solution eliminated the lamp's heat effect and kept the temperature at around $25^{\circ}C$. Magnetic stirring at 200 rpm was applied to make the suspension solution during the reaction. The photoreactor is located in an aluminum-sealed tube to enhance the radiation by reflection. A Philips lamp (23watt) was used as light source. Throughout the experiment, the appropriate concentration of PC 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 PC and residue organic carbon was measured using UV - visible spectrophotometer (shimadzu, uv-1650pc), TOC-VCSN analyzer, respectively. The UPLC was fitted with an Acquity BEH phenyl C_{18} column (10 cm × 2.1 mm × 1.7 µm) and the detector wavelength was 277nm. 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:

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

Where C_0=initial concentration of PC, C=concentration of PC after photoirradiation. All photocatalytic degradation experiments were carried out in duplicate. Photodegradation of PC was investigated in the absence of photocatalyst and at normal pH (7.49) as background. Results show 7% of PC was photolysed in the absence of photocatalyst. Therefore, PC is relatively stable under visible light irradiation. The concentration of PC was determined in the presence of photocatalyst in the dark. A 8% decrease in PC suggests it is adsorbed on the photocatalyst surface (Fox et al., 1993)

3. Results and Discussion

3.1 Photocatalyst loading

A series of experiments were carried out by varying the amount of catalyst (0.5 to 3.0 g/L) to establish the effect of photocatalyst loading and to avoid unnecessary excess photocatalyst. The percent of photodegraded PC (photodegradation%) vs. irradiation time was plotted in Fig. 2. The maximum photodegradation% 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 $^{\bullet}OH$ radicals. Moreover, the number of PC 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 PC adsorption, thus bringing little stimulation to the photocatalytic reaction.

3.2 p-cresol concentration

The photocatalytic degradation of various *p*-cresol concentrations, 25-100ppm, was studied (Fig. 3). With an increase in concentration of *p*-cresol, photodegradation% was decreased. As observed the concentration of 25ppm completely and the sample of 50ppm more than 60% were degraded however, with an increase in concentration of *p*-cresol, photodegradation% was decreased. At a high *p*-cresol concentration, the presumption is that active sites are covered by *p*-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 *p*-cresol concentration increases but the mass of photocatalyst, the intensity of light and illumination time are constant, then the •OH and O_2^{2-} species formed on the surface of photocatalyst are constant, so that the relative ratio of the •OH and O_2^{2-} for attacking *p*-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 *p*-cresol and H_2O molecules for photodegraded h^+ (Gaya, *et al*., 2008).

3.3 Photodecomposition kinetics

The rate of the photodegradation vs. *p*-cresol concentration exhibits a quadratic behaviour which has optimum values at 50 ppm (Fig.4). The rate is a nonlinear function of *p*-cresol concentration ($C_{p\text{-cresol}}$). The reason for this behavior may be related to the probability interaction between *p*-cresol and ZnO surface. At very low *p*-cresol concentration, the probability of interaction between *p*-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 *p*-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:

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

Where, the estimated value of $k_{p\text{-cresol}}$ ($mgL^{-1}min^{-1}ppm^{-1}$) and $K_{p\text{-cresol}}$ (ppm^{-1}) were 0.0088 and 0.0087 with R-squared value 0.98 respectively. Similar results were reported for photodegradation kinetics of aqueous sodium oxalate, sodium dodecyl sulphate, 4-nitrophenol solution using TiO_2 photocatalyst and *m*-cresol in our previous work (Abdollahi et al., 2011, Bangun, *et al*., 1998; Lea, *et al*., 1998, 2001, Hudaya, *et al*., 2009)

3.4 Effect of pH

The effect of pH on the photodegradation of PC was studied (Fig.5). The optimum amount of photocatalyst and PC were used as in the previous experiment. As observed the amount of PC photodegraded gradually increased with increasing pH from pH 5 to 9. The activity of photocatalyst seriously depends on adsorption of amount of pollutant over photocatalysis (Anandan et al., 2007). Increasing photodegradation may be due to the increase in adsorption of PC 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 PC because with increasing pH the number of positive species ($PC\text{-}H^+$) 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 PC 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 PC photodegraded by photocatalyst was observed at pH 10.

3.5 Mineralisation and photoproducts

Mineralisation is the main aim of photodegradation of PC, followed by measuring the total organic carbon (Heiland et al. 1959) and total inorganic carbon (TIC). Fig. 6 shows the TOC and TIC values of PC under visible light irradiation by ZnO. The amount of TOC was steadily decreased with increasing irradiation time, which indicates the decline of PC 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 94% organic carbon is exited from PC solution.

To confirm previous proposed pathway in the presence of $^\bullet OH$ radicals (Flox, 2007; Wang, 1998), determination of the some photoproducts of PC 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 intermediate is 4-hydroxy-benzaldehyde (R_t=2.150) that were detected at 120 min of irradiation time (Fig.7).

3.6 Reusability

The reusability of photocatalyst was investigated in order to establish the stability and degree of photo corrosion of the PC. While studying reuse of photocatalyst, all parameters including irradiation time, pH, PC 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.8) no significant reduction in photocatalytic performance in photodegrading PC, thus this indicates the stability of ZnO as a photocatalyst.

4 Conclusion

As a conclusion, the photodegradation of *p*-cresol was carried out by ZnO under visible light irradiation. The different variables studied included the amount of photocatalyst, concentration of *p*-cresol and pH impact on the efficiency of photodegradation. Under optimum conditions, the amount of photocatalyst and concentration of *p*-cresol were 1.5g/L and 25ppm respectively. *p*-cresol photodegradation was favorable in the range pH 7-9. TOC studies shows that 94% of total organic carbon is removed from the solution during irradiation time. The detected intermediate is 4-hydroxy-benzaldehyde. Reusability shows no significant reduction in photocatalytic performance in the photodegradation of *p*-cresol. This study indicates the great potential of ZnO to remove aqueous *p*-cresol under visible light irradiation.

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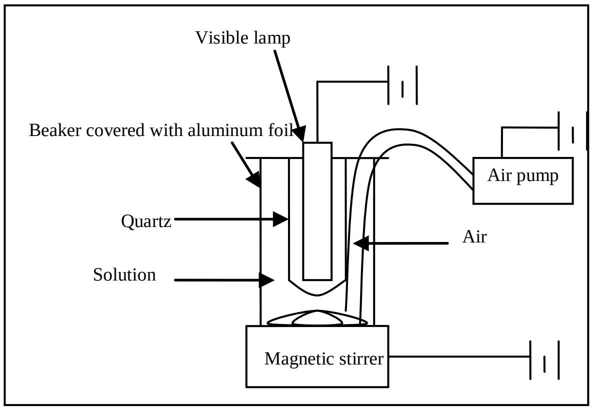

Fig.1. Schematic diagram of batch visible photoreactor

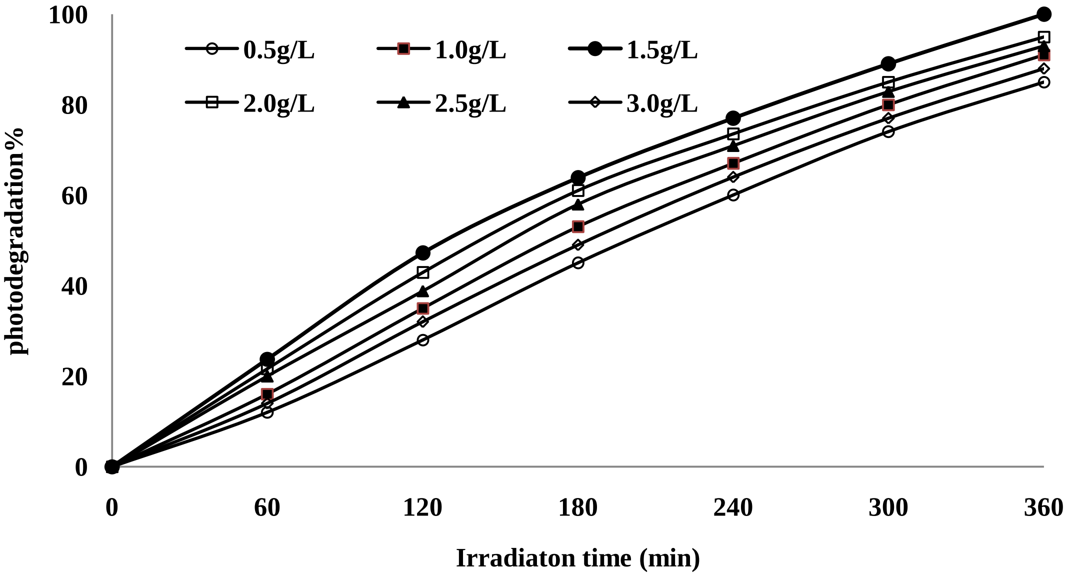

Fig.2 Effect of photocatalyst loading on photodegradation% of PC under visible irradiation, initial condition: PC concentration = 25 ppm, pH = 7.49, during 6h

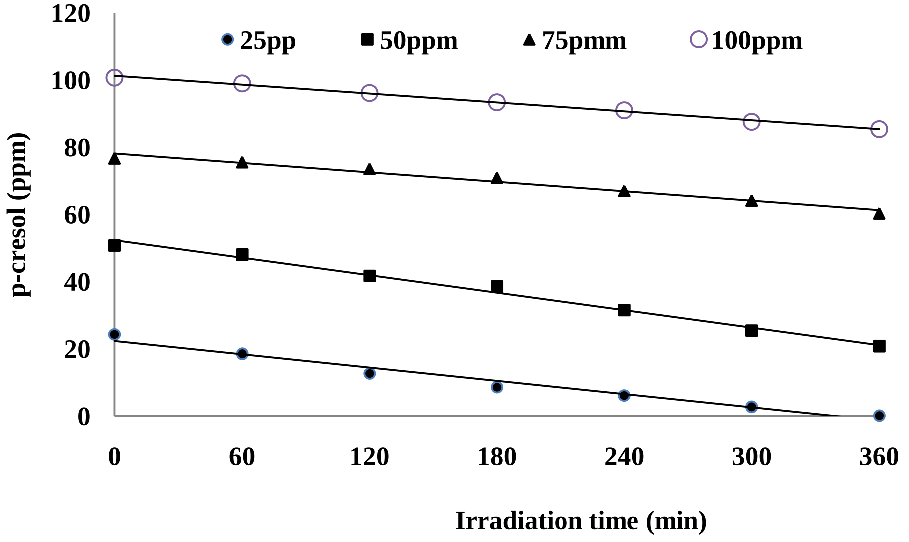

Figure 3. Effect of *p*-cresol concentration on photodegradation efficiency under visible light irradiation; Initial catalyst concentration = 1.5 g/L, pH=7.49

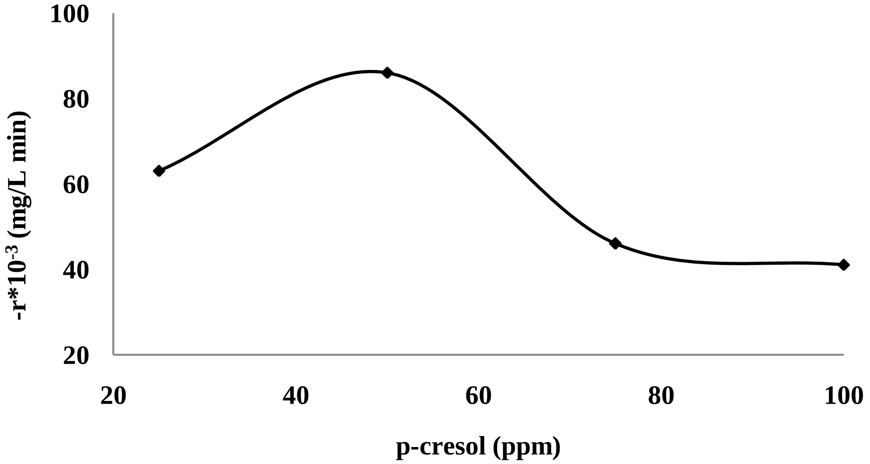

Figure 4. Rate constants (r) of photodegradation of different *p*-cresol concentration under visible-light irradiation. Initial condition: ZnO=1.5g/L, pH =7.49, at 25°C (Derived from Fig. 3)

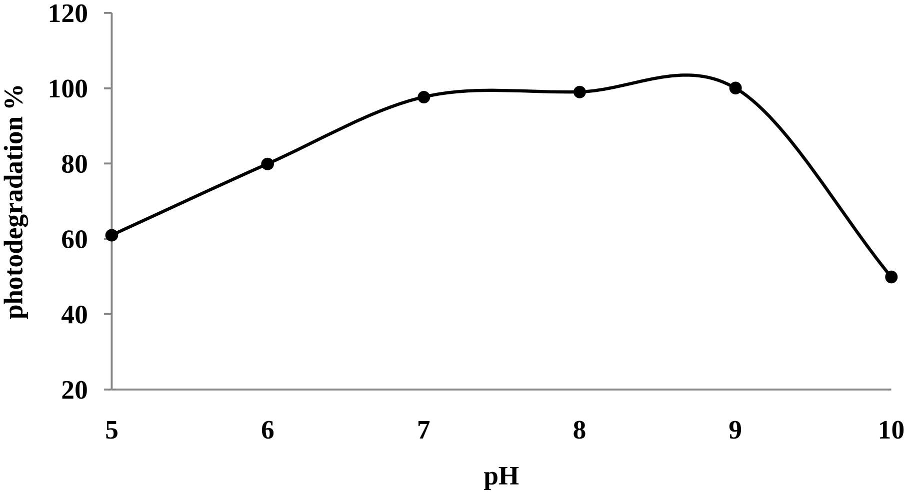

Fig.5. Photodegradation of *p*-cresol at variation initial pH under visible irradiation, initial *p*-cresol concentrations = 25ppm, photocatalyst = 1.5 g/L, end of 6h

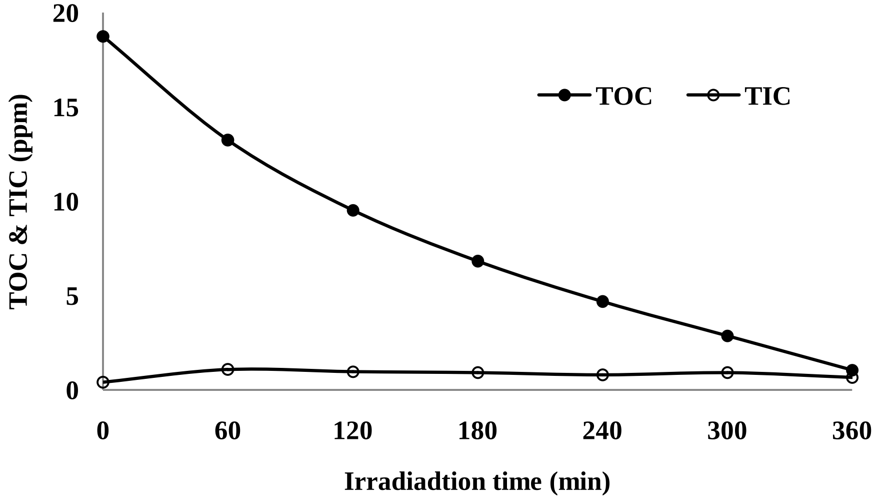

Fig.6 The amount of TOC and TIC during photodegradation of *p*-cresol under visible light irradiation, initial condition; PC concentration = 25ppm, ZnO = 1.5g/L and pH = 7.49

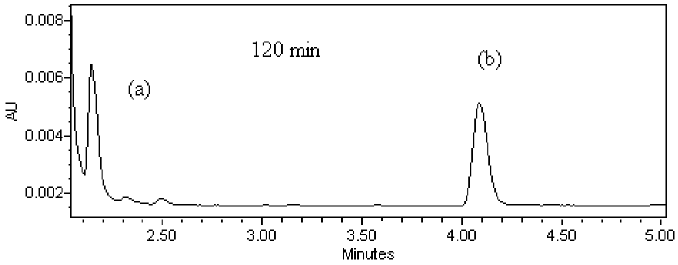

Fig. 7 Selected UPLC chromatograms of PC under visible light irradiation that shows (a) 4-hydroxy-benzaldehyde as intermediate and (b) *p*-cresol. Concentration of *p*-cresol= 25ppm at 120min

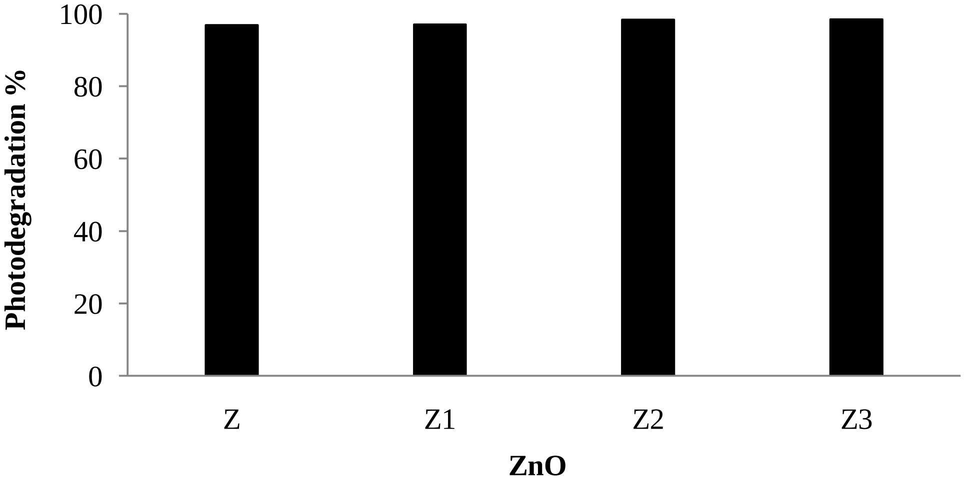

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Fig.8 Reusability of ZnO in photodegrading *p*-cresol solution under visible irradiation. Z is fresh ZnO cycle and Z1, Z2 and Z3 are reused ZnO cycle. Initial condition; Concentration of *p*-cresols = 25mg/L, ZnO = 1.5g/L, pH = 7.49, irradiation time = 6 h.