



Photocatalytic Degradation of Ortho-Cresol by Zinc Oxide-UV Process

R. Gladis Latha and M. Shanthi*

Department of Chemistry, Holy Cross College, Nagercoil-629 004, T. N., India

*Department of Chemistry, Annamalai University, Annamalai Nagar-608 002, T.N., India

Key Words:

Photocatalytic degradation
Ortho-cresol
UV-irradiation
Catalyst loading
Electron acceptors

ABSTRACT

The photocatalytic degradation of ortho-cresol over irradiated ZnO suspensions was investigated in aerated aqueous solution. Complete and relatively fast substrate degradation was achieved after irradiation with UV light, being the reaction rate dependent on the initial pH. The effect of various parameters such as catalyst loading, pH and initial concentration of o-cresol on degradation has been determined. The degradation was strongly enhanced in presence of electron acceptors such as H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$ and KBrO_3 .

INTRODUCTION

Toxic organic compounds released into the environment result in environmental damage as pollutants. The removal of toxic organic compounds from industrial water effluents is of growing concern and there is an urgent need to develop strategies to deal with organic compound contaminated waste waters. Ortho-cresol is one of the toxic organic compounds and is used as a chemical, pharmaceutical intermediate, reagent, solvent, disinfectant and chemical intermediate for a variety of products including resins, paints and textiles. Efficient water treatment technologies are required to reduce the concentration of chloroalkanes (Lee et al. 2001), aromatic hydrocarbons like benzene and toluene (Hennezel et al. 1998) and phenols (Ding et al. 2000) in wastewaters because these are hazardous even at low concentration.

The removal of o-cresol from aqueous media can be performed using different techniques including biological treatment (Maeda et al. 2005, Perron & Welander 2004). Heterogeneous photocatalysis, a promising advanced oxidation process developed in the past years allows to perform the degradation of a variety of organic compounds (Fujishima et al. 2000). In this study, an attempt has been made to investigate the advanced oxidative degradation of o-cresol using zinc oxide as catalyst under different conditions using UV light as the radiation source. The experiments have been carried out in a batch reactor.

MATERIALS AND METHODS

The photocatalyst zinc oxide, which has a particle size 0.1-4 μm and surface area $10\text{m}^2/\text{g}$, was used for the study. The experiments were carried out in slurry form of the catalyst. AnalaR grade reagents H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$ and KBrO_3 were used. The pH of the solution was measured by HANNA Phep digital pH meter.

Open borosilicate glass tube of 50mL of capacity, 40 cm height and 20mm diameter was used as the reaction vessel. The irradiation was carried out using four parallel medium pressure mercury

lamps in open air condition. The UV power of the four lamps was 32 W. The solution with ZnO and o-cresol was continuously aerated by a pump to provide oxygen and for complete mixing of reaction solution.

For the photolysis experiment, 50 mL of the o-cresol solution containing appropriate quantity of the catalyst dispersion was used. 20 minutes at the beginning and 30 minutes at the end, 3 mL of sample was with drawn and ZnO particles were removed by centrifugation. 1mL of the centrifugate was diluted to 10 mL. Changes in the concentration of o-cresol and intermediates were observed from their characteristic absorption at 270nm using UV visible spectrophotometer. All photocatalytic experiments were carried out at pH 7.

RESULTS AND DISCUSSION

Ortho-cresol (molecular formula C_7H_8O , molecular weight 108.14) is extensively used as a disinfectant. It has the absorption maxima at 270nm.

Photocatalytic degradability of o-cresol: In the absence of the photocatalyst, the o-cresol solution on irradiation with the UV light has been found to be stable even after 2 hrs. In presence of zinc oxide and in the absence of light there is a small decrease in o-cresol concentration initially and then found to be stable. The initial decrease is due to the absorption of the o-cresol by zinc oxide and the pollutant undergoes 85.6% degradation in 120 minutes on irradiation with light of 365nm. The photodegradation of o-cresol as a function of time is shown in Fig. 1.

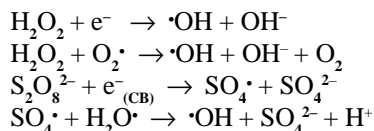
Effect of o-cresol concentration: The photocatalytic degradation of o-cresol has been carried out at different initial concentrations of o-cresol in the range 1×10^{-4} to 9×10^{-4} mol/L. Increase in concentration of o-cresol decreases the degradation from 72.3 to 50.6% at 90 minutes. The results are shown in Fig. 2.

Effect of catalyst weight: When the concentration of the catalyst is increased from 50mg to 100 mg/50mL, degradation efficiency increases from 38.8 to 72.3% at 90 minutes of irradiation time; further increase of catalyst loading from 100mg to 150mg/50mL makes no significant change.

Effect of solution pH: The efficiency of the catalyst is affected by pH of the solution. It is found that the degradation efficiency increases from 29.6 to 95.1% with increase in pH from 3 to 11 at 90 minutes. At acidic pH range, the degradation efficiency is minimum. The results are shown in Fig. 3.

Effect of UV light power: The increase of light intensity from 16 to 64 W increases the degradation from 61.1 to 91.5% at the time of 90 minutes. With the increase of the UV power, more photons are absorbed by the catalyst and this increases the hydroxyl radical concentration, hence the removal rate increases. The results are shown in Fig. 4.

Effect of oxidizing agents: The Photooxidation increases in the presence of H_2O_2 , $K_2S_2O_8$ and $KBrO_3$. H_2O_2 increases the concentration of hydroxyl radicals (Fig. 5) and $K_2S_2O_8$ can trap the photogenerated electrons and produce sulphate radical. The $SO_4^{\cdot-}$, a strong oxidant can participate in the degradation process.



The enhancement of the degradation rate by the addition of $KBrO_3$ is due to the reaction between

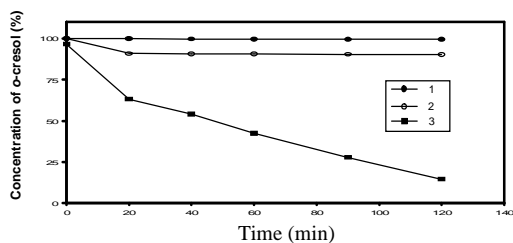


Fig. 1: Photodegradability of *o*-cresol using UV light and ZnO. ZnO = 100 mg/50 mL; [*o*-Cresol] = 1×10^{-4} mol/L; pH = 7.0 ± 0.1 ; Incident wavelength = 365 nm
1. *o*-Cresol solution irradiation with UV light in the absence of ZnO; 2. *o*-Cresol solution treated with ZnO in dark; 3. Degradation of *o*-cresol solution irradiation with UV light in the presence of ZnO.

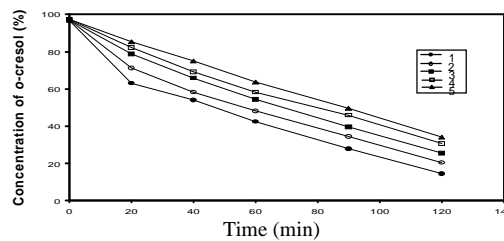
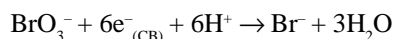


Fig. 2. Effect of various initial *o*-cresol concentrations on the degradation of *o*-cresol using UV light. ZnO = 100 mg/50 mL; pH = 7.0 ± 0.1 ; 1 = 1×10^{-4} mol/L; 2 = 3×10^{-4} mol/L; 3 = 5×10^{-4} mol/L; 4 = 7×10^{-4} mol/L; 5 = 9×10^{-4} mol/L

BrO_3^- and conduction band electron, which reduces the recombination of electron-hole.



Mechanism of photodegradation: The photocatalytic process is initiated by the illumination of a semiconductor catalyst with radiation of energy higher than the band gap energy of the semiconductor. This irradiation generates electrons (e^-) and holes (h^+) in the conduction band (CB) and valence band (VB) respectively as given by equation.



The electron hole pair formed may recombine in the bulk lattice where they can react with the absorbents (Turichi & Ollis 1990). Holes are trapped by OH^- and H_2O to form hydroxide radicals.



The electrons are trapped by dissolved oxygen resulting in the formation of super oxide ion.



The photocatalytic degradation by ZnO involved the hydroxyl radical and holes for oxidation of organic molecules (OM). The reactions are given below.



CONCLUSION

The photocatalytic degradation of *o*-cresol has been studied using UV light as radiation source in presence of zinc oxide as photocatalyst. The effects of various experimental parameters such as *o*-cresol concentration, catalyst concentration, pH and effect of electron acceptors (H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$ and KBrO_3) have been investigated. Optimum catalyst weight is found to be 100mg/50mL for UV degradation. Photodegradation increases with increases in pH. Photocatalytic degradation also increases by the addition of H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$ and KBrO_3 .

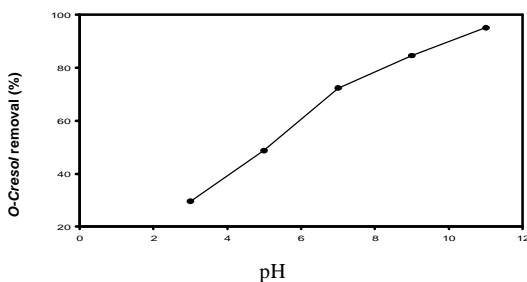


Fig. 3: Effect of initial pH on the degradation of *o*-cresol using UV light.
ZnO = 100 mg/50 mL; [*o*-Cresol] = 1×10^{-4} mol/L; Incident wavelength = 365 nm; Irradiation time = 90 minutes

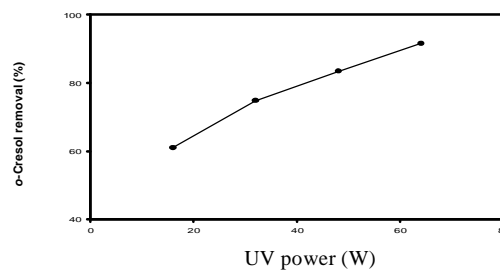


Fig. 4: Effect of UV power on the degradation of *o*-cresol.
ZnO = 100 mg/50 mL; [*o*-Cresol] = 1×10^{-4} mol/L; pH = 7.0 ± 0.1 ; Incident wavelength = 365 nm; Irradiation time = 90 minutes

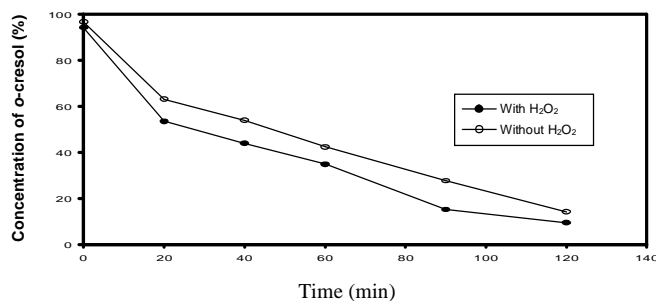


Fig. 5: Effect of H₂O₂ on the photocatalytic degradation of *O*-cresol using UV light; [*O*-Cresol] = 1×10^{-4} mol/L; pH = 7.0 ± 0.1 ; Catalyst = ZnO (100 mg/50 mL)

REFERENCES

- Ding, Z., Lu, G.Q. and Greenfield, P.F. 2000. Role of crystal like phase of TiO₂ in heterogeneous photocatalysis for phenol oxidation in water, *Journal of Physical Chemistry*, 104: 4815.
- Fujishima, A., Rao, T.N. and Tryk, D.A. 2000. Antifungal activity of TiO₂ photocatalysis against *Penicillium expansum* in vitro and in fruit tests. *Journal of Photochemistry and Photobiology, C: Photochem. Rev.*, 1: 1-21.
- Hennezel, O., Pichat, P.B. and Ollis, D.F. 1998. Degradation of azo dye Procion Red MX-5B by photocatalytic oxidation. *Journal of Photochemistry and Photobiology. A: Chem.*, 118: 197.
- Lee, S.H., Kang, M., Cho, S.M., Han, G.Y. and Chung C.H. 2001. Photocatalytic activity of dispersed TiO₂ thin films. *Journal of Photochemistry and Photobiology. A: Chem.*, 146: 121.
- Maeda, M., Itoh, A. and Kawase, Y. 2005. Kinetics for aerobic biological treatment of *o*-cresol containing wastewaters in a slurry bioreactor: Biodegradation by utilizing waste activated sludge. *Journal of Biochemical Engineering*, 22: 97-103.
- Perron, N. and Welander, U. 2004. Kinetics of 2,4-dichlorophenol and 4-cl-m-cresol degradation by *Pseudomonas* sp. cultures in the presence of glucose. *Chemosphere*, 55: 45-50.
- Turichi, C.S. and Ollis, D.F. 1990. Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack. *Journal of Catalysis*, 122: 178-192.