

Heterogeneous photocatalytic mineralisation of phenols in aqueous solutions

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Abstract

The photocatalytic oxidation of phenol and chlorophenols were studied in the presence of ZnO in a batch reactor configuration illuminated with a 6 W low pressure mercury lamp. The variables studied include catalyst usage, solution pH and phenol concentration. The degradation rate of phenol was favourable in the neutral pH range. However, *o*-chlorophenol and *p*-chlorophenol undergo degradation at a faster rate at lower pH values. The disappearance of phenols in each case approximately obeyed first-order kinetics with the apparent first-order decay constant increasing with decreasing solute concentration. Total organic carbon analysis indicated complete mineralisation of phenols on ZnO surface.

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1. Introduction

Important organic contaminants in industrial wastewaters are phenols and phenolic compounds. They are released to the environment, from effluents discharged by industries such as petroleum refining, coal tar, steel, dyestuff, synthetic resins, coal gasification and liquefaction, surface runoff from coal mines, byproducts of agricultural chemicals, paper and pulp mills, tanning, fiberboard production and paint stripping operations [1]. According to environment protection rules of Central Pollution Control Board (1992) the discharge limits of phenols in inland water is 1 mg/L. Among the list of priority of organic pollutants proposed by the U.S. Environmental Protection Agency, chlorophenols represent a group of organics frequently found in various industrial effluents and reported in hazardous waste sites. Chlorophenols are widely recognized as one of the most important types of pollutant in water and wastewater. The widespread utilization of chlorinated aromatic compounds as pesticides and

herbicides is attracting increased concern. More specifically, monochlorophenols constitute an important category of water pollutants [2]. Their presence in water stems principally from industries, which produce chemical intermediates or generate them during the chlorination of effluents containing phenolic compounds. They can also be formed by the degradation of phenoxy herbicides. They have been found in the river water, usually at levels of few ppb. Use of chlorine in the disinfection treatment of drinking water can also result in the formation of monochlorophenols.

In recent years advance oxidation processes (AOPs) involving hydrogen peroxide, ozone and/or Fenton reagents, with or without a source of UV light have been reported to be useful for the photo-oxidation of organic pollutants in waste waters [3–5]. It removes substantial amount of COD and TOC from industrial effluents. However, these oxidation methods results in partial oxidation of organics and more often lead to the generation of potentially harmful chemicals. Total oxidation of organics by these technologies is both cost and energy intensive. Among the various AOPs, semiconductor mediated photocatalysis has been accorded great importance over the last few years due to its potential to destroy a wide range

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of organic and inorganic pollutants at ambient temperatures and pressures, without the production of harmful byproducts [6–8]. Over the years, a large number of semiconductors have been used as photocatalysts. The most commonly studied catalyst are TiO_2 , ZnO and CdS . TiO_2 has become the bench mark catalyst against which photocatalytic activity of other semiconductors is measured because of its high photocatalytic activity. ZnO is a suitable alternative to TiO_2 and is in fact proved to be more efficient than TiO_2 in several applications. This study represents part of our investigation on the ZnO -mediated photo-destruction of phenols

2. Experimental

2.1. Materials

ZnO , phenol, *o*-chlorophenol, *p*-chlorophenol and other chemicals used in the present study are of reagent grade obtained from C.D.H and Merck. Brunauer–Emmett–Teller (BET) surface area of ZnO determined by flow method using Micromeritics Pulse Chemisorb 2700 was found to be $8 \text{ m}^2/\text{g}$. The desired concentrations of the phenol solutions were prepared using double distilled water. The pH of the solutions was adjusted to the desired values between 3.5 and 9.0 by using dilute solutions of dilute HCl or NaOH.

2.2. Photocatalytic reactor

The photodegradation studies were carried out in a batch reactor system. The solutions were illuminated in an open rectangular tray of $16 \text{ cm} \times 5 \text{ cm} \times 5 \text{ cm}$ made of borosilicate glass mounted on a magnetic stirrer. Low pressure mercury vapour lamp (6 W, 18 cm long) was used as an irradiation source. The lamp emitted ultra violet radiation with maximum intensity at 253.7 nm. The lamp was fitted on the top of the reactor. The light source used in the photocatalysis experiments was standardized by ferrioxalate actinometry and its intensity was found to be $2.48 \pm 0.1 \times 10^{19}$ quanta per second.

2.3. Procedures

The optimum conditions used in the present study were a batch volume of 250 ml, 8 cm distance between UV source and solution with a stirring speed of 70 rpm and 30 min for adsorption equilibrium. In all the experiments, the phenol solution of known concentration containing a suspension of known weight of catalyst powder was irradiated with UV light. Samples of 3 ml were withdrawn at regular intervals of time and centrifuged. The estimation of phenols were done spectrophotometrically using 4-aminoantipyrine method [9].

The estimation of TOC was done subjecting the solutions of phenols to photocatalytic degradation in a closed reactor to convert the organic carbon to carbon dioxide. The evolved carbon dioxide was trapped in an aqueous KOH solution of

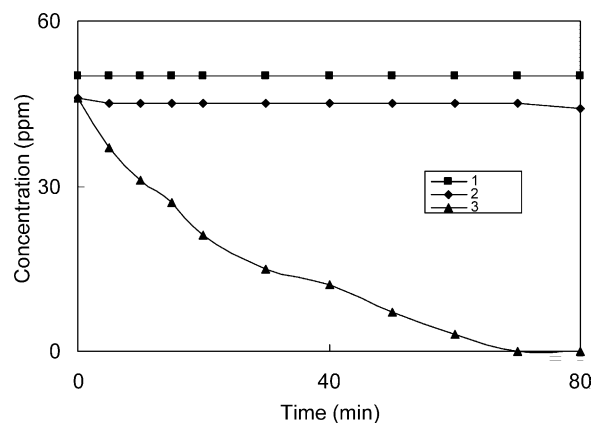


Fig. 1. Photodegradability of phenol. [Phenol] = 50 ppm; catalyst = ZnO (2.0 g/L); pH = 7.0 ± 0.1 ; temperature = 30.0 ± 0.1 °C. Incident wavelength = 254 nm; absorbance measured at 500 nm. (1) Phenol solution irradiated with UV light. (2) Phenol solution treated with 2.0 g/L of ZnO . (3) Phenol solution irradiated with UV light in the presence of 2.0 g/L of ZnO .

known concentration and unreacted KOH was titrated with HCl of known concentration [10]. In this 35 ml of the sample solution was filled up in the annular space between the UV lamp – quartz (6 W) assembly and the outer glass column of the tubular batch reactor and the inner wall of the glass column coated with ZnO . The inlet was connected to the aerator and the outlet tube was immersed into KOH solution of known concentration taken in a gas washing bottle. After irradiating the samples for a specific duration, the KOH solution was titrated against standardized HCl by volumetry. A blank was run with 35 ml of water to the same irradiation time, to nullify the errors due to dissolved CO_2 from aeration. The amount of KOH consumed by the liberated CO_2 and hence the amount of organic carbon present in the sample were calculated and compared with the theoretical values calculated on the basis of the known stoichiometry of the reaction.

The stability of ZnO was assessed by subjecting the irradiated solutions to atomic absorption spectroscopic (AAS-Perkin-Elmer 23800) analysis and the amount of zinc in solution resulting from dissolution or photo-corrosion was determined. The reusability of the catalyst was evaluated by reclaiming the catalyst after reaction in the batch mode, washing drying in air at 110 °C and using it for the phenol degradation under similar experimental conditions.

3. Results and discussion

3.1. Photodegradability of phenols

Phenols were degraded by illumination with UV light in ZnO suspension. The photodegradability of the phenols were investigated by exposing the phenol solutions to UV light in the absence and in the presence of ZnO photocatalyst (Fig. 1). In the absence of ZnO the phenols were found to be stable towards irradiation with UV light of 253.7 nm and photodegra-

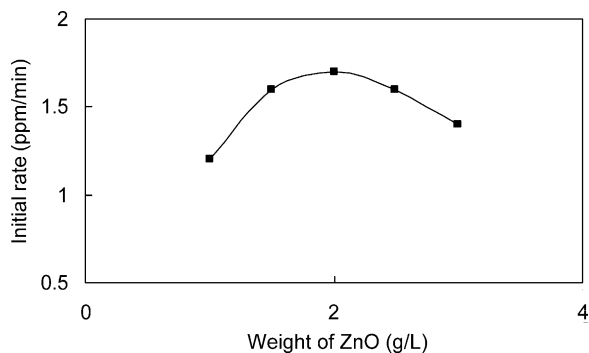


Fig. 2. Effect of catalyst weight on the initial rate of photocatalytic degradation of *o*-chlorophenol. [*o*-Chlorophenol] = 50 ppm; pH = 7.0 ± 0.1; catalyst = ZnO; incident wavelength = 254 nm; temperature = 30.0 ± 0.1 °C; absorbance measured at 500 nm.

degradation was negligible even after one hour of exposure. In the absence of UV light and in the presence of ZnO in dark about 10% of the phenols was adsorbed on ZnO surface under specified conditions. However, in the presence of UV light and ZnO (with a band gap energy of 3.2 eV), the phenols were completely mineralised to carbon dioxide, water and chloride in about an hour. The phenol solutions were analysed for TOC and inorganic ion. All the organic components were oxidised quantitatively to carbon dioxide as indicated by TOC determinations. Carbon dioxide determined experimentally was found to tally with theoretical value on the basis of molecular weight and concentrations employed. The percentage of carbon photo-oxidised in aqueous suspensions was 98% of the theoretical value.

3.2. Effect of catalyst weight

The effect of varying amounts of ZnO on the photodegradation of phenols was studied in the range 1.0–3.0 g/L. Fig. 2 shows the variation of initial rate of photodegradation of *o*-chlorophenol as a function of catalyst weight. The initial rate values indicated that the degradation rate increased with an increase in the weight of catalyst up to an optimum loading of ZnO (2.0 g/L). Similar results were obtained by Sehili et al. [11]. Further increase in the weight of the catalyst showed a negative effect. As the weight of the catalyst increased, the number of phenol molecules adsorbed were increased owing to an increase in the number of ZnO particles. So the rate was enhanced. The decrease in the initial rate beyond the catalyst loading of 2.0 g/L may be attributed to the screening effect of excess catalyst particles in the solution.

3.3. Effect of pH

The role of pH on the rate of photocatalytic degradation was studied in the pH range 3.5–9. The initial rates of photodegradation, expressed in terms of first-order rate constants were determined. It was observed that phenol degradation was favourable at mild acidic and neutral solutions. Similar

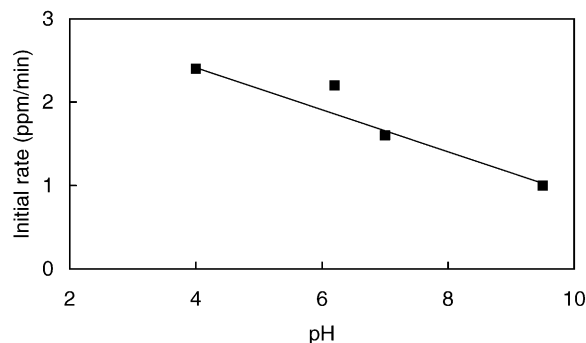


Fig. 3. Effect of pH on the initial rate of photocatalytic degradation of *p*-chlorophenol. [*p*-Chlorophenol] = 50 ppm; temperature = 30.0 ± 0.1 °C; catalyst = ZnO (2.0 g/L); incident wavelength = 254 nm; absorbance measured at 500 nm.

results were reported by Wei and Wan [12] for the photodegradation of phenol on TiO₂ surface. In the case of chlorophenols it was observed that the rate of degradation was enhanced at lower pH (as shown in Fig. 3) values. At higher pH, chlorophenols exist as negatively charged chlorophenolate anion. Higher removals of chlorophenols in acidic conditions may be attributed to the increased amount of undissociated chlorophenol species adsorbed on the catalyst surface. The zero point charge (zpc) of ZnO was reported as 8 [13]. When the pH > p*H*_{zpc}, the surface of ZnO is negatively charged and chlorophenolate anions may be repelled, resulting in no adsorption of chlorophenols. Similar results were reported by Ku et al. [14] in the photodegradation of *o*-chlorophenol on TiO₂.

3.4. Effect of phenol concentration

The photocatalytic degradation of the phenol and chlorophenols at different initial concentrations in the range 40–100 ppm was investigated. Fig. 4 shows the degradation of phenol as a function of time. The time required for complete mineralisation increased from 70 to 90 min when the initial

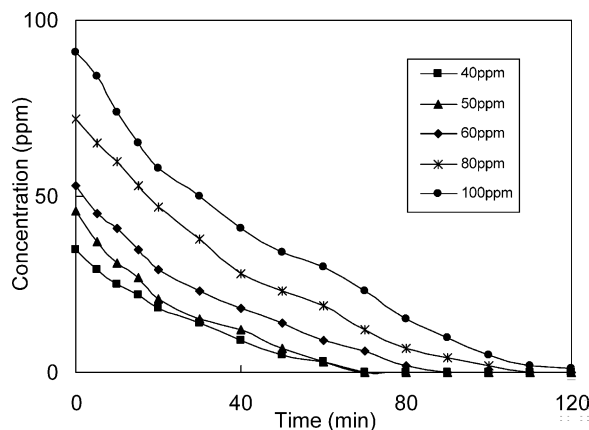


Fig. 4. Effect of concentration on the photocatalytic degradation of phenol. Catalyst = ZnO (2.0 g/L); pH = 7.0 ± 0.1; temperature = 30.0 ± 0.1 °C; incident wavelength = 254 nm; absorbance measured at 500 nm.

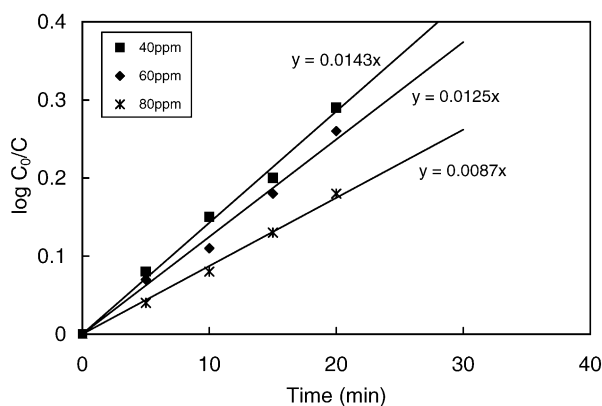


Fig. 5. Plot of $\log C_0/C$ vs. time for photocatalytic degradation of phenol. Catalyst = ZnO (2.0 g/L); pH = 7.0 ± 0.1 ; temperature = 30.0 ± 0.1 °C; incident wavelength = 254 nm; absorbance measured at 500 nm.

concentration was increased from 40 to 60 ppm. The initial rate increased from 1.2 to 1.8 ppm/min as the concentration increased from 40 to 50 ppm. Decrease in the initial rate was observed with further increase in concentration. In the case of chlorophenols, the initial rate increased with increase in the initial concentration range 40–60 ppm and decreased with further increase in concentration.

3.5. Kinetic analysis

Under constant conditions of pH, catalyst weight and photon flux the effect of variation of concentration of the phenols on its photodegradability were studied. Photocatalytic degradation of phenols at low concentrations obeyed pseudo first-order kinetics. A fairly linear relation between phenol concentration and irradiation time was observed as shown in the plot of $\log C_0/C$ versus time (vide Fig. 5). The computed data on the pseudo-first-order rate constants ' k ' at different concentrations of the phenol are given in Table 1. The rate constant values were found to decrease with increase in phenol concentration [15]. Similar results were obtained for the degradation of chlorophenols. Further evidence for the kinetic data was obtained from the studies of the phototransformation of chlorophenols on ZnO by Sehili et al. [11] and Lemaire et al. [16]. The reaction was reported to occur via

hydroxylation and the intermediates adsorbed on ZnO were found to decrease the rate of oxidation of the target compounds namely chlorophenols.

3.6. Reusability of ZnO catalyst

Reusability of ZnO for the degradation of phenols by photocatalysis was evaluated. The solutions resulting from the photocatalytic degradation of phenols was filtered, washed and the photocatalyst was dried. The dried catalyst samples were used for the degradation of phenols, employing similar experimental conditions. The filtrate was subjected to AAS analysis to assess the loss of Zn^{2+} ions to solution as a result of dissolution of ZnO. Under the present investigation it was observed that dissolution of ZnO was found to be negligible (0.04% loss of zinc was observed during two hours of reaction time). The percentage reduction in the rates of photocatalysis mediated by ZnO after five cycles for the degradation of phenols was found to be 3, 4 and 4.5 for phenol, *o*-chlorophenol and *p*-chlorophenol, respectively. ZnO samples showed considerably reproducible photocatalytic activity up to five cycles for the degradation of all phenols. The loss in activity and loss of zinc as zinc ions was more pronounced only after the fifth cycle of reuse.

4. Conclusions

Phenol and chlorophenols were completely mineralised by photocatalytic degradation on ZnO surface. The degradation rate of phenol was favourable in the neutral pH range. However, *o*-chlorophenol and *p*-chlorophenol was found to undergo degradation at a faster rate at lower pH values. Experimental results indicated that initial rate of photodegradation increased with increase in catalyst weight up to an optimum loading. Further increase in the catalyst weight showed a negative effect. The photocatalytic degradation of phenols were studied over wide concentration range 40–100 ppm. The initial rates of photodegradation were high at lower concentration range and it decreased with increase in concentration. The degradation of phenols on ZnO surface was found to follow first-order kinetics. The apparent rate constant values obtained was found to decrease with increase in the initial

Table 1
Rate constant values for the degradation of phenol

Time (min)	Concentration (ppm)	$\log C_0/C$	Concentration (ppm)	$\log C_0/C$	Concentration (ppm)	$\log C_0/C$
Before adsorption	40		60		80	
0	35	0.00	53	0.00	72	0.00
5	29	0.08	45	0.07	65	0.04
10	25	0.15	41	0.11	60	0.08
15	22	0.20	35	0.18	53	0.13
20	18	0.30	29	0.26	47	0.18
First-order rate constant values, k (min^{-1})	0.0333 \pm 0.0001		0.0287 \pm 0.0001		0.0200 \pm 0.0001	

pH = 7.0 ± 0.1 ; Temperature = 30.0 ± 0.1 °C; Catalyst = ZnO (2.0 g/L); Absorbance measured at 500 nm; Incident wavelength = 254 nm.

concentration. ZnO was quite stable and undergoes photo-corrosion only to a negligible extent. The photocatalytic activity of ZnO was retained even up to five cycles.

References

- [1] R.W. Matthews, S.R. McEvoy, *J. Photochem. Photobiol. A: Chem.* 64 (1992) 231.
- [2] K.R. Krijgheld, A. van der Gen, *Chemosphere* 15 (1986) 825.
- [3] G. Chen, L. Lei, P.L. Yue, *Ind. Eng. Chem. Res.* 38 (1999) 1837.
- [4] M.B. Borup, E.J. Middlebrooks, *Water Sci. Technol.* 19 (1987) 380.
- [5] F. Gahr, F. Hermanutz, W. Oppermann, *Water Sci. Technol.* 30 (1994) 255.
- [6] G. Al-Sayyed, J.C. D'Oliveria, P. Pichat, *J. Environ. Sci. Health A* 4 (1993) 28.
- [7] J.C. D'Oliveria, G. Al-Sayyed, P. Pichat, *J. Environ. Sci. Technol.* 24 (1990) 990.
- [8] A.A. Khodja, T. Sehili, J.F. Pilichowski, P. Boule, *J. Photochem. Photobiol. A: Chem.* 141 (2001) 231.
- [9] M.B. Ettinger, C.C. Ruchhoft, R.J. Lishka, *Anal. Chem.* 23 (1951) 1783.
- [10] R.W. Matthews, M. Abdullah, G.K.C. Low, *Anal. Chim. Acta* 233 (1990) 171.
- [11] T. Sehili, P. Boule, J. Lemaire, *J. Photochem. Photobiol. A: Chem.* 50 (1989) 117.
- [12] T.-Y. Wei, C.-C. Wan, *Ind. Eng. Chem. Res.* 30 (1991) 1293.
- [13] J. Peral, X. Domnech, *J. Chem. Technol. Biotechnol.* 53 (1992) 93.
- [14] Y. Ku, R.-M. Leu, K.-C. Lee, *Water Res.* 30 (1996) 2569.
- [15] R.W. Matthews, *Water Res.* 25 (1991) 1169.
- [16] J. Lemaire, P. Boule, T. Sehili, C. Richard, in: E. Pellizetti, M. Schiavello (Eds.), *Photochemical Conversions and Storage of Solar Energy*, Kluwer Academic Publishers, 1991, p. 477.