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Advanced Oxidation of Phenol by Ultraviolet Irradiation in Aqueous System

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Abstract: The photodegradation of phenol was studied in a batch reactor configuration illuminated with a 400 W medium pressure mercury lamp. The effects of parameters such as pH, kinetic constants and initial phenol concentration on the photolytic degradation and toxicity assay have been studied. The experimental results have shown that lower pH and lower concentration of phenol favor the phenol degradation. The disappearance of phenol in each case approximately obeyed first-order kinetics with the apparent first-order decay constant increasing with decreasing solute concentration. Bioassay tests showed that phenol were toxic to *D. magna* and so resulted in quite low LC_{50} values. Comparison of Toxicity Units (TU) between phenol and effluent toxicity has shown that TU value for effluent was 2.18 times lower than that obtain to phenol. Thus, photolysis able to eliminate the toxicity of by-products formed during the degradation of phenol.

Key words: Photodegradation, ultraviolet, phenol, bioassay, daphnia

INTRODUCTION

Phenol is one of the most abundant pollutants in industrial wastewater, i.e., chemical, petrochemical, paint, textile, pesticide plants etc (Alnaizy and Akgerman, 2000; Maleki *et al.*, 2005). The contamination of bodies of water with phenol is a serious problem in terms of environmental considerations due to its high toxicity. So far, several treatment methods such as chemical oxidation, biological treatment, wet oxidation, ozonolysis and activated carbon adsorption have been proposed for the removal of phenol from industrial effluents. However, each of these methods has some disadvantages. In recent years a new treatment technology, know as Advanced Oxidation Processes (AOPs), capable of the destruction of a wide range of organic compounds was developed (Akbal and Nuronar, 2003; Han *et al.*, 2004). One of these technologies is photolysis. This method is based on supplying energy to the chemical compounds as radiation, which is absorbed by reactant molecules that can pass to excited states and have sufficient time to promote reactions (Esplugas *et al.*, 2002). Direct photolysis has been always considered as one possible alternative because it is possible for molecules of most organic compounds to transform, to cleave bonds and even to undergo complete destruction in the presence of Ultraviolet (UV) irradiation (Bolton and Carter, 1994). In addition, UV irradiation causes dissociation of the water molecule and formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants (Wu *et al.*, 2001; Han *et al.*, 2004).

The main objective of this study is to focus on the degradation of phenol by the ultraviolet irradiation. The influences of various factors, such as initial pH, initial phenol concentrations and kinetic constant on the UV degradation of phenol have also been studied. Also, we determined the LC_{50} (the statistically determined concentration that causes 50% mortality in a given exposure period) of the aqueous phenol solution before and after photolysis (reaction by-products) using Daphnia magna as the test organisms. Such data can be considered as an indication of acute toxicity reduction resulting from treatment.

MATERIALS AND METHODS

The photodegradation studies were carried out in a batch reactor system. The photoreactor consist of a 2000 mL cylindrical glass body. A 400 W medium pressure mercury lamp (90 μW cm^{-2}, 7 cm long) surrounded by quartz jacket was located in the center of the reactor. The lamp bandwidth was in the range of 185-800 nm. The reactor walls were covered by aluminum foil to avoid release of radiation. The temperature of the reactor contents was maintained at 30°C. The apparatus is open to air. The initial concentration of phenol was in the range of 1-100 mg L^{-1}. The photolysis reactions were carried out for 2 h. The pH value of the sample was adjusted to a constant value of 3. Phenol analysis was done according to the direct colorimetric method using 4-aminoantipyrine (APHA, 1995). Color was determined

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spectrophotometrically at 500 nm using UV/VIS Spectrometer (Lambada 25 Perkin Elmer, Shelton). Phenol (analytical grade) was obtained from Merck. All other chemicals were of at least 99% purity and were used without further purification. Deionized water was used for preparing all aqueous solutions.

Acute toxicity of phenol and the toxic effects of its degradation products after ultrasonic irradiation were studied with *Daphnia magna* test according to Standard Methods (APHA, 1995). Primary daphnia was caught from their living site, then, one of them was cultured alone, after infants of primary daphnia were used for culture in large amounts. Dilution water which was used for tests was groundwater and the general characteristics were as follows: pH 8.1, total hardness 130 mg L^{-1} as $CaCO_3$, total alkalinity 306 mg L^{-1} as $CaCO_3$, electrical conductivity 1197 μS cm^{-1}, calcium 36 mg L^{-1}, magnesium 10 mg L^{-1}, chloride 75 mg L^{-1}, sulfate 147 mg L^{-1} and nitrate 44 mg L^{-1}.

D. magna was maintained in a 10 L glass vessel containing culture medium in a temperature-controlled condition of 22±2°C and a 12/12 light-dark cycle. Culture medium was made of sheep manure. *D. magna* was fed with yeast at a concentration of 100 mg L^{-1} every two day.

For running the experiment, 10 infants (age<24h) were exposed to the test volume of 100 mL in a 250 mL glass beaker. The initial concentration of phenol was 100 mg L^{-1} and the concentration of phenol in mixture was 5 mg L^{-1} after 90 min sonication (according to percent of phenol conversion from Fig. 1). Experimental concentrations tested were, 100, 75, 50, 40, 30, 20, 10 and 5% of ultrasonic effluent diluted with dilution water. After the setting periods of 24, 48, 72 and 96 h, LC_{50} values were calculated for toxicity tests by use of the special computer program [PROBIT] (Goi *et al.*, 2004). Finally, for a certain comparison, the toxicity values were converted to Toxic Units (TU). The TU of an effluent or mixture is equal to 100% divided by the LC_{50} of that effluent or mixture (Jin *et al.*, 1999; Guerra, 2001). All experiments were run in triplicate to ensure reproducibility.

RESULTS AND DISCUSSION

The photolysis degradation of the phenol at different initial concentration in the range 1-100 mg L^{-1} was investigated. Figure 1 shows the degradation of phenol as function of time. The time required for complete degradation increased from 3 to 120 min when the initial concentration was increased from 1 to 100 mg L^{-1}. Chun *et al.* (2000) have reported 96% removal for phenol (C_0 = 100 mg L^{-1}) by a bath UV equipment (500 W,
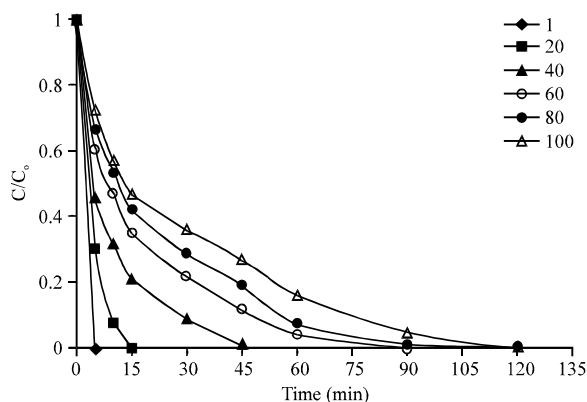

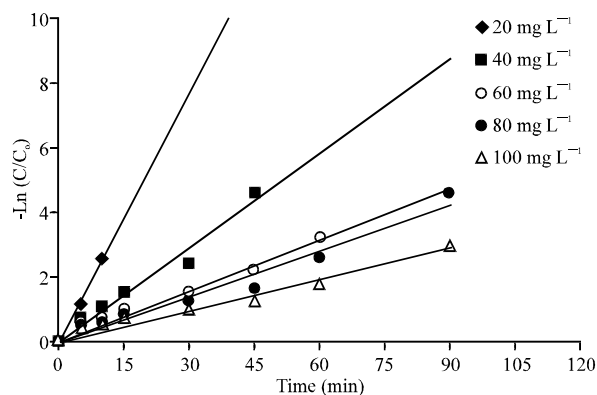Fig. 1: Effect of concentration on the photodegradation of phenol

Fig. 2: Plot of Ln C/C_0 vs. time for photodegradation of phenol

λ>200 nm, high pressure) during 60 min irradiation (Chun *et al.*, 2000). Also, 92% degradation has been reported by Wu *et al.* (2001) by means of UV at 254 nm (9 W) for initial phenol concentration of about 1.06×10^{-4} mmol L^{-1} during 60 min (Wu *et al.*, 2001).

It can be concluded that UV light had high potential to degrade phenol. This may be because the main oxidant responsible for the oxidation of phenol is the highly reactive hydroxyl radical that produce very much during the irradiation of solution using medium pressure mercury lamp (400 W). This is in agreement with results obtained later (Han *et al.*, 2004). Also, supplying energy to the chemical compounds as radiation, which is absorbed by reactant molecules that can pass to excited states and have sufficient time to promote reactions is high at this condition.

Figure 2 shows that the rates of degradation of the phenol at the initial period of the reaction are rapid but the rate slows down later on. The initial rates decreased from 0.255 to 0.034 min^{-1} as the concentration increased from
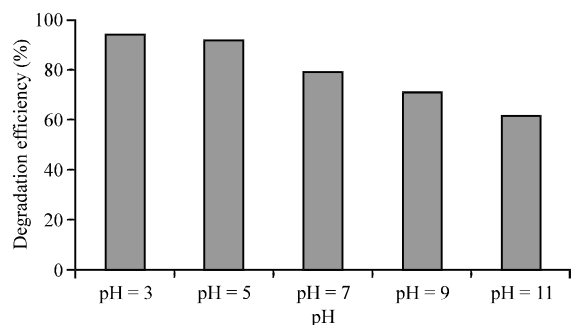
Fig. 3: Effect of pH on phenol photodegradation (Phenol concentration = 60 mg L^{-1}, Time = 60 min)

Table 1: First order kinetic values for phenol photodegradation at different initial phenol concentrations

Phenol concentration (mg L^{-1})	20	40	60	80	100
Rate constant (min^{-1})	0.255	0.097	0.053	0.047	0.034
Correlation Coefficient	0.99	0.96	0.97	0.97	0.97

Table 2: Toxicity data for phenol solution and photolysis effluent

Test sample	Phenol				Photolysis effluent			
Time (day)	24	48	72	96	24	48	72	96
LC_{50} (% v/v)	33.1	19.5	18.1	15.70	66.5	42.4	32.3	22.3
Toxicity Unit (TU)	3.02	5.13	5.52	6.36	1.5	2.35	3.09	4.35

20 to 100 mg L^{-1}. In the initial period of the reaction, rate is higher because of the presence of the high concentration of produced oxidants (OH• and H_2O_2) and the phenol. Afterwards, a number of intermediates are formed with compete with phenol to react with available oxidants and vice versa. Similar results have been reported by Lathasree *et al.* (2004).

First order kinetics with respect to phenol concentrations were found to fit all the experimental data and first order rate constants were estimated (Fig. 2), as is commonly found in the literature (Esplugas *et al.*, 2002; Akbal and Nuronar, 2003; Lathasreea *et al.*, 2004). The rate of disappearance of phenol may be described by following equation:

$$r_{uv} = -\frac{dc}{dt} = kc$$

Where, r_{uv}, k and C are the photochemical reaction rate of phenol, first order constant and phenol concentration, respectively. Table 1 shows the major calculated reaction rate coefficients.

Figure 3 shows the degradation of phenol by the photolysis process at different pH. It is clearly shown that lower pH values favored the phenol degradation. The degradation of phenol attained 94% at pH 3, 91.5% at pH 5, 71% at pH 9 and 62% at pH 11. For photolysis of phenol other researcher have reported that the rate of degradation under acid condition were faster than in alkaline condition (Wu *et al.*, 2001; Esplugas *et al.*, 2002; Bali *et al.*, 2003).

In the present study, the ionic species of phenol is predominant when the pH exceeds 10.0 (equal to pKa value of phenol at 25°C), but the molecular species predominates when pH is less than the pKa. The fraction in the molecular state of phenol was larger when the pH was smaller. Therefore, it has been concluded that photolysis of phenol are pH dependent and increases when more acid conditions are carried out. This might be the reason why lower pH favored the ultrasonic degradation of phenol.

It is found that daphnia is the most sensitive organism to phenol (Guerra, 2001). So bioassay was done using daphnia. The acute toxicity of phenol and mixture of its photodegradation by-products is presented in Table 2.

Results showed that phenol was toxic to *D. magna* and resulted in quite low LC_{50} values (LC_{50} 96 h of 15.7% v/v). As can be seen from Table 2, 24 and 48 h LC_{50} (% v/v) values ranged from 33.1 and 19.5 for phenol to 66.5 and 42.4 for effluent mixture, respectively. Comparison of Toxicity Unit (TU) between phenol and effluent toxicity showed that TU value for effluent was 2.18 times lower than that obtain to phenol (according to 48 h LC_{50}). Thus, photolysis was able to eliminate the toxicity of by-products formed during the degradation of phenol. This reduction was achieved by phenol degradation and transformation of aromatics by-products to aliphatic products by ring opening reactions (Goi *et al.*, 2004). However, the end-product solutions were somewhat more toxic than would be predicted from the known concentration of initial phenol. This situation was reported by Guerra for phenolic compound decomposition due to production of hydroquinone, benzoquinone and catechol (Guerra, 2001). Data of this study showed that bioassay can be used as a suitable method for evaluation of the efficiency of treatment procedures by ultraviolet waves.

CONCLUSIONS

This study shows the potentialities of UV radiation in water and wastewater treatment. Photolysis can be an alternative treatment method for those pollutants resistant to conventional methods. Photodegradation can be used for complete decomposition of phenol. First order expression can be used to describe photodegradation reaction of phenol. It was found that The rate of phenol degradation increased with decreasing solution pH and phenol concentration. The data point to the possible use of photodegradation as an effective method for completely removal of phenol.

Despite high percentages of phenol removal, the samples taken from the batch reactor at the end of reaction had a low toxicity. Thus, the mineralization was incomplete and intermediate products existed in the low concentration. Although some of these intermediates such as hydroquinone are very toxic but this low toxicity may be explained by the produce of intermediates in the low concentration. Hence, the effluent toxicity was less than the toxicity of phenol. Thus, photolysis was able to eliminate the toxicity of by-products formed during the degradation of phenol. Of course the toxicity of the primary intermediates threatens human health; there is need to sufficient irradiation time to make the intermediates degrade as completely as possible.

ACKNOWLEDGMENTS

NOMENCLATURE

C   Phenol concentration at time t, mg L^{-1}
C_0 Initial Phenol concentration, mg L^+
k   First order constant, min^{-1}
I   Intensity of ultraviolet radiation, W cm^{-2}
LC_{50} The statistically determined concentration that causes 50% mortality in a given exposure period, mg L^{-1}
R^2 Regression coefficient
r_{uv} Photochemical reaction rate of phenol, mg L^{-1} min^{-1}
TU   Toxicity Unit,%

REFERENCES

Akbal, F. and A. Nuronar, 2003. Photocatalytic degradation of phenol. Environ. Monit. Assess., 83: 295-302.

Alnaizy, R. and A. Akgerman, 2000. Advanced oxidation of phenolic compounds. Adv. Environ. Res., 4: 233-244.

APHA., AWWA. and WEF., 1995. Standard Methods for the Examination of Water and Wastewater. 19 Edn, Washington.

Bali, U., E.C. Catalkaya and F. Sengul, 2003. Photochemical degradation and mineralization of phenol: A comparative study. J. Environ. Sci. Health Envir., 38: 2259-2275.

Bolton, J.R. and S.R. Carter, 1994. Homogeneous photodegradation of pollutants in contaminated water: An introduction in aquatic and surface photochemistry. Lewis Publishers, Boca Raton, USA., pp: 467-490.

Chun, H., W. Yizhong and T. Hongxiao, 2000. Destruction of phenol aqueous solution by photocatalysis or direct photolysis. Chemosphere, 41: 1205-1209.

Esplugas, S., J. Gimenez, S. Contreras, E. Pascual and M. Rodriguez, 2002. Comparison of different advanced oxidation processes for phenol degradation. Water Res., 36: 1034-1042.

Goi, A., M. Trapido and T. Tuhkanen, 2004. A study of toxicity, biodegradability and some by-products of ozonised nitrophenols. Adv. Environ. Res., 8: 303-311.

Guerra, R., 2001. Ecotoxicological and chemical evaluation of phenolic compounds in industrial effluents. Chemosphere, 44: 1737-1747.

Han, W., W. Zhu, P. Zhang, Y. Zhang and L. Li, 2004. Photocatalytic degradation of phenols in aqueous solution under irradiation of 254 and 185 nm UV light. Catal. Today, 90: 319-324.

Jin, H., X. Yang, D. Yin and H. Yu, 1999. A case study on identifying the toxicant in effluent Discharged from a Chemical Plant. Mar. Pollut. Bull., 39: 122-125.

Lathasreea, S., R.A. Nageswara, B. SivaSankarb, V. Sadasivamb and K. Rengarajb, 2004. Heterogeneous photocatalytic mineralisation of phenols in aqueous solutions. J. Mol. Catal. A-CHEM., 223: 101-105.

Maleki, A., M.A. Zazoli and A. Eslami, 2005. Adsorption of phenol by commercial powdered activated carbon in aqueous solution. Al-Haitham. J. Sci. Technol., 1: 73-78.

Wu, C., X. Liu, D. Wei, J. Fan and L. Wang, 2001. Photosonochemical degradation of phenol in water. Water Res., 35: 3927-3933.