

## Photo-oxidation of phenol in aqueous solution: Toxicity of intermediates

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(Received 4 March 2006 • accepted 1 September 2006)

**Abstract**—The photodegradation of phenol was studied in a batch reactor system illuminated with a 400 W medium pressure mercury lamp. The effects of parameters such as pH, reaction time 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 rate constants increasing with decreasing solute concentration. Bioassay tests showed that phenol was toxic to *Daphnia magna* and so resulted in quite low LC<sub>50</sub> 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 obtained for phenol. Thus, photolysis is able to decrease the toxicity of by-products formed during the degradation of phenol.

Key words: Photodegradation, Ultraviolet, Phenol, Bioassay

### 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; Wu et al., 2002; 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, known as Advanced Oxidation Processes (AOPs), capable of the destruction of a wide range of organic compounds was developed [Akbal and Nuronar, 2003; Wu et al., 2002; 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; Xiaoli et al., 2003; Lee et al., 2006]. 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; Lee et al., 2003; Han et al., 2004].

The main objective of this work 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 reaction time on the UV degradation of phenol, have also been studied. Also, we determined the LC<sub>50</sub> (the statistically determined concen-

tration that causes 50% mortality in a given exposure period) of the aqueous phenol solution before and after photolysis (reaction by-products) using *D. magna* as the test organisms. For certain comparisons, the toxicity values were converted to toxic units (TU). 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 consists of a 2,000 ml cylindrical glass body. A 400 W medium pressure mercury lamp ( $I = 90 \mu\text{W cm}^{-2}$ , 7 cm long) surrounded by a 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<sup>-1</sup>. 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 spectrophotometrically at 500 nm by using a UV/VIS Spectrometer (Lambda 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 *D. magna* test according to Standard Methods [APHA, 1995]. Primary *D. magna* was caught from their living site, then one of them was cultured alone, after infants of primary *D. magna* were used for culture in large amounts. Dilution water which was used for tests was ground-water and the general characteristics were as follows: pH 8.1, total hardness 130 mg L<sup>-1</sup> as CaCO<sub>3</sub>, total alkalinity 306 mg L<sup>-1</sup> as CaCO<sub>3</sub>,

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electrical conductivity  $1,197 \mu\text{S cm}^{-1}$ , calcium  $36 \text{ mg L}^{-1}$ , magnesium  $10 \text{ mg L}^{-1}$ , chloride  $75 \text{ mg L}^{-1}$ , sulfate  $147 \text{ mg L}^{-1}$  and nitrate  $44 \text{ mg L}^{-1}$ .

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

For running the experiment, 10 infants (age < 24 h) were exposed to a test volume of 100 mL in a 250 mL glass beaker. The initial concentration of phenol was  $100 \text{ mg L}^{-1}$  and the concentration of phenol in mixture was  $5 \text{ mg L}^{-1}$  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 hours,  $\text{LC}_{50}$  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  $\text{LC}_{50}$  of that effluent or mixture [Jin et al., 1999; Guerra, 2001].

$$\text{TU} = \frac{100\%}{\text{LC}_{50}}$$

All experiments were run in triplicate to ensure reproducibility.

## RESULTS AND DISCUSSION

The photolysis degradation of phenol at different initial concentrations in the range 1-100  $\text{mg L}^{-1}$  was investigated. Fig. 1 shows the degradation of phenol as a 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  $\text{mg L}^{-1}$ . Chun et al. [2000] have reported 96% removal for phenol ( $C_0=100 \text{ mg L}^{-1}$ )

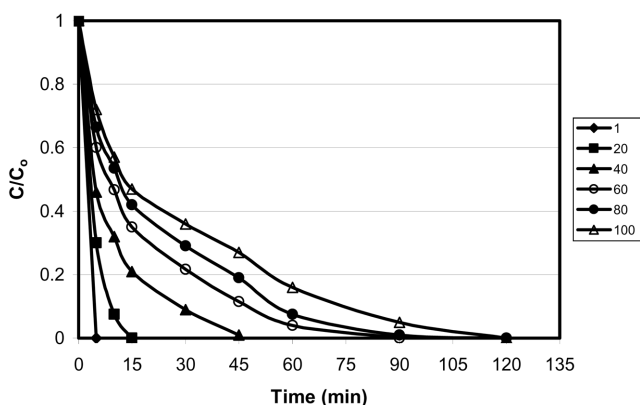


Fig. 1. Effect of the initial concentration of phenol on the photodegradation.

by a bath UV equipment (500 W,  $\lambda > 200 \text{ nm}$ , high pressure) during 60 min irradiation [Chun et al., 2000]. Also, 92% degradation has been reported by Wu [2001] by means of UV at 254 nm (9 W) for initial phenol concentration of about  $1.06 \times 10^{-4} \text{ mmol L}^{-1}$  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 was produced very much during the irradiation of solution by using a medium pressure mercury lamp (400 W). This is in agreement with results obtained later [Han et al., 2004].

Fig. 1 shows that the rate of degradation of the phenol at the initial period of the reaction is rapid but it slows down later on. The initial rates decreased from 0.255 to  $0.034 \text{ min}^{-1}$  as the concentration increased from 20 to  $100 \text{ mg L}^{-1}$ . In the initial period of the reaction, the rate is higher because of the presence of the high concentration of produced oxidants ( $\text{OH}^\bullet$  and  $\text{H}_2\text{O}_2$ ) and the phenol. Afterwards, a number of intermediates are formed which 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 was 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; Lathasree et al., 2004]. The rate of disappearance of phenol may be described by following equation:

$$r_{\text{av}} = -\frac{dc}{dt} = kc$$

Where,  $r_{\text{av}}$ ,  $k$  and  $C$  are the photochemical reaction of phenol, rate constant and phenol concentration, respectively. Table 1 shows the major calculated rate constant.

Fig. 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

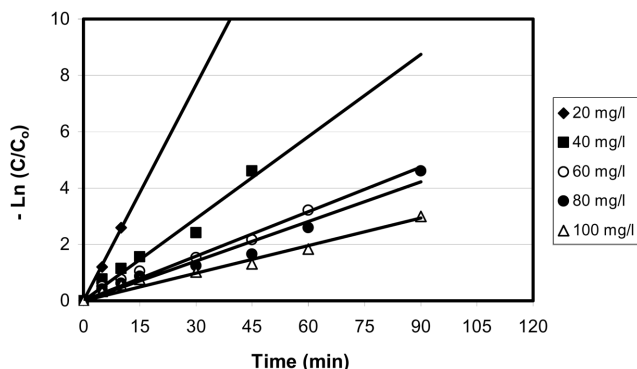


Fig. 2. Plot of  $-\ln C/C_0$  vs. time for photodegradation of phenol.

Table 1. First order rate constant for phenol photodegradation at different initial phenol concentrations

Initial phenol concentration ( $\text{mg L}^{-1}$ )	20	40	60	80	100
Rate constant ( $\text{min}^{-1}$ )	0.255	0.097	0.053	0.047	0.034
Correlation coefficient	0.99	0.96	0.97	0.97	0.97

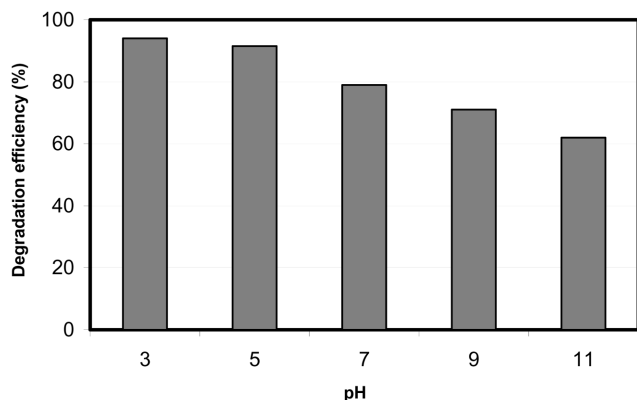


Fig. 3. Effect of pH on phenol photodegradation (Initial phenol concentration=60 mg L<sup>-1</sup>, Time= 60 min).

of phenol other researchers have reported that the rate of degradation under acid condition was faster than that 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 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 pH was smaller. Therefore, it has been concluded that photolysis of phenol is pH dependent and increases under more acidic conditions. This might be the reason why lower pH favored the ultrasonic degradation of phenol.

It is found that *D. magna* is the most sensitive organism to phenol [Guerra, 2001]. So bioassay was done by using *D. magna*. 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<sub>50</sub> values (96 h-LC<sub>50</sub> of 15.7% v/v). As can be seen from Table 2, 24 and 48 h LC<sub>50</sub> (% 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 obtained with phenol (according to 48 h-LC<sub>50</sub>). Thus, photolysis was able to decrease the toxicity of by-products formed during the degradation of phenol. This reduction was achieved by phenol degradation and transformation of aromatic 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.

Table 2. Toxicity data for phenol solution and photolysis effluent

Test sample	Phenol				photolysis effluent			
	24	48	72	96	24	48	72	96
Time (day)	24	48	72	96	24	48	72	96
LC <sub>50</sub> (% v/v)	33.1	19.5	18.1	15.7	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

## CONCLUSION

This study shows the potential of UV radiation in water and wastewater treatment. Photolysis can be an alternative treatment method for those pollutants instead of 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 imply the possible use of photodegradation as an effective method for complete 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. Therefore, it has been concluded that photolysis was able to decrease the toxicity of by-products formed during the degradation of phenol. Of course, the toxicity of the primary intermediates threatens human health; there is a need of sufficient irradiation time to make the intermediates degrade as completely as possible.

## ACKNOWLEDGMENTS

The authors would like to thank Tehran University of Medical Sciences for their financial supported. We would also thank laboratory staff of the Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences for their assistance in the handling of experiments.

## NOMENCLATURE

C	: phenol concentration at time t [mg L <sup>-1</sup> ]
C <sub>0</sub>	: initial phenol concentration [mg L <sup>-1</sup> ]
k	: first order constant [min <sup>-1</sup> ]
I	: intensity of ultraviolet radiation [W cm <sup>-2</sup> ]
LC <sub>50</sub>	: the statistically determined concentration/dilution that causes 50% mortality in a given exposure period [mg L <sup>-1</sup> or ml L <sup>-1</sup> ]
R <sup>2</sup>	: regression coefficient
r <sub>w</sub>	: photochemical reaction rate of phenol [mg L <sup>-1</sup> min <sup>-1</sup> ]
TU	: toxicity unit [%]

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