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DEGRADATION AND TOXICITY REDUCTION OF PHENOL BY ULTRASOUND WAVES

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ABSTRACT. The effects of parameters such as pH, kinetic constants and initial phenol concentration on the sonochemical degradation of phenol and toxicity assay were studied. The experimental results showed that lower pH and lower concentration of phenol favor the phenol degradation. But the rates of phenol degradation under sonication have always been quite low. It is found that the rate of ultrasonic degradation of phenol for initial concentration of 1 mg/L is 0.018 min^{-1} but later it reduces with increasing of phenol initial concentration substantially and the experimental data fitted well with pseudo first-order reaction rate equation. Bioassay tests showed that phenol was toxic to *Daphnia magna* and so resulted in quite low LC_{50} values. Comparison of toxicity units (TU) between phenol and effluent toxicity showed that the TU value for effluent was 1.21 times lower than that obtained for phenol solely. Thus, the toxicity of metabolites formed during the degradation of phenol is lower than the toxicity of phenol itself.

KEY WORDS: Phenol, Ultrasound, Sonochemistry, Toxicity assay

INTRODUCTION

In recent years, considerable interest has been shown in the application of ultrasound as an advanced oxidation process for the treatment of hazardous contaminants in water. Sonochemistry has been demonstrated as a promising method for the destruction of aqueous pollutants [1, 2]. The chemical effects of ultrasound (US) are due to the phenomenon of acoustic cavitation [3]. Sound is passed through a liquid as a wave consisting of alternating compression and rarefaction cycles. If the rarefaction wave has a sufficiently high negative pressure, it can overcome the intermolecular forces bonding fluid. As a result, the molecules are torn apart from each other and tiny microbubbles will be created. These microbubbles gradually grow during compression and rarefaction cycles until they reach a critical size. Subsequent compression causes these cavities to collapse almost instantaneously, with a large amount of energy being released [3]. Thus, sonochemical destruction of pollutants in aqueous phase generally occurs as the results of imploding cavitation bubbles and involves several reaction pathways and zones such as pyrolysis inside the bubble and/or at the bubble-liquid interface and hydroxyl radical-mediated reactions at the bubble-liquid interface and/or in the liquid bulk [4].

Important organic contaminants in industrial wastewaters are phenolic compounds and phenols. Phenol is 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, paint stripping operations, pesticides, medications, pharmaceuticals and even from food-processing industries [5-8]. If present in even small quantities (of the order of a few mg/L), phenol causes toxicity and foul odor to the water. It has been listed as the priority pollutant in the list of EPA (USA). Most of the countries specify the maximum allowable concentration of phenol in the effluent streams to be less than 1 mg/L [9].

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The main objective of this work is to focus on the degradation of phenol by ultrasonic equipment operating at 130 kHz. The influences of various factors, such as initial pH and initial phenol concentrations on the ultrasonic degradation of phenol were also studied. Also, we determined the LC_{50} (the statistically determined concentration that causes 50 % mortality in a given exposure period) of an aqueous phenol solution before and after sonication (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.

EXPERIMENTAL

Phenol (analytical grade) was obtained from Merck. All other chemicals add company from which they were purchased were of at least 99 % purity and were used without further purification. Deionized water was used for preparing all aqueous solutions.

In each case, the reaction volume was 2 L and the initial concentration of phenol was in the range of 1-100 mg/L. The ultrasonic reactions were carried out for 300 min. The pH of samples was changed by condense sulfuric acid and sodium hydroxide for determination of pH effect on sonodegradation of phenol and finally the pH value of the sample was adjusted to a constant value of 3. Sonication was achieved at frequency of 130 kHz (500 W) with an ultrasonic generator (Elma TI-H-5, Germany) with two piezoelectric transducers having a diameter of 5 cm fixed at the bottom of the vessel. Dimensions of ultrasonic bath were 250 cm x 130 cm x 150 cm. Ultrasonic energy dissipated in the reactor was set at 2.5 W cm^{-2} through the calorimetric method. The apparatus was open to air. The solution was irradiated with ultrasound for 15 min and then sonication was stopped for the next 10 min. This process was continued till the solution was irradiated for a predetermined time (300 min). The temperature of the solution was kept constant at 32 ± 2 °C using cold water circulation around the beaker. Phenol analysis was done according to the direct colorimetric method using 4-aminoantipyrine method [10]. Color was determined spectrophotometrically at 500 nm after filtrate samples through Whatman filter paper using UV/VIS Spectrometer (Lambada 25 Perkin Elmer, Shelton). HPLC was also used for the analysis of degradation products.

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 [10]. 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 as $CaCO_3$, total alkalinity 306 mg/L as $CaCO_3$, electrical conductivity 1197 µS cm^{-1}, calcium 36 mg/L, magnesium 10 mg/L, chloride 75 mg/L, sulfate 147 mg/L and nitrate 44 mg/L.

Daphnia magna was maintained in a 10 L glass vessel containing culture medium in a temperature-controlled condition of 22 ± 2 ºC and a 12/12 light-dark cycle. Culture medium was made of sheep manure. *Daphnia magna* was fed with yeast at a concentration of 100 mg/L every two days.

For running the experiment, 10 infants (age < 24 h) were exposed to the test volume of 100 mL in a 250 mL glass beaker. The initial concentration of phenol was 100 mg/L and the concentration of phenol in mixture was 89 mg/L after 120 min sonication (according to percent of phenol conversion from Figure 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, LC_{50} values were calculated for toxicity tests by use of the special computer program (PROBIT) [11]. 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 [12, 13].

$$TU = \frac{100\%}{LC_{50}}$$

All experiments were run in triplicate to ensure reproducibility.

RESULTS AND DISCUSSION

Phenol degradation was for 300 min irradiation time. Figure 1 shows the change in concentration of phenol over time. Only 23 % degradation of phenol was observed after 300 min of sonication of 100 mg/L initial phenol concentration. This may be because phenol is hydrophilic in nature. Phenol is a moderately soluble compound in water (C_w^{sat} = 0.63 M) with a relatively low vapor pressure (4.6 x 10^{-4} atm) and Henry's constant of phenol (4.0 x 10^{-4} L atm M^{-1}). These physiochemical properties preclude significant concentrations of phenol molecule diffusing into the vapor phase of the acoustic cavitation bubbles, so it remains in the bulk of the solution during cavitation. Most of the hydroxyl radicals that are formed within the cavity during the sonication might be recombined before they attack the phenol molecules in the bulk liquid. The reaction of hydroxyl radicals on phenol was confirmed through the formation of small quantities of catechol, hydroquinone and resorcinol (Figure 4). The lack of pyrolysis products (e.g. acetylene and methane) during the sonolysis of aqueous phenol indicates that the sonochemical reactions primarily occur within the bulk solution rather than within the superheated regions of the interfacial zone surrounding the cavitation bubble. There are many reports, which have proven the formation of hydroxyl radicals during sonication [5]. Petrier reported that this low efficiency is mainly due to the low concentrations of phenol [14]. The experimental data fitted well with pseudo first-order reaction rate equation (Figure 2), as is commonly found in the literature [14, 15]. The initial first order rate constants of phenol degradation were estimated to be 0.018 min^{-1} to 0.0019 min^{-1} for initial concentration of 1 mg/L to 100 mg/L, respectively. Table 1 shows the major calculated reaction rate coefficients.

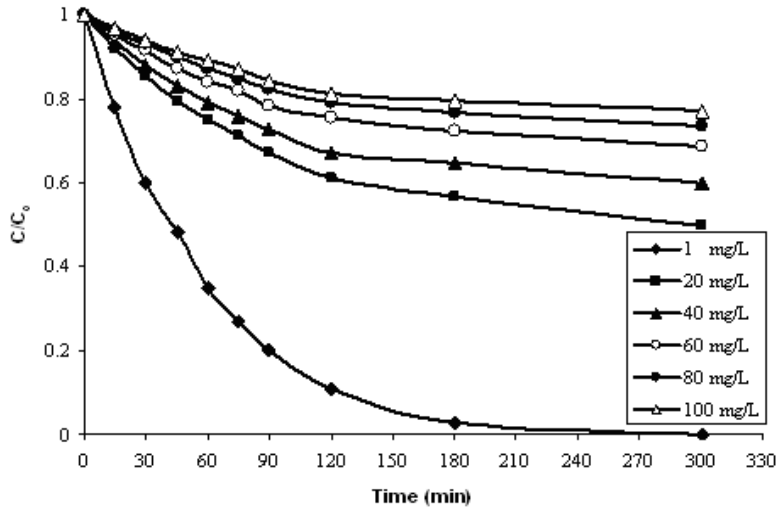

Figure 1. Effect of the initial concentration of phenol on the sonodegradation at 130 kHz.

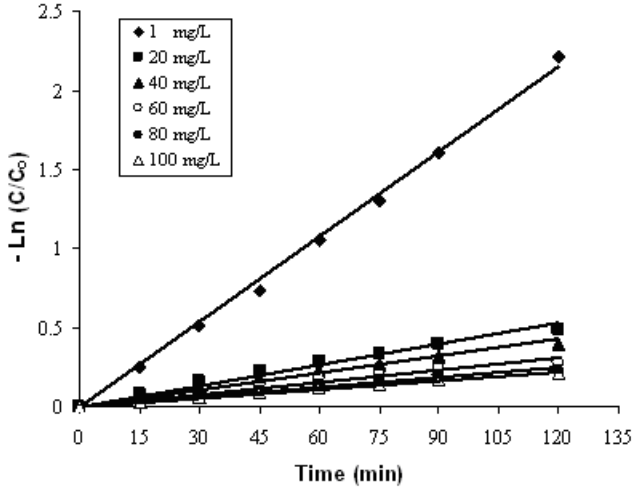

Figure.2. Plot of Ln C/C_o vs. time for sonodegradation of phenol.

Table 1. Pseudo first order kinetic values for degradation of phenol at different initial phenol concentrations by ultrasound irradiation

Initial phenol concentration (mg/L)	1	20	40	60	80	100
Rate constant (min^{-1})	0.018	0.0044	0.0036	0.0026	0.0021	0.0019
Correlation coefficient	0.98	0.98	0.98	0.97	0.98	0.99

We observe that initially the rate of ultrasonic degradation of phenol is high but later it reduces substantially. This can be explained by the fact that whatever dissolved air is present in the solution, it is degassed after the initial period of sonication resulting in a decrease in the amount of hydroxyl radicals generated. Also, there could be a competition between the oxidation of the phenol and the intermediates formed resulting into a net reduction in the degradation rate.

Figure 3 demonstrates the removal of phenol by the sonochemical process at different pH. It is clearly seen that lower pH values favored the phenol degradation. The degradation of phenol attained 65 % at pH 3, 61 % at pH 5, 47 % at pH 9 and 39 % at pH 11.

For sonication, many researchers have found the sonochemical degradation rate increases with decreasing solution pH [3, 16]. In the present study, the ionic species of phenol is predominant when the pH exceeds 10.0 (equal to pK_a value of phenol at 25 ºC), but the molecular species predominates when pH is less than the pK_a. The fraction in the molecular state of phenol was larger when the pH was smaller. The phenolate ions are uncomfortably concentrated in the gas-water interfaces of bubbles, where the hydrophobicity is strong, and cannot vaporize into the cavitation bubbles; they can react only outside of the bubble film with the OH radicals cleaved from water. However, in the molecular states phenol more easily enters the gas-water interfaces of bubbles and even vaporize into cavitation bubbles; they can react both inside by thermal cleavage and outside with OH radicals [3]. Therefore, it has been concluded that sonolysis of phenol is 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 [3].

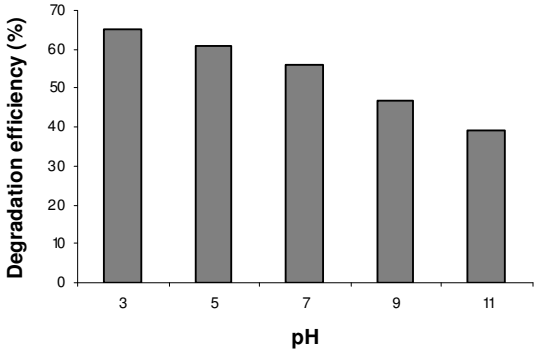

Figure 3. Effect of pH on phenol degradation under 130 kHz ultrasound irradiation (phenol concentration = 1 mg/L, Time = 60 min).

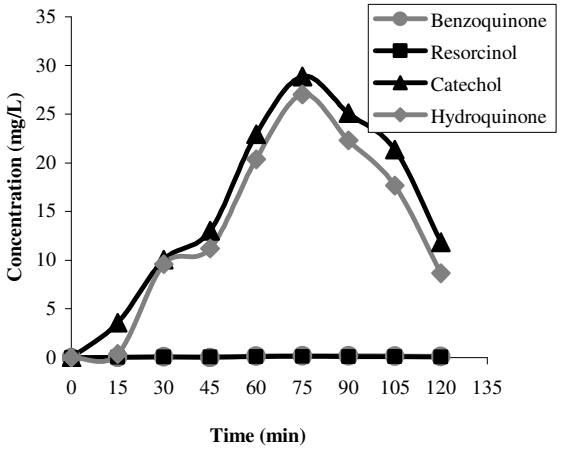

Figure 4. Concentration of the main intermediate of sonodegradation of phenol in different reaction time (Phenol concentration = 100 mg/L).

It is found that *daphnia* is the most sensitive organism to phenol [12]. So bioassay was done using daphnia. The acute toxicity of phenol and mixture of its sonodegradation by-products is presented in Table 2. Results showed that phenol was toxic to *Daphnia 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 41.2 and 23.6 for effluent mixture, respectively. Comparison of toxicity unit (TU) between phenol and effluent toxicity showed that TU value for effluent was 1.21 times lower than that obtain to phenol (according to 48 h-LC_{50}). Thus, sonication was able to reduce 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 [11]. 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 [12].

Table 2. Toxicity data for phenol and the toxic effects after its sonication at 130 kHz.

Test sample	Phenol				Sonicated effluent			
Time (day)	24	48	72	96	24	48	72	96
LC_{50} (% v/v)	33.1	19.5	18.1	15.7	41.2	23.6	20.1	16.1
Toxicity Unit (TU)	3.02	5.13	5.52	6.36	2.42	4.24	4.97	6.21

Data of this study showed that bioassays could be used as a suitable method for the evaluation of the efficiency of treatment procedures by ultrasound.

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