INTRODUCTION
Phenol is a potential hazard to human health and the environment. This compound has attracted public attention due to its presence in groundwater, rivers and drinking waters (Entezari et al., 2003). Acute exposure to phenol and its quinone analogues is known to cause skin irritation, kidney damage, gastrointestinal discomfort, and headaches. Aesthetically, this compound also poses a nuisance with detectable taste and odors in water at concentrations as low as 1-8 mg/L (Lesko, 2004). It has been listed as the priority pollutant in the list of USEPA (Mahamuni and Pandit, 2005). Most of the countries specify the maximum allowable concentration of phenol in the effluent streams to be less than 1 mg/L (Mahamuni and Pandit, 2005).

Phenol can be found in aqueous effluents from various industries such as the manufacturing of resins and plastics, petroleum refining, steel production, coal gasification and conversion, surface runoff from coal mines, byproducts of agricultural chemicals, dyestuff, textiles, tanning, fiberboard production and paint stripping operations, pulp and paper, pesticides, medications, pharmaceuticals and even from food processing industries (Lesko, 2004; Entezari and Petrier, 2004; Entezari and Petrier, 2005; Mahamuni and Pandit, 2005; Lathasree et al., 2004; Beltran et al., 2005). Due to its toxicity, hazardous character and an increasing social concern on environment, the discharge of such compounds in the environment has become more restrict. Therefore, there is more demand for improved methods of treatment (Entezari and Petrier, 2004; Beltran et al., 2005). Traditional methods of removal such as conventional chemical, physical and biological treatments for dephenolization of wastewater have their own limitations (Entezari and Petrier, 2004; Entezari et al., 2003). Lately, there has been a lot

ULTRASONIC DEGRADATION OF PHENOL AND DETERMINATION OF THE OXIDATION BY-PRODUCTS TOXICITY
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ABSTRACT
Phenol is a potential hazard to human health and the environment. The sonochemical degradation of phenol in aqueous solution was investigated by use of a 35 kHz bath sonicator. Experiments were performed at initial phenol concentrations varying from 1 to 100 mg/L. The effects of parameters such as pH and initial phenol concentration on the sonochemical degradation and bioassay test have been studied. The results of the study showed that the ultrasonic phenol degradation increased with decreasing the pH values and phenol concentration. But the rates of phenol degradation under different conditions had always been quite low. It was found that the rate of ultrasonic phenol degradation was first high but it was later substantially reduced and the experimental data fitted well with first order reaction rate equation. Bioassay tests showed that phenol was toxic to Daphnia magna and so resulted in quite low LC50 values. Comparison of toxicity units (TU) of phenol and the effluent flow showed that TU value for effluent was 1.65 times lower than that obtained for phenol. Thus, sonication was able to eliminate the toxicity of by-products which were formed during the degradation of phenol.

Key words: Ultrasound, sonochemistry, phenol, bioassay, daphnia magna
of interest in application of the advanced oxidation processes (AOPs) for the removal of phenol from the effluent streams (Mahamuni and Pandit, 2005). Ultrasound irradiation is a novel advanced oxidation process that has emerged as an answer to the growing need for lower levels of contaminants in wastewater (Wu et al., 2001; Nikolopoulos et al., 2005). Since 1990, several studies have focused on the use of ultrasound to remove organic xenobiotics from water (Pétrier et al., 1994; Kruus et al., 1997; Pétrier et al., 2001; Entezari et al., 2003). Ultrasonic irradiation introduces cavitation bubbles into an aqueous solution. These bubbles form, grow and subsequently collapse through compression-rarefaction cycles. The temperature in the collapsing bubbles can reach up to 3000-5000 °K and the pressure to 500-10,000 atm. Under such extreme conditions, water molecules undergo homolysis to yield hydroxyl radicals and hydrogen atoms. Since oxidation by hydroxyl radical is an important degradation pathway, the amount of the hydroxyl radicals present in the sonolysis system is directly related to the degradation efficiency (Zheng et al., 2005).

The main objective of this work was to focus on the degradation of phenol by the ultrasonic equipment operating at 35 kHz. The influences of various factors, such as initial pH and phenol concentrations on phenol ultrasonic degradation have also been studied. Also, the LC₅₀ (the statistically determined concentration that causes 50% mortality in a given exposure period) of the aqueous phenol solution before and after sonication (reaction by-products) using Daphnia magna as the test organisms, was studied. Such data can be considered as an indication of acute toxicity reduction resulting from treatment.

MATERIALS AND METHODS
Analytical grade phenol (from Merck) was used for the experiments. All other chemicals were of at least 99% purity and were used without further purification. Deionized water was used for preparing all aqueous solutions. For each of the experiments, the reaction volume was 2000 mL and the initial concentration of phenol was in the range of 1–100 mg/L. The ultrasonic reactions were carried out for 5 hr. The initial pH value of the sample was adjusted to a constant value of 3. Sonication was accomplished at the frequency of 35 kHz (500 W) with an ultrasonic generator (Elma TI-H-5, Germany) equipped with two piezoelectric transducers (5cm diameter) fixed at the bottom of the vessel. The apparatus was open to air. Dimensions of ultrasonic bath were: L=25 cm, W=13 cm, H=15 cm. Ultrasonic energy dissipated in the reactor was set at 2.5 W/cm² through the calorimetric method. The solution was irradiated 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 (15-300 min). Phenol analysis was then done according to a direct colorimetric method using 4 aminoantipyrine reagent (Anonymous, 1995). Color was measured spectrophotometrically at 500 nm by the use of a UV/VIS apparatus (Lambada 25 Perkin Elmer, Sheltom), after the filtration of samples through Whatman filter paper had been performed. Acute toxicity of phenol and the toxic effects of its degradation products after ultrasonic irradiation were studied with Daphnia magna test according to the procedure described in Standard Methods (Anonymous, 1995). Daphnia was found to be the most sensitive organism to phenol (Guerra, 2001), so bioassay tests were done using this organism. Primary daphnia was caught from their living site; then, one of them was cultured alone, and infants of primary daphnia were used for culture in large amounts. Dilution water which was used for tests was groundwater with the general characteristics of as follows: pH =8.1, total hardness =130 mg/L as CaCO₃, total alkalinity =306 mg/L as CaCO₃, electrical conductivity = 1197 µS/cm, 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 temperature-controlled condition of 22±2 °C 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 day. For running the experiment, 10 infants (with the age of < 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 phenol conversion percent from Fig. 1). Experimental samples concentrations were, 100, 75, 50, 40, 30, 20, 10 and 5 % of phenol sonicated effluent diluted with dilution water. After the setting periods of 24, 48, 72 and 96 hrs, 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 (Guerra, 2001; Jin et al., 1999). All experiments were run in triplicate to ensure reproducibility.

**RESULTS**

Study on phenol degradation was carried out for 5 h irradiation time. Fig. 1 shows the variations of phenol concentration with time. Only 13% degradation of phenol has been observed for 300 min sonication of 100 mg/L phenol solution. The experimental data from this study fitted well with first order reaction rate equation (Fig. 2). We observed that the initial rate of ultrasonic degradation was high but later it reduced substantially. Fig. 3 demonstrates the removal efficiency of phenol by the sonochemical process at different pH values. It clearly shows that lower pH values had favored the phenol degradation. The maximum and minimum efficiencies of phenol degradation were determined to be 37 % and 19 % at pH value of 3 and 11, respectively.

The LC$_{50}$ values of phenol and the mixture of its sonodegradation by-products are presented in Table 2. Results showed that, as it was expected, phenol was toxic to Daphnia magna and resulted in quite low LC$_{50}$ values (LC$_{50}$ 96 h of 15.7 % v/v). As it can be seen from Table 2, 24 and 48 h LC$_{50}$ (% v/v) values have ranged from 33.1 and 19.5 for phenol to 51.3 and 32.2 for the effluent mixture, respectively.

![Fig. 1: Effect of 35 kHz sonication on phenol decomposition at different initial phenol concentrations](image-url)
Fig. 2: Neperian logarithm of different concentrations of phenol vs. time for sonication of phenol

Fig. 3: Effect of pH on phenol degradation under 35 kHz ultrasound irradiation (phenol concentration = 1 mg/L, time= 60 min)

Table 1: First order kinetic values for degradation of phenol at different initial phenol concentrations by ultrasound irradiation

<table>
<thead>
<tr>
<th>Phenol concentration (mg/L)</th>
<th>1</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant (min⁻¹)</td>
<td>0.0076</td>
<td>0.0028</td>
<td>0.002</td>
<td>0.0016</td>
<td>0.0013</td>
<td>0.0011</td>
</tr>
<tr>
<td>Correlation coefficient</td>
<td>0.995</td>
<td>0.99</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 2: Toxicity data for phenol and sonicated phenol solution at 35 kHz

<table>
<thead>
<tr>
<th>Test sample</th>
<th>Phenol</th>
<th>Sonicated effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (day)</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>LC₅₀ (% v/v)</td>
<td>33.1</td>
<td>19.5</td>
</tr>
<tr>
<td>Toxicity Unit (TU)</td>
<td>3.02</td>
<td>5.13</td>
</tr>
</tbody>
</table>
DISCUSSION

As Fig. 1 shows, only 13% degradation of phenol has been observed after 300 min sonication of phenol solution with initial concentration of 100 mg/L. Mahamuni et al. reported 17% removal for phenol (C_0 = 85 mg/L) by a bath of ultrasonic equipment working at 20 kHz (120 W) during 60 min (Mahamuni and Pandit, 2005). Also, 20% degradation has been reported by Entezari et al. by means of ultrasound at 35 kHz (50 W) for initial phenol concentration of about 60 mg/L during 150 min (Entezari et al., 2003). This may be related to the hydrophilic nature of phenol. Phenol is a moderately soluble compound in water (C_{sw} = 0.63 M) with a relatively low vapor pressure (4.6 × 10^{-4} atm) and Henry’s constant (4.0 × 10^{-4} L atm M^{-1}). These physicochemical 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 get recombined before they attack the phenol molecules in the bulk liquid. The attack of hydroxyl radicals on phenol was confirmed through the formation of small quantities of catechol, hydroquinone and resorcinol. The lack of pyrolysis products (e.g. acetylene and methane) during 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 proved the formation of hydroxyl radicals during sonication (Lesko, 2004). Petrier reported that this low efficiency is mainly due to the low concentrations of phenol and of hydroxyl radicals that escape from the cavitation bubble at 35 kHz frequency (Petrier and Francony, 1997). Similar to the previous work (Petrier and Francony, 1997; Naffrechoux et al., 2000; Nikolopoulos et al., 2005), the experimental data in this study fitted well with first-order reaction rate equation. The initial first order rate constants of phenol degradation were estimated to be 0.0076 min^{-1} to 0.0011 min^{-1} for initial concentrations of 1 mg/L to 100 mg/L, respectively. Table 1 shows the major calculated reaction rate coefficients.

The initial rate of ultrasonic degradation was observed to be high but later it was reduced substantially. This can be explained by the fact that whatever dissolved air is present in the solution is degassed after the initial period of sonication and resulted in a decrease in the amount of hydroxyl radicals generated. Also, there could be a competition between the oxidation of phenol and the intermediates formed resulting into a net reduction in the degradation rate. This phenomenon has proved by other researcher (Mahamuni and Pandit, 2005).

As shown in Fig. 3, pH values influenced the phenol degradation. It is observed that phenol degradation can be favored by lowering the pH of solution and the sonochemical degradation rate of phenol increases with decreasing solution pH, because 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. 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 state, phenol more easily enters the gas–water interfaces of bubbles and even vaporizes into cavitation bubbles; thus can react both inside by thermal cleavage and outside with OH radicals. Therefore, it has been concluded that sonolysis of phenol is pH dependent and increases when more acidic conditions are carried out. This might be the reason why lower pH favored the ultrasonic degradation of phenol. The results from previous studies (Okouchi et al., 1992; Wu et al., 2001) showed that lower pH values favored for degradation of phenol by ultrasound.

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). Comparison of TUs of phenol and effluent toxicity showed that TU value of effluent was 1.65 times less than that obtained for phenol (according to 48 h-LC_{50}). Thus, sonication was able to eliminate the toxicity of by-products.
which were 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. 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 ultrasound.

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REFERENCES


