Intensification of sonochemical degradation of phenol using additives at pilot scale operation

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ABSTRACT

The present work reports the use of sonochemical reactors for the degradation of phenol in the presence of additives with an objective of enhancing the rates of degradation at a pilot scale operation. Process intensification studies have been carried out using additives such as hydrogen peroxide (H$_2$O$_2$) (0.5–2.0 g/L), sodium chloride (0.5–1.5 g/L) and solid particles viz. cupric oxide (CuO) and titanium dioxide (TiO$_2$) (0.5–2.5 g/L). Optimum concentration for H$_2$O$_2$ and sodium chloride has been observed beyond which no beneficial effects are obtained even with additional loadings. Maximum extent of degradation has been observed by using ultrasound/H$_2$O$_2$/CuO approach at a solid loading of 1.5 g/L followed by ultrasound/H$_2$O$_2$/TiO$_2$ approach at a loading of 2.0 g/L. The obtained results at pilot scale operation in the current work are very important especially due to the fact that the majority of earlier studies are at laboratory scale which cannot provide the design related information for large scale operation as required scale up ratios are quite high adding a degree of uncertainty in the design. The novelty of the present work lies in the fact that it highlights successful application of sonochemical reactors for wastewater treatment at pilot scale operation.

Key words | cavitational reactors, hydrogen peroxide, intensification using additives, phenol degradation, pilot scale operation, ultrasound

INTRODUCTION

Rising population and new developments in a variety of fields to meet the ever-increasing requirements of human beings have also led to the presence of new compounds in the effluent streams of processing plants, which are not readily degraded by the conventional effluent treatment methods (Gogate & Pandit 2004). Until recent years, the treatment schemes were mainly comprised of the conventional physical (screening, mixing, flocculation, sedimentation, flotation, filtration, etc.), chemical (precipitation, adsorption, disinfection, oxidation using chemicals, etc.) and biological (removal of contaminants brought about by biological activity) methods. These conventional methods, however, failed to meet the demands of the newer and more stringent environmental regulations. With increased understanding of the environmental effects, possible adverse long-term effects, increased scientific knowledge and an expanded information base, wastewater treatment has begun to focus on the health concerns related to toxic and potentially toxic chemicals released into the environment. This gave rise to development of new methods such as advanced oxidation processes (AOPs), membrane separation, wet air oxidation, radiolysis, and electrochemical oxidation. AOPs are defined broadly as those aqueous phase oxidation processes which are based primarily on the generation and attack of the hydroxyl radicals resulting in the destruction of the target pollutant (Gogate & Pandit 2004). In the present work, AOPs based on the use of ultrasound and its intensification using different additives has been investigated for degradation of phenol. Phenol is one of the most common compounds found in the effluents of many industries such as petroleum refining and petrochemicals, pharmaceuticals, pesticides, paint and dye industries, organic chemicals manufacturing, etc. with typical concentrations ranging from 10 to 3,000 mg/L.

Ultrasonic waves can induce the reaction through the chemical process inside the cavitation bubble, or at the interface of the bubble. Solute molecules that cannot diffuse to these two places are likely to undergo attack by hydroxyl radicals formed from the dissociation of water in the bulk water (Adewuyi 2003). The two major pathways for the
sonolytic degradation of a pollutant are pyrolysis of the molecules evaporated inside the bubble and the attack of OH radical on the pollutant molecules in the bulk solution leading to hydroxylated products that are further degraded to the final products. In the case of phenol degradation using ultrasound induced cavitation, the main degradation products have been reported to be catechol and hydroquinone, which points at attack of OH radical (i.e. hydroxylation reaction) produced by the cavitation bubbles on the phenol molecule in the bulk liquid medium as the foremost degradation pathway (Petrier & Francony 1997; Entezari et al. 2003; Mahamuni & Pandit 2006; Sivasankar & Moholkar 2009). The efficacy of cavitation can be significantly enhanced by combining cavitation with other oxidation processes or by using catalysts and/or additives. With this intensification, cavitation can be a suitable technology for degradation of wastewater streams or at the minimum it can be used for lowering the toxicity levels of the effluent stream so that conventional biological oxidation can be readily applicable. It is also important to note here that the beneficial effects obtained by the use of additives or combination with other processes should be compared with the possible increase in the cost of operation due to additional use of chemicals or energy consumption in combined processes, and based on the superiority of the beneficial effects, optimum operational strategies should be selected.

**MATERIALS AND METHODS**

**Ultrasonic reactors**

In the present work, two different ultrasonic reactors have been used for the degradation of phenol. The experimental set up consists of an ultrasonic bath equipped with a single transducer, which was procured from Roop Telesonic Ultrasonic, India. One of the ultrasonic baths has an operating frequency of 25 kHz and a rated power output of 1 kW, whereas the second ultrasonic bath has an operating frequency of 36 kHz and 150 W power dissipation. The reactor with 25 kHz frequency has dimensions of 35 cm length, 12 cm width, 20 cm height and is provided with a single large transducer with dimensions of length 25 cm and diameter 30 mm at the bottom of the reactor. The reactor with 36 kHz frequency has dimensions of 33 cm length, 15 cm width, 21 cm height and is provided with a single large transducer with dimensions of length 22.5 cm and diameter 30 mm at the bottom of the reactor. The schematic representation of the reactors can be obtained from earlier work (Bhirud et al. 2004; Pradhan & Gogate 2010).

Energy efficiency, i.e. fraction of the total supplied electrical energy actually dissipated into the system and hence available for cavitation events (based on calorimetric measurements) has been estimated as a function of the volume of the reaction mixture with an aim of quantifying the zone of influence of the ultrasonic irradiations (Bhirud et al. 2004). Energy efficiency studies were undertaken using water and with varying capacity in the range of 2–7 L for a 1 kw reactor and 4–9.5 L for a 150 W reactor. Experiments with actual pollutant were then performed using this optimum volume.

**Materials**

Phenol crystals (99.5%), hydrogen peroxide (H2O2; 30% w/v), titanium dioxide (TiO2), cupric oxide (CuO) and sodium chloride (NaCl) were procured from S.D Fine Chem Pvt. Ltd, Mumbai, India and were of analytical reagent grade. The chemicals were used as received from the supplier.

**Experimental methodology**

Based on the results obtained in the calorimetric study, the optimum capacity was selected for experiments for degradation of phenol. Each experiment was performed for 90 min and sample was collected after every 15 min. The reactor was allowed to cool for 5–10 min to prevent any significant increase in the operating temperature. Distilled water was used for preparation of aqueous solution of phenol. Phenol solutions in various concentrations were prepared in the range from 0.5 to 2.0 g/L. Initially, experiments were carried out in the presence of ultrasound alone. Further studies related to intensification of the ultrasound degradation process were carried out by adding H2O2 in different concentrations ranging from 0.5 to 2.0 g/L, NaCl with different concentrations in the range 0.5–1.5 g/L and addition of CuO/TiO2 with different concentrations in the range 0.5–2.5 g/L. Degradation of phenol was also studied in a stirred reactor with different concentrations of H2O2. A six blade pitched blade turbine stirrer was used at an operating speed of 480–500 rpm in a 1,000 ml glass beaker.

All the experiments were repeated two times and the reported values are an average of the two runs. The experimental errors were within 2% of the value of extent of degradation.
Analysis

The sample collected after each 15 min interval was analyzed using an ultraviolet/visible UV/VIS Chemito –2,500 spectrophotometer. Dilutions were made using 25 μl of the sample + 9.975 ml of distilled water and the spectrophotometer was set at 270 nm, which shows maximum absorbance for phenol. It should be noted here that as the main objective of the current work was to quantify the extent of intensification obtained due to the presence of different additives in the sonochemical reactors, a simpler analysis technique in terms of monitoring the removal of phenol using a spectrophotometer has been used. Care has been taken to check whether there is any interference of the intermediate products or H2O2 generated in the system on the extent of absorbance of phenol at the desired wavelength of 270 nm. The analysis of the absorbance spectrum indicated that there was no interference of H2O2 as the peak for H2O2 was observed at 192 nm. Also the nature of the absorbance spectrum remained similar for pure phenol solution as well as for the samples used during the monitoring of the extent of degradation. Use of a spectrophotometer for monitoring the extent of degradation of phenol has been used commonly in reported literature (Gogate et al. 2004; Mahamuni & Pandit 2006; Rokhina et al. 2010).

The formation of H2O2 in the sonochemical reactor has also been quantified using a spectrophotometer. H2O2 showed a maximum absorbance around 192 nm and hence analysis was carried out based on a calibration plot. Wang et al. (2000) have also reported a similar analysis technique.

RESULTS AND DISCUSSIONS

Calorimetric results

The obtained results for calorimetric measurements of energy as a function of the operating capacity indicate that the energy increases with an increase in the capacity. The power dissipated at an operating capacity of 7 L for 1 kW reactor is 206.3 kJ, whereas for a 150 W reactor, maximum energy dissipation of 80 kJ was observed at an operating capacity of 9.5 L. The sound wave emission is from the transducer (from the entire surface) located at the bottom of the reactor in a direction perpendicular to the base of the reactor. As the operating capacity increases, the enhanced quantum of liquid volume is capable of absorbing the energy transferred from the vibrating transducer. If the operating capacity is lower than the maximum, the liquid height achieved in the reactor with the given geometry is not sufficient to absorb all the supplied energy from the vibrating transducer and is possibly lost in reflections from the air–water interface. Based on these results, the optimum operating capacity was selected for further studies.

H2O2 formation

The controlling mechanism of sonochemical reactors in degradation of phenol is the generation of free radicals and their subsequent attack on the pollutant species. H2O2 measurements were done in absence of phenol to investigate the efficacy of different sonochemical reactors in generating free radical species. It has been observed that the generation of H2O2 increases linearly with time of ultrasonic irradiation. Also, the extent of formation of H2O2 was higher in the reactor operating at 25 kHz and 1 kW power (by about 100%) as compared to that operating at 36 kHz and 150 W as power dissipation. This can be attributed to the fact that the acoustical power per unit volume in a 25 kHz reactor is substantially higher than 36 kHz (0.143 W/mL for 25 kHz, 0.0158 W/mL for 36 kHz). Earlier work by Hua & Hoffmann (1997) showed increased H2O2 formation at 300 kHz as compared to 520 kHz was attributed to about four times more acoustic power per unit volume (0.129 and 0.033 W/mL, respectively) as measured calorimetrically.

Phenol degradation using ultrasonic irradiations alone

Initially, degradation of phenol was carried out only using ultrasonic irradiations over a concentration range from 0.5 to 2.0 g/L. It has been observed that the extent of phenol degradation was the maximum for lowest concentration of 0.5 g/L. The typical extents of degradation using this approach were in the range 5–11% depending on the operating conditions as represented in Table 1. The increase in the extent of degradation with a decrease in the initial concentration of the pollutant has also been reported for various pollutants (Bhirud et al. 2004; Abbasi & Asl 2008).

It has also been observed that the extent of degradation is higher in the reactor with power dissipation as 1 kW, attributed to the higher number of cavitational events, leading to enhanced generation of the hydroxyl radicals which control the extent of phenol degradation. This has also been confirmed by the quantification of H2O2, as discussed earlier.

Phenol degradation using ultrasound/H2O2

Sonochemical degradation of phenol was investigated in the presence of H2O2 in different concentrations in the range of
0.5–2.0 g/L and for three initial concentrations of phenol. It has been observed that due to the addition of H₂O₂, the extent of phenol degradation increases up to an optimum concentration of H₂O₂. The obtained trend was similar for all the concentrations of phenol and the final extent of degradation in 90 min of treatment have been given in Table 1.

Comparing the degradation of phenol in the case of two ultrasonic reactors, it has been observed that the extent of increase in the degradation due to addition of hydrogen peroxide in the reactor with power dissipation as 1 kW, attributed to a higher number of cavitational events, leading to enhanced generation of the hydroxyl radicals which control the extent of phenol degradation. The maximum extent of degradation obtained using this combination approach was 25% for the 1 kW reactor and for initial concentration of phenol as 1 g/L, indicating about 100% improvement as compared to the use of ultrasound alone. Guo et al. (2008) have also reported similar extents of intensification for the degradation of 2,4-dinitrophenol.

The effect of addition of H₂O₂ depends strongly on the rate of generation of hydroxyl radicals and relative rates of recombination reaction as well as the utilization of the hydroxyl radicals by the pollutant molecules. The observed increase in the extent of degradation at lower concentrations of H₂O₂ can be attributed to the fact that the additional hydroxyl radicals produced are indeed consumed by the pollutant molecules. The dissociation in the presence of ultrasound was also confirmed with experiments based on only stirring and H₂O₂, which showed much lower extents of degradation (only about 5%). At higher loadings of H₂O₂, however, all the molecules of H₂O₂ are not dissociated; some are also formed due to the recombination reaction of the unutilized hydroxyl radicals and these molecules play a major role in scavenging the available hydroxyl radicals. It can be clearly seen from the Table 1 that the extent of degradation is higher for 1 g/L loading of H₂O₂ as compared to 2 g/L loading for all the initial concentrations of phenol. The undesired reaction occurring due to excess H₂O₂ has been given below (Gogate & Pandit 2004):

\[
\text{OH}^* + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^*.
\]

Teo et al. (2001) also reported that degradation of 0.4 mmol/L p-chlorophenol increased with an increase in the concentration of H₂O₂ up to 30 mmol/L beyond which extent of degradation decreased with an increase in the concentration of H₂O₂. Similar results for optimum concentration of H₂O₂ have also been reported by Quesada-Peñate et al. (2009). It should be also noted here that though similar studies have been reported earlier as regards the effects of H₂O₂, all the studies have been at laboratory scale operation with capacity of the order of few ml whereas the current study has established the existence of an optimum concentration of H₂O₂ at pilot scale operations.

### Table 1: Extent of phenol degradation in 90 min of treatment using different approaches

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Approach</th>
<th>Extent of degradation of 0.5 g/L phenol (%)</th>
<th>Extent of degradation of 1.0 g/L phenol (%)</th>
<th>Extent of degradation of 2.0 g/L phenol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>US alone (150 W, 36 kHz reactor)</td>
<td>8</td>
<td>6.5</td>
<td>5.5</td>
</tr>
<tr>
<td>2</td>
<td>US alone (1 kW, 25 kHz reactor)</td>
<td>11</td>
<td>9.5</td>
<td>8.5</td>
</tr>
<tr>
<td>3</td>
<td>Stirring + 0.5 g/L H₂O₂</td>
<td>4.5</td>
<td>7.5</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>Stirring + 1.0 g/L H₂O₂</td>
<td>7.5</td>
<td>9</td>
<td>8.0</td>
</tr>
<tr>
<td>5</td>
<td>Stirring + 2.0 g/L H₂O₂</td>
<td>9</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>US (150 W) + 0.5 g/L H₂O₂</td>
<td>9.5</td>
<td>13.5</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>US (150 W) + 1.0 g/L H₂O₂</td>
<td>12</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>US (150 W) + 2.0 g/L H₂O₂</td>
<td>10</td>
<td>12.0</td>
<td>8.5</td>
</tr>
<tr>
<td>9</td>
<td>US (1 kW) + 0.5 g/L H₂O₂</td>
<td>12.5</td>
<td>18</td>
<td>9.0</td>
</tr>
<tr>
<td>10</td>
<td>US (1 kW) + 1.0 g/L H₂O₂</td>
<td>15</td>
<td>25</td>
<td>13.5</td>
</tr>
<tr>
<td>11</td>
<td>US (1 kW) + 2.0 g/L H₂O₂</td>
<td>13.5</td>
<td>17.5</td>
<td>11</td>
</tr>
<tr>
<td>12</td>
<td>US (150 W) + 0.5 g/L NaCl</td>
<td>8</td>
<td>7.5</td>
<td>6.0</td>
</tr>
<tr>
<td>13</td>
<td>US (150 W) + 1.0 g/L NaCl</td>
<td>9.5</td>
<td>9.5</td>
<td>6.5</td>
</tr>
<tr>
<td>14</td>
<td>US (150 W) + 1.5 g/L NaCl</td>
<td>11</td>
<td>13.5</td>
<td>8.5</td>
</tr>
<tr>
<td>15</td>
<td>US (1 kW) + 0.5 g/L NaCl</td>
<td>11</td>
<td>10.5</td>
<td>9.0</td>
</tr>
<tr>
<td>16</td>
<td>US (1 kW) + 1.0 g/L NaCl</td>
<td>12</td>
<td>13.5</td>
<td>10</td>
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<tr>
<td>17</td>
<td>US (1 kW) + 1.5 g/L NaCl</td>
<td>13</td>
<td>14.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>
scale operation and is valuable design related information especially for establishing sound scale up strategies.

**Phenol degradation using ultrasound/NaCl**

The majority of oxidation reaction occurs in the bubble–bulk interface area. Pollutants present in that region undergo degradation due to exposure to free radicals and conditions of high temperature and pressure. Using theoretical analysis, Bapat et al. (2008) have clearly established the dependency of the extent of degradation of phenolic compounds on the interfacial concentration of the pollutants. To enhance concentration of the pollutant in the bubble–bulk interface, additives can be used with an objective of enhancing the extent of degradation. NaCl in different concentrations in the range of 0.5–1.5 g/L was used as an additive to alter the interfacial concentration of phenol. The extent of degradation was found to increase with an increase in the concentration of NaCl and similar results have been obtained for the case of initial concentration of phenol as 1 and 2 g/L. The final extent of degradation after 90 min of treatment has been given in Table 1. Comparison of the results of phenol degradation in the presence of ultrasound alone and a combination of ultrasound/NaCl indicates that the degradation was higher in the case where NaCl was used. The obtained results can be attributed to enhanced interfacial concentration resulting in an increase in the overall degradation rate (Seymour & Gupta 1997). Addition of NaCl does not take part in the degradation process but only selectively transfers the phenol molecules to the cavity collapse site where it is subjected to intense cavitational conditions.

**Phenol degradation using ultrasound/H2O2/catalyst**

The combined effect of ultrasound and H2O2 may further be improved by addition of catalyst as solid particles. In the present work, CuO and TiO2 have been used as additives over a concentration range of 0.5 g/L to 2.5 g/L. The main role of solid particles is expected to be enhancing the cavitational intensity by virtue of surface cavitation. Tuziuti et al. (2005) have suggested that the existence of particles in liquid provides a nucleation site for cavitation bubbles due to its surface roughness. An overall increase in the cavitational intensity is likely to produce additional free radicals leading to enhanced degradation of phenol. The presence of these solids can also catalyze the H2O2 dissociation. However, the presence of solids has a detrimental effect as well in terms of the decreased transfer of ultrasound energy and hence an optimum loading of solids may exist. The extents of degradation of 0.5 g/L and 1 g/L initial concentration of phenol have been investigated with 1 g/L H2O2 in 25 kHz ultrasonic reactor with power dissipation 1 kW. The obtained results have been shown in Figure 1 for the case of CuO and TiO2 solids at 1 g/L initial concentration of phenol.

It can be seen from the figure that the extent of degradation of phenol increased with an increase in the solid loading only till an optimum value. For the case of CuO, the optimum loading was 1.5 g/L, whereas for TiO2 the optimum concentration was 2.0 g/L, above which a decrease in the extent of degradation was observed. The observed results can be attributed to the scattering effects due to the presence of solid particles especially at higher loadings, which results in a decrease in the transferred ultrasonic energy. Nakui et al. (2007) have reported similar existence of optimum concentration of solid catalyst (coal ash) for degradation of phenol. However, Kubo et al. (2005) have reported that the degradation of phenol increased with an increase in the concentration of TiO2 from 0 to 10 g in 25 ml of solution. The observed optimum in the present case can be attributed to the dependency on the rate of hydroxyl radical generation, its utilization by the pollutant molecules as well as differences in the reactor geometry which decides the extent of scattering of the incident sound waves. It should be also noted here that for the case of CuO as catalyst, the magnitude of optimum concentration is lower as compared to the case of TiO2 as catalyst which can be possibly attributed to the differences in the particle size distributions leading to different degree of surface cavitation as well as scattering effects. Also, presence of CuO generates a Fenton chemistry-like mechanism in the system generating additional free radicals as compared to TiO2 at similar loadings. Kim & Metcalfe (2007) have
reported the fact that presence of CuO plays a role in enhancing the dissociation of H₂O₂ yielding a higher quantum of hydroxyl radicals in the system and hence resulting in enhanced rates of degradation of the pollutants.

CONCLUSIONS

The present work has clearly established the utility of sonochemical reactors for phenol degradation and the role of different additives in enhancing the cavitation activity. Amongst the two ultrasonic reactors, the extent of degradation was higher in the reactor with 25 kHz frequency and 1 kW power dissipation, elucidating the dominant role of power dissipation in enhancing the cavitation activity and hence the extent of degradation. Studies related to quantification of H₂O₂ generated in the system have also confirmed this hypothesis. Presence of NaCl as an additive showed increase in the degradation of phenol with an increase in the concentration of NaCl over the entire concentration range, whereas for H₂O₂ addition in the presence or absence of solid particles as catalyst, an optimum concentration as well as optimum loading of catalyst was observed. The current work has clearly established the fact that different additives can be effectively used to increase the extent of degradation of the model pollutant (phenol) at pilot scale operation.

REFERENCES


