Effects of operating parameters on sonochemical decomposition of phenol

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Abstract

Ultrasonic removal of phenol under irradiation at 20, 300 and 520 kHz was investigated to assess the impacts of operating parameters on the efficiency of the systems. It was found under our experimental conditions that 20 kHz was the least effective frequency for ultrasonic decomposition of phenol, owing to the low volatility of phenol and the slow rate of OH radical ejection to the bulk solution at this frequency. Assessment of relative rates of destruction and ultrasonic yields showed that maximum efficiency was accomplished with 300 kHz employed in a reactor enclosed with an ultrasonic energy of 14.7 W. The same reactor and frequency was found to provide maximum ejection of hydroxyl radicals to the solution. Impacts of pH and initial concentration on the efficiency of phenol removal were such that acidic pH and high concentrations accelerated the process as related to the increased likelihood of phenol at these conditions to approach the cavity sheath. Separate injection of equivalent volumes of air and argon into the reactors showed that the decomposition was enhanced in the presence of air by virtue of the production of additional reactive species via the reaction of nitrogen with molecular oxygen.
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1. Introduction

Phenols are widely consumed in the industry such as in preservers of paint, leather and textile goods, and in the production of resins, disinfectants, medicine, caprolactam and bisphenol A. Improper handling of these compounds and/or inappropriate disposal of their wastes into water is a major pollution, as many of phenolic compounds are resistant to conventional water treatment processes, and some are recognized as suspected carcinogens [1].

Methods of destroying phenolic wastes in water has been widely investigated and found that advanced oxidation processes (AOPs) are promising alternatives, owing to their potential to generate hydroxyl radicals in solution [2–5]. Among many tools of producing hydroxyl radicals in AOPs (e.g. UV irradiation, ozonation, addition of hydrogen peroxide, Fenton's agent and combinations thereof), ultrasound is a novel method, by which water molecules undergo molecular fragmentation to release hydroxyl and hydrogen radicals [6]. The underlying mechanism for this phenomenon is acoustic cavitation, which consists of the formation, growth and implosive collapse of gaseous cavity bubbles, resulting in local extremes of temperatures and pressures, at which molecules undergo pyrolysis [7]. As some of these radicals escape into the aqueous phase, they readily attack organic molecules therein for oxidative destruction.

Sonochemical effects can be enhanced by inserting solid particles and/or injecting a soluble gas in solution [6]. However, the effects are more strictly related to the applied frequency, power and the reactor geometry. In general, frequency selection is based on the vapor pressure, solubility and octanol–water partition coefficient of the target chemical. Hydrophobic compounds with high vapor pressures tend to diffuse into the gaseous bubble interior, so that they may easily be destroyed in the bubble–liquid interface and/or the bubble itself. The most suitable frequencies for destroying such compounds lie between 20 and 100 kHz, by which long-lived "stable" cavities are generated [8]. In contrast, hydrophilic compounds particularly at low concentrations tend to remain in the bulk liquid and their destruction is possible only by aqueous phase oxidation caused by the "unstable cavity"

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collapse (at 200–800 kHz), during which the probability of radical escape to the bulk liquid is high [9–10].

There are many studies on sono-degradation of phenol in water, focusing mainly on parameteric effects. In principle, short frequency ultrasound was found ineffective, while medium frequencies, particularly 200 and 500 kHz were found to provide sufficiently high decomposition yields [11–15]. In addition, it was found the efficiency of removal at all frequencies could be improved by the addition of catalysts such as Fenton's reagent or CCl$_4$, which by reacting with hydrogen radicals increased the availability of uncombined hydroxyl radicals in solution [15,16].

The purpose of this study was to cover a detailed study on ultrasonic decomposition of phenol to fulfill the gaps in the literature and to assess single and interactive effects of operating parameters (e.g. frequency, reactor volume, hydrogen peroxide production, solute concentration and pH, type of saturating gas) on the rate of decomposition and the product yield. The test frequencies were 20, 300 and 520 kHz employed in three different reactors with 80, 150 and 1200 ml, respectively.

2. Experimental

2.1. Material

Phenol was purchased from Riedel Häen (97% pure) in solid form, and was dissolved in deionized water. Potassium ferro cyanide (K$_3$Fe(CN)$_6$), 4-aminoantipyrine, ammonium chloride (NH$_4$Cl), ammonium hydroxide (NH$_4$OH), sulfuric acid and all other reagents were obtained from Fluka and used as received.

2.2. Apparatus

Three different ultrasonic equipment with three distinct frequencies, power outputs and cell volumes were used throughout the study. The first one was a horn-type sonicator (tip diameter = 12 mm) connected to a 20 kHz Bandelin Sonopuls HD2200 generator with a capacity of 180 W. The tip of the horn was submersed into the liquid from the top of an 80 ml cylindirical glass reactor. The second one was made of a 300 kHz piezo-electric transducer located at the bottom of a 150 ml cell and connected to a generator with a maximum capacity of 25 W (UNDATIM ULTRASONICS). The third equipment consisted of a piezo-electric transducer emitting ultrasonic pressure at 520 kHz and mounted on a titanium plate at the bottom of a cylindrical Pyrex reactor of 1200 ml with a generator capacity of 100 W (UNDA-TIM ULTRASONICS). In all systems, the cells were equipped with a water-cooling jacket to maintain constant liquid temperature.

2.3. Analysis

Phenol was monitored spectrophotometrically by the aminoantipyrine method [17] using a UNICAM-Heλios, alpha/beta double beam spectrophotometer with an optical path-length of 1 cm. The method is based on the reaction of phenol with 4-aminoantipyrine in the presence of potassium ferro cyanide at pH 7.9 to form a colored antipyrine complex (AMPH) as shown:

4-aminoantipyrine   phenol   AMPH   (1)
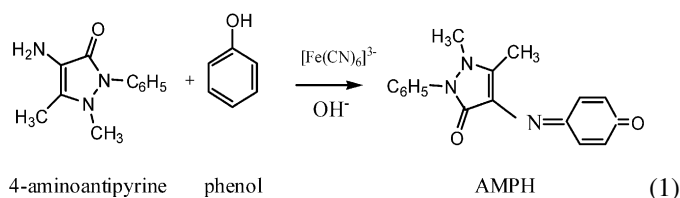
Concentration of phenol in solutions of AMPH was estimated via a calibration curve generated from the absorption of the solutions in the visible band. Hydrogen peroxide was monitored by the analytic procedure described by Klassen et al. [18].

2.4. Procedure

A stock phenol solution of 0.5 M was made in deionized water and stored at 4 °C in the dark. Test samples of 0.1, 0.25, 0.5, 1, 2 and 5 mM were prepared from the stock using deionized water. Sample volumes in 20, 300 and 520 kHz reactors were respectively 80, 100 and 300 ml. The test solutions were bubbled with air or argon for 30 min prior to sonication and the same gas was continually injected into the solution throughout a contact time of 90 min. Samples were withdrawn from the reactors every 10 min for duplicate analysis of the antipyrine complex by spectrometry.

3. Results and discussion

3.1. Effect of initial concentration and the applied frequency

The UV–vis spectrum of AMPH showed that it had two principle absorptions: one at the visible band (508 nm) corresponding to the phenolic chromophore, and the other at near UV (332 nm). Spectral changes in AMPH prepared by reacting the effluents of 300 kHz reactor during 90 min sonication of 5 mM phenol is presented in Fig. 1. Note that sonication not only rendered decolorization (and decomposition) of the phenol complex but also induced UV absorption abatement.
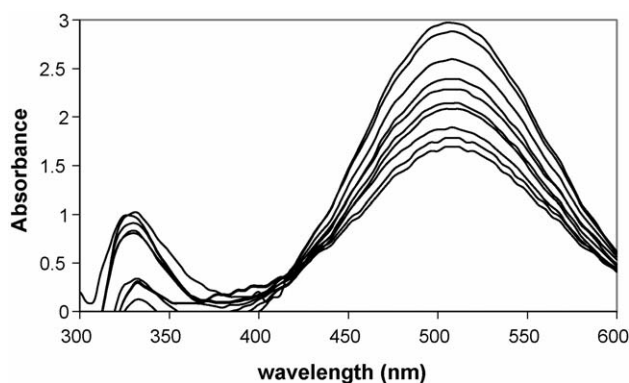
Fig. 1. Changes in the the spectrum of AMPH during sonication of 5 mM phenol (300 kHz) for 0, 10, 20, 30, 40, 50, 60, 70, 80 and 90 min at pH 2.0 and in the presence of air flowing at 1.5 l min^{-1}.
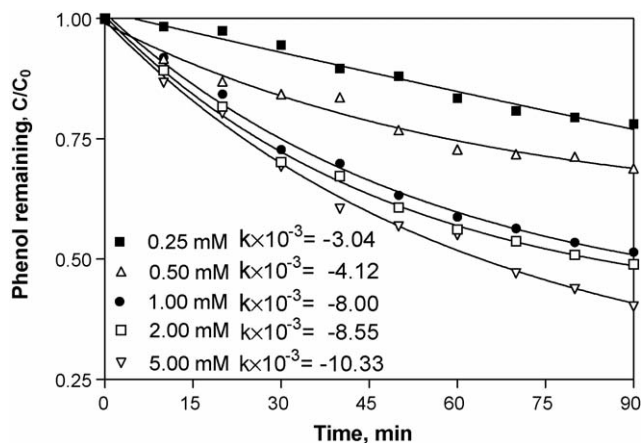
Fig. 2. Variation of time–rate decomposition of phenol with initial concentration. Operating conditions are: frequency = 300 kHz, pH 2.0 and air injection at $1.5 \, l \, min^{-1}$.

The effect of concentration on the rate of decomposition was determined by monitoring the reactor effluents for phenol during 90 min sonication of 0.25, 0.50, 1.0, 2.0 and 5.0 mM phenol at 300 kHz. The data revealed that the rate was pseudo-first order with respect to the instantaneous concentration of phenol in solution, and the rate constants were estimated accordingly using the integrated form of the related rate equation:

$$\frac{C}{C_0} = e^{-kt} \tag{2}$$

where C and C_0 are concentrations of phenol at time t and zero, and k is the pseudo-first order degradation rate coefficient. Profiles of phenol removal at the selected test concentrations and values of k estimated by non-linear regression are presented in Fig. 2.

The data and the estimated rate coefficients showed that the rate of decomposition increased with increasing input concentrations of phenol, as typical of pseudo-first order decay reactions of low concentration-solutes. The observation also verifies the hypothesis proposed in the literature that at increasing concentrations of low volatility solutes, an additional destructive pathway emerges, as demonstrated by the formation of pyrolysis products along with hydroxylated intermediates [19]. The probable site for thermal decomposition of concentrated non-volatile solutes is the interfacial bubble sheath, at which solutes may accumulate via diffusive sorption during the formation and growth of acoustic cavities.

It is also significant that while the rate of decomposition was highly sensitive to increases in C_0 from low to medium levels (e.g. k was enhanced nearly by 100% when C_0 was doubled from 0.5 to 1.0 mM), it turned out to be less sensitive to further increases above that level (e.g. the enhancement was only 20% with an increase of C_0 from 2 to 5.0 mM). This implies saturation type of kinetics as typical of adsorption of highly concentrated non-volatile solutes on non-polar surfaces [6].

The efficiencies of the test frequencies were assessed by comparing the observed ultrasonic yields after 90 min sonication of the test concentrations at pH 2.0. The yield as defined by the change in chemical concentration in the experiment volume per

Table 1
Relative power inputs and product yields obtained with 5 mM phenol exposed to 90 min sonication at pH 2.0 during air injection

Frequency (kHz)	20	300	520
Power applied (P_a), W	59.0	25.0	40.0
Power deposited (P_d), W	36.5	14.7	33.7
Solution volume, l	0.08	0.10	0.30
ΔC (mM)	1.64	3.41	2.01
$G \times 10^{-2}$ (mmol/W)	0.36	2.34	1.79
$^\bullet OH \times 10^{-5}$ (mmol/W)[a]	0.18	2.06	1.52

[a] OH radical yield in deionized water containing no phenol (All other conditions are the same as above).

power of the sonic energy deposited in that volume [20] was calculated by:

$$G = \frac{\Delta C \times V}{P_d} \tag{3}$$

where G is the ultrasonic yield of products (mol W^{-1}), ΔC the change in the concentration of the test chemical (M), V the volume of the solution (l) and P_d is the sonic energy deposited in the given volume (W). Values of P_d in each test system as estimated by calorimetry [21], and the calculated yields for 5 mM phenol are listed in Table 1. Note that the reason for different input powers and different solution volumes in each scheme is that the systems were operated at their previously optimized conditions.

Values of G in Table 1 show that relative efficiencies of the test frequencies as applied in the specified reactor volumes are in the order 300 > 520 > 20 kHz. The fact that the degradation was remarkably inefficient at 20 kHz is consistent with the literature, and can be related to the interactive effects of long collapse duration at this frequency that inhibits radical escape to the bulk liquid and low volatility of phenol (vapor pressure = 0.41 mmHg at 25 °C) that resists its diffusion into the gas phase. Higher decomposition efficiencies observed at 300 and 520 kHz, at which bubble lives and collapse durations are shorter to allow radical escape confirm that ultrasonic degradation of phenol is mainly dominated by OH radical chemistry in the bulk liquid, as reported by others [22].

The larger efficiency of destruction at 300 kHz irradiation than at 520 kHz is inconsistent with the well-accepted knowledge that radical production rates increase with increasing applied frequency [23]. However, although shorter bubble life (or shorter collapse duration) at 520 kHz is more favorable for radical production and ejection out of the gas phase, it must have been unfavorable for the "quality" or the violence of collapse [24]. In most cases, therefore, there exists an optimum frequency, at which the rate of radical production and the duration of cavity collapse provide the "best" conditions for the destruction of the target chemical. Hence, our observation that 300 kHz (and the related reactor properies) was much better than 520 kHz for phenol destruction must be due to longer lived bubble advantages at 300 kHz over shorter lasting but less energetic cavity collapse at 520 kHz that allows larger spread of OH radicals into solution.

It is also possible to compare the systems for the efficiency of OH radical ejection to the bulk solution, based on the previous discussion that decomposition takes place mainly in the aque-
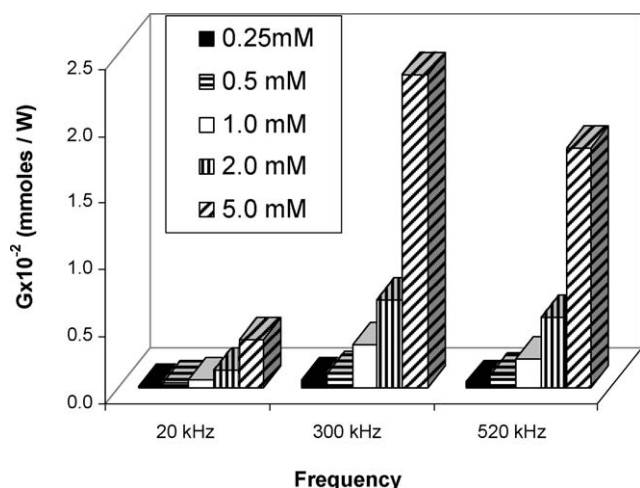
Fig. 3. Variation of G with initial phenol concentration and the applied frequency (Operating conditions are pH 2.0 and continuous air injection at $1.5 \, l \, min^{-1}$).
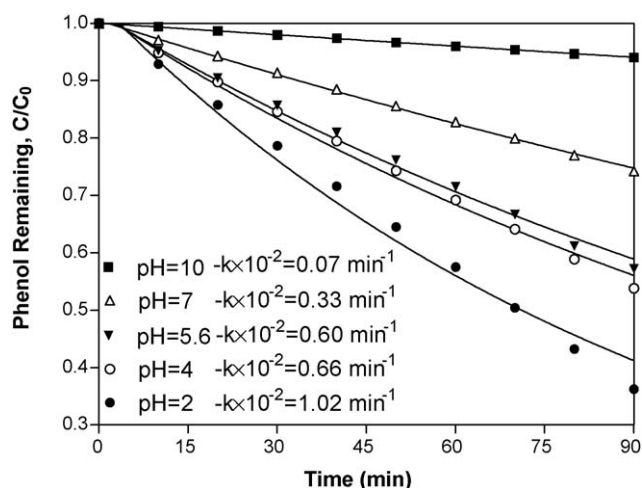

Fig. 4. Impact of pH on the rate of phenol removal during irradiation of 5.0 mM phenol at 300 kHz.

ous phase. An indirect method of determining the amount of OH radicals in solution is to monitor the accumulation of H_2O_2 in solution with time. The observed H_2O_2 concentrations in deionized water (containing no phenol) were converted to yield units and added to the very last row of Table 1 for comparison with G. It is noteworthy that the yield of product formation from phenol decomposition (G) and that of $^\bullet$OH ejection into solution are perfectly consistent, verifying again the dominance of aqueous phase oxidation reactions and the larger efficiency of the 300 kHz reactor system.

Calculated decomposition yields for each test concentration at the applied frequencies are compared in Fig. 3 in a bar chart. Note the remarkable enhancement in G as C_0 was increased from 2.0 to 5.0 mM as was noted previously in discussing rate enhancements with increasing concentrations. The improvement in G must be related to the increased probability of phenol transfer to the bubble–liquid interface followed by its sorption at the sheath, where it may undergo thermal decomposition upon collapse.
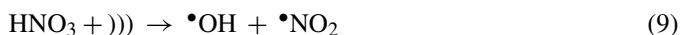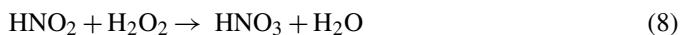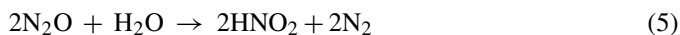
3.2. Effects of pH and the sparge gas

In aqueous solutions of phenol the degree of ionization from molecular state to the phenolate ion increases as pH is raised, and at $pH > pK_a$ (=10) phenolate ion is the major species, which due to repulsive forces are unable to approach the negatively charged cavity bubbles or even the bubble–liquid interface, where uncombined OH radical concentration is at a maximum [10]. As pH is lowered and the fraction of molecular phenol increases, the probability of solutes approaching the interfacial area also increases, resulting in enhanced rates of phenol removal. This is demonstrated by the rate profiles plotted in Fig. 4 for five different pH.

The impact of the sparge gas was tested by continuous injection of argon and air separately, each at $1.5 \, l \, min^{-1}$ into buffered and non-buffered solutions of phenol and sonicating the test solutions at 300 and 520 kHz. Despite the theory-based knowledge that the presence of monoatomic gases in sonicated liquids

are more favorable than diatomic gases for the output temperatures generated at collapse [25], we found higher sonochemical yields in the presence of air than that of argon. Comparative impacts of the test sparge gases on the ultrasonic yield are given in Table 2 for 5 mM phenol sonicated in 300 and 500 kHz reactors at pH 2.0 and 5.6.

Larger yields in the presence of air despite its lower polytropic gas ratio is due to the reactions of nitrogen with molecular oxygen to yield nitric acid and radical species such as $^\bullet$OH, $^\bullet$NO$_2$, and $^\bullet$NO$_3$ that accelerate the oxidation process. Chemical reactions that take place during air injection into a sonoreactor are as follows [26]:

$$2N_2 + O_2 \rightarrow 2N_2O \tag{4}$$

$$2N_2O + H_2O \rightarrow 2HNO_2 + 2N_2 \tag{5}$$

$$^\bullet H + N_2O \rightarrow N_2 + {}^\bullet OH \tag{6}$$

$$^\bullet OH + N_2O \rightarrow 2NO + {}^\bullet H \tag{7}$$

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \tag{8}$$

$$HNO_3 +))) \rightarrow {}^\bullet OH + {}^\bullet NO_2 \tag{9}$$

$$HNO_3 +))) \rightarrow {}^\bullet H + {}^\bullet NO_3 \tag{10}$$

While the formation of nitrous and nitric acids (reactions (5) and (8)) favor the decomposition process via pH reduction, generation of excess $^\bullet$OH and other radicals such as nitrite and nitrate, which are comparably strong oxidants of organic com-

Table 2
Effect of the sparge gas on sonochemical yield of 5 mM phenol (gas flow = $1.5 \, l \, min^{-1}$)

Frequency (kHz)	$G \times 10^{-2}$ (mmol/W)			
	pH 5.6		pH 2.0	
	Air	Argon	Air	Argon
300	1.69	1.61	2.34	2.04
520	1.37	1.15	1.79	1.61

pounds ($k_{\cdot N_{ox}} = 10^7 \, l \, mol^{-1} \, s^{-1}$; $k_{\cdot OH} = 10^{12} \, l \, mol^{-1} \, s^{-1}$ [27]) further accelerates the oxidation process.

4. Conclusions

Ultrasonic decomposition efficiency of phenol is significantly related to the applied frequency ($300 > 520 > 20 \, kHz$), solution pH (acidic > neutral > alkaline), initial concentration ($5 > 2 > 1 > 0.5 \, mM$, etc.) and the injected gas type (air > argon). Frequency effects are due to the resonating bubble size and the nature of bubble collapse in addition to the physical–chemical properties of phenol and the reactor properties, while pH and concentration effects rise because of enhanced probability of the solute to approach the cavity sheath, where radical species are at a maximum. More effective decomposition in the presence of air despite its lower polytropic gas ratio is a consequence of the reactions of nitrogen in ultrasonic media to produce additional radicals.

Acknowledgement

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