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# Mechanistic insight on the sonolytic degradation of phenol at interface and bulk using additives

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## Abstract:

Present work investigated the degradation of phenol based on theoretical knowledge of bubble dynamic and experimental studies. Optimum parameters of theoretical knowledge such as initial concentration of phenol: 1.1 mole/L; concentration of additive: 2 g/L; liquid medium temperature: 35°C and pressure of liquid medium: 101325 Pa were considered for the experimental study. The degradation was further explored in the presence of zinc oxide (effect of particle size), hydrogen peroxide (effect on hydroxyl radical concentration), and sodium chloride (effect of a change in liquid properties) and its effect on degradation of phenol. The degradation of phenol increased in the presence catalyst such as  $0.61 \pm 0.013$  moles  $L^{-1} min^{-1}$  (hydrogen peroxide),  $0.44 \pm 0.014$  moles  $L^{-1} min^{-1}$  (zinc oxide), and  $0.5 \pm 0.013$  moles  $L^{-1} min^{-1}$  (sodium chloride) compare to the absence of catalyst  $0.24 \pm 0.009$  moles  $L^{-1} min^{-1}$ . The results confirmed that maximum degradation of phenol obtains in the presence of hydrogen peroxide (cavitation yield:  $15.9 \times 10^{-5}$  mg/J, the rate constant:  $4.8 \times 10^{-5} min^{-1}$ , and TOC removal 28.5%). The presence of sodium chloride showed the considerable effect on degradation and TOC removal. Results confirmed that the degradation of phenol is driven by the hydroxyl radicals' mechanism and increased with increase in the concentration of hydroxyl radicals. The degradation of phenol was highly dependent on the concentration of phenol near vicinity of the liquid-bubble interface.

**Keywords:** Mechanistic approach, Bubble Dynamics, Sonication, phenol degradation, cavitation yield, additives

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## Nomenclature

$A_s$ : surface area of bubble

$C_p$ : concentration of pollutant molecules in the bubble

$C_{pi}$ : heat capacities of species at constant pressure

$C_{p,mix}$ : heat capacity of gaseous mixture at constant pressure

$C_{pr}$ : concentration of pollutant molecules at bubble wall

$C_{v,mix}$ : heat capacity of mixture at constant volume

$C_w$ : concentration of water molecules in the bubble

$C_{wr}$ : concentration of water molecules at bubble wall

$dV$ : change in volume of bubble

$D_p$ : diffusion coefficient of pollutant.

$D_w$ : diffusion coefficient of water

$E$ : net energy in the bubble

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$h$ : radius of Wander Vaals hard sphere

$h_w$ : molecular the enthalpy of water

$k$ : Boltzman constant

$K$ : thermal conductivity of species

$L_p$ : length scale of diffusion in the presence of pollutants

$L_{th}$ : thermal diffusive penetration length

$L_w$ : length scale of diffusion or thickness of diffusive water layer around bubble

$N_{tot}$ : total number of molecules in the bubble

$N_w, N_{Ar}$  and  $N_p$ : number of molecules of water, argon, and pollutants respectively

$P_i$ : pressure inside the bubble

$Q$ : net heat in the bubble

$R$ : radius of bubble at any time 't'

$R_0$ : initial radius of bubble

$T$ : temperature inside bubble

$T_0$ : temperature at interface

$U_w$ : internal energy of water molecule

$W$ : work done by the bubble

$\rho_i$ : densities of species

$\rho_{mix}$ : density of gas mixture

$\lambda_{ij}$ : thermal conductivity of bubble

## 1 Introduction

Phenol and its derivatives are considered as one of priority chemicals and highly persistent in the environment. These chemicals need to be treated before discharge to surface water. Worldwide, phenol production is more than 6 million ton/year. It is increasing with growing demand of globalization [1-5]. About 95% of the total phenol is produced by Hock process [6]. Major contributing industries of phenolic wastewater are refineries (6-500 mg/l), coking operation (28-3900 mg/l), coal processing (9-6800 mg/l), petrochemicals (2.8-1220 mg/l) and other industries like cosmetic and pharmaceuticals [7-10].

Phenol has health effects through an inhalation and ingestion. It rapidly absorbs into the body through the skin and may cause skin and eye burns. The overdose of phenol leads to comas, convulsions, cyanosis which may further result in death. Phenol can also affect the liver, kidneys, lungs and vascular system [14-17]. Due to toxic nature, Environmental Protection Agency (EPA) has set limits for discharging of the phenolic wastewater. It should be less than 1 ppb (parts per billion) in surface water, > 0.5 ppm (parts per million) for industrial water and >1 ppm for municipal sewage wastewater system [14-16]. Currently, several technologies used for the treatment of phenolic wastewater such as distillation, liquid-liquid extraction (membrane extraction), adsorption (using activated carbon /resin /enzymatic oligomerization) and pervaporation [6]. These methods are typically useful for the treatment of lower concentration of phenol and required higher processing conditions (temperature and pressure). Solid waste generated during the treatment may cause additional disposal problem. The biological method has the limitation of maintaining the single microbial species/stain for degrading phenol and require higher residence time. Therefore, the complete mineralization of phenol is a major challenge for the conventional methods [18-19].

An advanced oxidation process (AOP) is useful for the treatment of phenol. Several AOP techniques are available for oxidation of phenol, such as ozonation, Fenton-oxidation, electro-oxidation, photocatalytic, sonochemical and their sequential/combination approach [10-15]. Fenton-based oxidation increases the phenol degradation but generate secondary solid waste. Ozonation has the limitation of global warming issues, and electrolysis requires higher current density [1-5]. Photo-catalysis can overcome limitation associated with other AOP techniques and another advantage of minor safety issues. It has typical limitations of the lower penetration depth of UV light and separation of the catalyst. These factors may affect the scale-up aspects of the photocatalytic reactor [14-18].

A broad spectrum of sonochemical effects (ambient process conditions) is suitable for the treatment of phenolic wastewater. It works on the principle of cavitation and produces the highly reactive radicals to oxidize the target pollutants [1-4]. Most of the work reported in the literature at different frequencies, a lower concentration of phenol, effect of additives and fewer volume of operation [21-22]. The lower frequency operation produced, the more transient collapse of cavities at million location in the reactor and produce more numbers of hydroxyl radicals. This activity is highly useful for enhancing degradation kinetics of phenol [1-8]. Megasonic scale frequency produced a higher number of stable cavitation activity. Stable cavitation is helpful in degradation of hydrophobic compounds with low pka value [9-11]. Due to the hydrophilic nature of the phenol, it remains in bulk of the solution. The lower frequency operation preferred for treatment of phenol.

Moholar and et al. reported the work on the mechanistic understanding of the sonochemical process [1-2, 24-25]. Recent work mechanistic degradation of organic pollutants was highlighted on kinetic and thermodynamic analysis of degradation using different protocols. They observed that sonochemical process is driven by a negative change in activation energy and enthalpy. Sono-enzymatic process controlled by the positive change in activation energy and enthalpy [23]. Mechanistic aspect sonochemical degradation of perchloroethylene observed that frequency operation plays a major role in degradation of volatile compounds. The cleavage  $\text{Cl}^-$  ion from perchloroethylene increased with a decrease in frequency of operation [24]. Mechanistic understanding sonochemical degradation of two kinds of pollutants revealed that degradation of volatile pollutants occurs primarily by thermal pyrolysis. The hydroxyl radicals are predominant for the treatment of nonvolatile pollutants [1-2]. Reported work on the mechanistic analysis of cavitation is limited to the understanding of cavitation physics. The correlating findings of experimental and theoretical work will be useful for the development of scale aspects of the sonochemical reactor.

In the present work, links relation between the theoretical knowledge based on bubble dynamic model with experimental results in the presence of different additives viz. zinc oxide, hydrogen peroxide, and sodium chloride. Optimum parameters based on theoretical knowledge utilized for the experimental study. Results were analyzed based on the initial concentration of phenol, the effect of additives, cavitation yield, kinetic of degradation and removal of total organic carbon (TOC).

## 2 Materials and Method

### 2.1 Materials

Phenol, zinc oxide, hydrogen peroxide, sodium chloride procured from M/s Newneeta Chemicals, Pune, India. The stock solution of phenol was prepared in distilled water, obtained from distilled water (Millipore) plant of AISSMS College of Engineering, Pune, India. All the chemicals used as received from the providers.

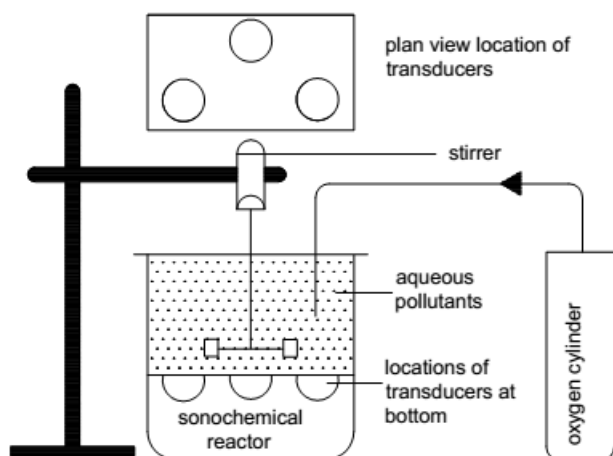
### 2.2 Reactor Details

The experiments were performed in an ultrasonic bath. Bottom of bath attached with three transducers (triangular pitch). Operating frequency of bath is 20 kHz, power dissipation of 120 W, the dimension of a reactor of 25cm×17.5cm×10 cm and procured from M/s Oscar Ultrasonics Pvt Ltd, Mumbai, India. The calorimetric efficiency (the power dissipation to liquid medium) of the bath was 46 W (~ 38.3 %) for 3 L of solution. Schematic of the reactor have been shown in Figure 1. The stirrer (350 rpm) was introduced into the reactor for maintaining the uniform concentration of phenol, suspension of additives and cavitation effects. The temperature of the reactor was maintained at constant desired value of 35±2°C by operating reactor cyclic mode of 'on' and 'off' condition ('on' time: 15 min and 'off' time: 10 min).

### 2.3 Experimental Procedure

A stock solution of phenol was prepared by dissolving known mass of phenol in distilled water. Initially, the

sonochemical reactor was filled with the aqueous solution of phenol (3 L). The solution was saturated with oxygen by bubbling with oxygen gas for 30 min. A blanket of oxygen gas was maintained for throughout the experiment. The experiments were performed in the presence and absence of additives. A constant stirring (400 rpm) was maintained for all experiments. The reaction was stopped by quenching the samples in an ice bath (temperature range between 0°C to 5°C). Standard deviation immediate analysis of withdrawn samples and quenched samples were  $\pm 0.25 \mu\text{M}$ . It was very small, so the results of quenched samples were reported in the manuscript.



**Figure 1:** Schematic of sonochemical reactor (bath)

## 2.4 Analysis

Collected samples were filtered before analysis to remove the traces of suspended particles (if any). Initially, the samples were diluted (5-20 times) by dissolving samples in distilled water (absorbance of high concentration of phenol cannot be measured using the UV spectrophotometer. Hence the samples were diluted). The concentration of phenol measured using CHEMITO SPECTROSCAN UV 2600 at 270 nm (maximum absorbance of phenol). Calibration plot of a standard solution of phenol was prepared. The concentration of unknown samples was measured based on the calibration curve. The concentration of carbon was monitored using Shimadzu total organic carbon (TOC) analyzer (Model: TOCLCPH) and procedure for measuring the concentration of TOC reported in our earlier work [25].

## 3 Mathematical model

Bubble dynamic model estimates the physical and chemical effects of cavitation based on boundary layer approximation. There are two approaches to bubble dynamic modeling viz single bubble and cluster approach (1-2). Cluster bubble approach has the limitation of the unknown of a number of cavities present in the system. Moreover, ultrasound provides resistance to coalescence or aggregation. The coalescence is very less in ultrasound assisted system (3-4). Thus, single bubble approach was used for modeling and simulations. The differential equations (Equations 1-6) were solved by Runge-Kutta-Felberg Step Adaptive size (RKF) method iteratively till significant reduction in error. Step size was adjusted based on error value and the progress of the numerical simulation. MATLAB 7.8 (2009a) was used to simulate these models. By applying laws of conservation over a bubble, the summarized basic modeling equations are as follows (2-8).

By applying conservation law of energy, total energy balance over single cavity (bubble) is

$$\frac{dE}{dt} = \frac{dQ}{dt} - \frac{dW}{dt} + h_w \frac{dN_w}{dt} \quad (1)$$

Where,  $h_w = 4kT_0$  [21]. The bubble is considered as continuously expanding and work done by the system (bubble) may be assumed as the expansion of bubble ( $W = P_i dV$ ). The pressure generated inside the bubble is due to molecular motion molecules, and it increases with increasing number of molecules. Mass transfer across bubble is occurring due to diffusion of water only. Since the time scale of oscillation of bubble is minuscule as compare to the time scale of diffusion of gasses inside the bubble [18, 22-24]. The diffusion of gasses may be neglected and entire diffusion occurs in the film thickness ( $L_w$ ). Mass transfer across the gas-liquid interface (bubble) is given by Fick's law of diffusion (equation 2a).

$$\frac{dN_w}{dt} = A_s D_w \frac{\delta C_w}{\delta r} \text{ at } r=R \approx A_s D_w \left( \frac{C_{wr} - C_w}{L_w} \right) \quad (2a)$$

Where surface area of bubble is  $A_s = 4\pi R^2$  and  $C_{wr} = \frac{P_v(T_0)}{kT_0}$ . Vapour-liquid equilibrium is assumed at the interface. The properties at the gas-liquid interface are considered as same as that of the liquid medium. If nature of pollutant is volatile then the mass transfer of pollutants across the gas-liquid interface is considered same as that of water and calculated as:

$$\frac{dN_p}{dt} = A_s D_p \frac{\delta C_p}{\delta r} \text{ at } r=R \approx A_s D_p \left( \frac{C_{pr} - C_p}{L_p} \right) \quad (2b)$$

The net heat generated in the bubble ( $Q$ ) is:

$$\frac{dQ}{dt} = A_s \lambda_{ij} \left( \frac{T_0 - T}{L_{th}} \right) \quad (3)$$

The pressure generated inside the bubble is:

$$P_i = \frac{N_{tot}(t)kT}{V - V_b} \quad (4a)$$

Where,  $N_{tot} = N_w + N_{Ar} + N_p$ . Volume of bubble is  $V = \frac{4\pi}{3} R^3$ . There are various types of molecules present in the bubble (Vander Waal consider a molecule as hard sphere). The average molecular volume of a hard sphere is  $V_b = \frac{4\pi}{3} h^3$ .  $h$  is Vander Waals hard core radius and equivalent to  $\approx \frac{R_0}{8.86}$  [18]. Pressure is considered in terms of Laplace form. The external influences of the pressure fluctuations (i.e. Laplace pressure) generated in the liquid medium due to sound waves and it may consider as follows:

$$P_t = P_A \sin(2\pi ft) \quad (4b)$$

$P_t$  is time variant pressure of liquid medium due to wave oscillations.  $f$  is frequency of the wave and  $t$  is time. Energy across bubble is function as  $V$ ,  $T$  and  $N_w$ ; it can be considered as (3):

$$\frac{dE}{dt} = U_w \frac{dN_w}{dt} + C_{v,mix} \frac{dT}{dt} \quad (5)$$

Energy equation in terms of temperature gradient is,

$$\frac{dT}{dt} = \frac{\left[ \frac{dQ}{dt} - P_i dV + (h_w - U_w) \frac{dN_w}{dt} \right]}{C_{v,mix}} \quad (6)$$

Instantaneous diffusive penetration depth ( $L_w$ ) and thermal diffusion length ( $L_{th}$ ) are the thickness of the film formed inside the bubble and near the gas-liquid interface (where heat, mass, and all phenomena occur) (18, 23). The temperature of the film may be considered as constant and calculated as follows:

$$L_w = \min \left( \sqrt{\frac{RD_w}{|dR/dt|}}, \frac{R}{\pi} \right) \quad (7a)$$

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