

## Sonochemical degradation of Phenol and Para-Chlorophenol in an Ultrasonic bath in the Presence of inorganic salts and H<sub>2</sub>O<sub>2</sub>

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### Abstract

Phenol (Ph) and some of its derivatives such as para chloro-phenol (PCP) have received considerable attention from environmental scientists and engineers, due to their undesirable effects in the water environment, where they end up as a result of improper disposal methods. As a consequence, research has been conducted all around the world with the common goal of reducing their concentrations to allowable limits or converting them to non-toxic, non-hazardous forms that may easily be handled by natural decay processes. This report describes a system developed to degrade these substances using sonochemical reactions. Sonochemical degradation of phenolic compounds were carried out in the presence and absence of NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. In sonochemical degradation of phenol in sonicator high degradation rate was obtained in the presence of additives H<sub>2</sub>O<sub>2</sub> and followed the order: Ph+H<sub>2</sub>O<sub>2</sub> > Ph+Na<sub>2</sub>SO<sub>4</sub> ≈ Ph+NaCl > Ph (0 mM salt & additive) ≈ Ph+NaNO<sub>3</sub> > Ph+Na<sub>2</sub>CO<sub>3</sub>. Whereas, in case of parachlorophenol (PCP) high rate was obtained in the presence of H<sub>2</sub>O<sub>2</sub> and they followed the order: PCP+H<sub>2</sub>O<sub>2</sub> > PCP+NaCl > PCP+Na<sub>2</sub>SO<sub>4</sub> ≈ PCP (0 mM salt & additive) > PCP+Na<sub>2</sub>CO<sub>3</sub> > PCP + NaNO<sub>3</sub>.

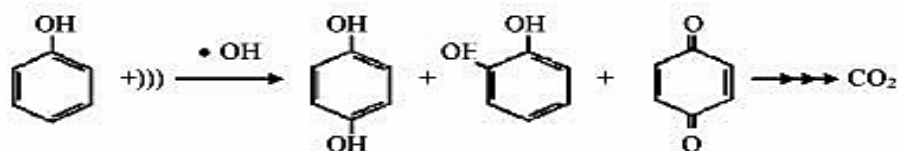
**Keywords:** Phenolic compounds, Sonolysis, Inorganic salts, H<sub>2</sub>O<sub>2</sub>.

## 1. Introduction

Wastewater from the industries has to be treated because it causes toxicity and foul odor to the water that can be a potential hazard to human health and the environment. Phenol and its derivatives are the one of the common and important hazardous chemical compounds in wastewater. Its high stability and solubility in water is the main reasons why the degradation of this compound to acceptable levels is a relatively difficult process. These chemicals 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, PCP stuff, textiles, tanning, fiberboard production and paint stripping operations, pulp and paper, pesticides, medications, pharmaceuticals and even from food processing industries [1-6] Phenol is one of the most abundant pollutants in industrial wastewater. [7, 8] Even though the concentration of phenolic compound in wastewater is low, it is considerable as toxicity. It has to be handled with great care because it causes immediate white blistering to the skin. The major hazard of phenolic compound is its ability to penetrate the skin rapidly, particularly when liquid, causing severe injury which can be fatal. These chemicals also have a strong corrosive effect on body tissue causing severe chemical burns. This compound has attracted public attention because of its exposure that can result acute and chronic effects to human health. [9] Due to its toxicity, hazardous character and increasing social concern on the environment, the discharge of such compounds in the environment has become more restrict. Therefore, there is more demand for improved methods of treatment. [2, 6] Ultrasonic oxidation is a novel advanced oxidation process that has emerged as an answer to the growing need for lower levels of contaminants in wastewater [10, 11] Nowadays, the application of ultrasonic (US) in wastewater treatment has attracted great interest. It has been proposed as one of the alternative techniques for degradation of hazardous organic compounds. Ultrasonic technology as an innovative technology may be used for water and wastewater treatment for pollution removal.

Ultrasonic irradiation results in the formation and collapse of micro scale bubbles and generating local high temperature. The bubbles are thought to work as the reaction field and the local high temperature caused by the collapsed bubbles forces the decomposed water to generate hydroxyl radicals, which promotes the degradation reaction of the organic compounds. Phenol and its chloro derivatives are largely soluble in water so that the main reaction site for them destruction during ultrasonic irradiation is the bulk liquid, where the attack of hydroxyl radicals on the ring carbons results in various oxidation intermediates.

After sufficiently long contact times mineralization occurs.



**Fig.1:** Structure of Degradation of Phenol.

Phenol 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. [4] But degradation of phenol to such low levels has not been possible by conventional biological treatment processes. Many process such as wet air oxidation, radiolysis, Fenton oxidation, photocatalytic oxidation, electrochemical oxidation, ozonation and peroxidation had been used in the past for the degradation of phenol to the required low levels. [9]

All these processes have their inherent limitations such as low rates of degradation, or lower mineralization or high costs of operation or severe operating conditions. Sonication for phenol and phenolic compounds degradation has proved to be an attractive process in terms of its normal operating conditions and lower costs. There had been some efforts to increase the rates of phenol degradation using hybrid techniques. [12, 13] The aim of these researches is to investigate the optimum condition for the degradation of phenol and phenolic compounds in the absence and presence of inorganic salts and H<sub>2</sub>O<sub>2</sub>. To the best of our knowledge sonochemical degradation of phenol and para-chlorophenol degradation in a sonicator is the first time.

## 2. Basic principles of sonochemistry

In chemistry, the study of sonochemistry is concerned with understanding the effect of sonic waves and wave properties on chemical systems. The chemical effects of ultrasound do not come from a direct interaction with molecular species. Studies have shown that no direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry or sonoluminescence. Instead, sonochemistry arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. This is demonstrated in phenomena such as ultrasound, sonication, sonoluminescence, and sonic cavitation. Firstly, sonochemistry can cause real chemical changes to a solution without the necessity of adding any other compounds. Secondly, sonochemistry is often conducted at low temperatures and pressures; thus, no heating or pressurization is required. These two features simplify enormously the design and operation of reactors. Thirdly, in many cases, the peculiar nature of sonochemical reactions offers alternative pathways, providing a faster or environmentally safer degradation of contaminants. The present challenge for

sonochemists and acoustical physicists in the field of environmental remediation is to provide cost-effective sonochemical solutions to large-scale problems. Sonochemistry proceeds because the passing of acoustical waves of large amplitude, called finite amplitude waves, through solutions causes cavitation.

### 3. Sound theory

Most modern ultrasonic devices rely on transducers which are composed of piezoelectric materials. Such materials respond to the application of an electrical potential across opposite faces with a small change in dimensions. This is the inverse of the piezoelectric effect. If the potential is alternated at high frequencies, the crystal converts electrical energy to mechanical vibration (sound) energy. At sufficiently high alternating potential, high frequency sound (ultrasound) will be generated. When more powerful ultrasound at a lower frequency is applied to a system, it is possible to produce chemical changes as a result of acoustically generated cavitation. Frequencies above 18 kHz are usually considered to be ultrasonic. The frequencies used for ultrasonic cleaning, range 20 kHz to over 100 kHz. The most commonly used frequencies for industrial cleaning are those between 20 and 50 kHz. [14, 9, 15] Ultrasound has wavelengths between successive compression waves measuring roughly 10 to  $10^{-3}$ cm. Because of this mismatch, the chemical effects of ultrasound cannot result from a direct interaction of sound with molecular species. [16]



**Fig. 2:** Compression and expansion cycle of ultrasound [9, 14, and 15]

### 4. Experimental procedure

Phenol and parachlorophenol were purchased from Popy chemicals, Dhaka, Bangladesh. Sodium chloride, sodium sulfate, sodium carbonate, sodium nitrate and hydrogen peroxide were purchased from Merck KGaA 64271 Darmstadt, Germany. All chemicals were reagent grade and used as received. An ultrasonicator model soniclean 250HT, 50-60 Hz was used to degrade phenolic compound in aquatic medium. The schematic diagram of the experimental setup is shown in the **Fig. 3**. A conical flask with a total volume of 100 ml of 50 mg/L sample solution was used for ultrasonic irradiation under air at room temperature around 24°C. The sonicated solution was extracted every (0, 3, 7 and 10 min) by a glass syringe (1 ml) without exposing the

sample to air. The glass vessel was flat bottomed and was mounted at a constant position (4.0 mm from the oscillator). The sonicated solutions were analyzed by a UV-Vis spectrophotometer (Shimadzu UV-1650).



**Fig. 3:** Schematic diagram of the experimental set-up.

### 5. Calorimetric power measurement during sonication

A technique for quantitatively evaluating an ultrasonic reaction field has been investigated. Ultrasonic power is one of the important factors for sonochemistry. Calorimetry is one of the most frequently used methods for measuring the actual ultrasonic power input for a solution. <sup>[16, 17]</sup> Equation (1) gives the calculated ultrasonic output power  $P$ .

$$P = MC_p \frac{dT}{dt} \quad (1)$$

Here,

$C_p$  = heat capacity of water

$M$  = mass of water

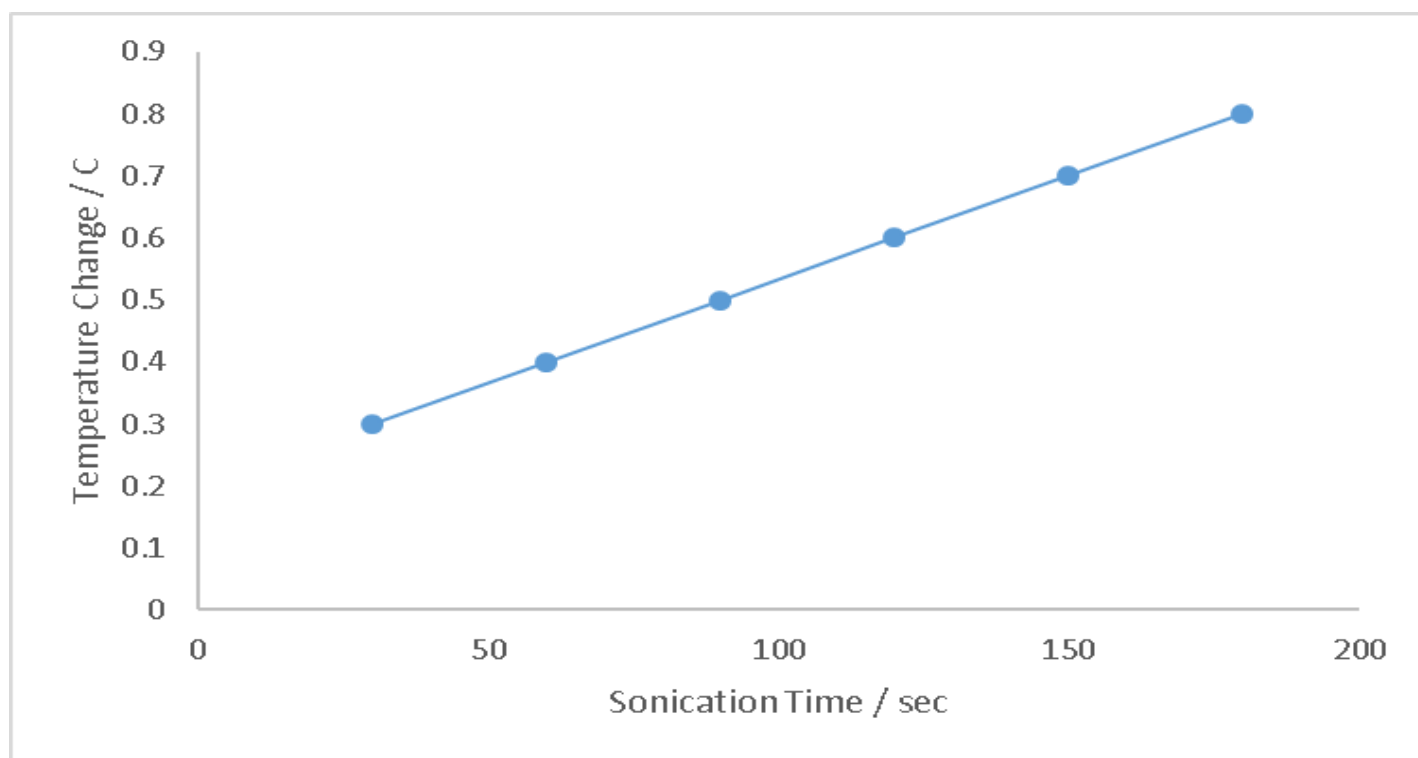
$T$  = temperature of the sample solution

$t$  = ultrasonic irradiation time.

<i>Observation</i>	<i>Sonication Time</i> )sec(	<i>Initial Temperature</i> )°C(	<i>Final Temperature</i> )°C(	<i>Temperature Change</i> )°C(	<i>Acoustic power</i> (W)
1	30	24.7	25.0	0.3	4.180
2	60	25.2	25.6	0.4	2.787
3	90	25.6	26.1	0.5	2.322
4	120	26.0	26.6	0.6	2.090
5	150	26.4	27.1	0.7	1.951
6	180	26.7	27.6	0.8	1.858

**Table 1:** Measurement of temperature change.

**Graphical presentation of temperature change:**

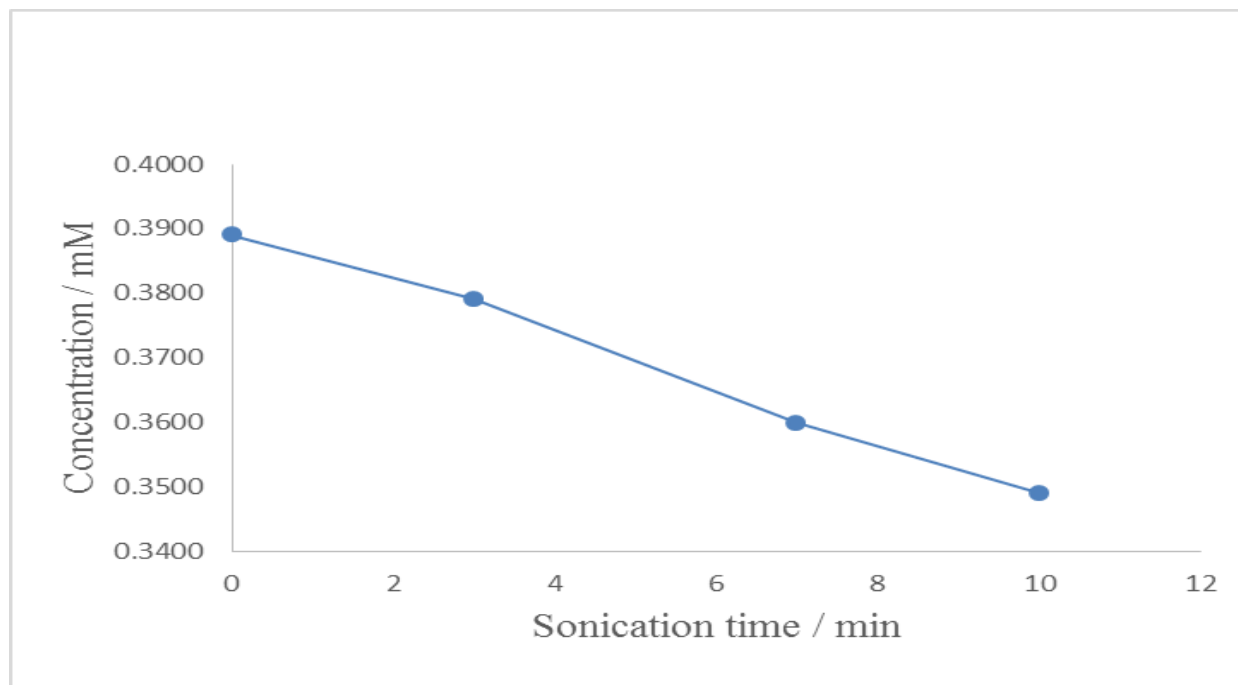


**Fig. 4:** Graphical chart for measurement of temperature change with increasing sonication time.

From the **Table-1** and **Fig. 4**, indicate that the temperature in the site of the reaction is increasing with sonication time. Again, reaction rate increases with temperature. Therefore, degradation rate of the phenolic compounds would increase with the elongation of sonication time.

## 6. Results and Discussion

Fig.5 Show the sonochemical degradation of PCP in the absence of inorganic salts and additives. The figure indicates that the rate constants increase with increasing sonication time. At the initial PCP concentration was 0.3889 mM. After sonicating for 3 mins, 7 mins and 10 mins, the concentrations became 0.3791mM, 0.3599 mM and 0.3490 mM respectively. The graphical representation is shown in fig.5.

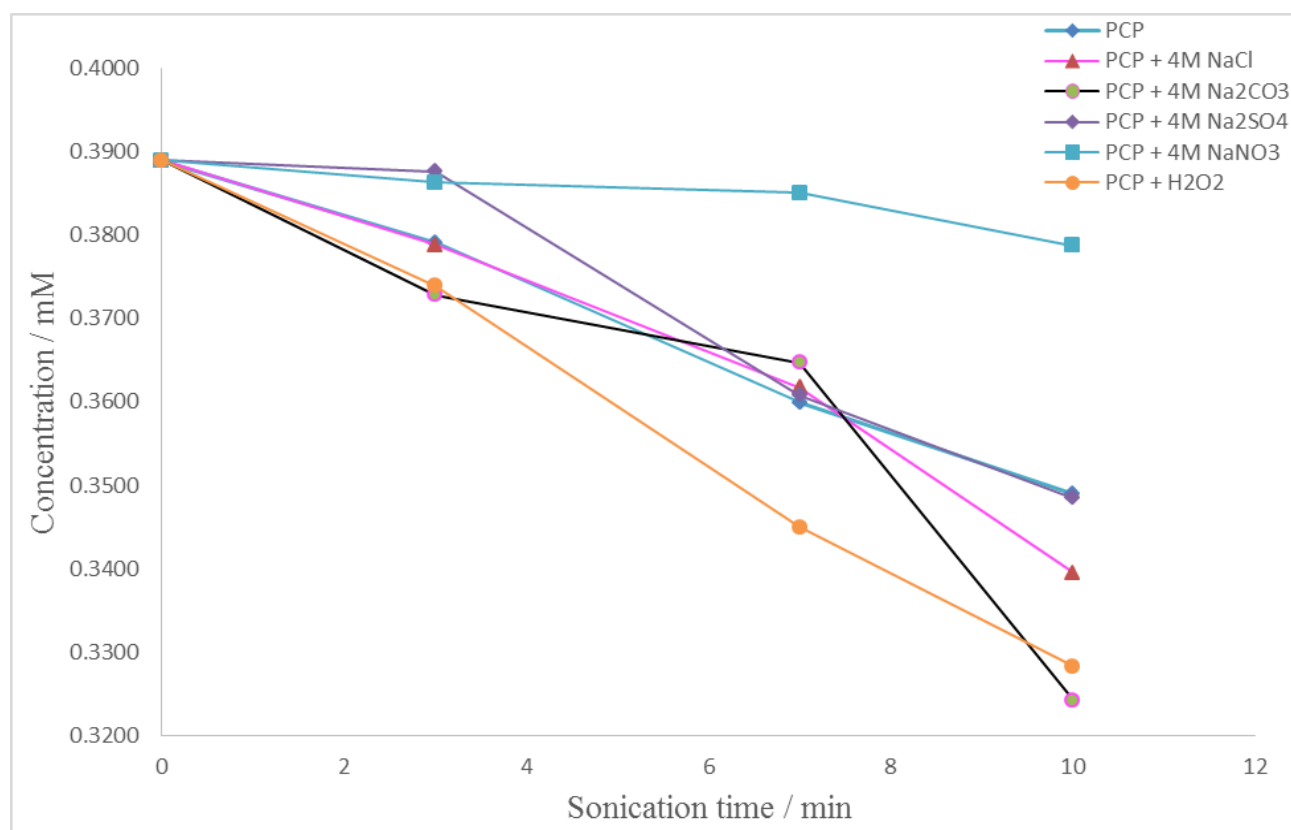


**Fig. 5:** Time dependence of sonochemical degradation of para-chlorophenol (50mg/ L).

The fact that the degradation rate increases proportionally with concentration despite the increased competition for hydroxyl radicals in the bulk solution shows that at higher concentrations decomposition occurs not only in the bulk liquid but also at the bubble-liquid interface. However, a linear relationship was not observed, as expected, for a first order kinetic law. The initial degradation rate can be expected to be dependent on the concentration of OH radicals produced and the concentration of the PCP molecules at the interface of the cavitation bubble. At the surface of the collapsed bubble, the OH radical concentration is remarkably high. At lower PCP concentrations, a considerable part of these OH radicals will recombine yielding  $H_2O_2$  and the degradation is carried out in the bulk of the solution where there is a lower concentration of OH radicals because only about 10% of the OH radicals generated in the bubble can diffuse into the bulk solution, which conduct to lower degradation rates. On an increase in the PCP concentration,

the probability of OH radical attack on PCP molecules increases, thus leading to an increase in the degradation rate. However, if the PCP molecules at higher concentration reach a saturation limit at the bubble surface during the persistence time of the bubble, an almost constant degradation rate at higher solute concentrations is reached. At higher PCP concentration, an increasing proportion of the OH radicals will be scavenged and the  $H_2O_2$  yield progressively reduced and because PCP is a non-volatile compound, the sonochemical reaction with the hydroxyl radical is expected to take place at the cavitation bubble interface where the hydroxyl radical concentration attains an upper limit.

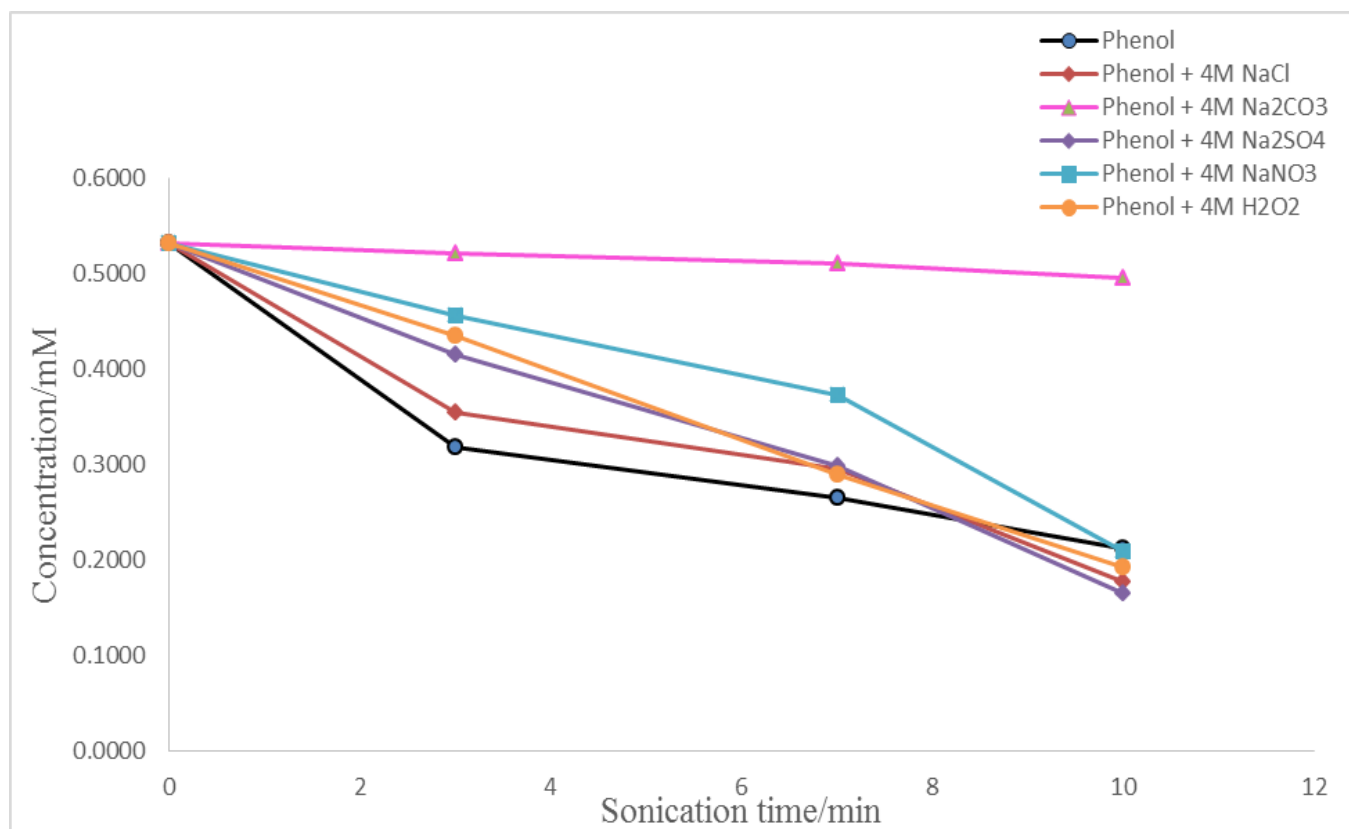
Fig.6: Shows the time dependence comparison of para-chlorophenol in the absence and presence of salts and additive.



**Fig.6:** Time dependence comparison of sonochemical degradation of PCP with and without salt and additive.

This figure indicates that, the addition of salt and additives enhance the degradation of Para -chlorophenol compared to the degradation of Para-chlorophenol alone. Though in cases of some salt the degradation rate was comparatively slow at initial state, but finally the rate increased noticeably. The degradation rate is much higher in case of  $H_2O_2$ . Fig.7: Also shows the time dependence comparison of phenol in the absence and presence of salts and additive.





**Fig.7:** Time dependence of comparison of degradation of phenol with and without salt and additive.

One of the popular advanced oxidation process (AOP) methods for degradation of phenolic compounds is the oxidation with H<sub>2</sub>O<sub>2</sub>. Presence of H<sub>2</sub>O<sub>2</sub> is a key parameter for phenol and para-chlorophenol decomposition in AOP technique, depending on its concentration and nature of reductants. Hydrogen peroxide increases the formation of rate of hydroxyl radicals in two ways. First, the reduction of H<sub>2</sub>O<sub>2</sub> at the conduction band would produce hydroxyl radicals. Second, the self-decomposition as a result of ultrasound irradiation would also produce hydroxyl radicals. Generally, the degradation rate of phenolic compounds increase as the H<sub>2</sub>O<sub>2</sub> concentration increase until an optimal concentration is achieved. <sup>[18]</sup> Recently, ultrasonic irradiation was described as a possible generator of highly active OH, HOO<sup>•</sup> and H<sup>•</sup> radicals. <sup>[19]</sup> The resulting plots of percentage of phenolic compounds removal versus time implying the H<sub>2</sub>O<sub>2</sub> effect are shown in the figure.

## 8. Conclusions

Sonochemical degradation of phenol and para-chlorophenol has been studied at room temperature. This work has shown that phenolic compounds can be effectively degraded by ultrasonic irradiation. This study

demonstrates that sonochemical degradation occurs mainly through reactions with hydroxyl radicals. It was found that the initial degradation of phenolic compounds increased. The addition of salt and additives enhanced the rate of degradation. In the presence of H<sub>2</sub>O<sub>2</sub> phenol and para-chlorophenol significantly degraded.

## References

1. Lesko, T. M., (2004), Chemical Effects of Acoustic Cavitation, Ph.D. thesis reported in California Institute of Technology, Pasadena, California, USA.
2. Entezari, M. H. and Petrier, C., (2004), A combination of ultrasound and oxidative enzyme: sonobiodegradation of phenol. *Appl. Catal. B- Environ*, 53, 257-263.
3. Entezari, M. H. and Petrier, C., (2005), A combination of ultrasound and oxidative enzyme: sono-enzyme degradation of phenols in a mixture. *Ultrason. Sonochem.* 12, 283-288.
4. Mahamuni, N. N. and Pandit, A. B., (2005), Effect of additives on ultrasonic degradation of phenol. *Ultrason. Sonochem*, 13 (2), 165-174.
5. Lathasreea, S., Nageswara, R. A., SivaSankarb, B., Sadasivamb, V. and Rengarajb, K., (2004). Heterogeneous photocatalytic mineralisation of phenols in aqueous solutions. *Mol. Catal. A- Chem.*, 223, 101-105.
6. Beltran, F. J., Rivas, F. J. and Gimeno, O., (2005), Comparison between photocatalytic ozonation and other oxidation processes for the removal of phenols from water, *Chem. Technol. Biot*, 80 (9), 973-984(12).
7. Alnaizy, R.; Akgerman, A., (2000), Advanced oxidation of phenolic compounds. *Adv. Environ. Res.*, 4 (3), 233-244.
8. Maleki, A., Zazoli, M. A.; Eslami, A., (2005), Adsorption of phenol by commercial powdered activated carbon in aqueous solution. *Al-Haitham. J. Sci. Tech.*, 1 (1), 73- 78.
9. Entezari, M. H.; Petrier, C.; Devidal, P., (2003), Sonochemical degradation of phenol in water: a comparison. A comparison of classical equipment with a new cylindrical reactor, *Ultrason. Sonochem.* 10 (2) 103-108.
10. Wu, C., Liu, X., Wei, D., Fan, J. and Wang, L., (2001), Photosonochemical degradation of phenol in water. *Water. Res.*, 35 (16), 3927-3933.

11. Nikolopoulos, A. N., Igglessi-Markopoulou, O. and Papayannakos, N., (2005), Ultrasound assisted catalytic wet peroxide oxidation of phenol: kinetics and intraparticle diffusion effects. *Ultrason. Sonochem.*, 13(1), 92-97.
12. Naffrechoux, E., Chanoux, S., Pe'trier, C. and Suptil, J., (2000), Sonochemical and photochemical oxidation of organic matter. *Ultrason. Sonochem.*, 7, 255-260.
13. Esplugas, S.; Gimenez, J.; Contreras, S.; Pascual, E.; Rodriguez, M., (2002), Comparison of different advanced oxidation processes for phenol degradation. *Water Res.*, 36 (4), 1034-1042.
14. Suslick KS, Price G (1999), Applications of ultrasound to materials chemistry. *Annu Rev Matl Sci*, 29: 295-326.
15. Zheng W (2004), Mechanistic study of pollutant degradation. [PhD thesis] Department of Chemistry, University of New Oriends.
16. Goel M., Hongqiang H., Mujumdar A.S., Ray M.B., Sonochemical decomposition of volatile and non-volatile organic compounds—a comparative study, *Water Res.* 38 (2004) 4247–4261.
17. Kormann C., Bahnemann D.W., Hoffmann M.R., Photocatalytic production of H<sub>2</sub>O<sub>2</sub> and organic peroxides in aqueous suspensions of TiO<sub>2</sub>, ZnO, and desert sand, *Environ. Sci. Technol.* 22 (1988) 798–806.
18. Mahmoodi N.M, Arami M, Limaee N.Y, Tabrizi N.S, Decolorization and aromatic ring degradation kinetics of direct red 80 by UV oxidation in the presence of hydrogen peroxide utilizing TiO<sub>2</sub> as a photocatalyst, *Chem. Eng. J.* 112 (2005) 191-196.
19. Suslick K.S, Sonochemistry, *Science* 247 (1990) 1439-1445.



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