

ULTRASONIC DEGRADATION OF BISPHENOL A AND 4-TERT-OCTYLPHENOL

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Abstract

Bisphenol A (BPA) and 4-tert-octylphenol (OP) were well known as endocrine disrupting compounds. Ultrasonic degradation of BPA and OP was carried out by optimizing different parameters. Optimum parameters for ultrasonic degradation of BPA and OP were found to be 5 pH, 45 KHz frequency & 500 W power of sonication bath and 100-200 mg/L of Sodium persulfate in presence of air. Both degradation processes were monitored under UV absorption spectra. It was observed that both the reaction followed first order kinetics. During BPA and OP degradation the intermediates formed were identified by GC-MS analysis. The degradation rate was strongly affected by pH in both processes.

Keywords: Ultrasonic degradation, Sodium persulfate, Aeration, Bisphenol A, 4-tert-Octylphenol.

1. INTRODUCTION

Now a day's advanced oxidation processes (AOPs) are highly efficient method to remove low to trace amount of organic compounds from both aqueous and gaseous wastes (Goel et al. 2004). AOPs are well known for remediation of such contaminated water/effluent treatment without generating any sludge of hazardous character (Ince et al. 2001). Generally AOPs involve generation and utilization of hydroxyl radicals which are highly reactive in nature having an oxidation potential of 2.33V and able to oxidize the toxic and non biodegradable organic compound in the waste water (Pradhan et al. 2010).

Sonochemical oxidation involves use of ultrasound that results in the cavitation phenomenon. There is formation, growth, and subsequent collapse of microbubbles (Gogate et al. 2004). This results in local hot spot having temperature 5000K and pressure 1000 atm respectively [Joseph et al. 2009, Chakinal et al.2007, Zheng et al. 2005, Martinez-Tarifa et al. 2010]. Two main reaction mechanisms have been proposed for sono-degradation. The first is pyrolysis of hydrophobic compound with high volatility at high temperature and pressure inside the bubble, and second is generation and utilization of hydroxyl radical to oxidize the organic matter which is hydrophilic and less or non-volatile in nature (Pang et al. 2011).

Generally BPA is used for manufacturing of raw materials of epoxy and polycarbonate

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resins (Li et al. 2007, Watanbe et al. 2003). BPA also used in the manufacturing of medical device and dental materials (Shintani 2001). OP belongs to alkylphenol ethoxylates group and widely used as nonionic surfactants in large variety of industrial and commercial applications (Cruceru et al. 2012).

An endocrine disrupting chemicals (EDCs) are defined as xenobiotic and exogenous substance which can affect adversely on natural action of endocrine system of animals and human such as synthesis, secretion, transport, and binding (Chang et al.2009). Among these EDCs, BPA and OP are highly toxic in nature and mainly present in sediments and almost in every water supply, such as surface waters, waste water and even in drinking water up to 670 µg/kg and 0.1 µg/L (Ulutas et al. 2011). BPA as pollutant causes not only endocrine disruption but also cancer (Huange et al. 2012).

2. MATERIAL AND METHODS

BPA (CAS number 80-05-7), OP (CAS number 140-66-9), and Sodium persulphate were purchased from Sterling Labcare and used without further purification. All other chemicals used were of analytical grade. All the solutions were prepared in demineralized water. Stock solution of BPA (100 mg/L) and OP (10 mg/L) were prepared by dissolving it in demineralized water and stored carefully throughout the experiment.

2.1 Experimental procedure for Ultrasonic degradation experiment

The sonication process was carried out in a sonication bath at low frequency 45 KHz and power 500 W at room temperature. Experiment was conducted in 120 ml flat bottom beaker and sample amount was 40 ml. BPA and OP degradation experiment was carried out at initial concentration of 2 mg/L and 5 mg/L respectively. During sonication BPA and OP concentration were measured at regular time interval. The major UV absorption spectra of BPA was observed at wavelength 224 nm and 276 nm and of OP at 193 nm, 220 nm and 276 nm respectively in UV-VIS spectroscopy (HACH) .

3. RESULTS

3.1 Effect of pH

Effect of pH was studied at different pH for both BPA and OP degradation respectively. The effect of pH for BPA degradation studied at 5, 6, and 9 pH and for OP degradation studied at 4, 5, and 9 pH. The maximum degradation found at 5 pH in both the degradation processes. This have been investigated that, at lower pH the compound exists mainly in the molecular form, whereas at basic pH it is completely ionic in nature so the diffusion of the molecule at lowers pH to the bubble liquid interface, where the concentration of hydroxyl radicals is a maximum

which degrade the organic compound. Gultekin et al. (2008) and P. Gogate (2008) also found that the acidic pH was effective for degradation while the basic condition was not favorable for degradation of BPA. So in rest of the experiment, 5 pH was maintained.

3.2 Effect of applied frequency

The experiment was carried out at low frequency (45 KHz). This have been investigated that, frequency is a critical parameter in sonochemical action. It can affect cavitations by modifying bubble number, bubble size, cavitations threshold, and temperature reached during cavitation (Torres et al. 2008). Higher ultrasonic frequency lowered the average size of the cavitation bubbles and increased the number of cavitation bubbles with higher frequency (Park et al. 2012). 45 KHz frequency showed better degradation efficiency as compared to 25 KHz frequency. So both BPA and OP degradation were carried out at 45 KHz frequency.

3.3 Effect of ultrasonic power

Power supply was varied from 10 % to 100% of the total power supply. It was observed that maximum degradation obtain at 100 % power supply i.e. 500 W (fig.1 and fig.2) power as increasing in power causes more number of collapsing cavities, leading to enhanced degradation (Torres et al. 2008). Also the number of active cavitations bubbles and there implosive energy increases as applied power increases, leading to an increase in the amount of hydroxyl radical generated (Park et al. 2012). The thermal efficiency was calculated as 0.32 % (the ultrasonic energy dissipated in the reactor was ≈ 2 % of the total electrical power input) (Mason et al. 1992).

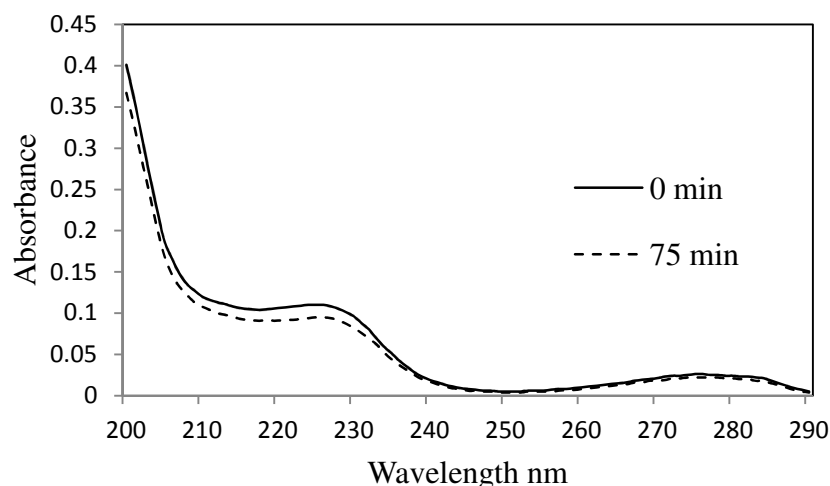


Figure 1: Effect of Ultrasonic power on ultrasonic degradation of BPA at Co: 2 mg/L; ultrasonic frequency: 45KHz, pH: 5; ultrasonic power: 500W, time: 75 min

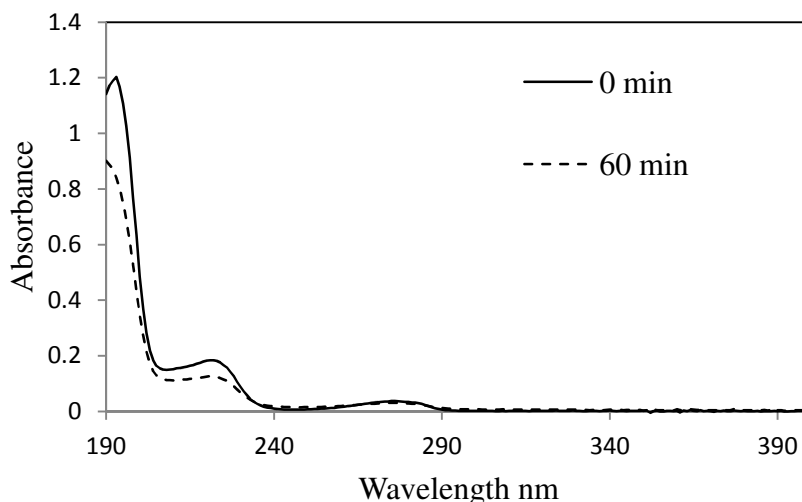


Figure 2: Effect of Ultrasonic power on ultrasonic degradation of OP at Co: 5 mg/L; ultrasonic frequency: 45KHz, pH: 5; ultrasonic power: 500W, time: 60 min.

3.4 Effect of aeration

The effect of aeration was observed at moderate air flow rate. It was observed that major spectra of BPA increases continuously at 224 and 276 nm wavelengths during aeration. After 10 min there was disappearance at 224 nm peak but 276 nm was remained and there was increase in absorbance (fig.3). This is because of formation of intermediates as observed by Ioan et al. (2007) in sono-Fenton process and Katsumuta et al. (2004) in photo-Fenton process. Intermediates found during BPA degradation were 2-pyrrolidinone,1-methyl; 1,4-dioxane-2,5-dione, 3,6-dimethyl-, (3S-CIS)- and 2-Prpanol, 1,1'-[(1-metyhl-1,2-ethanediyl)bis(oxy)]bispropanol.

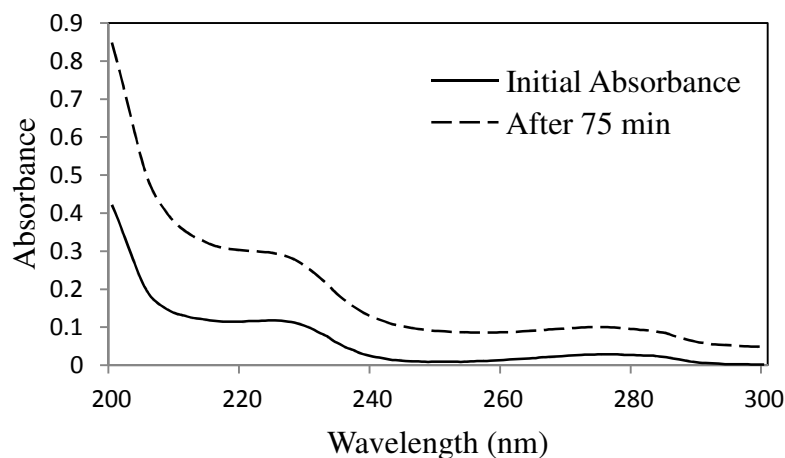


Figure 3: Effect of Aeration on ultrasonic destruction of BPA at Co: 2 mg/L, time: 75 min, pH: 5, ultrasonic power: 500W, ultrasonic frequency: 45 KHz.

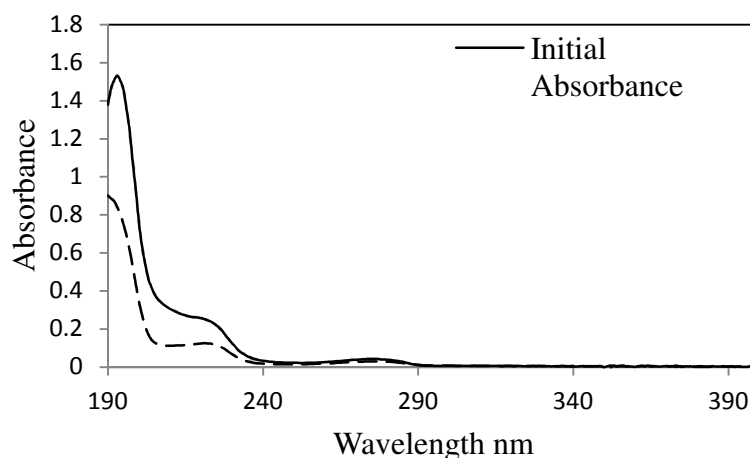


Figure 4: Effect of Aeration on ultrasonic destruction of OP at Co: 5 mg/L, time: 60 min, pH: 5, ultrasonic power: 500W, ultrasonic frequency: 45KHz.

This increase in absorbance was remained about 3 to 4 h and then slowly decreased with time. But in case of OP there was no increase in absorbance in presence of air. It was observed that there was continuous decrease in absorbance of OP (fig.4). This attributed that there was increase in degradation rate in presence of air (Mishra et al. 2012). Intermediates was identified by GC-MS technique namely Tridecane; Hexadecane; Octadecane; phthalic acid, isobutyl octyl ester; hexadecanoic acid, methyl ester; 2-methyl-tridecane.

3.5 Effect of Sodium persulfate

Sodium persulfate is a strong oxidizer which oxidizes BPA and formed intermediates in presence of air easily. It was observed that higher the concentration of sodium persulphate higher the rate of degradation of BPA. The major UV spectra of BPA obtained at 224 and 276 nm were disappeared after treatment. After 13 h, 70 % degradation of BPA was observed. The UV absorbance spectrum of initial BPA concentration; after aeration; and after sodium persulfate treatment addition is shown in fig.5. In case of OP degradation we observed that after addition of sodium persulfate initial UV absorbance spectra of OP soon just slightly increase without any treatment as shown in fig.6. During treatment the major spectra of OP at 193, 220 and 276 nm decreased continuously and 55 % degradation of OP was observed.

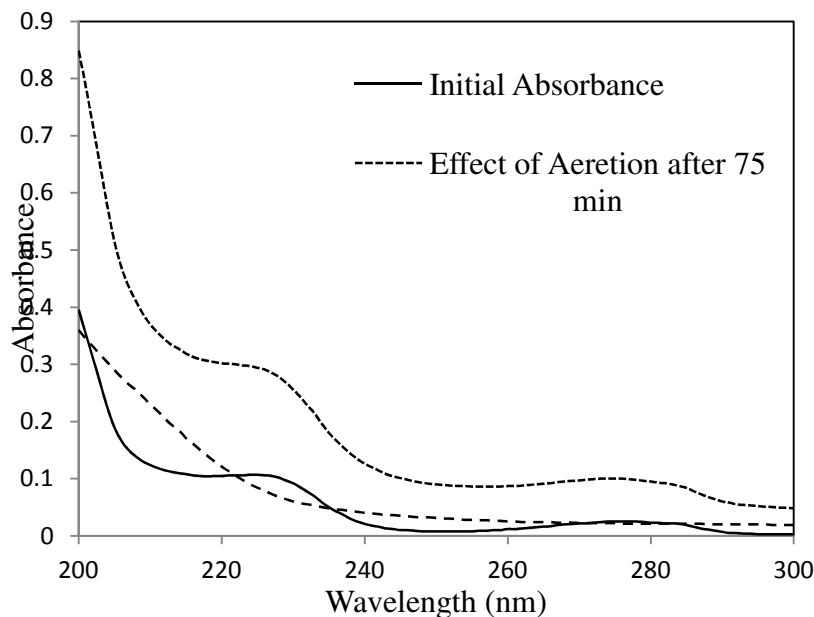


Figure 5: Effect of Sodium persulfate concentration on ultrasonic destruction of BPA at Co: 2 mg/L; pH=5; ultrasonic power: 500W; ultrasonic frequency: 45 KHz; Sodium persulfate : 200 mg/L.

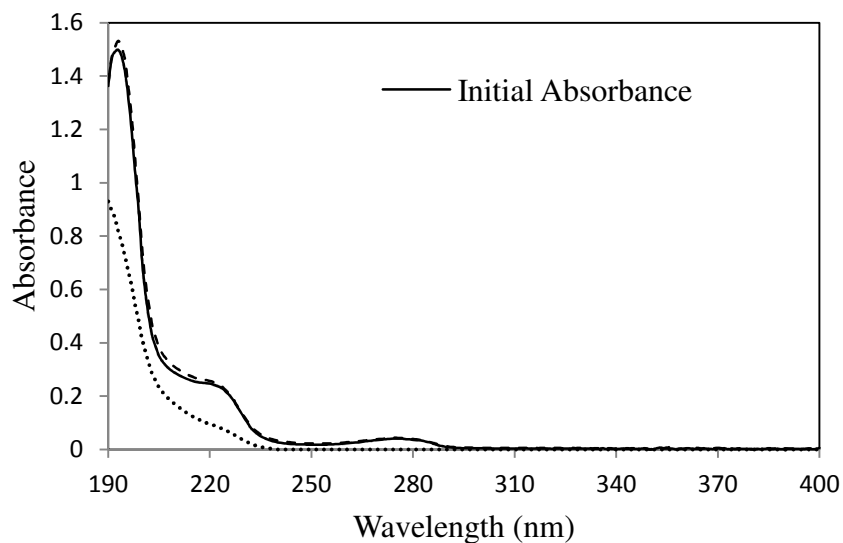


Figure 6: Effect of Sodium persulfate (SPS) concentration on ultrasonic destruction of OP at Co: 5 mg/L, ultrasonic power: 500W; ultrasonic frequency: 45 KHz; Sodium persulfate: 100 mg/L.

3.6 Effect of initial concentration of BPA and OP

The effect of initial BPA concentration studied at 5 pH, 45 KHz frequency, 500 W power and 200 mg/L concentration of sodium persulfate. The major spectrum of BPA at 224 and 276 nm

disappeared at different time as shown in Table 1. It was observed that BPA of initial concentration 20 mg/L required 10 h to degrade. This attributes that BPA exist lower fugacity and it cannot enter in the bubble and most probably present at bubble liquid interface where hydroxyl radicals present which oxidize the BPA, but more concentration of BPA reduces the production of hydroxyl radical's, so required more time for degradation reaction (Torres et al. 2008). In case of OP, the major spectrum of OP at 193; 220 and 276 nm disappeared at different time. It was observed that higher the OP concentration lower the rate of degradation

Table 1: Effect of initial BPA concentration

Sr.No.	pH	Initial BPA concentration mg/L	Sodium persulfate concentration mg/L	Time required to disappear at 224 and 276 nm (h)
1	5	2	200	1
2	5	5	200	2
3	5	10	200	3
4	5	20	200	10

3.7 Study of reaction kinetics of BPA and OP

By plotting $\ln(C/C_0)$ vs time obtained the reaction rate constants and correlation coefficients in both processes. It was found that both degradation processes followed first order kinetics.

$$\ln(C / C_0) = - k * t \text{ -----(1)}$$

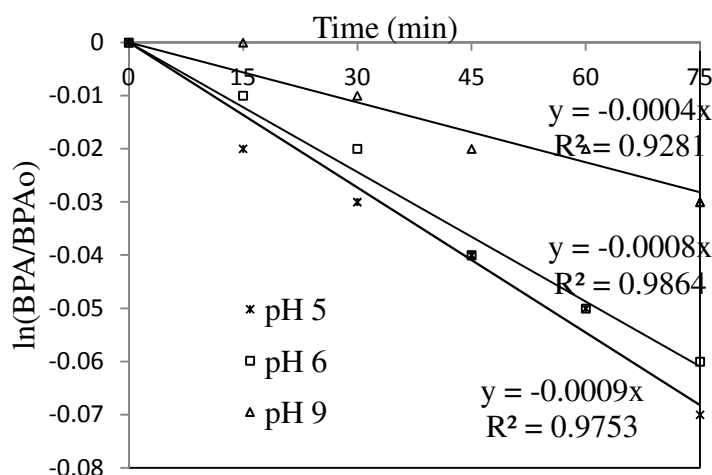


Figure 7: Degradation kinetics of BPA at different pH

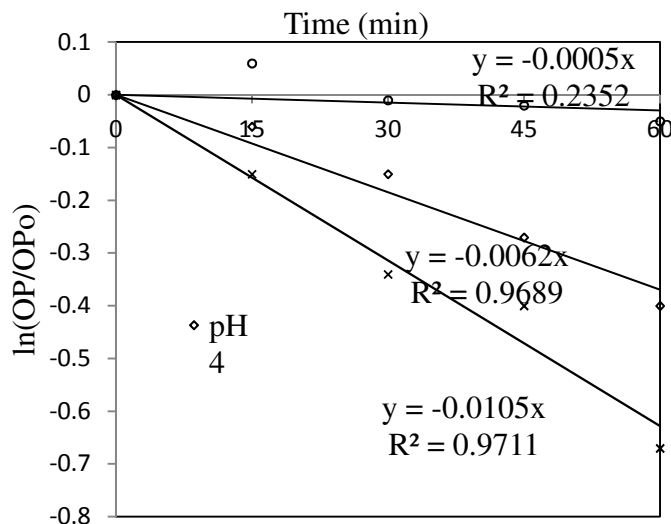


Figure 8: Degradation kinetics of OP at different pH

Degradation kinetics (fig. 7 & 8) were studied and rate constant values were calculated from equation (1). It was found rate constant value was higher (0.0009 min^{-1} and 0.0105 min^{-1}) at 5 pH for both degradation processes.

4. CONCLUSION

The degradation rate was strongly affected by pH of the system for both BPA and OP degradation. The addition of sodium persulfate was required for complete and faster degradation for both BPA and OP. Intermediates were identified in both degradation processes.

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