PHENOL OXIDATION UNDER PULSED MODE OF ULTRASONIC IRRADIATION

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ABSTRACT

This study demonstrates ultrasound assisted Fenton oxidation of phenol present in waste water produced as a result of synthetic processes. The degradation of phenol was investigated at isothermal conditions under 20 kHz ultrasonic frequency, under pulsed and continuous mode of irradiations. The ultrasonic system was calibrated by calorimetric measurements. Various experimental conditions of H_2O_2, $FeSO_4.7H_2O$, aeration, initial pH and acoustic intensity have shown that phenol oxidation was enhanced using ultrasound at pulsed mode instead of continuous mode. It was found that optimum oxidation of phenol was achieved at 80 mM H_2O_2, $8.9x10^{-4}$ mM $FeSO_4.7H_2O$, pH of 3 and 20 Wcm^{-2} of ultrasonic acoustic intensity. Pseudo first order rate kinetics were observed at different phenol concentrations of 2 mM, 4 mM and 5 mM. A fitted regression model by R software confidently provided a tool for quantifying the main factors involved in oxidation. Multiple linear regression analyses showed that phenol oxidation is enhanced by increasing concentrations of H_2O_2 and $FeSO_4$ and reducing pH of solution.

Keywords: *Ultrasonic irradiation, fenton oxidation, sonofenton kinetics, half-life studies, regression model, phenol oxidation*

1. INTRODUCTION

The waste stream discharged by leather, textile, dyes, oil refineries, and paint industries contains substantial amount of phenol. These waste streams when exposed to ambient environment can cause severe tribulations and even minute concentrations of phenol ($<3.3x10^{-2}$ mM) are intolerable in water. Higher concentrations of phenol in water not only kill fish, but also completely act as biogenic compound (Saha, et al., 1999; Jain, et al., 2011). The presence of phenol in water bodies contributes to severe pollution and causes carcinogenic and mutagenic effects to human and aquatic life. Hence, prior treatment of phenol containing waste stream is requisite before it is discharged to environment.

Previous investigations introduced various methods for the treatment of hazardous organic pollutants from the wastewater (Berlan, et al., 1994; Pera-Titus, et al., 2004; Bremner, et al., 2009; and Babuponnusami and Muthukumar, 2011). However, biological, chemical and physical treatment processes suffer from either inefficiency, phase transfer of pollutants, or toxic end-products (Kušić, et al., 2006).

Recently, advanced oxidation processes are gaining momentum for oxidation of phenol as its oxidation is inhibited by conventional chemical and biological methods.

Advanced Oxidation: Process (AOP) has shown potential to mineralize organic pollutants, including phenols. However, AOP requires transition metals, e.g., Fe, Cu, etc. along with a large amount of H_2O_2, which themselves contribute towards pollution (Siddique, et al., 2014). The decomposition of organic pollutants occurs by its OH• radicals that are generated by H_2O_2 in the presence of ultraviolet light, ultrasound radiations or microwaves (Barros, et al., 2013).

The use of ultrasound leads to the formation of acoustic cavitation by pressure fluctuation in a liquid and the collapse of these cavitation bubbles develop hotspots with extremely high local conditions of temperature and pressure, which allow the formation of reactive radicals, such as H•, OH•, O•. Ultrasonic oxidation of organic compounds can be enhanced by using oxidizing agents. Particularly, the Fenton's reagent ($FeSO_4.7H_2O$, H_2O_2), along with the ultrasound irradiation leads to much higher oxidation efficiency in very short span (Segura, et al., 2009; Bach, et al., 2010; Luis, et al., 2009; APHA, 1998). Hence the hydroxyl radicals (2.33 V oxidation potential) formed by cavitations quickly remove hydrogen from the aromatic ring of phenol, resulting in a series of oxidation reactions to mineralization and non-toxic end-products (Bhargava, et al., 2006). Studies on sonofenton oxidation of phenol have been restricted to continuous mode of ultrasonic irradiation. However, little attention is paid to investigate sonofenton oxidation of phenol using pulsed mode of ultrasonic irradiation. During pulsed mode of ultrasonic irradiation, it was observed that the specific energy consumption is lower in the case of concentrated aqueous effluents. This trend indicates that the process is more efficient in terms of energy consumption for more polluted streams (Cailean, et al., 2014).

Therefore, the present study was performed to determine sonofenoton oxidation of phenol under various experimental conditions using pulsed and continuous mode of ultrasonic irradiation and to

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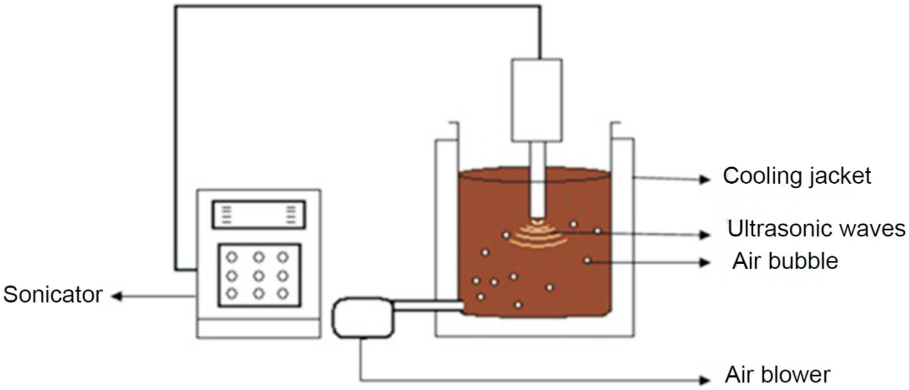

Figure-1: Experimental setup of Sonofenton oxidation of phenol

present a statistical model at optimized conditions to understand the relationships between different factors with oxidation of phenol.

2. MATERIALS AND METHODS

Sonofenoton oxidation of phenol under various experimental setups, including continuous, pulsed, continuous aerated, and pulsed aerated irradiation of ultrasound was conducted. The effect of ultrasonic intensity on phenol oxidation was also investigated. Kinetics of reactions were determined and the results were interpreted using statistical model at optimum experimental conditions. Sonofenton oxidation of phenol at continuous mode of irradiation has been investigated previously (Babuponnusami and Muthukumar, 2013; Pétrier and Francony, 1997). The present study involved the comparison of pulsed with continuous mode of ultrasonic irradiation for percentage removal, order of reaction/rate constants determination, and half-life of phenol oxidation.

Phenol and ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) hydrogen peroxide (35% w/v) (H_2SO_4, NaOH) were obtained from Sigma Aldrich and NH_4OH was obtained from Merk. The aqueous solutions of phenol (2 - 5 mM) were prepared while dissolving 10-100 mM H_2O_2 and 0 - 1.0 mM $FeSO_4.7H_2O$.

Sonofenton process was carried out in 500 ml cylindered Pyrex vessel as a batch reactor and ultrasonic waves were introduced by VCX500 ultrasonic processor outfitted with a titanium horn-probe (13 mm of diameter) for continuous and pulsed wave at a frequency of 20 kHz (Figure-1). Air-flow of 1 mL min^{-1} was maintained throughout the experiments. All the reactions were performed at atmospheric pressure in isothermal condition (25±1°C) for 60 minutes.

The effect of ultrasonic power density on oxidation of phenol was probed at 0, 5, and 10, 20 and 40 Wcm^{-2} in aerated solutions. Energy input was determined (equation-1) using calorimetric method (Price and Lenz, 1993) by recording temperature increase after every every 5 minutes for 30 minutes.

$$q = mc\, dT/dt \qquad (1)$$

where, 'q' is energy input, 'm' is the mass of water, 'c' is heat capacity of water, and 'dT/dt' is the temperature gradient over time. Ultrasonic power density (Wcm^{-2}) was calculated by dividing energy input over area of ultrasonic probe.

The samples were collected at regular intervals and oxidation process in samples was immediately ceased by bringing pH at 9 using 0.5 N NH_4OH for analysis. The concentration of phenol was measured on calibrated UV-Vis spectrophotometer (O.R.I Germany UV 4000 Spectrophotometer) by 4.aminoantipyrine method at pH 7.9±0.1 (Eaton, et al., 2005).

The percentage decomposition was determined using Equation-2.

$$\text{Phenol \% decomposition} = (1-C_t/C_0)x100 \qquad (2)$$

In Equation 2, 'C_t' and 'C_0' are the concentrations of phenol at reaction time of 't' and '0' minutes, respectively. The change in phenol concentration was determined using Beer–Lambert Law (Shu and Chang, 2005).

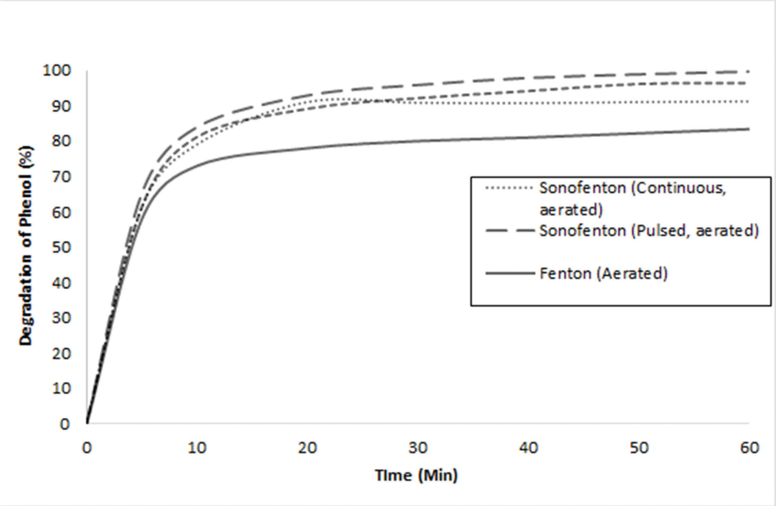

Figure-2: Effect of pulsed and continuous wave ultrasound on fenton oxidation of phenol in aerated and non-aerated systems

Preliminary experiments are conducted to find concentrations of hydrogen peroxide, ferrous sulfate and pH where maximum oxidation of phenol takes place. The optimum conditions were found to be 8 mM H_2O_2, 8.99 x10^{-4} mM concentration of ferrous sulphate at pH level 3 (supplementary data) and are kept constant throughout current investigation.

The kinetic study of phenol oxidation by ultrasound assisted Fenton oxidation in aqueous solutions of phenol was undertaken at its various initial concentrations of 2, 4 and 5 mM, while keeping all parameters constant.

A latest version of 'R' software was used for statistical modeling. Hence, the multiple linear regressions are performed to observe the effect of pH, H_2O_2 and $FeSO_2.7H_2O$ on percentage degeneration of phenol. Analysis of variance test was performed to evaluate the reliability of fitted regression model.

3. RESULTS AND DISCUSSION

3.1 Ultrasonic Irradiation and Phenol Oxidation

The oxidation of compounds in ultrasonic field depends upon three major factors, including adsorption of contaminates on its gas / solution interface, number and shielding effect of cavitations.

Sonofenton oxidation rate has significantly enhanced over fenton alone (Figure-2). This is due to increased dissociation of H_2O_2 and H_2O and formation of OH• radicals, which, in turn, are used for phenol oxidation. The volatile phenol compound may interact with the bubble-water interface and enter cavitation bubbles and react with OH• radicals in gas, interfacial, and regions of cavitation bubbles.

In an attempt to determine the ultrasound-induced oxidation efficiency of phenol, pulsed ultrasound was compared with continuous ultrasound in its aqueous solutions. The lifetime of the gas/solution interface increases during the pulse intervals which in turn increases adsorption of contaminants on chemically active bubbles. This adsorption depends on the ratio of the ultrasonic pulse length (T) to pulse interval (T_0). The ratio of the ultrasonic pulse length (T) to pulse interval (T_0), in current study was kept at 3:3. While in continuous mode, ultrasound is irradiated continuously. The effect of pulsed and continuous mode on percentage oxidation of phenol for the same parametric conditions is shown in Figure-2. During continuous mode of sonication, shielding effect of ultrasonic waves by bubbles is reported. Where size of some bubbles becomes more than their resonance size causing them to be unresponsive regarding the generation of cavitational effect (Ishtiaq, et al., 2009). Therefore, in continuous mode of sonication, some of the acoustic energy profligates into just heat, vibrations and degasification of liquid. While in the case of pulsed mode of sonication, the shielding effect is minimized as bubbles are generated below their resonance size. The high sonochemical oxidation by pulsed ultrasound, compared with that by continuous-wave ultrasound, can be due to the residual pressure amplitude during the pulse-off time and the spatial enlargement of active reaction sites. During pulsed

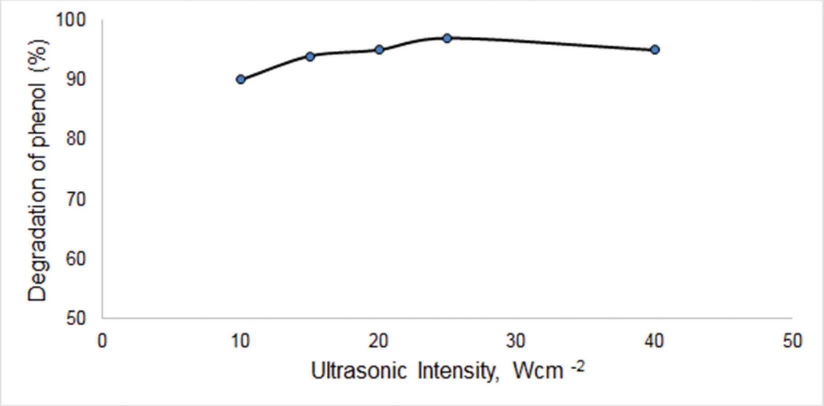

Figure-3: Effect of Power Intensity on Phenol Percentage Oxidation

ultrasound, it allows time for diffusion in bubble–water interfaces, the sources of reactivity between two successive pulses (Tuziuti, et al., 2008).

The amount of dissolved gases in solutions affects cavitational events and reaction rates. The effect of aeration in continuous as well as pulsed wave ultrasound on sonofenton process was studied at 2.5 l/min flow rate of air and was compared with non-aerated sonofenton process (Figure-2). Experimental results showed that by introducing the aeration in the system, phenol oxidation was increased. This could be explained based on the fact that air bubbles act as a nucleation site for cavitation and the number of bubbles formation might increase leading to the increase in events of bubble collapse via rectified diffusion. Moreover, bubbled air imparts an additional advantage in mass transfer increment by enhancing free turbulent fluidic movement.

The sonofenton phenol oxidation at different ultrasonic intensities at pulsed mode of operation was probed. At acoustic intensity of 25 Wcm^{-2}, maximum oxidation was achieved. Further increment in its intensity leads to decrease in phenol oxidation (Figure-3). Current study showed that maximum removal of 97% is achieved at very low intensity of 25 Wcm^{-2v} as compared to previous studies where 69.77 % removal efficiency was achieved at 40.76 Wcm^{-2} using continuous mode of operation (Cailean, et al., 2014). This can be explained based on the fact that the excessive power intensity may lead to bubble shielding effect, according to which a dense cloud of these bubbles gather around the ultrasonic transducer which ultimately decreases the oxidation rate (Chen, 2012; Cintas, 2012; Vijayanand S. Moholkar, et al., 2012).

3.2 Kinetic of Phenol Oxidation

Kinetic of phenol oxidation at its various concentrations of 2, 4 and 5 mM, apparently follows pseudo first order reaction (Figure-4). The half-life $t_{1/2}$ and regression coefficient R^2 obtained for pseudo first order reaction at different concentrations of phenol are shown in Table-1.

3.3 Statistical Model for Phenol Oxidation

A statistical model is developed for determining the effect of hydrogen peroxide, ferrous sulphate and pH of the solution on phenol sonofenton oxidation at pulsed mode of irradiation (supplementary data in Figures 1, 2 and 3). The model confidently provided quantitative information regarding the significance of these parameters and their consequence on oxidation of phenol in aqueous medium. A latest version of R software was used for statistical modeling and multiple

Table-1: Pseudo first order rate constant kobs, half-life $t_{1/2}$, and regression coefficients R^2 for oxidation of Phenol at different initial concentration

Phenol concentration (mM)	k(obs) (min^{-1})	$t_{1/2}$(min)	R^2
2	0.96	6.93	0.98
4	0.98	6.89	0.99
5	0.98	6.97	0.99

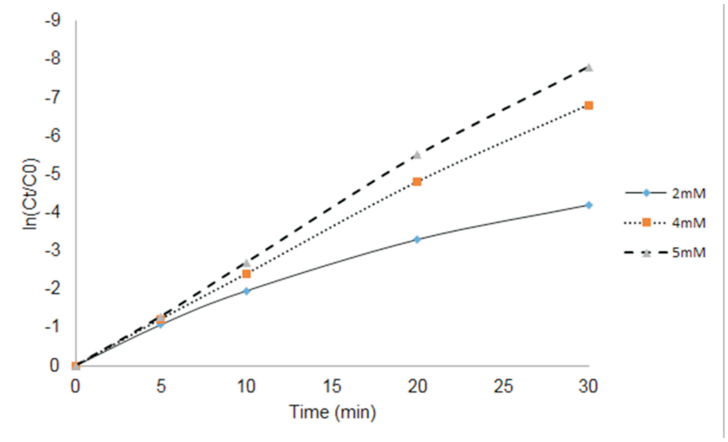

Figure-4: Pseudo First Order Relationship of Phenol Oxidation by Fenton Oxidation at Different Initial Concentration

linear regressions are performed to observe the effect of pH, H_2O_2 and $FeSO_4.7H_2O$ on percentage degeneration of phenol (Equation-3).

Phenol Degeneration=
39.164 - 9.511(pH) + 475.726(H_2 O_(2)) +
54650.073(FeSO_4.7H_2 O) (3)

In above model, 39.164 is known as an intercept of the fitted regression model. The pH has negative relationship with phenol degeneration; the one unit increase in pH results 9.51 units decrease in phenol degeneration. H_2O_2 and $FeSO_4$ have highly positive relationship with phenol degeneration. The coefficient of determination of fitted regression model is 84.79%, which means 84.79 percent variation of the degeneration is explained by the pH, H_2O_2 and $FeSO_4$. More explicitly, it can be said that the results of the model are 84.79% reliable for further predictions. It is to be noted that the above model is valid only if the independent variables pH, H_2O_2 and $FeSO_4.7H_2O$ takes the values within 3, 7; 10, 100 mM; and 0.0, $1x10^{-4}$ mM, respectively. Analysis of variance test is performed to evaluate the reliability of fitted regression model. The results of ANOVA are presented in Table-2. It is observed (Table-2) that all p-values are less than 0.01; representing significant contribution of pH, H_2O_2 and $FeSO_4.7H_2O$ for predicting phenol oxidation.

4. CONCLUSIONS

Fenton oxidation of phenol in aqueous medium under pulsed mode of ultrasonic irradiation showed that 99.5% of phenol was degraded when experiments were conducted at 80 mM H_2O_2, $8.9x10^{-4}$ mM $FeSO_4.7H_2O$, pH of 3. Sonofenton oxidation is proved to be an effective tool as compared to simple Fenton for oxidation of phenol. Kinetic study shows that phenol oxidation followed pseudo first order reaction having specific rate constant k= 0.1 min^{-1} and half-life of 6.93 min. Finally, a latest version of R software was used to develop regression model by quantifying pH, concentration of hydrogen peroxide and concentration of ferrous sulphate. The regression model elucidated that pH increase has negative whereas increase of H_2O_2 and $FeSO_4.7H_2O$ has a positive impact on phenol oxidation.

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Table-2: Statistical Analysis of Phenol Oxidation at Different Response (pH, H_2O_2 and $FeSO_4.7H_2O$)

Response	Sum of square	Mean square	F-value	p-value
pH	1386.7	1386.7	21.647	8.41E-05
H_2O_2	1392.8	1392.8	21.742	8.41E-05
$FeSO_4$	3229.0	3229.0	50.406	1.54E-07

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