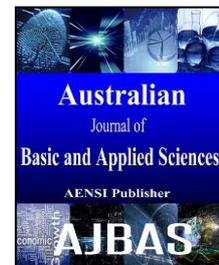




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### Degradation efficiency, kinetic and intermediates of phenol by ozonation

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#### ABSTRACT

Phenol contamination is unavoidable as a result from industrialization. Though phenol contamination is not a new issue and extensive studies on phenol degradation had been done; but wastewater matrixes changes over time thus alternative treatments are necessitated. Ozonation has the capability to treat wide range of wastewaters, including phenolic wastewater, utilized molecular ozone and hydroxyl radicals to oxidize organic compounds. The aim of this study is to evaluate the performance of ozonation to degrade phenol. Spectrophotometric analysis was done to assess the phenol concentration and its degradation spectrum by ozonation. Initial concentration and pH of phenol solution were manipulated to assess their influence on degradation efficiency based on concentration and COD reduction. Whereas, the trend of phenol degradation and the characteristic of degradation intermediates were observed via Ultraviolet-Visible spectrophotometer. The findings show the degradation efficiency of phenol by ozonation decreases as the initial concentration increased; and increases as the initial pH increased from pH 3 to pH 11. Phenol initial concentration of 100 mg/L of phenol, with COD value of 216 mg/L, can be effectively degraded by ozonation, with concentration and COD reduction of 93.9% and 64.8%, under the experimental conditions. The degradation kinetic of phenol by ozonation is of pseudo first order; the kinetic constant decreased as the initial phenol concentration increased. The UV spectrum at wavelength region of 210 to 400 nm of phenol degradation by ozonation suggests the possible degradation intermediates are of carbonyl group such as aldehydes, ketones and carboxylic acids.

#### INTRODUCTION

Contamination is often the consequence of industrialization for the purpose of economic growth. Phenol, as one of the most common used organic compounds in industrials, its contamination to the environment is unavoidable. Phenol mostly found in wastewater of petrochemical, refineries, coke, pesticide, dye and textile industries; its concentration range from 0.1 to 3900 mg/L, depends on the type of industrial (Contreras *et al.*, 2003; Gami *et al.*, 2014; Tasic *et al.*, 2014; Zhang *et al.*, 2009).

Phenol is classified as a Group D by the Environmental Protection Agency (EPA). Though the carcinogenic effects of phenol in humans and animals are still not clear due to insufficient supported data, its risks to human and the environment cannot be neglected. Phenol is an organic aromatic with a hydroxyl group, which makes it readily to be substituted or undergoes various reactions. The formation of other phenolic compounds, e.g., chlorophenols, methylphenols and alkylphenols, is the main concern as they are more toxic and persistent compared to phenol (Gami *et al.*, 2014). In Malaysia and those countries employ chlorination in water treatment plants, the presence of phenol is critical as it will react with chlorine to form chlorophenol (Michalowicz, 2004). Due to this reason, the Malaysia's environmental law, Environment Quality Act (EQA) 1974 regulates the limit

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for phenol concentration in sewage and industrial effluent as 0.001 mg/L for standard A and 1.0 mg/L for standard B.

Biological methods and adsorption are the two most common methods used in phenolic wastewater. Biological methods are preferable in treating wastewater as its cost-effectiveness; however biological methods have drawbacks in treating phenolic wastewater due to the toxicity of phenol and its derivatives. This is because phenol inhibits the growth of microorganisms (El-Naas *et al.*, 2010), and the inhibitory effect on phenol biodegradation increases as the phenol concentration increases (Yusoff *et al.*, 2016). Adsorption is very effective in removal of phenolic compounds, but it involves high treatment cost. Though phenol contamination is not a new issue and phenol degradation has been studied intensively, but wastewater matrixes change over time; thus alternative treatments are necessitated.

Advanced oxidation processes (AOPs) are the emerging wastewater treatment technology. AOPs involving strong oxidants or free radicals to degrade organic compounds (Moussavi *et al.*, 2009). Ozonation as one of the AOPs has the capability to treat wide range of wastewaters, including phenolic wastewater. Ozonation utilizes molecular ozone and hydroxyl radicals to oxidize organic compounds. Ozone oxidation process contains two ways of oxidizing reaction. Ozone can react with organic compounds via direct molecular reaction in acidic pH; and via indirect oxidation by hydroxyl radical ( $\cdot\text{OH}$ ) produced during ozonation in alkaline pH (Esplugas *et al.*, 2002; Venkatesh *et al.*, 2015). Kulkarni & Kaware (2013) and Yogeswary *et al.* (2010) remarked that ozonation is efficient for phenol degradation compared to conventional aerobic and anaerobic wastewater treatment methods. Other than high treatment efficiency, the other advantages of ozonation are short treatment time, easy installation and operation, compact, generated on-site, and less problems associated to shipping and handling chemicals (Forero *et al.*, 2001; Sano *et al.*, 2007).

Numerous studies were done by researchers on phenol degradation by ozonation with different emphasis. Huang & Shu (1995) studied the reaction kinetics, decomposition pathways and intermediate formations of phenol in ozonation, UV/O<sub>3</sub> and UV/H<sub>2</sub>O<sub>2</sub> processes. Forero *et al.* (2001) examined the feasibility of ozone for phenol treatment in industrial wastewater. Esplugas *et al.* (2002) studied and compared the effect of pH, kinetic constants, stoichiometric coefficient and optimum oxidant to pollutant ratio of different advanced oxidation processes for phenol degradation. Hsu *et al.* (2007) enhanced the COD removal of the phenol degradation by ozonation using calcium binding. Ramseier & Gunten (2009) presented the mechanisms and the formation of primary and secondary reaction products in phenol ozonation. Whereas Sun *et al.* (2012) studied on the degradation mechanism of phenol induced by ozone in waste system. Whilst Wang *et al.* (2016) optimized self-design ozone generator to degrade phenol in wastewater.

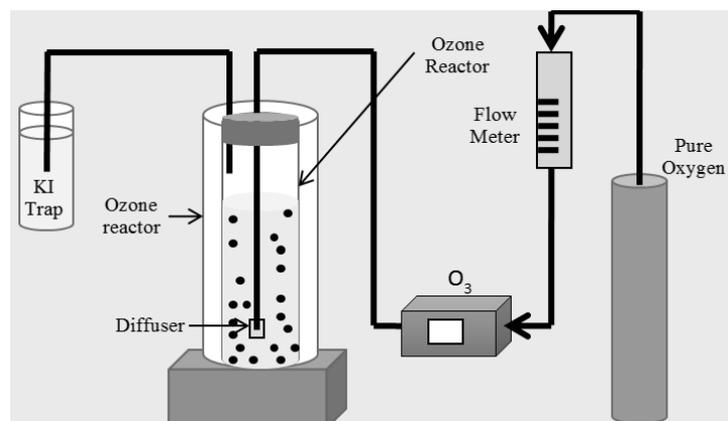
Though there are abundant published literatures related to phenol degradation by ozonation, limited documentation on characterization of phenol degradation intermediates via ultraviolet-visible (UV-Vis) spectrophotometer can be found. In this study, ozonation was used to degrade phenol in aqueous solution. Degradation efficiency of phenol by ozonation at different initial concentrations and pH were evaluated based on phenol concentration and COD reduction. The mechanism involved in acidic and alkaline conditions was discussed. Besides, the kinetic order of the phenol degradation by ozonation under the experimental conditions was calculated. Lastly, the degradation trend and intermediates characteristic of phenol by ozonation were observed via spectrophotometric analysis.

## MATERIAL AND METHODS

Phenol (Bendosen), sodium hydroxide (HmbG), sulphuric acid (95-98%, Fisher Chemical) and other required chemicals were of reagent grade. All solutions were prepared with deionized water produced from Elga Purelab Option-Q water system. Fig. 1 shows the schematic diagram of experimental set-up for ozonation experiment. The reactor set-up for ozonation experiments comprised of a 2.0 L of glass measuring cylinder as ozone reactor, A2Z ozone generator (model Z-3G), oxygen cylinder (99.8% of oxygen concentration), flow meter, diffuser and potassium iodide (KI) trap. The ozone gas was produced by ozone generator with 2.0 L/min of O<sub>2</sub> inflow at 10 g/m<sup>3</sup> of O<sub>3</sub> generation. The concentration of dissolved ozone used in ozonation experiment was predetermined using KI method (Rakness *et al.*, 1996). The pH of phenol sample was adjusted by 1.0/0.1 N of NaOH and 1.0/0.1 N of H<sub>2</sub>SO<sub>4</sub>.

Ozonation experiments were conducted in a semibatch mode. During ozonation experiment, phenol samples with different initial concentration (e.g., 100, 200 and 500 mg/L), and initial pH (e.g., pH 3, 5, 7, 9, and 11) were used to examine their effects on degradation efficiency. Samples were taken at specific time intervals for further analysis. Phenol concentration was analyzed using Hitachi U2810 UV-Vis spectrophotometer at 269 nm wavelength; whereas the COD of samples was measured according to Standard Method 5220D: closed-reflux, calorimetric method, in Standard Methods for the Examination of Water and Wastewater (1989), using HACH DR200 COD reactor and HACH DR2800 spectrophotometer. The degradation efficiency (DE) of phenol by ozonation were evaluated using formula,  $DE (\%) = [(C_o - C_f) / C_o] \times 100\%$ , where, DE = degradation efficiency in percent; C<sub>o</sub> = initial concentration or COD of sample in mg/L; and C<sub>f</sub> = final concentration or COD of treated

sample in mg/L. The ultra-violet (UV) spectrums of phenol degradation by ozonation over time were observed using UV-Vis spectrophotometer, at wavelength region of 210 to 400 nm.

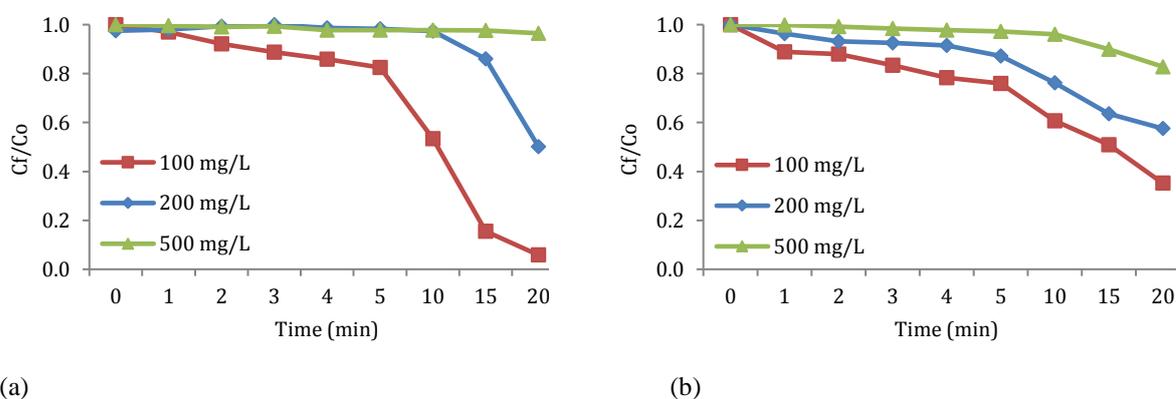


**Fig. 1:** The schematic diagram of experimental set-up for ozonation experiment. (pls cite figure 1 in material and methodology section)

## RESULTS AND DISCUSSION

### Degradation efficiency:

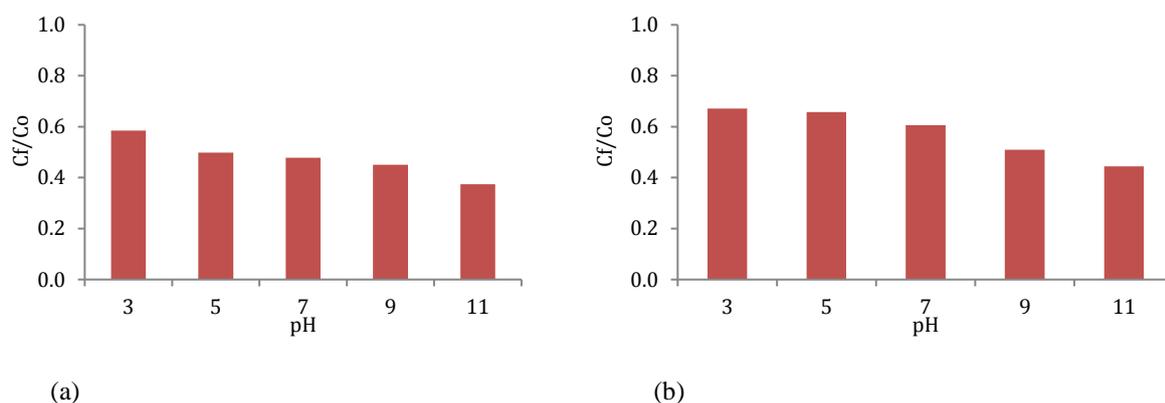
Initial concentration of phenol in the ozonation experiments was varied to assess the DE of phenol by ozonation within 20 minutes. Fig. 2 (a) and (b) show the influence of the initial concentrations on phenol degradation based on concentration and COD reduction. The DE for concentration and COD, as expected, decrease as the initial concentration increased. The findings show 100 mg/L of phenol (COD = 216 mg/L) can be effectively degraded by ozonation, with concentration reduction of 93.9% and COD reduction of 64.8%. As the phenol initial concentration increased to 200 mg/L (COD = 412 mg/L), the DE for concentration and COD decreased to 70.7% and 42.5% respectively. Whilst for 500 mg/L of phenol, the DE for concentration is 9.9%; however unlike the others, its COD reduction is 17.2%, which is higher than concentration reduction. Generally, the DE based on COD reduction is lower than those of phenol concentration reduction due to production of degradation intermediates which contributes to the COD value (Wang *et al.*, 2016). The higher DE for COD reduction than concentration reduction for 500 mg/L of phenol suggests that the intermediates produced competed for  $O_3$ , results in less available  $O_3$  for phenol degradation. This can be supported by the findings of Turhan & Uzman (2008) in which longer ozonation time and higher ozone dosage are requires for the destruction of some organic compounds produced during phenol degradation by ozonation. Moreover, as the phenol concentration increases, more intermediates will be produced during degradation; thus longer treatment time and higher ozone dosage are necessitated to achieve the same DE as those low concentration phenol solutions.



**Fig. 2:** Influence of phenol initial concentrations on phenol degradation by ozonation, based on (a) phenol concentration reduction; (b) COD reduction, at pH 7, contact time = 20 minutes.

### Initial pH:

The effect of initial on phenol degradation by ozonation was examined as pH affects the oxidation pathways of ozone with organic compounds in aqueous solution (Alvares *et al.*, 2001; Wang *et al.*, 2016; Yogeswary *et al.*, 2010). The treatment time for ozonation of phenol solution with initial concentration of 100 mg/L at varies pH was reduced to 10 minutes; as shown in Fig. 2 (a), 10 minutes of ozonation was adequate to assess the effect of initial pH on the degradation performance for 100 mg/L of phenol. Fig. 3 (a) and (b) depict the influence of the initial pH on phenol degradation based on concentration and COD reduction within 10 minutes of treatment time. The results show both DE for concentration and COD increases as the pH increased from pH 3 to pH 11. The highest DE was achieved at pH 11, with concentration reduction of 62.9% and COD reduction of 55.6%. In contrast, the DE at initial pH of 3 was the lowest with concentration reduction of 42.0% and COD reduction of 32.87%. Due to the fact that ozone is predominant in acidic condition, and hydroxyl radical ( $\cdot\text{OH}$ ) only produced in ozonation at elevated pH; it is suggested that phenol degradation achieved higher DE via the route of indirect oxidation by  $\cdot\text{OH}$  since higher DE was found at high pH. At low pH, ozone is less likely to decompose; the route of degradation is ozone direct oxidation on organic compounds by breaking its double bonds or aromatic rings (Gunten, 2003; Van and Trinh, 2013). Whereas, at high pH, indirect oxidation by  $\cdot\text{OH}$  is predominant. This is because the instability of ozone and abundant hydroxyl ion ( $\text{OH}^-$ ) in alkaline condition favour the production of  $\cdot\text{OH}$ , a highly reactive radical species with higher oxidation power ( $E^0 = 2.80 \text{ V}$ ) than ozone ( $E^0 = 2.07 \text{ V}$ ) (Kow *et al.*, 2016; Staehelin *et al.*, 1984; Staehelin and Hoigne, 1982). Furthermore, phenol dissociates into its conjugate base, phenoxide ion ( $\text{C}_6\text{H}_5\text{O}^-$ ), at high pH (Forero *et al.*, 2001). The presence of  $\cdot\text{OH}$  in the solution and higher reactivity of phenoxide ion with ozone and  $\cdot\text{OH}$  ( $k_{\text{O}_3} = 1.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ;  $k_{\text{OH}} = 9.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ) compared to those of phenol ( $k_{\text{O}_3} = 1.3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ ;  $k_{\text{OH}} = 11.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ) (Buxton *et al.*, 1988; Hoigne and Bader, 1983), without doubt, contribute to the high DE in the treatment.

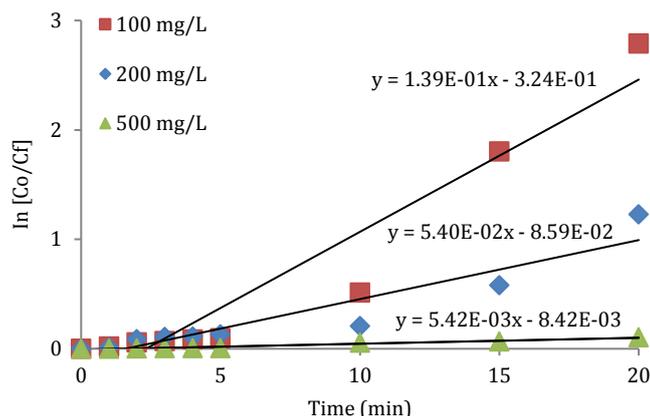


**Fig. 3:** Influence of initial pH on phenol degradation by ozonation, based on (a) phenol concentration reduction; (b) COD reduction; phenol concentration = 100 mg/L, COD = 216 mg/L, contact time = 10 mins.

### Degradation kinetic:

Simple mathematical model for phenol degradation was developed. Since the ozonation experiments were carried in a semibatch mode, liquid flow rate,  $Q_L = 0$ ; the mass balance for phenol in the liquid phase became:  $dc(\text{Ph})/dt = -r(\text{Ph})$ . Second order rate equation was adopted considering all direct and/or indirect reactions occurred during the degradation of phenol by ozonation:  $r(\text{Ph}) = [k_D c_L + k_R c(\cdot\text{OH})] \cdot c(\text{Ph})$ , where  $r(\text{Ph})$  = reaction rate of phenol;  $k_D$  = reaction rate constant for the direct reaction;  $k_R$  = reaction rate constant for the indirect reaction;  $c_L$  = concentration of molecular ozone in liquid;  $c(\cdot\text{OH})$  = concentration of hydroxyl radical;  $c(\text{Ph})$  = concentration of phenol. Besides, the ozone was supplied continuously at constant gas flow and pressure; therefore, the concentrations for ozone and the radicals involved in the reactions were assumed to be at steady state,  $k' = k_D c_{LSS} + k_R c(\cdot\text{OH})_{SS}$ , where  $k'$  = reaction rate coefficient, pseudo-first-order; subscript ss = steady-state conditions. Thus, the reaction rate of phenol degradation by ozonation was simplified to a pseudo-first-order relationship:  $dc(\text{Ph})/dt = r(\text{Ph}) = k'c(\text{Ph})$ . An integrated rate equation was obtained by solving the mathematical model by using integration of rate laws:  $\ln([Ph]_t - [Ph]_0) = -k't + C$ , where  $C$  = constant.

A graph was plotted by fitting the experimental data to a straight line using the integrated rate equation in order to estimate the  $k'$  for phenol degradation by ozonation. Fig. 4 shows the influence of initial concentration on the phenol degradation rate by ozonation, under the experimental conditions, 76.6 mg dissolved  $\text{O}_3$  per 2 L phenol, pH 7, with 20 minutes of ozonation time. The findings show that the degradation kinetic of phenol by ozonation decreases from  $1.39 \times 10^{-1} \text{ min}^{-1}$  to  $5.42 \times 10^{-3} \text{ min}^{-1}$  as the initial phenol concentration increased from 100 to 500 mg/L. The decreased in phenol degradation kinetic at high initial phenol concentration is due to phenol molecules are present in large excess, exceeded those of oxidants. Therefore, longer ozonation time or higher ozone dosage is required to degrade higher concentration of phenol.

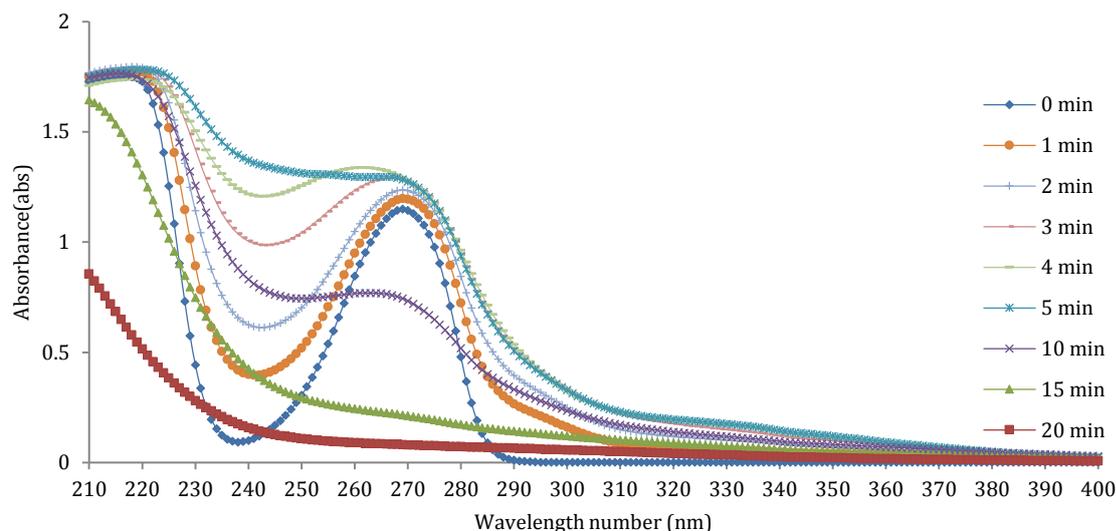


**Fig. 4:** Influence of initial concentration on the phenol degradation rate by ozonation.

#### **Degradation intermediates:**

The general mechanism of oxidation phenol is the formation of cyclic intermediates; followed by ring-opening reactions of the intermediates produced and the formation of organic acids; lastly, mineralization of organic acids (Tasic *et al.*, 2014). UV spectrum evolution of phenol degradation by ozonation was analyzed by UV-Vis spectrophotometer. The structures of degradation intermediates of phenol were identified based on the absorption spectra at different wavelength range. Through comparison of UV spectrum of toluene and phenol, it was suggested that OH group lies within the wavelength range of 220 – 250 nm. Whereas, aromatic ring at 250-270 nm, C=O group of aldehydes and ketones at 270-300nm, C=O group conjugated with double bond at 300-350 nm (Patrick, 2012).

Fig. 5 shows the evolution of UV spectrum of phenol degradation by ozonation over ozonation time at initial phenol concentration of 100 mg/L, pH 7 and 20 minutes of treatment time. Peak for the phenol was observed at  $\lambda_{\max}$  of 269 nm. The UV spectrum shows there was an increase in absorbance at the wavelength range of 220-250 nm at the first 5 minutes, which indicates the phenol degradation starts with the cleavage of OH group of phenol. Wu *et al.* (2000) and Youmin *et al.* (2012) also proposed that the OH bond in phenol is first attack by ozone; consequently formed cyclic intermediates. With the cleavage of OH bond, the absorbance at the wavelength range 270-350 nm also increased indicates the generation of carbonyl group of saturated aldehydes and ketones. After that, the absorbance of UV spectrum for phenol degradation from 210-400 nm was decreased over ozonation time; the decreases in absorbance at 250-270 nm indicates that the aromatic ring was oxidized into organic acid; hence, decrease in aromaticity (Forero *et al.*, 2001; Tasic *et al.*, 2014). Other than aldehyde and ketone, organic acid such as carboxylic acid is also possible degradation intermediate in phenol degradation. The drop in pH~3 after ozonation suggests the formation of weak acid; this acidic nature of ozonated sample was a common phenomena observed by numerous researchers (Soares *et al.*, 2006; Wang *et al.*, 2003). In addition, Langlais *et al.* (1991) also reported that there was an increase in aliphatic groups such as carboxyl group, hydroxyl group and carbonyl group during ozonation. This finding shows that UV-Vis spectrophotometer can be used to characterize the degradation intermediates of organic compounds by observing the trends of degradation spectrum at different wavelength region.



**Fig. 5:** Evolution of UV spectrum of phenol degradation by ozonation over ozonation time at initial phenol concentration of 100 mg/L, pH 7 and 20 minutes of treatment time.

### Conclusions:

Based on the experimental results, a few conclusions can be drawn. Ozonation is capable to degrade phenol effectively. High DE was achieved for phenol of 100 mg/L (COD = 216 mg/L), with concentration and COD reduction of 93.9% and 64.8%, respectively. The DE of phenol by ozonation decreases as the initial concentration increased; but increases as the initial pH increased from pH 3 to pH 11. The high DE of phenol degradation by ozonation at high pH suggest  $\cdot\text{OH}$  was produced during the ozonation process, subsequently contributed in oxidation of phenol. From the results obtained, the degradation kinetic of phenol by ozonation is of pseudo first order; the kinetic constant decreases as the initial phenol concentration increased. This indicates longer ozonation time or higher ozone dosage is requires to degrade higher concentration of phenol. This study also shows the characterization of the degradation intermediates of phenol degradation can be done via spectrophotometric analysis by using UV-Vis spectrophotometer. The UV spectrum of phenol degradation suggests the possible degradation intermediates are of carbonyl group such as aldehydes, ketones and carboxylic acids.

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