Oxidation of p-Cresol by Ozonation
(Pengoksidaan p-Cresol oleh Pengozonan)

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ABSTRACT
Oxidation of p-Cresol was investigated by using ozonation process. The aim of this research is to assess the effectiveness of ozonation on oxidation of micropollutant such as p-Cresol. Ozonation performance was evaluated based on p-Cresol concentration reduction and chemical oxidation demand (COD) reduction. It was found ozonation at pH11 achieved the highest p-Cresol degradation, with 95.8% of p-Cresol reduced and 96.0% of COD reduced, for an initial 50 mgL\(^{-1}\) of p-Cresol. The degradation of p-Cresol could be expressed by second-order of kinetic model. The second-order rate constant \(k\) increases as the initial pH increased, but decreases with the increasing of initial p-Cresol concentrations. Besides, the absorption spectra of p-Cresol over ozonation time were analyzed by spectrophotometry. The evolution of absorption spectra of p-Cresol degradation suggests that the oxidation of p-Cresol follows three stages mechanisms with cycloaddition as the first step to produce aromatic intermediates followed by ring-opening reactions, degradation of the intermediates, and subsequently achieved mineralization.

Keywords: Absorption spectra; mechanism; micropollutant; ozonation; p-Cresol

ABSTRAK

Kata kunci: Mekanisme; pencemar mikro; pengozonan; p-Cresol; spektrum penyerapan

INTRODUCTION
p-Cresol is an emerging micropollutant found in environment due to their wide applications as well as inadequate wastewater treatment prior discharges in industries. It is extensively used in formulation of antioxidant and fragrance and dye industrials (Lewis 2001; O’Neil et al. 2001). The occurrence of p-Cresol in environment was of concern as it is persistent and bioaccumulative. The United State Environment Protection Agency (EPA) classified p-Cresol as group C priority pollutant due to its toxicity and persistency in environment. According to Centers for Disease Control and Prevention (CDC), p-Cresol is corrosive to the eyes, skin and respiratory tract; corrosive if ingested and can affect organs as well as the central nervous system of living organisms (CDC 2007). Animal studies also showed that p-Cresol can affect the liver, kidney and central nervous system (CNS) from acute inhalation of mixed cresols (ATSDR 2008). Other than that, the presence of p-Cresol can greatly degraded the water quality due to its toxicity (Kavitha & Palanivelu 2005).

Conventional treatment methods of p-Cresol include adsorption, membrane filtration, incineration and activated sludge system. Amongst all, adsorption is commonly adopted in industrial wastewater due to its easy operation, cost effective and high efficiency for low concentration of pollutants (Bello et al. 2013; Das et al. 2013). However, it eventually generates another hazardous waste because the pollutants are adsorbed on the surface of activated carbon. This method do not destroy nor degrade p-Cresol, but only removed from the wastewater. Various studies on p-Cresol biodegradation had been carried out using bacteria, algae and fungi (Singh et al. 2008; Surkatti & El-Naas 2014). The use of microorganism is environmental friendly and cost effective but it requires relatively long treatment time and is not feasible for industrial application.
Advanced oxidation processes (AOPs) is an emerging wastewater treatment method as it is highly efficient in treating wide range of wastewater within a short duration. AOPs can achieve complete mineralization of organic compounds into water and carbon dioxide or partial mineralize it into readily-biodegradable compounds. To date, only a few researchers study $p$-Cresol degradation using AOPs such as photocatalysis (Abdollahi et al. 2012; Rattabal & Grisdanurak 2016) and electrochemical oxidation (Escudero et al. 2017). Though those methods were proved effective, it still requires hours of treatment time.

Ozonation is one of the AOPs and had been widely used as a part of wastewater treatment scheme to remove persistent organic pollutant. Ozonation utilizes both molecular ozone (O$_3$) and hydroxyl radicals (•OH) to degrade pollutants into intermediates and further oxidize the intermediates subsequently achieved mineralization. This study aimed to investigate the effectiveness of oxidation of $p$-Cresol by ozonation. The influence of operating parameters, such as initial $p$-Cresol concentration and initial pH, on ozonation performance were also assessed. Based on experimental results, the degradation kinetic of oxidation of $p$-Cresol by ozonation was calculated. Other than that, the evolution of absorption spectra of $p$-Cresol degradation was presented, and the possible pathways and intermediates were proposed.

### MATERIALS AND METHODS

#### REAGENTS

$p$-Cresol (C$_7$H$_8$O) was purchase from SIGMA-ALDRICH, USA, sulfuric acid (H$_2$SO$_4$) was obtained from Fisher Scientific, UK; sodium hydroxide (NaOH) and potassium iodide (KI) were supplied by HmbG Chemicals, Germany.

All and other not-mentioned chemicals were of analytical reagent grade.

#### OZONATION EXPERIMENTS

Ozonation experiments were conducted in semibatch mode in laboratory scale. The experimental set-up comprised of oxygen tank, gas flow meter, ozone generator, glass reactor, gas diffuser and KI trap. Ozone gas was generated on-site using Z3G ozone generator (AZZ Ozone, USA) supplied with purified oxygen at a constant gas flow rate of 3.0 L min$^{-1}$ (Figure 1). The outlet gas was passed through 2.0 N of KI solutions to trap ozone residue before vent out to atmosphere. Performance of $p$-Cresol degradation by ozonation was evaluated based on $p$-Cresol degradation, COD reduction, pH changes and kinetic, with respect to initial concentration as well as initial pH. $p$-Cresol with initial concentration of 50, 100, 200 mg L$^{-1}$ were prepared using deionized water produced from Purelab Option-Q water system (Elga, UK) and initial pH of 3, 5, 7, 9, 11 were adjusted by 1.0/0.1 N of NaOH and H$_2$SO$_4$ solutions prior experiment. Samples were taken at specific time intervals to analyze the concentration and COD of the treated samples.

#### ANALYTICAL METHODS

Concentration reduction and degradation spectrum of $p$-Cresol were analyzed by U2810 UV-Vis spectrophotometer (Hitachi, Japan) via photometry and wavelength scan mode. Whereas, COD of treated samples were measured according to the Standard Method 5220D: closed-reflux, calorimetric method, using HI839800 COD test tube heater (Hanna Instruments, USA) and DR2800 spectrophotometer (HACH, USA). The percent reduction based on concentration and COD reduction was calculated using equation:

![](https://example.com/figure1.png)
is obvious especially at initial ozonation. The concentration reduction of p-Cresol improved from 17.6% to 73.8% within 5 min as the initial pH increased from pH7 to pH11. Considering both degradation performance, pH11 is the optimum pH for oxidation of p-Cresol by ozonation, with 95.8% of p-Cresol concentration reduced and 96% of COD reduced. Generally, the degradation performance improved as the initial pH increasing. This is due to the fact that ozone decomposes rapidly in basic condition causing the production of •OH which has higher oxidation power, 2.8 V, compared to O₃, 2.1 V. Moreover the concentration of hydroxyl ion (OH⁻) increases as the pH increasing, favours the production of •OH consequently enhances the degradation of p-Cresol (Buxton et al. 1988; Kurniawan et al. 2006).

However, p-Cresol degradation at pH9 was found has the lowest efficiency, with 95.3% of p-Cresol concentration reduced and 52.7% of COD reduced. The decreases in performance at higher pH values in this study may attribute to the presence of bicarbonate ions (HCO₃⁻) and carbonate ions (CO₃²⁻). As shown in equation (1), HCO₃⁻ and CO₃²⁻ produces from the dissociation of dissolved carbon dioxide during ozonation. HCO₃⁻ ($k_{\text{OH}} = 8.5 \times 10^8 \text{M}^{-1}\text{s}^{-1}$) and CO₃²⁻ ($k_{\text{OH}} = 3.9 \times 10^9 \text{M}^{-1}\text{s}^{-1}$) have high reactivity with •OH in the solution thus scavenging the •OH in solution, as shown in equation (2) and (3). Figure 3(c) depicted the scavenging pH range of HCO₃⁻ and CO₃²⁻. It is known that H₂CO₃ convert to HCO₃⁻ at approximately pH4.3; and HCO₃⁻ starts to dissociate to CO₃²⁻ at pH8.3 and the dissociation completed at pH10.2. The scavenging effect of HCO₃⁻ and CO₃²⁻ can be seen in Figure 3(d). The decreases in $k$ over ozonation time at higher pH values, and the dropped of $k$, especially in pH9, indicates the reaction between p-Cresol and •OH is scavenged. Nevertheless, p-Cresol degradation by ozonation at pH11 achieved excellent performance in both concentration and COD reduction. This is because at elevated pH, also undergoes hydrolysis. The scavenging effect at pH3 is negligible. The produced enables higher production of •OH subsequently partially overcomes the scavenging effect of CO₃²⁻. The scavenging effect at pH9 is noticeable.
as ozone is predominant at acidic condition. Moreover the reactivity of ozone with \( \text{CO}_3^{2-} \) \((k_{O3} = <1 \times 10^{-2} \text{M}^{-1} \text{s}^{-1})\) and \( \text{HCO}_3^- \) \((k_{O3} = 1\times 10^{-2} \text{M}^{-1} \text{s}^{-1})\) is lower than that of •OH (Hoigne & Bader 1976),

\[
\text{H}_2\text{O} + \text{CO}_2 \rightarrow + \text{H}^+ + \text{HCO}_3^-
\]

\(\text{•OH} + \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \)  

\(\text{•OH} + \text{CO}_3^{2-} \rightarrow \text{CO}_3^{2-} + \text{OH}^- \)

\(\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^- \)

**INFLUENCE OF OPERATING FACTORS ON OXIDATION RATE OF \( p\)-CRESOL**

In this study, the reaction of \( p\)-Cresol with •OH and \( O_3 \) during ozonation, under experimental conditions, can be expressed by the second-order of kinetics as follows:

\[
d'[pC]/dt = k_{\text{OH}}[pC][•OH] - k_{\text{O}_3}[pC][O_3]
\]

where \( k_{\text{OH}} \) is the reaction rate constant of \( p\)-Cresol with •OH and \( k_{\text{O}_3} \) is the reaction rate constant of \( p\)-Cresol with \( O_3 \). Figure 4(a) and 4(b) shows the ozonation of \( p\)-Cresol under experimental conditions followed second-order of kinetics, which is consistent with the findings of other researchers (Hoigne & Bader 1983). The second-order rate constant, \( k \) decreased from 0.0092 to 0.0007 M⁻¹min⁻¹ as the \( p\)-Cresol initial concentration increasing from 50 to 200 mgL⁻¹. Whereas, increasing in initial pH value shows positive influence on \( k \) before affected by scavengers in which the \( k \) increases from 0.0034 to 0.0139 M⁻¹min⁻¹ as the initial pH increases from pH3 to pH11 within 10 min of ozonation, as shown in Figure 3(d).

**EVOLUTION OF ABSORPTION SPECTRA OF \( p\)-CRESOL DEGRADATION**

In this study, the absorption spectra of \( p\)-Cresol degradation over ozonation time were analysed by spectrophotometry. The absorption value represents the ability of a substance to absorb light. The higher the absorption value the greater the absorption by the substance. The absorption at wavelength regions for functional groups, e.g., O-H (220-250 nm), aromatic ring (250-270 nm) and C=O (270-350 nm) were of attention. Figure 5 shows the evolution of absorption spectra of \( p\)-Cresol degradation by ozonation. The evolution can be distinguished into three stages. First, the increased in absorbance value at wavelength regions of O–H and C=O while almost no changes at the aromatic region within 4 min of ozonation; indicates the build-up of OH adducts (Wojnárovits et al. 2002) and the aromatic ring are not likely cleaved. Second, the dropped of absorbance value at aromatic region; suggests the ring-opening reaction of aromatic compounds. Third, the decreased in absorbance values for all wavelength regions over time; indicating
$p$-Cresol and its intermediates were degraded to simpler by-products. Based on the evolution trend, it is believed that the oxidation of $p$-Cresol by ozonation follows three stages mechanisms (Hsu et al. 2005; Valsania et al. 2012). First, the formation of aromatic intermediates followed by ring-opening reactions; degradation of the intermediates; and finally mineralize into water and carbon dioxide.

The possible aromatic intermediates of oxidation $p$-Cresol by ozonation are presented in Figure 6. The mechanism of $p$-Cresol degradation can occur through H-atom abstraction from hydroxyl substituent and methyl substituent; and addition at the aromatic ring (Olariu et al. 2002). The abstraction of hydroxyl-H and methyl-H will form $p$-methylphenoxyl radical (A) and benzyl-type radical (B). The latter is a more preferable abstraction pathway and is expected to generate $p$-hydroxybenzyl alcohol (C), $p$-hydroxybenzaldehyde (D) and $p$-hydroxybenzoic acid (E) (Olariu et al. 2002; Rattabal & Grisdanurak 2016). However, abstraction reaction is slower and has smaller contribution to the overall reactions compared to addition reaction (Atkinson 1986). It is well-accepted that the addition to the aromatic is the first step of oxidation of aromatic compounds due to the fact that $O_3$ and $•\text{OH}$ are strong electrophiles. The cycloaddition is most probably follows the ortho and meta addition pathway (Sun et al. 2012; Wojnárovits et al. 2002; Wu et al. 2012) subsequently produce $p$-methylcatechol (F) and $p$-methylresorcinol (G).

**CONCLUSION**

This study demonstrated ozonation is highly effective in oxidation of micropollutant such as $p$-Cresol. The oxidation of $p$-Cresol by ozonation was favorable at high pH. The oxidation of $p$-Cresol by ozonation under experimental conditions was abided by second-order of kinetics. Generally, the second-order rate constant $k$ increases as the initial pH increased, but decreases with the increasing of initial $p$-Cresol concentration. Though the ozonation performance decreased as the initial $p$-Cresol concentration increased, longer ozonation time can be employed to achieve the same efficiency. The evolution of absorption spectra of $p$-Cresol degradation suggests the $p$-Cresol degradation followed three stages mechanisms; the formation of aromatic intermediates and ring-opening reactions, degradation of the intermediates and subsequently achieved mineralization.
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REFERENCES


FIGURE 6. Possible mechanism of p-Cresol degradation by ozonation.


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