Degradation of phenol and 2,4-dichlorophenol wastewater by ozonation in multi-injection bubble column reactor

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Abstract. The presence of phenolic compounds, such as phenol (carbolic acid or phenylic acid) and 2,4-DCP (2,4-dichlorophenol), in trace amounts in the agricultural environment and in chemical industries wastewater has been considered a potentially large risk for the environment and human health. Therefore, it is very important to develop effective techniques for removing phenolic compounds in wastewater. This research was conducted specifically to observe the effect of temperature of ozone production in the ozonation process to remove phenol and 2,4-DCP in the agricultural aquatic environment and industrial wastewater. This experimental study was conducted using a semi-continuous multi-injection bubble column reactor with initial concentrations of phenol and 2,4-DCP 50 ppm for 60 minutes ozonation. The effect of parameters namely, waste water flow rate, air flow rate, pH of the solution, and temperature were evaluated and optimized. Degradation efficiency, COD concentration, hydroxyl radical concentration were also monitored. It was found that the degradation efficiency at room temperature and low temperature (cold conditions) of phenol were 98.79% and 98.22%, respectively, while 2,4-DCP degradation at room and cold temperatures was 99.83% and 99, 99%, respectively.

1. Introduction

Phenolic compounds have long been used in the petrochemical, pulp and paper, pesticides, herbicides, disinfectants, and pharmaceutical industries. Phenol and chlorinated phenols are commonly found as micropollutant in water. They have harmful effects on living organisms, and endanger human health even at low concentration [1,2] United States Environmental Protection Agency (EPA) put phenol to the list of priority substances in the wastewater that must be eliminated [3]. They could be formed indirectly during chlorination of municipal or industrial wastewater, bleaching in the paper industry, or during bioconversion of low molecular weight compounds. These contaminants are difficult to decompose in wastewater [4,5]. On the other hand, it seems increasingly clear that some conventional wastewater treatment methods have still not succeeded in treating persistent organic pollutants, especially phenol compounds until the concentration remains below the standard (≤ 0.5 mg/L).

Various methods have so far been used to remove excessive quantities of phenols and phenolic compounds including biological processes, chemical oxidation, extraction by solvents, burning, reverse osmosis, and electrochemical and radiation methods [6]. Most of these methods have drawbacks such as high cost, low efficiency, long time required, and production of excessive byproducts [7]. Recently, the combination of biodegradation with initial ozonation for water treatment has attracted attention because of its dual function as a strong oxidizing agent and disinfectant [8]. The unique characteristic of ozone is decomposition into hydroxyl radicals which are strogest oxidizing agents in water.
In this study, decomposition using the ozonation technique for phenol and 2,4-DCP (2,4-dichlorophenol) compounds in synthetic liquid waste was examined specifically for the effect of temperature conditions. The aim of this study was to compare the degradation efficiency of the appropriate phenolic compound. UV absorbance is used to control the initial decomposition level. The size of the COD concentration is proposed for comparison of the biodegradability of the initial compound and the final product.

2. Materials and methods

2.1. Materials
Phenol or carboxylic acid (99%) was obtained from Merck and 2,4-Dichlorophenol (99%) was obtained from Sigma-Aldrich. All solutions were prepared by using demineralized water. In addition, all chemicals used in this work were 0.1 N KI, 0.0001 N KMnO4, 4 M NaOH, 0.01 N Na2S2O3, 2 N H2SO4, Merck Millipore ozone test kit 100607.0001.

2.2. Experimental installation and procedure
This research was carried out in a bench scale multi-injection column reactor. Samples tested in the laboratory were prepared synthetically using phenol, 2,4-DCP and demineralized water with initial concentration of 500 ppm. Cylinder ozonation reactor with useful volume 12 L is used. The reactor is equipped with a multi-injection system to supply ozone into waste water. Ozone is produced by the release of a dielectric barrier. The diameter and height of the reactor are 9 cm and 190 cm, respectively. Figure 1 shows a schematic diagram of experimental settings for catalytic ozonation techniques.

![Figure 1. The schematic diagram of the experimental setup](image-url)
Ozone production rate test was conducted in the early stage of this study at room temperature (about 29 °C) and cold temperature (-12 °C), using two bubblers containing 0.1 N KI. The solubility of ozone in water was determined with Merck Millipore ozone test kit 100607.0001, and the hydroxyl radical generated during the ozonation process was determined by permanganometric titration using 0.0001 N KMnO4. Several experimental parameters had been examined and it was determined that the experiment was be carried on air flow rate of 12 L/min, wastewater flow rate of 495 mL/min, and solution pH of 12. The initial concentration of phenol and 2,4 DCP in all experiments were 50 ppm. The experiment was conducted for 60 minutes with sampling at minute 0, 15, 30, 45, and 60. Degradation efficiency, COD concentration, and hydroxyl radical concentration were monitored. All samples were reacted with Merck Millipore phenol test kit 1.00856.0001 and the concentration of the phenolic compound was measured by spectrophotometer at λ = 512 nm. The degradation efficiency of the phenolic compound was calculated via Equation (1), where Ct is the concentration of phenol or 2,4-DCP after several regular intervals of time (t) and C_{t=0} is the initial concentration of phenol or 2,4-DCP.

Degradation efficiency (%) = \frac{C_{t=0} - C_t}{C_{t=0}} \times 100 \tag{1}

3. Results and discussion

3.1. Ozone production rate

The air was discharged from a compressor and used as oxygen source for ozone generation (in ozonator). Variations of air flow rate from 4 to 12 L/min achieved ozone production rate as shown in fig. 2.

![Figure 2. Ozone production rate test at 29°C and -12°C](image)

The higher the air flowrate passed through the ozonator, the more oxygen was available to generate ozone, resulting in higher ozone production rate. The highest ozone production rate at room temperature in the laboratory (29 °C) was obtained at 12 L/min air flow rate with a dosage of ozone is 956.10 mg/h. Meanwhile, the ozone generated at cold temperature (-12 °C), reached a production rate of 1779.95 mg/h at the air flow rate of 12 L/min. The cold temperature of -12 °C only represents the temperature of ozone generation and does not represent the temperature in the bubble column reactor. The higher ozone production rate at cold temperature is due to the increasing half-life of ozone as temperature decreases, both in gaseous phase and in water.

3.2. Ozone solubility and hydroxyl radical concentration

This part of the study aims to determine the optimum condition for the degradation process. The rate of ozone decomposition increases as pH grows because of the catalytic action of hydroxyl ions OH-.
The half life of ozone at pH 10 is approximately less than one minute [9]. The mechanism of interaction is fairly complex and includes a successive chain of reactions that yield H$_2$O$_2$, O$_3$, and •OH and HO$_2$• radicals [10]. As a result of the chain reactions, ozone solubility in water decreases and more hydroxyl radicals are formed. This is shown in Table 1, where ozone solubility is highest at pH 7 (0.079 mg/L at 60 minutes) and lowest at pH 12, while hydroxyl radical concentration is lowest at pH 7 and highest at pH 12 (0.9435 mg/L at 60 minutes). Hydroxyl radical has stronger relative oxidation power (2.80 V) than ozone (2.07 V) [11]. The indirect mechanism of ozone involving reaction via free hydroxyl radicals which are produced during the decomposition of ozone is preferred in the degradation of phenolic compounds, since the reactions are faster than the direct reaction with ozone.

The effect of initial pH on the degradation of phenolic compounds has been researched widely, and the results show that the degradation is more effective at higher pH [8,11,12] and it is suggested that phenol degradation achieved higher degradation efficiency via the route of indirect oxidation by •OH. Based on the similar studies and the concentration of hydroxyl radicals formed, pH 12 was selected as the condition for the degradation of phenol and 2,4-DCP.

| Time (min) | Ozone solubility (mg/L) | Hydroxyl radical concentration (mg/L) |
|------------|-------------------------|-------------------------------------|
| pH = 7     | pH = 8                  | pH = 10                             | pH = 12                             |
| 15         | 0.0350                  | 0.0120                              | 0.0092                              | 0.0064                              | 0.3060                              | 0.3995                              | 0.6205                              |
| 30         | 0.0450                  | 0.0180                              | 0.0129                              | 0.0079                              | 0.3927                              | 0.5330                              | 0.7225                              |
| 45         | 0.0540                  | 0.0410                              | 0.0285                              | 0.0160                              | 0.4675                              | 0.6452                              | 0.7735                              |
| 60         | 0.0690                  | 0.0210                              | 0.0147                              | 0.0084                              | 0.5610                              | 0.7956                              | 0.9435                              |

3.3. The influence of ozone production temperature on the degradation of phenol and 2,4-DCP

3.3.1. Degradation of phenol.

Figure 3 shows the degradation efficiency of phenol and 2,4-DCP at room temperature (29 °C) and cold temperature (-12 °C). The effect of temperature significantly affected the percentage of phenol degradation. The mechanism of electrophilic reaction between ozone and phenol occurs actively in ambient temperature (28-29 °C). Otherwise in cold condition, phenol structure becomes more rigid which inhibit ozone to attack the electrophilic group (OH group) in phenol compound. Thus, phenol in cold condition become more ozone-resistant than in ambient temperature. Based on Figure 3, phenol degradation in ambient temperature could reach 98.79% by 60 minutes of ozonation process remaining 0.6 mg/L of phenol concentration and 98.22% in cold temperature remaining 0.86 mg/L of phenol concentration.

Indirect mechanism is more dominant in this condition due to the instability of ozone and the abundance of hydroxyl radicals. This mechanism needs high rate of ozone decomposition to be hydroxyl radicals, which was affected by temperature. The rate of ozone decomposition increases as the temperature grows [10]. Furthermore, phenol dissociates into its conjugate base, phenoxide ion (C$_6$H$_5$O$^-$), at high pH [13]. The presence of •OH in the solution and higher reactivity of phenoxide ion with ozone and •OH ($k_{O3} = 1.4 \times 10^9$ M$^{-1}$s$^{-1}$; $k_{OH} = 9.6 \times 10^{-9}$ M$^{-1}$s$^{-1}$) compared to those of phenol ($k_{O3} = 1.3 \times 10^9$ M$^{-1}$s$^{-1}$; $k_{OH} = 11.0 \times 10^{-9}$ M$^{-1}$s$^{-1}$) [14,15] contribute to the high degradation efficiency in the treatment. Comparable result was obtained by [10] where 100 mg/L of phenol at pH 11 was ozonated for 10 minutes and achieved 62.9% in the first 10 minutes (compared to 69.39% and 63.56% in the first 15 minutes of our study).
3.3.2. Degradation of 2,4-dichlorophenol.

2,4-DCP was fairly easier to oxidize than phenol due to the substitution of hydrogen by two electron donors (-Cl), which activates the aromatic ring. Consequently, in these positions, 2,4-DCP react actively with ozone, with the initial attack of ozone molecules taking place at the ortho or para position of the hydroxyl group or the negative-charged oxygen group. Since there is a chlorine atom bonded to the para position of the hydroxyl group or the negatively charged oxygen group of 2,4-DCP, the electrophilic addition of an ozone molecule to the para molecule to the para position releases the chlorine atom \([16]\). Both the direct ozonation mechanism and the more complex indirect mechanism took place in this condition, but the indirect mechanism by •OH is more dominant due to the instability of ozone and abundant hydroxyl radicals in alkaline condition. At cold temperature, the amount of ozone and hydroxyl radicals available to oxidize 2,4-DCP was higher. Thus, the initial degradation rate was significantly higher than that at room temperature, as it reached 98.34%, compared to 84.18% within the first 15 minutes of ozonation. The rate of degradation slowed down over time, and after 60 minutes of ozonation, the degradation efficiency of 2,4-DCP at cold condition reached 99.99%, with the remaining 2,4-DCP concentration of 0.0066 mg/L, while at ambient temperature, the degradation efficiency reached 99.83% with the remaining concentration of 2,4-DCP of 0.085 mg/L. Comparable result was obtained by \([8]\) where 100 mg/L of 2,4-DCP solution at pH 12 was treated for 30 minutes by ozonation and achieved 100% degradation efficiency.

![Figure 3](image)

**Figure 3.** Degradation efficiency of (a) phenol and (b) 2,4-DCP at ozone production temperature of 29 °C and -12 °C

3.4. Evaluation of COD degradation

Among those proposed in literature, the COD degradation is commonly used as a biodegradability measure. The effect of ozonation to the biodegradability of the studied compounds by the determination of COD degradation before and after ozonation was investigated. The decrease in COD concentration shows the decrease of the oxygen demand required to oxidize the chemicals in the sample. Table 2 presents the COD concentration and its degradation efficiency with and without preliminary ozonation.

Based on the obtained results, we observe that the initial COD concentration of phenol is higher than that of 2,4-DCP. The COD degradation of phenol in room temperature and cold temperature are 74.01% and 42.76% respectively. This supports the result that the degradation of phenol is higher at room temperature than that at cold temperature. The COD degradation of 2,4-DCP at room temperature and cold temperature were 84.31% and 65.5%.
Table 2. COD concentration and degradation of phenol and 2,4-DCP at room and cold temperature

| Temperature | Time (min) | Phenol | 2,4-Dichlorophenol |
|-------------|------------|--------|-------------------|
|             |            | COD concentration (mg/L) | COD degradation (%) | COD concentration (mg/L) | COD degradation (%) |
| 29°C        | 0          | 96.13 | 0.00 | 55.4 | 0.00 |
|             | 15         | 77.67 | 19.19 | 41.82 | 24.51 |
|             | 30         | 59.68 | 37.92 | 29.06 | 47.55 |
|             | 45         | 39.92 | 58.47 | 19.82 | 64.22 |
|             | 60         | 24.98 | 74.01 | 8.69 | 84.31 |
| -12°C       | 0          | 112.43 | 0.00 | 58.12 | 0.00 |
|             | 15         | 102.65 | 8.70 | 39.65 | 31.78 |
|             | 30         | 97.49 | 13.29 | 32.32 | 44.39 |
|             | 45         | 70.61 | 37.20 | 24.98 | 57.02 |
|             | 60         | 64.36 | 42.76 | 20.01 | 65.57 |

4. Conclusions
In view of the results obtained we may conclude the following:

- The ozonation of aqueous solutions containing phenol and 2,4-DCP at ozone generation temperature of 29°C and -12°C was studied to evaluate the potential of ozonation for treating waters containing these toxic chemicals and to compare the degradation efficiency at these temperatures.
- The ozone production rate was significantly higher at cold temperature (1779.95 mg/h) than at room temperature (956.1 mg/h).
- Ozone solubility in water was highest at pH = 7 (0.069 mg/L) while hydroxyl radical concentration was highest at pH = 12 (0.9435 mg/L).
- The degradation efficiency of phenol at room and cold temperature were 98.79% and 98.22% while the degradation efficiency of 2,4-DCP was higher, which reached 99.83% at room temperature and 99.99% at cold temperature.
- The COD degradation of phenol at room and cold temperature were 74.01% and 42.76%, while the degradation efficiency of 2,4-DCP at room and cold temperature were 84.31% and 65.57%.

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