

Article

## Degradation of 2,4-Dichlorophenol in Aqueous Solution by Ozonation in the Presence of Iron Oxide Compound in Bubble Column Reactor

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**Abstract.** Chlorophenols are a group of chemical substances given special attention by experts and researchers of industrial wastewater due to their high toxicity and low biodegradability. The degradation of these compounds, often used in studies is 2,4-Dichlorophenol (2,4-DCP), either use conventional processing methods or contemporary approaches such as catalytic ozonation and AOPs (Advanced Oxidation Processes). The laboratory-scale 2,4-DCP degradation technique in this study was carried out in a multi-injection bubble column, with very satisfactory processing results. This is mainly due to the ability of hydroxyl radicals to decompose almost all 2,4-DCP in wastewater as well as not giving out a dangerous product. Specifically, the chlorophenol waste used here is a synthetic wastewater or dilute 2,4-DCP solution focused on investigating the effect of air flow rate, wastewater flow rate, and the amount of iron oxide (FeO and / or Fe<sub>2</sub>O<sub>3</sub>) involved. This bench scale processing of 2,4-DCP degradation is a semi-continuous, with an initial concentration of 2,4-DCP of 50 ppm and 60 minutes of ozonation time. In this study, the use of FeO and/or Fe<sub>2</sub>O<sub>3</sub> catalysts does not significantly affect the degradation efficiency of 2,4-DCP. With the non-catalytic ozonation technique, the highest percentage of phenolic and COD degradation obtained was 99.83% and 84.31% at an air flow rate of 12 L / min and a wastewater flow rate of 495 mL / min. For catalytic ozonation, the highest phenolic and COD degradation under the same operating conditions was 99.64% and 86.44%.

**Keywords:** 2,4-Dichlorophenol, ferrolite, ozonation, wastewater treatment, bubble column reactor.

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## 1. Introduction

Industrial wastewater containing chlorinated organic compounds, especially phenol substances, has been widely reported as a threat to the environment and human health. They have harmful effects on living organisms and endanger human health even at low concentration [1]. There are six chlorophenol isomers; 2,3-dichlorophenol, 2,4-dichlorophenol, 2,5-dichlorophenol, 2,6-dichlorophenol, 3,4-dichlorophenol, and 3,5-dichlorophenol. The use of 2,4-DCP is more common than other chlorophenols with an estimated annual worldwide production of 40,000 tonnes [2]. Exposure to phenolic compounds, particularly 2,4-DCP, one of the very toxic and common chlorophenol, cause kidney, liver, and pancreas damage, weaken the central nervous system, and denature protein molecules. As one of the most common chlorophenols used in industries, 2,4-DCP is widely used as a raw material or intermediate product in the pulp and paper industries, drugs, disinfectants, herbicides, and petrochemicals. The contaminants include those difficult to decompose in wastewater [3] [4]. In herbicide production, 2,4-DCP is used as an intermediate to prepare 2,4-dichlorophenoxyacetic acid. This compound is commonly used as it eliminates broad leaf weeds selectively without harming other plants. In many countries, the 2,4-DCP compound has been classified as hazardous waste and it is therefore very important to develop an effective method for removing it in wastewater, within a relatively short time and without dangerous byproducts. The Environmental Protection Agency (EPA) has set a limit for 2,4-DCP concentration in wastewaters to 60 µg/L because of possible contamination of drinking water sources by industrial activities. In drinking water, the maximum concentration of 2,4-DCP is 0.03 µg/L [5].

Several 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]. One of the most effective methods for removing organic pollutants is the use of ozonation at elevated pH, which is considered as an advanced oxidation process (AOP), due to the rapid decomposition of ozone in water, producing hydroxyl radicals with high oxidation potential. Some of the advantages of this method include the ease of use, low cost, low space requirement, and high efficiency in addition to harmless organic products [8] [9]. An opportunity to accelerate ozonation reactions is to use heterogeneous or homogeneous catalysts. Several metal oxides and ions have been studied and sometimes a significant acceleration in the decomposition of the target compound has been achieved, although the reaction mechanism in most cases remain unclear [10].

This study investigates the degradation of 2,4-DCP using ozonation and catalytic ozonation with Fe-based catalyst in multi-injection bubble column reactor. To achieve the purpose of this study, a special examination

was carried out on the decomposition process with ozonation technique applied to 2,4-DCP compounds in synthetic liquid waste. This was meant to determine the effect of air flow rate, wastewater flow rate, and catalyst weight to allow investigation on the efficiency of 2,4-DCP degradation. Spectrophotometric analysis with UV absorbance was used to measure the level of decomposition in each process, while the amount of COD concentration was used as a comparison of biodegradability for the initial phenolic compounds and the final products of the degradation process. LC/MS analysis was conducted to analyze the intermediates and final products of the 2,4-DCP degradation.

## 2. Materials and Methods

### 2.1. Materials

2,4-Dichlorophenol was obtained from Sigma-Aldrich. Ferrolite (granular activated sand) containing iron oxide (FeO/Fe<sub>2</sub>O<sub>3</sub>), which is claimed to have a good adsorption capacity and be able to reduce the iron and manganese content in wastewater, was acquired and readily used. All solutions were prepared using demineralized water. In addition, all the chemicals used in this work were of extra purity or analytical grade. Supporting materials include sodium hydroxide, potassium iodide, sodium thiosulfate, sulfuric acid, potassium permanganate, and starch.

### 2.2. Experimental Installation

This research was carried out in a laboratory scale multi-injection bubble column reactor. The samples tested were prepared synthetically using 2,4-DCP and demineralized water. Cylinder ozonation reactor with useful volume 12 L with diameter and height of 9 cm and 190 cm respectively was used. The reactor was equipped with a multi-injection system to supply ozone into wastewater. The ozone was produced through the release of a dielectric barrier, injected to the reactor through silicone hose and discharged to the reactor by air diffuser. The catalyst named *Ferrolite* was placed in a 200-micron stainless-steel wire mesh bag which tied to a stainless-steel wire on top of the reactor. Figure 1 shows a schematic diagram of experimental settings for catalytic ozonation techniques.

In liquid-phase direct oxidation with in-situ generated ozone, the contact must occur as soon as possible. Generally, ozonation reaction in water is classified into two categories: 1) Fast reaction where the rate of reaction is affected by mass transfer rate of ozone to the liquid, and 2) Slow reaction where the rate-limiting step is the reaction rate. This research falls under the first category since ozonation of phenolic compounds occur very rapidly. The mass transfer of ozone to the liquid is affected by solubility of the ozonated compound in water, concentration of ozone in the gas, type of carrier gas, method and contact time, bubble size, pressure, and temperature. The solubility of ozone at low partial pressure is very low. Hence, a contactor is required to aid

the contact of ozone with liquid to increase the effectivity of mass transfer of ozone from gas to liquid. Bubble column reactor is a modification of gas bubble-dispersing unit with two steps of dispersion to liquid [11], [12]. The rapid movement of gas bubbles helps the gas and liquid to mix, so an impeller is no longer needed. The use of multi-injection system increases the contact area for heat and mass transfer. It also yields a more homogeneous mixture. In the bubble column, oxidation reactions such as degradation, sterilization, and chemical bond severance [13], [14], [15], [16].

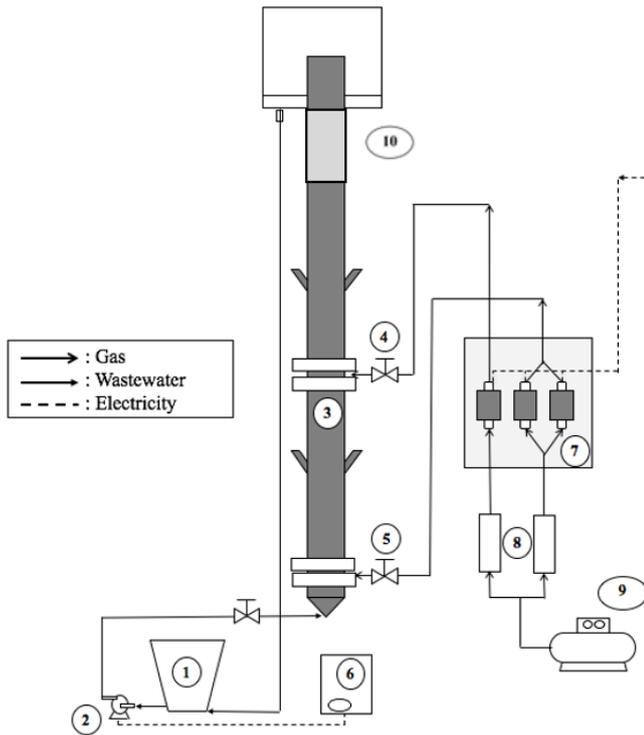


Fig. 1. The schematic diagram of experimental setup for catalytic ozonation of 2,4-dichlorophenol in bubble column reactor.

Table 1. Description of the schematic diagram of the experimental setup.

No.	Description
1	Reservoir
2	Pump
3	Bubble Column Reactor
4	Air Injection 1 ( $I_1$ )
5	Air Injection 2 ( $I_2$ )
6	Power Supply
7	Ozonator Circuit
8	Flowmeter
9	Compressor
10	Catalyst

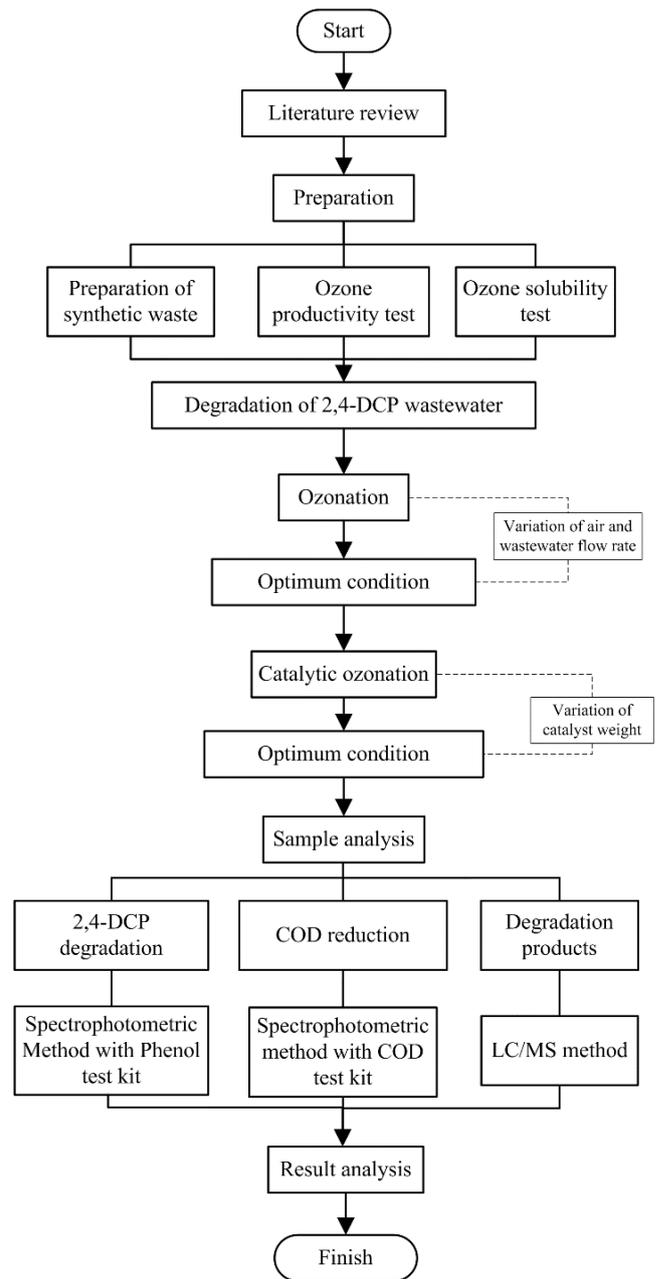


Fig. 2. Flow chart of the experimental procedure.

### 2.3. Procedure

The experimental procedure of this research is summarized in Fig. 2. Ozone production rate test was conducted in the early stage of the study using two bubblers containing 0.1 N KI. The solubility of ozone in water was determined with Merck Millipore ozone test kit 100607.0001. The hydroxyl radical generated during the ozonation process was determined by permanganometric titration using 0.0001 N  $\text{KMnO}_4$ . Several experimental parameters had been examined and it was determined that the experiment was to be carried on air flow rate of 12 L/min, wastewater flow rate of 495 mL/min, and solution of pH 12. The initial concentration of 2,4-DCP was 50 ppm and the total volume of the wastewater was 15 L. The reactions were carried out at room temperature ( $29^\circ\text{C}$ ) for 60 minutes with 15-minute sampling interval. Degradation efficiency (DE), 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 2,4-DCP compound was measured by UV-Vis Spectrophotometer (BEL Engineering UV-M51) at  $\lambda = 512$  nm. The degradation efficiency of 2,4-DCP was calculated via Eq. (1), where  $C_t$  is the concentration of 2,4-DCP after several regular intervals of time ( $t$ ) and  $C_{t=0}$  is the initial concentration of 2,4-DCP.

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

### 3. Results and Discussion

#### 3.1. Bubble Column Reactor Hydrodynamics

This test aims to learn about the mass transfer profile and behavior of liquid and gas in the bubble column reactor. This test is the foundation to determine the variation of power supply voltage and air flow rate in the succeeding experiments. The effect of power supply voltage to the residence time of liquid in the reactor is shown in Fig. 3.

The increase of power supply voltage causes the increase of wastewater flow rate as well, decreasing the residence time of the wastewater in the reactor. The expected residence time of wastewater in the reactor is between 18 to 40 minutes, with power supply voltage of 6, 8, and 10 V, and wastewater flow rate of 255, 405, and 495 mL/min.

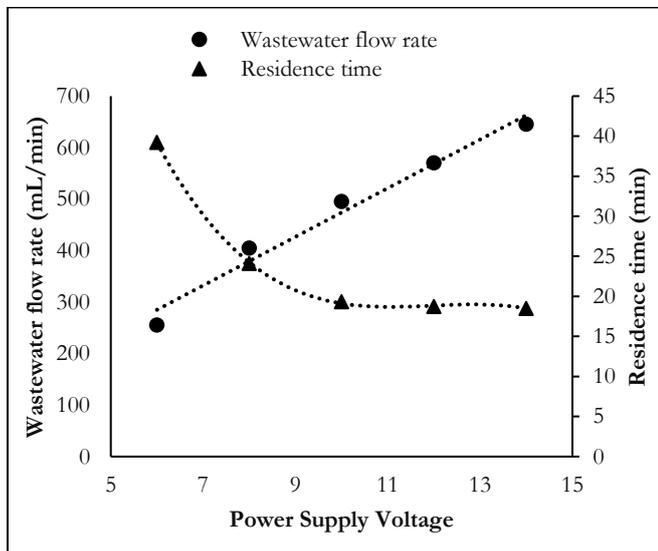


Fig. 3. The effect of power supply voltage on wastewater flow rate and residence time.

Along with power supply voltage, air flow rate also affects the average wastewater circulation flow rate. Air is injected from the bottom and middle part of the reactor. It is shown in Fig. 4 that the wastewater flow rate with the addition of air injection is larger than that of with no air injection. The air that flows upwards thrusts the liquid axially to the top of the reactor and increases the contact area between the liquid and the gas phase. The air flow

rate selected for the succeeding experiments are 8, 10, and 12 L/min due to the fairly high amount of bubbles formed and causes the liquid hydrodynamics to be more turbulent, which are favorable conditions for the degradation of 2,4-DCP. The air flow rate of 14 L/min was not selected as the reactor's base becomes unstable in this condition and causes the liquid to periodically spill from the reactor.

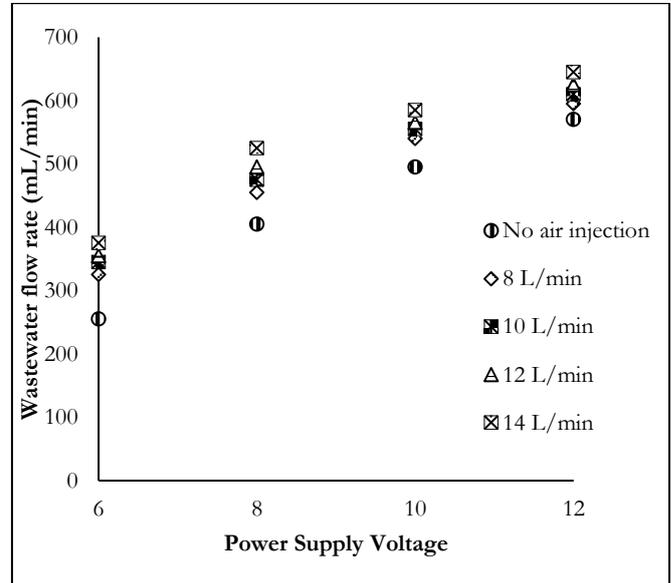


Fig. 4. The effect of air flow rate on wastewater flow rate (air injection at  $I_1$  and  $I_2$ )

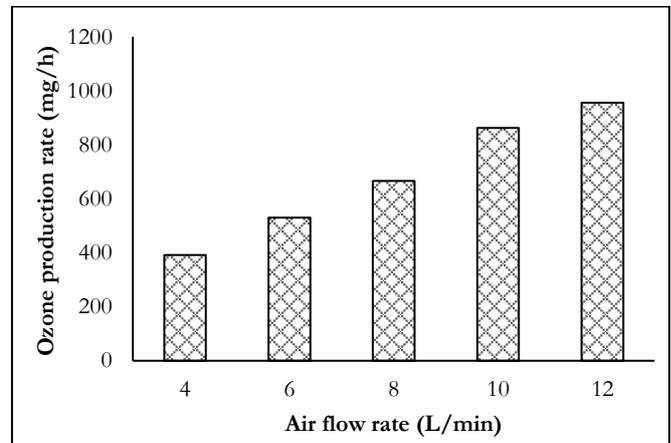
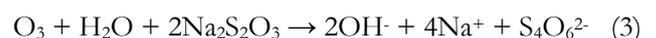
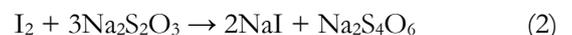


Fig. 5. Ozone production rate test.

#### 3.2. Ozone Production Rate

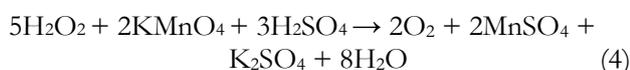
Air was discharged from a compressor and used as oxygen source for ozone generation in the ozonator. At laboratory temperature ( $29^\circ\text{C}$ ), variations of air flow rate from 4 to 12 L/min achieved ozone production rate as shown in Fig. 5. The test was performed by iodometric titration, the method and reactions were according to a previous research by Birdsall et al. [17].



The higher the flow rate passed through the ozonator, the more oxygen was available to generate ozone, resulting in highest production rate, 956.10 mg/h, obtained at 12 L/min air flow rate.

### 3.3. Ozone Solubility and Hydroxyl Radical Concentration

This section was carried in demineralized water and aimed to determine the optimum condition for the degradation process. The rate of ozone decomposition increases as pH grows because of the catalytic action of hydroxide ions. The mechanism of interaction is fairly complex and includes a successive chain of reactions which yield  $H_2O_2$ ,  $O_3^-$ , and  $OH^\bullet$  and  $HO_2^\bullet$  radicals [18]. The formed hydroxyl radicals tend to react with each other and form hydrogen peroxide ( $H_2O_2$ ). The oxidation of  $H_2O_2$  and  $KMnO_4$  follows the following reduction-oxidation reaction principal:



From Table 2 and 3, as the pH increases, the ozone solubility decreases and consequently generate more and stronger hydroxyl radicals which degraded 2,4-DCP more effectively. Hydroxyl radical has stronger relative oxidation power (2.80 V) than ozone (2.07 V) [19]. 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 [20] [21] and it is suggested that phenol degradation achieved higher degradation efficiency via the route of indirect oxidation by  $\bullet OH$ . 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. Ozone solubility was highest at pH = 7.00, where it reached 0.079 mg/L. The hydroxyl radical generated was highest (0.9435 mg/L) at solution of pH 12.00.

Table 2. Ozone solubility at pH 7, 8, 10, and 12

Time (min)	Ozone solubility (mg/L)			
	pH=7	pH=8	pH=10	pH=12
15	0.035	0.012	0.0092	0.0064
30	0.045	0.018	0.0130	0.0079
45	0.054	0.041	0.0285	0.0160
60	0.069	0.021	0.0147	0.0084

Table 3. Hydroxyl Radical Concentration at pH 8, 10, and 12.

Time (min)	Hydroxyl radical concentration (mg/L)		
	pH=8	pH=10	pH=12
15	0.3060	0.3995	0.6205
30	0.3927	0.5330	0.7225
45	0.4675	0.6452	0.7735
60	0.5610	0.7956	0.9435

In various studies [19], the increase of pH results to shorter ozone half-life. The result obtained from this experiment corresponds to previous works, where the increase of pH decreases the concentration of ozone due to its shorter half-life. The solubility of ozone can also be reviewed from Ozone's Henry's Constant in water, with the relation of:

$$\frac{p}{K_H} = x \quad (5)$$

The  $K_H$  at 25 °C at pH 7, 8, and 10 are  $6.35 \times 10^3$ ,  $6.88 \times 10^3$ , and  $8.09 \times 10^3$ , respectively. Since all the conditions except for pH in this experiment are set constant, the partial pressure is considered the same. If  $K_H$  increases, then  $x$  (mole fraction, which can also represent solubility at very low concentration) decreases [19].

The decomposition rate of ozone increases as pH increases. The half-life of ozone can be less than 1 minute at pH 10. Combination of reactions with molecular ozone and reactions with  $\bullet OH$  radicals may cause oxidation of organic species. The reaction between ozone and hydroxide ions produce hydroperoxyl radical  $HO_2^\bullet$  and super-oxide anion radical  $O_2^\bullet$ . By the reaction between ozone and the super-oxide anion radical, the ozonide anion radical  $O_3^\bullet$  is formed, which decomposes rapidly, giving  $\bullet OH$  radical. The reaction three ozone molecules to produce two  $\bullet OH$  radicals is summarized by [22].



### 3.4. Effect of Air Flow Rate on 2,4-DCP Degradation

The ozone generated results from the oxygen passed through the ozonator and was injected to the reactor by air diffuser. Variations in air flow rate were 8 L/min, 10 L/min, and 12 L/min with wastewater flowrate of 495 mL/min. Air flow rate correlates to the amount of oxygen available to generate ozone. The higher the rate, the higher the oxygen available to generate ozone, hence more hydroxyl radicals form. Based on Fig. 6, the highest degradation efficiency of 2,4-DCP was obtained at 12 L/min, where it reached 84.18% in the first 15 minutes, compared to 75.59% at 8 L/min and 82.02% at 15%. This trend continued until the 45th minute, where the highest degradation efficiency, 99.28%, was achieved at 10 L/min. At the 60th minute, the highest degradation efficiency, 99.83%, was achieved at 12 L/min with remaining 2,4-DCP concentration of 0.085 mg/L. The air flow rate of 12 L/min was to be used as the control variable for the

next part. Comparable result was obtained by [19] where 100 mg/L of 2,4-DCP solution at pH 12 was treated for 30 minutes by ozonation and achieved 100% degradation efficiency.

Initial attack of 2,4-DCP molecules by hydroxyl radicals and ozone take 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 [23]. Both the direct ozonation mechanism and the more complex indirect mechanism took place in this condition, but the indirect mechanism by  $\bullet\text{OH}$  is more dominant due to the instability of ozone and abundant hydroxyl radicals in alkaline condition.

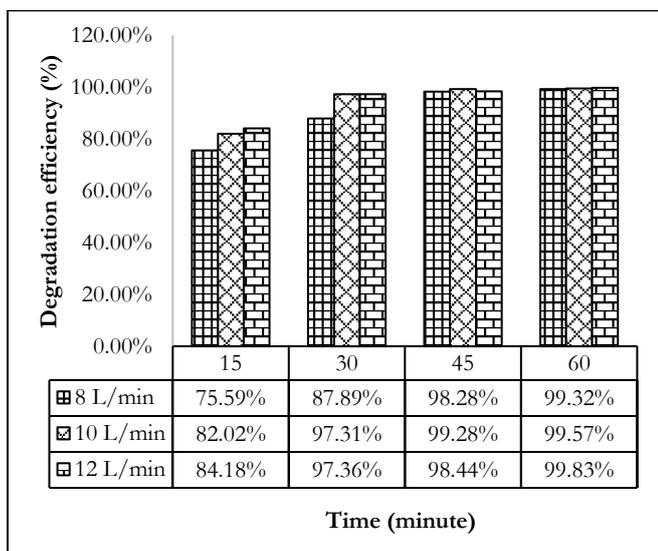


Fig. 6. Effect of air flow rate on the degradation of 2,4-DCP by ozonation.

### 3.5. Effect of Wastewater Flow Rate on 2,4-DCP Degradation

The variations in the wastewater flow rate were 255, 405, and 495 mL/min with air flow rate of 12 L/min. the results of degradation of 2,4-DCP with different wastewater flow rate were as shown in Fig. 7. In the first 15 minutes, the highest degradation efficiency, 495 mL/min was achieved. This was around 84.18% of 2,4-DCP degradation, followed by 405 mL/min (81.58%), and 255 mL/min (80.28%). This result was consistent up to the 45th minute, where the highest degradation efficiency was achieved at 405 mL/min (99.25%). At the 60th minute, the end of the experiment, the highest 2,4-DCP degradation, 495 mL/min, was achieved, followed by 405 mL/min, and 255 mL/min. Wastewater or circulation rate contributed to the residence time of liquid in the reactor, which affected the contact time between 2,4-DCP in the liquid and ozone [24] [25]. The residence time was longest at 255 mL/min, but since the system was semi-continuous and a portion of the liquid stayed in the reservoir, this had the least frequent circulation of liquid. Conversely,

residence time was shortest at wastewater flow rate of 495 mL/min, but resulted in the most frequent circulation of liquid in the reservoir to the reactor.

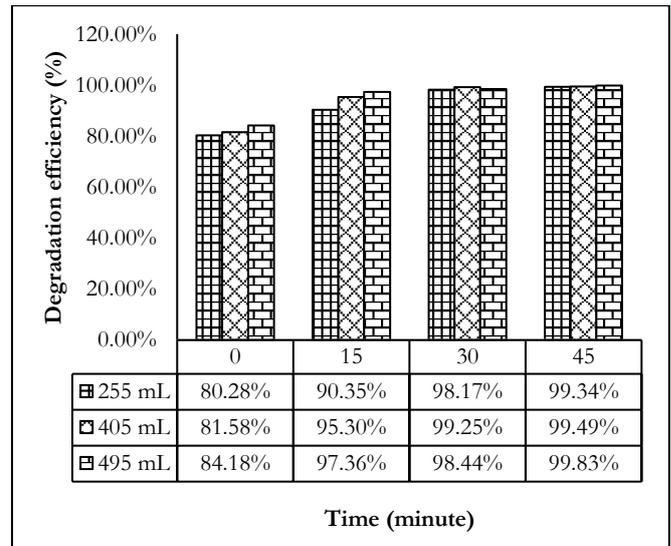


Fig. 7. Effect of wastewater flow rate on the degradation of 2,4-DCP by ozonation.

### 3.6. Effect of Catalyst Weight on 2,4-DCP Degradation

A set of reactions was carried out by varying the catalyst (ferrolite) weight while keeping the wastewater flow rate at 495 mL/min and air flow rate at 12 L/min. The degradation efficiency increased with the increase of ferrolite weight, as shown in Fig. 8.

In the first 15 minutes, the highest degradation efficiency, 91.40%, was obtained at catalyst load of 200 g, followed by 100 g and 50 g with 87.94 and 82.04% respectively. This result was consistent up to the end of the reaction time, where the catalyst load of 200 g achieved the highest degradation efficiency, 99.64%, and the remaining 2,4-DCP concentration was 0.19 mg/L, followed by at 100 g (98.54%), and 50 g (98.24%). The degradation efficiency of 2,4-DCP was notably higher in catalytic ozonation under the same condition (91.40% with 200 g catalyst weight), in contrast to ozonation (84.18%). However, the difference gradually declines over time, and at the 60th minute, the degradation efficiency of catalytic ozonation was finally lower than that of ozonation, although the difference between the two methods was not significant. This is predicted due to the saturation of the catalyst over time, or that the presence of wire mesh bag in which the catalyst was placed in increases pressure drop and decreases the contact surface between the gas phase and liquid phase.

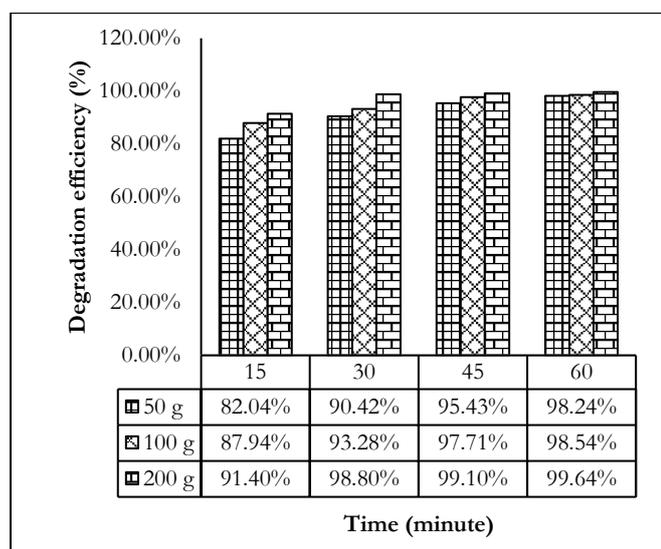


Fig. 8. Degradation efficiency of 2,4-DCP by catalytic ozonation: effect of catalyst weight.

### 3.7. Comparison of 2,4-DCP Degradation by Ozonation and Catalytic Ozonation

Based on Fig. 9, it can be inferred that the catalytic ozonation is more effective in the first 15 minutes than that of ozonation, as the degradation of 2,4-DCP by catalytic ozonation reached 91.40% while it only reached 84.18% by ozonation. The presence ferrolite gave positive result on the initial degradation as it helps with the adsorption of 2,4-DCP on the micropores of ferrolite and the catalytic process. However, as the reaction proceeds the presence of ferrolite becomes insignificant and in the end of the reaction, the catalytic ozonation process reached a slightly lower degradation efficiency (99.64%) compared to ozonation (99.83%). This is due to the presence of catalyst wire mesh bag placed in the reactor that hinders the circulation of wastewater flow rate in the reactor. As a result, the mass transfer from the aqueous solution to the surface of ferrolite declines, so the degradation process becomes more ineffective. The presence of ferrolite in the wire mesh bag also increases the pressure drop along the reactor. Furthermore, during the 60 minutes of degradation, the micropores of ferrolite may become saturated with 2,4-DCP and its degradation products, lowering its ability to bind ozone and accelerate radical components.

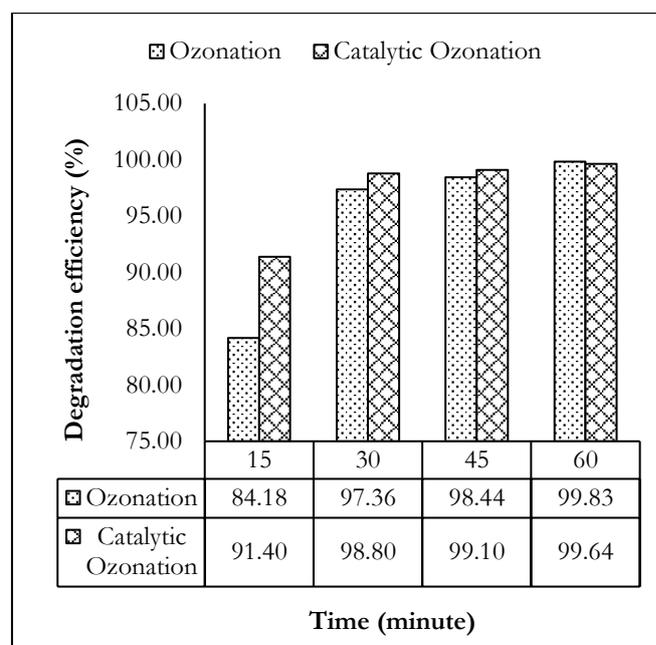


Fig. 9. Comparison of 2,4-DCP Degradation by Ozonation and Catalytic Ozonation with 200 g ferrolite (Air flow rate of 12 L/min, Wastewater flow rate of 495 mL/min, pH 12)

Based on Table 4, there is a decrease in solution pH, which started off at the same pH (12). Degradation of 2,4-DCP by ozonation had higher pH than that by ozonation, although the difference is insignificant. The decrease in pH is an indication of the formation of various intermediates, including aldehydes, carboxylic compounds, and other organic acids that increases the concentration of H<sup>+</sup> in the solution [19].

Table 4. Comparison of degradation efficiency (DE), Final 2,4-DCP concentration ( $C_{t=60}$ ), and final pH.

Configuration	DE (%)	$C_{t=60}$	Final pH
Ozonation	99.83	0.085	8.46
Catalytic Ozonation	99.64	0.190	8.82

### 3.8. Evaluation of COD Degradation

From various literature, COD degradation is commonly used as a biodegradability measure [19] The effect of ozonation on the biodegradability of 2,4-DCP through the determination of COD degradation before and after ozonation was investigated. The decrease in COD concentration shows the reduction in oxygen required to oxidize the chemicals in the sample. The COD test was carried out only on the optimum condition for each method at air flow rate of 12 L/min and wastewater flow rate of 495 mL/min. Figure 10 presents the COD concentration and its degradation efficiency with and without preliminary ozonation.

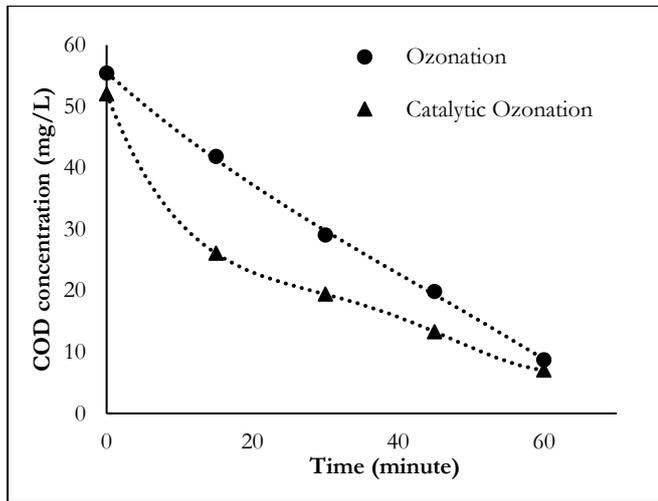


Fig. 10. COD concentration of the 2,4-DCP wastewater by ozonation and catalytic ozonation.

Based on the results, the COD degradation of 2,4-DCP by catalytic ozonation is higher than that by ozonation. In the first 15 minutes, the COD degradation of 2,4-DCP by catalytic ozonation reached 49.92% with COD concentration of 26.07 mg/L. Contrastingly, ozonation technique only achieved 24.51% with COD concentration of 41.82 mg/L. The difference of COD degradation between the two methods shrunk over time. By the end of the experiment, the COD concentration and degradation by catalytic ozonation was 7.06 mg/L (86.44%), while that of ozonation was 8.69 mg/L (84.31%).

### 3.9. Intermediates and Final Species in the Ozonation of 2,4-DCP

LC-MS Spectrum of the degradation products at the end of the reaction (60 minutes) is presented in Fig. 11 and Fig. 12 while the identified products are shown in Table 5 and Table 6.

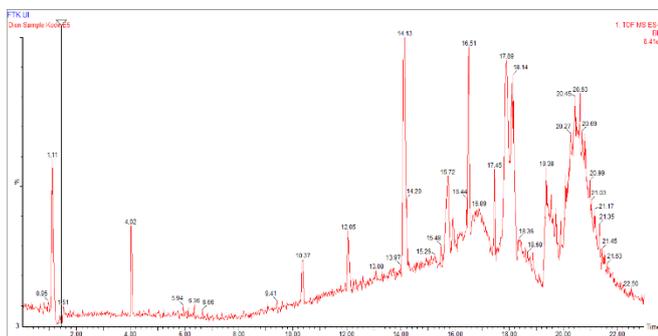


Fig. 11. Chromatogram of 2,4-DCP degradation products by ozonation.

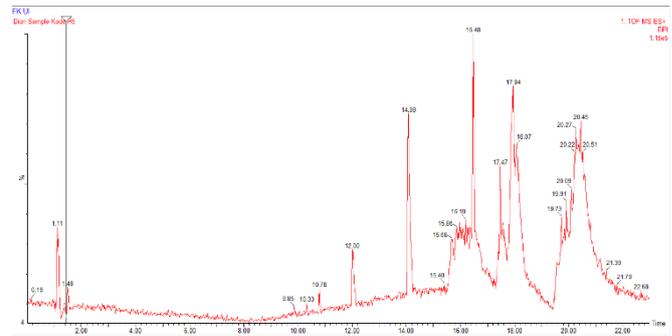


Fig. 12. Chromatogram of 2,4-DCP degradation products by catalytic ozonation.

Table 5. Identified products of 2,4-DCP degradation by ozonation.

No.	Retention time (min)	Formula	Name	Area (%)
1	1.11	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	2-oxopropyl acetate	12.48
2	14.12	C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup>	Benzoate ion	9.52
3	15.91	C <sub>10</sub> H <sub>7</sub> O <sub>5</sub> <sup>-</sup>	3-[(1-carboxyvinyl)oxy]benzoate	21.91
4	18.10	C <sub>7</sub> H <sub>4</sub> Cl <sub>2</sub> O	2-chlorobenzoyl chloride	19.30
5	18.10	C <sub>8</sub> H <sub>5</sub> O <sub>3</sub>	2-oxomethylbenzoic acid	19.30

Table 6. Identified products of 2,4-DCP degradation by catalytic ozonation.

No.	Retention time (min)	Formula	Name	Area (%)
1	10.04	C <sub>8</sub> H <sub>5</sub> O <sub>3</sub>	2-oxomethylbenzoic acid	0.19
2	14.10	C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> <sup>-</sup>	Benzoate ion	5.93
3	14.10	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	2-oxopropyl acetate	5.93
4	15.95	C <sub>7</sub> H <sub>4</sub> Cl <sub>2</sub> O	2-chlorobenzoyl chloride	33.61
5	17.62	C <sub>10</sub> H <sub>7</sub> O <sub>5</sub> <sup>-</sup>	3-[(1-carboxyvinyl)oxy]benzoate	7.13
6	18.13	C <sub>8</sub> H <sub>5</sub> O <sub>3</sub>	2-oxomethylbenzoic acid	27.94

Nearly all of the identified products in Table 5 and 6 has aromatic ring except for 2-oxopropyl acetate. These compounds may be formed by hydroxyl radical attack in the para position of 2,4-DCP's aromatic ring, yielding 2-chlorohydroquinone [26] [27] [28]. Further attack by hydroxyl radical ( $\bullet$ OH) produces compounds such as 2-chloro-1,4-benzoquinone. Further oxidation produces maleic and fumaric acid, which are then degraded into

organic molecules with a simpler functional group such as acetic acid. The reaction mechanism is proposed by [25]:

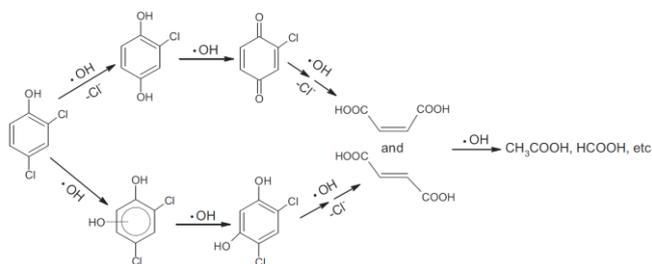


Fig. 13. Mechanism of 2,4-DCP degradation with catalyst addition.

Most of the degradation products haven't been degraded into acetic acid, oxalic acid, or maleic acid. The identified products still has cyclic or aromatic rings, such as benzoate ion, 4-chlorobenzoyl chloride, and 2-oxomethylbenzoic acid. This suggests that since the COD reduction reached 84.31% and 86.44%, there is still non-degradable organic compounds. 2,4-DCP and other phenolic compounds are not identified in the degradation product. This supports the result of 2,4-DCP degradation which nearly reached 100% in all configurations.

#### 4. Conclusion

Several experiments were conducted to degrade 2,4-DCP by ozonation and catalytic ozonation in multi-injection bubble column reactor. All reactions were carried out at pH = 12.00 since in this condition the accumulated hydroxyl radical formed had the highest concentration, 0.9435 mg/L by the end of the reaction time. The results were satisfactory, as the ozonation technique was able to degrade 2,4-DCP up to 99.83%, while catalytic ozonation technique degraded 99.64%, slightly lower than the ozonation technique. The optimum air flow rate and wastewater flow rate for both ozonation and catalytic ozonation was 12 L/min and 495 mL/min, respectively.

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#### References

- [1] S. Chaliha and K. G. Bhattacharyya, "Wet oxidative method for removal of 2,4,6-trichlorophenol in water using Fe (III), Co (II), Ni (II) supported MCM41 catalysts," *J. Hazard. Matter*, vol. 150, no. 3, pp. 728-736, 2008.
- [2] J. Desmurs and S. Raton, "Chlorophenols," in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed. New York: John Wiley and Sons, 1993, ch. 6, pp. 156-168.
- [3] G. Boari, A. Brunetti, and A. Rozzi, "Anaerobic digestion of olive oil mill wastewater," *Agricultural Wastes*, vol. 10, no. 3, pp. 161-175, 1984.
- [4] M. Hamid, "Toxicity and biodegradability of olive mill wastewater in batch and anaerobic digestion," *J. Phys. Chem*, vol. 37, no. 2, 155-163, 1991.
- [5] L. Mohammadi, E. Bazrafshan, N. Meissam, A. A. Moghaddam, F. Barahuie, and D. Balarak, "Removing 2,4-dichlorophenol from aqueous environments by heterogeneous catalytic ozonation process using synthesized MgO nanoparticles," *Water Science and Technology*, vol. 76, pp. 76-90, 2017.
- [6] A. E. Navarro, R. F. Portales, M. R. Sun-Ko, and B. P Llanos, "Effect of pH on phenol biosorption by marine seaweeds," *J. Hazard. Mater*, vol. 156, no. 1, pp. 405-411, 2008.
- [7] E. J. Rosenfeldt, K. G. Linden, S. Canonica, and U. von Gunten, "Comparison of the efficiency of OH radical formation during ozonation and the advanced oxidation processes O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>," *Water Research*, vol. 40, no. 20, pp. 3695-3704, 2006.
- [8] G. Bayramoglu, I. Gursel, Y. Tunali, and M. Y. Arica, "Biosorption of phenol and 2-chlorophenol by *Funaliatrogii* pellets," *Bioresource Technology*, vol. 100, no. 1, pp. 2685-2691, 2009.
- [9] J. C. Kruithof, P. C. Kamp, and B. J. Martijn, "UV/H<sub>2</sub>O<sub>2</sub> treatment: a practical solution for organic contaminant control and primary disinfection," *Ozone: Science & Engineering*, vol. 29, no. 4, pp. 273-280, 2007.
- [10] R. Munter, "Advanced oxidation processes—Current status and prospects," in *Proc. Estonian Acad. Sci. Chem*, 2001, vol. 50, no. 2, pp. 59-80.
- [11] N. Annisa, "Pengolahan Limbah Cair yang Mengandung Senyawa Fenolik dengan Teknik Ozonasi Katalitik dalam Reaktor Kolom Gelembung Multi Injeksi [Removal of wastewater containing phenolic compound by catalytic ozonation in multi injection bubble column reactor]," thesis, Chem. Eng. Dept., Univ. Indonesia, Depok, 2018.
- [12] E. F. Karamah, S. B. S. Bismo, L. Annasari, and W. W. Purwanto, "Mass Transfer Study on Micro-Bubbles Ozonation in A Bubble Column," *IJCER*, vol 2, no. 2, pp. 243-252, 2010.
- [13] E. F. Karamah, S. Bismo, and W. W. Purwanto, "Significance of acoustic and hydrodynamic cavitations in enhancing ozone mass transfer," *Ozone: Science & Engineering*, vol. 35, no. 6, pp. 482-488, doi: 10.1080/01919512.2013.820640.
- [14] W. Pryhanto, "Kinerja Penyisihan Senyawa Fenolik dengan Teknik Ozonasi pada Suasana Basa dalam Kolom Sistem Injeksi Ozon Berganda [Performance of phenolic compound removal by ozonation in alkaline condition in double-injection ozone column system]," thesis, Chem. Eng. Dept., Univ. Indonesia, Depok, 2000.
- [15] S. V. Ghaisani, D. P. Wahyudi, E. Enjarlis, E. F. Karamah, and S. Bismo, "Performance of phenolic wastewater degradation with ozonation and catalytic

- ozonation technique in multi injection bubble column reactor,” in *AIP Conference Proceedings*, 2019, vol. 2175, p. 020004. [Online]. Available: <https://doi.org/10.1063/1.5134568>
- [16] D. P. Wahyudi, S. V. Ghaisani, and S. Bismo, “Degradation of phenol and 2,4-dichlorophenol wastewater by ozonation in multi-injection bubble column reactor,” *Journal of Physics Conference Series*, vol. 1349, p. 012074, 2019, doi: 10.1088/1742-6596/1349/1/012074.
- [17] C. M. Birdsall, A. C. Jenkins, and E. Spadinger, “Iodometric determination of ozone,” *Anal. Chem.*, vol. 24, pp. 662-664, 1952.
- [18] B. G. Ershov and P. A. Morozov, “The kinetics of ozone decomposition in water: the influence of pH and temperature,” *Russ. J. Phys. Chem*, vol. 83, no. 8, pp. 1457-1462, 2009.
- [19] D. Gardoni, A. Vailati, and R. Canziani, “Decay of ozone in Water: A review,” *Ozone: Science & Engineering: The Journal of the International Ozone Association*, vol. 34, no. 4, pp. 233-2432, 2012.
- [20] T. Poznyak and J. Vivero, “Degradation of aqueous phenols and chlorinated phenols by ozone,” *Ozone: Science and Engineering*, vol. 27, no. 6, 447-458, 2005.
- [21] S. H. Kow, M. R. Fahmi, Z. A. Abidin, and S. A. Ong, “Degradation efficiency, kinetic and intermediates of phenol by ozonation,” *Aust. J. Basic & Appl. Sci.*, vol. 11, no. 3, pp. 71-78, 2017.
- [22] C. Gottschalk, J. A. Libra, and A. Saupe, *Ozonation of Water and Waste Water*. Wiley-VCH, 2000.
- [23] Y. Qiu, C. H. Kuo, M. E. Zappi, and E. C. Fleming, “Kinetic and mechanistic study of ozonation of three dichlorophenols in aqueous solutions,” *J. Environ. Eng.*, vol. 125, no. 5, pp. 441-450, 2012.
- [24] N. Annisa, M. S. Nadisti, E. F. Karamah, N. Saksono, and S. Bismo, “Degradation of batik dye wastewater in basic condition by ozonation technique in bubble column reactor,” in *E3S Web of Conferences*, 2018, vol. 67, p. 04019.
- [25] M. S. Nadisti, N. Annisa, E. F. Karamah, N. Saksono, and S. Bismo, “Waste treatment of remazol blue compounds based on ozonation/AOP in a bubble column reactor,” in *E3S Web of Conferences*, 2018, vol. 67, p. 04017.
- [26] L. J. Xu and J. L. Wang, “Fenton-like degradation of 2,4-dichlorophenol using  $Fe_3O_4$  magnetic nanoparticles,” *Applied Catalysis B: Environmental*, vol. 123, pp. 117-126, 2012.
- [27] H. Wang, Y. Zhao, Y. Su, T. Li, M. Yao, and C. Qin, “Fenton-like degradation of 2,4-dichlorophenol using calcium peroxide particles: performance and mechanisms,” *RSC Adv.*, vol. 7, pp. 4563-4571, 2017.
- [28] P. J. D. Ranjit, K. Palanivelu, and C. Lee, “Degradation of 2,4-dichlorophenol in aqueous solution by sono-Fenton method,” *Korean J. Chem. Eng.*, vol. 25, pp. 112-117, 2008, doi:10.1007/s11814-008-0020-7.





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