

## Removal of 2,4,6-Trichlorophenol in Simulated Wastewater via Ozonation

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This study aimed to investigate the ability of ozonation to degrade 2,4,6-trichlorophenol (2,4,6-TCP) in simulated wastewater. Independent variables such as initial 2,4,6-TCP concentration and pH were investigated. The results showed that 100.0% degradation efficiency was achieved for an initial 2,4,6-TCP concentration of 10 ppm and reaction time of 25 minutes. Higher initial concentrations had lower degradation rates. The results also revealed that the degradation of 2,4,6-TCP fitted well with first order reaction kinetics, with an apparent rate constant of 0.0947 min<sup>-1</sup> at an initial concentration of 10 ppm. The degradation of 2,4,6-TCP increased significantly with the increase in initial pH of the solution from pH 4 to pH 7 and then to pH 10. The highest degradation effect was found at pH 10.0 with a rate constant of 0.0443 min<sup>-1</sup>, which was attributed to the production of more powerful hydroxyl radicals. Evaluation of BOD<sub>5</sub>/COD ratios showed some enhancement in the biodegradability of the effluent treated by ozonation. A chemical oxygen demand (COD) reduction of 42.10% was achieved after ozonation treatment and this result indicated that only partial mineralization of 2,4,6-TCP could be achieved by ozonation alone. These findings suggest that future studies should focus on the application of catalytic ozonation or a combination of ozonation with other conventional treatments such as biodegradation or filtration in order to achieve complete degradation of this toxic organic contaminant.

**Key words:** 2,4,6-TCP; ozonation treatment; degradation effect

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Significant amounts of toxic and hazardous pollutants are released to the environment due to domestic, industrial and agricultural activities [1,2]. The occurrence of phenolic compounds as a major pollutant in the environment could be due to anthropogenic activities or may be naturally derived from dead animals and plants that decompose in water [3]. Chlorophenols (CPs) or chlorinated phenols are organic chemicals with Kekulé structures that are widely employed in the chemical, forestry, and wood-working industries. CPs are often used as chemical intermediates, wood preservatives, herbicides, insecticides, and fungicides [4]. However, there has been increasing concern about the effects of chlorophenol on the environment and human health. The United States Environmental Protection Agency (US EPA) has classified CPs as a specific group of priority toxic contaminants due to their genotoxic, mutagenic and carcinogenic properties [5].

In this study, 2,4,6-trichlorophenol (2,4,6-TCP) was used as the target pollutant. It is an organic pollutant that affects the human nervous system and causes human respiratory problems such as chronic bronchitis, cough and altered pulmonary function [4]. Most of its 18 derivatives are considered toxic, mutagenic, and carcinogenic [6–10]. They can also severely damage flora and fauna besides affecting the water quality [11]. There are various conventional pollutant treatment methods such as biological, thermal and chemical treatments [12] which can be used to remove 2,4,6-TCP from aqueous solution. However, the slow metabolic rate of dechlorinating bacteria populations and accumulation of potentially toxic by-products are among the limitations of bioremediation methods [13]. 2,4,6-TCP is also resistant to microbial degradation [14]. Therefore, researchers are now investigating the use of innovative and effective methods such as ozonation to destroy chlorinated organic compounds such as chlorophenols *in situ* [15,16].

Advanced oxidation processes (AOPs) have gained critical importance in the detoxification of industrial wastewater [17]. Examples of AOPs include ozonation, persulfate-based AOPs, the Fenton process, ultrasound, microwaves, sonolysis, electrochemical oxidation, wet oxidation, photolysis and photocatalysis [18]. Various efforts are being made to establish AOPs as efficient and environmentally friendly wastewater treatment methods, e.g. the development of a plasmonic metal particle-incorporated TiO<sub>2</sub>-SiO<sub>2</sub> composite as the solar photocatalyst for a photocatalysis method [19] and the novel application of industrial waste products such as red mud as a catalyst support for the catalytic processes of AOPs [20].

Ozonation processes based on the generation of mainly hydroxyl radicals can serve as an alternative to conventional treatment methods [2]. When using ozone gas in a treatment process, two reactions may occur: ozonolysis or ozonation. Ozonolysis is the direct attack of the ozone on the C=C bond of the target pollutant molecule. This only occurs in acidic environments and is a rather selective reaction. Ozonation occurs in a basic/neutral environment when the ozone undergoes decomposition into OH radicals which oxidises the target pollutant. These radicals react unselectively with nearly

all organic pollutants. Ozonation is considered an AOP treatment method as it uses OH radicals to oxidize the target pollutant while ozonolysis is not. A higher removal efficiency of pollutants by ozonation can be attained under alkaline conditions [2].

Ozone-based methods have been used in the treatment of various derivatives of chlorophenol (CP) such as 2-CP, 4-CP, 2,4-CP [21–24], 2,4,6-TCP [15,16,25,26], pentachlorophenol (PCP) [27,28] and phenol [29,30]. Selected important findings for phenols and substituted phenols degraded by ozonation are summarized and tabulated in Table 1. Most of the research were conducted on phenol, mono- or dichlorophenol degradation. A comprehensive investigation of the influences of the independent variables including initial 2,4,6-TCP concentration and pH is still needed, and the present study attempts to fill this void. The mineralisation degree of 2,4,6-TCP by ozonation was determined using chemical oxygen demand (COD). The complex degradation mechanism of 2,4,6-TCP by ozonation and the feasibility of using solely ozonation for the mineralisation of 2,4,6-TCP are discussed in detail. The perspective for future studies and recommendations for ozonation degradation of phenolic compound are also discussed.

**Table 1.** Summary of important findings on the degradation of phenols and substituted phenols by ozonation

Target Pollutants	Experimental Conditions	Highlights of the work	Ref.
2-CP (50 mg/L)	Ozone concentration: 0.5 mg/L	The highest removal of CPs was achieved under alkaline conditions.	[21]
4-CP (50 mg/L)	pH: 2.5 and 9.5	There was a decrease in pH indicating the presence of acidic degradation products. Incomplete dechlorination indicated the presence of chlorinated aliphatic intermediates.	
2,4-DCP (65 mg/L)	Reaction time: 2.5-45 min		
2,4,6-TCP (50 mg/L)			
2,3,4,6-TCP (90 mg/L)			
PCP (105 mg/L)			
4-CP (6 mg/L)	Ozone concentration: 7-40 mg/L	Removal efficiencies of 98.9%, 99.8% and 98.9% achieved for phenol, 4-CP, and 2,4-DCP respectively.	[23]
2,4-DCP (6 mg/L)	pH: 2.5 and 9.5		
Phenol (6 mg/L)	Reaction time: 24 and 96 hrs		
Phenol	2 different reactors are used: i) With injector ii) Bubble column	The reactor with injector had a higher mass transfer rate. Better results were obtained at higher pH.	[29]
Phenol (93-105 mg/L)	pH: 2.7 -11.3		
	Ozonation, O <sub>3</sub> /UV, O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> , O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> , UV, UV/H <sub>2</sub> O <sub>2</sub> , O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub> , Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub>	Lower costs were achieved with ozonation. Among the ozone-based treatment methods, single ozonation achieved the best results (100% degradation at pH 9.4).	[30]
	UV light source: mercury vapor lamp with 253.7 nm		
	Ozone dosage: 0.2-0.3 g/h		
	pH: 3, 7.2, 9.4		
4-CP (200 mg/L)	Ozone concentration: 23 mg/L	Ozonation of the target pollutant started with dechlorination and the degradation process was similar to phenolic decomposition. The cleavage of the aromatic ring was confirmed by the presence of unsaturated acids. The pre-ozonation step increased the biodegradability of all the pollutants.	[31]
2,4-CP (200 mg/L)	pH: 2-12		
Phenol (200 mg/L)			

**Table 1.** Summary of important findings on the degradation of phenols and substituted phenols by ozonation (continued)

Target Pollutants	Experimental Conditions	Highlights of the work	Ref.
2,4,6-TCP (10-100 mg/L)	Adsorption using high-silica FAU zeolite combined with ozonation pH: 6.2-6.5 Ozone concentration: 7 mg/L	2,4,6-TCP was effectively absorbed onto the zeolite. Ozone helped to regenerate the loaded zeolite and enhanced the adsorption capacity. TCP removal of 87%.	[32]
2,4,6-TCP (0.1 mmol/L)	Ozone concentration: 24 mg/L pH: 7.5 (This value dropped to 3.25 after reaction.) Reaction time: 25 min	TCP removal of 99% within 6 min. The intermediate products of H <sub>2</sub> O <sub>2</sub> , Cl <sup>-</sup> , formic acid, and oxalic acid were found. Direct and indirect degradation pathways were proposed in this study.	[16]
2,4,6-TCP	pH: 3-11 NaCl or NaBr was dissolved to achieve the required Cl <sup>-</sup> (0-300 mM) or Br <sup>-</sup> (0-100 mM) concentrations	The effect of halide ions on the decomposition of 2,4,6-TCP were investigated. With halide ions, the toxicity of 2,4,6-TCP solution increased after O <sub>3</sub> treatment. The bromide ion was found to have a stronger negative impact on 2,4,6-TCP degradation than the chloride ion in the O <sub>3</sub> system. Stronger basicity inhibited the formation of halogenated by-products.	[15]
2-CP, 3CP, 4-CP, 2,4-DCP, 2,5-DCP, 2,4,6-TCP	Ozone concentration: 30-50 mg/L	Pre-ozonation for chlorination of seawater samples. Significantly lower concentrations of halophenol compounds formed during chlorination.	[25]
2- Bromophenol (BP), 4-BP, 2,4-BP, 2,4,6-TBP	Reaction time: 30 min pH: 2-7.5	Dechlorination and formation of 2,6-dichloro-benzo-1,4-quinone (DCQ) detected	[26]

## EXPERIMENTAL

### 1. Materials

Solid 2,4,6-TCP (98%) obtained from Aldrich was used without further purification. The characteristics of 2,4,6-TCP are given in Table 2. Ozone gas was generated from a laboratory-scale ozone generator and

used directly. All experiments were carried out at a constant concentration and volume of ozone gas and at constant pressure. The experimental duration was 30 minutes long for all parameters tested. The experiments were conducted in batches and repeated in triplicate. Experimental errors were within 2% of the reported average value of the extent of degradation.

**Table 2.** Characteristics of 2,4,6-TCP [33,34]

Properties	2,4,6-TCP
Formula	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub> O
CAS No.	88-06-2
Molecular weight (g/mol)	197.5
Melting point (°C)	246.0
Boiling point (°C)	69.0
Solubility (g/L)	0.5
pKa	6.0-7.4

## 2. Preparation of 2,4,6-TCP solution

The initial concentrations of 2,4,6-TCP used in the experiments were 10 ppm, 20 ppm, 30 ppm, 40 ppm and 50 ppm, prepared by dilution from a stock standard solution of 1000 ppm. To test the pH parameter, the solutions were adjusted to pH 4, pH 7 or pH 10 by adding sodium hydroxide (NaOH) or hydrochloric acid (HCl). After treatment via ozonation, the 2,4,6-TCP solutions were analyzed with a UV-vis spectrophotometer (Agilent Cary 3500) to determine the extent of degradation. After the optimised parameters were determined, further COD and BOD<sub>5</sub> analyses were carried out.

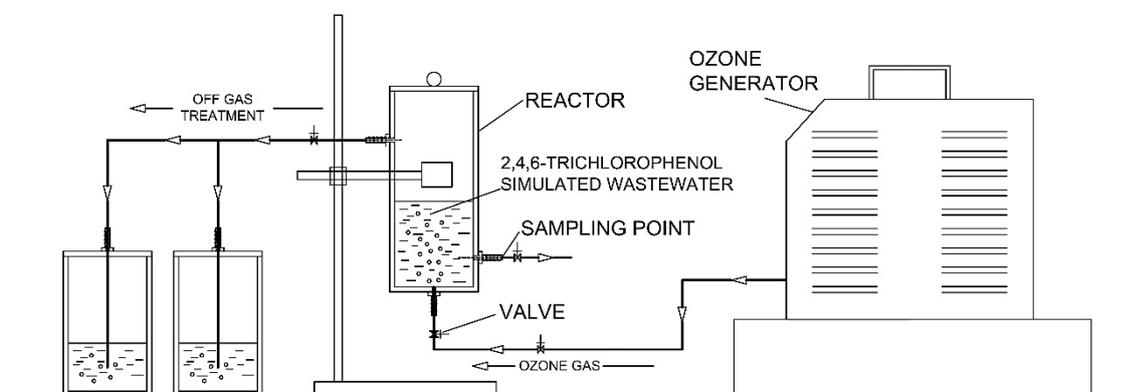
## 3. Experimental Setup

The ozonation treatment process for the degradation of

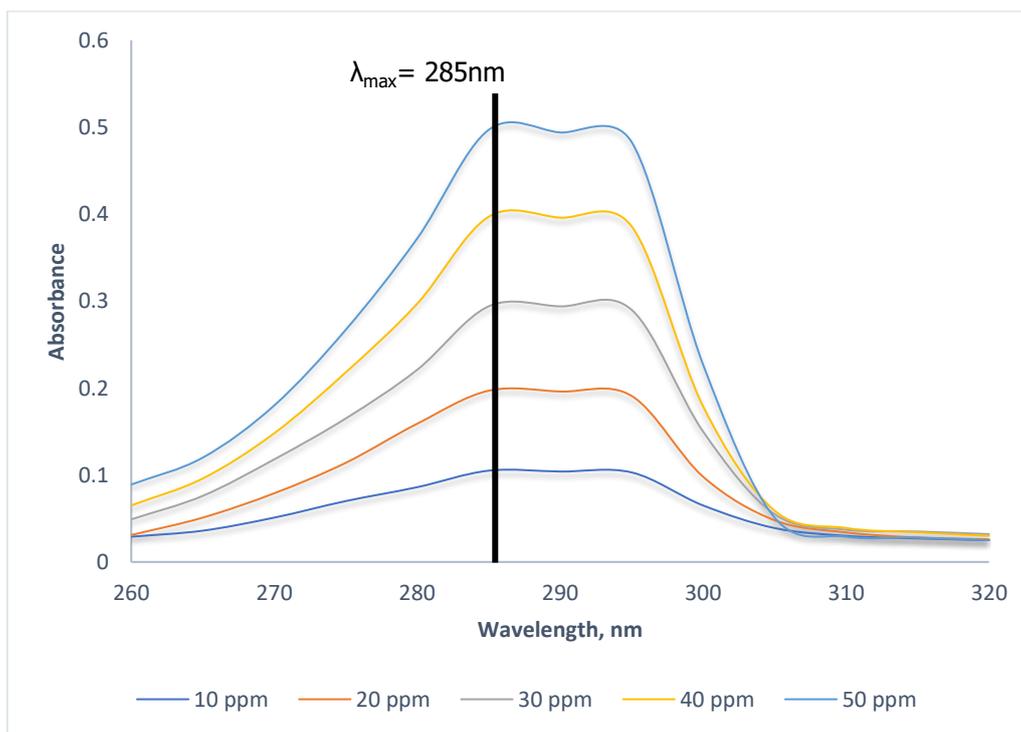
2,4,6-TCP was carried out using the experimental setup shown in Figure 1. Ozone was generated by an ozone generator (Vroex Lab, China) with a capacity of 2.2 g/h ozone in which atmospheric oxygen was used to produce ozone at a constant flow rate of 15 L/min. Ozone was introduced into the bottom of the reactor containing the sample solution of 2,4,6-TCP. The residual ozone in the off-gas treatment system was captured in 2% potassium iodide (KI) solution.

## 4. Analytical method

Figure 2 shows the maximum absorbance wavelength ( $\lambda_{\max}$ ) of 285 nm for 2,4,6-TCP as measured by UV-Vis spectroscopy [35]. The various concentrations chosen for 2,4,6-TCP were 10, 20, 30, 40 and 50 ppm.



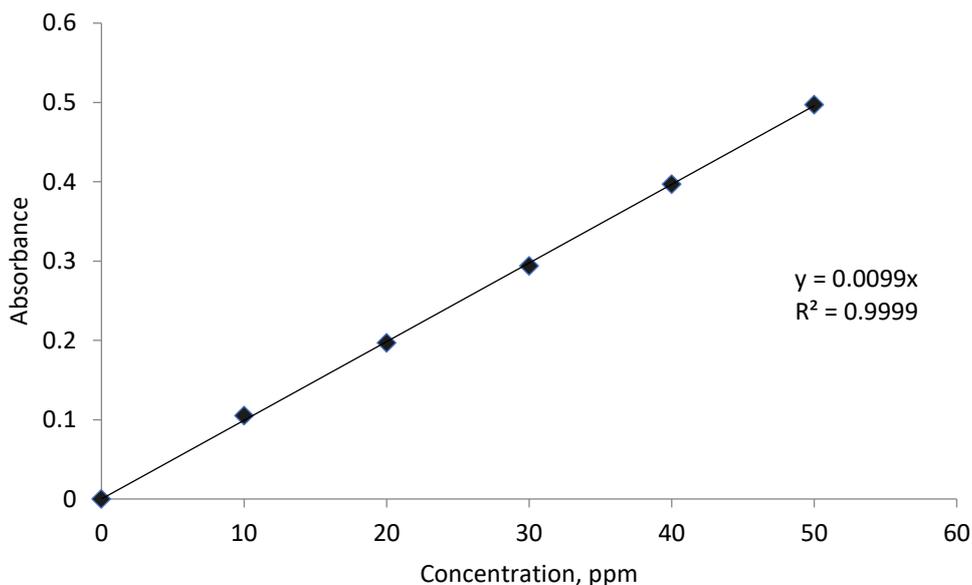
**Figure 1.** Experimental setup for 2,4,6-TCP degradation by ozonation treatment.



**Figure 2.** Wavelength scan for the pre-determined set of initial concentrations of 2,4,6-TCP

**Table 3.** The calibration plot of absorbance against concentration of 2,4,6-trichlorophenol data ( $\lambda_{\max} = 285 \text{ nm}$ )

Concentration of 2,4,6-Trichlorophenol (mg/L)	Absorbance, A.U.			
	1	2	3	Average
0	0	0	0	0
10	0.1041	0.1052	0.1045	0.1046
20	0.1978	0.1922	0.1932	0.1944
30	0.2968	0.2926	0.2938	0.2944
40	0.3934	0.3972	0.3977	0.3961
50	0.4994	0.4993	0.5007	0.4998



**Figure 3.** The calibration plot of absorbance against concentration of 2,4,6-trichlorophenol ( $\lambda_{\max} = 285 \text{ nm}$ )

The calibration curve of 2,4,6-TCP at 285 nm showed a good regression coefficient ( $R^2=0.9997$ ) and agreed well with the Beer-Lambert Law [23, 24] as shown in Table 3 and Figure 3.

The kinetics study was performed to determine the rate constants for the direct 2,4,6-trichlorophenol-ozone decomposition reaction [38]. According to previous studies [39], the ozonation degradation of 2,4,6-TCP followed first-order reaction kinetics. The equation is given by:

$$\ln\left(\frac{C_0}{C_t}\right) = k_c t \quad (1)$$

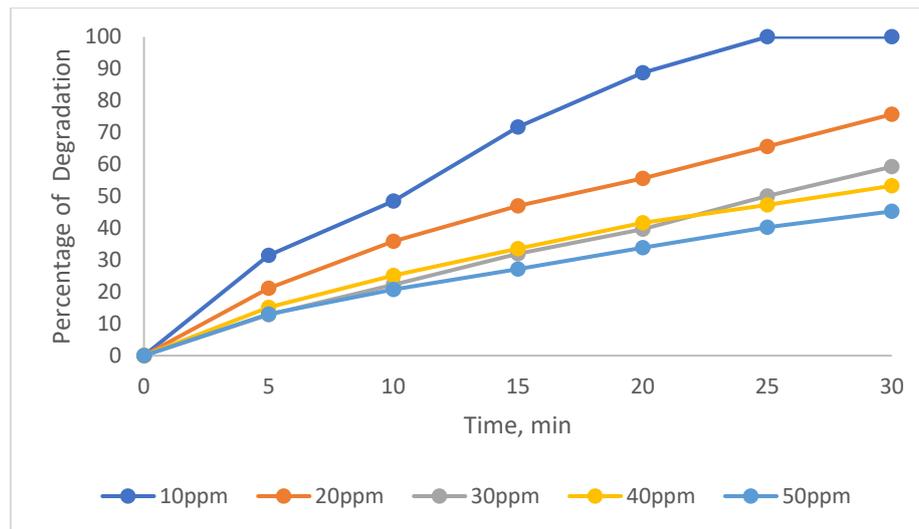
where

- $C_0$  = initial concentration (ppm)
- $C_t$  = final concentration (ppm)
- $k_c$  = rate constant
- $t$  = reaction time (min)

## RESULTS AND DISCUSSION

For 2,4,6-TCP, initial concentrations of 10, 20, 30, 40

and 50 ppm were prepared using the dilution method. The contact time parameter for ozonation treatment was fixed at 30 minutes. Figure 4 showed the effect of the initial concentration of 2,4,6-TCP as a function of contact time between the ozone gas and the 2,4,6-TCP solution throughout the whole procedure. The removal rate was rapid in the initial stages, then reduced slightly, and reached a maximum in 30 minutes. This may be due to the availability of a large number of vacant surface sites. Based on this result, the contact time was fixed at 30 minutes. The first 10 minutes are defined as fast ozone demand, varying from just a few seconds to as much as 9 or 10 minutes. During this period, an instantaneous or very rapid consumption of ozone takes place. During the tenth or long ozone decomposition period, ozone decomposes slowly. It is in this latter period that the kinetics studies were performed for the decomposition of ozone in the trichlorophenol molecule. The initial ozone fast-demand period is caused by the existence of substances that readily react with ozone through direct reactions. Once the concentrations of these substances decrease or the substances disappear, the longer ozone decomposition period begins [40].



**Figure 4.** The degradation efficiency of 2,4,6 TCP at various initial concentrations under ozonation treatment for 30 minutes

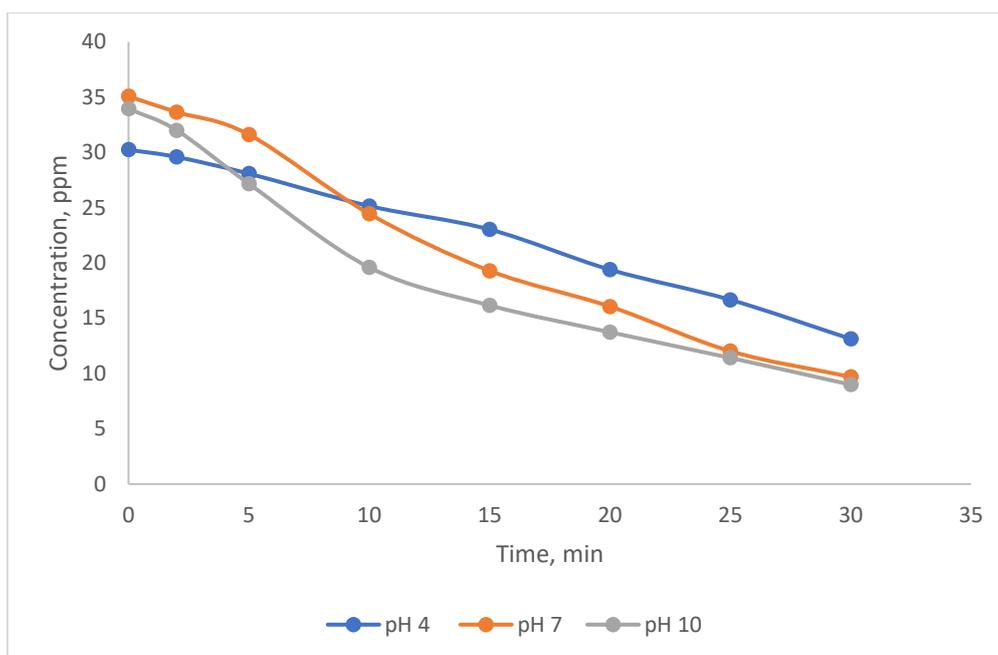
A graph with different degradation efficiencies against time was plotted and presented in Figure 4. According to Figure 4, the pattern of ozonation degradation for different initial concentrations of 2,4,6-TCP indicated that higher initial 2,4,6-TCP concentrations had lower degradation rates and vice versa [41,42]. Increasing the initial 2,4,6-TCP concentration from 10 ppm to 50 ppm decreased the degradation efficiency. The initial concentration of 10 ppm achieved 100% degradation efficiency under ozonation treatment within 25 minutes. Therefore, the initial 2,4,6-TCP concentration of 10 ppm gave the best degradation effect as shown in Figure 4. Researchers have previously determined that when the initial 2,4,6-TCP concentration increases, the residual concentration increases as well while the 2,4,6-TCP degradation efficiency decreases. This indicates that there is a negative correlation between residual 2,4,6-TCP concentration and initial 2,4,6-TCP concentration, and this is supported by previous studies [42]. At low concentrations of 2,4,6-TCP, the probability of collisions between ozone and TCP molecules is low, and the unreacted ozone therefore has a higher likelihood of producing free radicals. However, the production of free radicals is decreased greatly at high concentrations due to the higher probability of collisions between ozone and TCP molecules [39].

The 2,4,6-TCP concentration reduced significantly with the increase in initial pH from pH 4 to pH 10. Ozonation of 2,4,6-TCP under acidic conditions yielded 56.6% degradation. The ozonation of 2,4,6-TCP was found to work best under alkaline conditions, which gave a degradation efficiency of 72 to 75%. From a previous study, the degradation of 2,4,6-TCP decreased at lower pH but increased at higher pH [38]. It is well-known that the self-decomposition of ozone would be higher at a higher pH, which means a higher concentration of hydroxide ions, and this would generate more hydroxyl free radicals through a series

of chain reactions [2,43]. Hydroxyl radicals are stronger oxidants which have a higher standard oxidation potential of 2.80 V compared to molecular ozone which has an oxidation potential of 2.07 V. Under acidic conditions, the selective reactions of molecular ozone include electrophilic, nucleophilic or dipolar addition reactions [2].

Figure 5 shows 2,4,6-TCP degradation during ozonation under acidic, alkaline and neutral conditions. The dissociation constants (pKa) for 2,4,6-TCP are in the range of 6.0 to 7.4 [34]. The production of hydroxyl radicals is favoured in this pH range. A reduction in 2,4,6-TCP concentration in all three experiments was observed at different pH values. TCP has a much lower pKa value compared to mono- and di-chlorophenols, which are mainly deprotonated when dissolved in wastewaters with pH > 7. It has been indicated that there is much higher reactivity with ozone due to the dissociation of phenols and substituted phenols, making them easily influenced by the ozonation treatment process. Both the hydroxyl group and aromatic ring of 2,4,6-TCP can react via electrophilic and nucleophilic substitution by ozonation [44]. Subsequently, it is expected that a high reactivity would be shown between 2,4,6-TCP and ozone under neutral or alkaline pH conditions.

The lower pKa value is related to the electron withdrawal impact of chlorine substitution on the aromatic ring, which decreases its comprehensive electron density [45]. This is because under acidic conditions, 2,4,6-TCP is not dissociated and the dispersion correlation predominates. However, 2,4,6-TCP dissociates under basic conditions, and will form phenolate anions with surface functional groups that are either negatively charged or neutral. The electrostatic repulsion between identical charges causes capacities to be lower and thus the reaction rate between ozone and 2,4,6-TCP decreases [46].



**Figure 5.** Ozonation degradation of 2,4,6-TCP under acidic, neutral and alkaline conditions

**Table 4.** Experimental data for the rate constants and regression correlations for 2,4,6-trichlorophenol at different initial concentrations and pH values

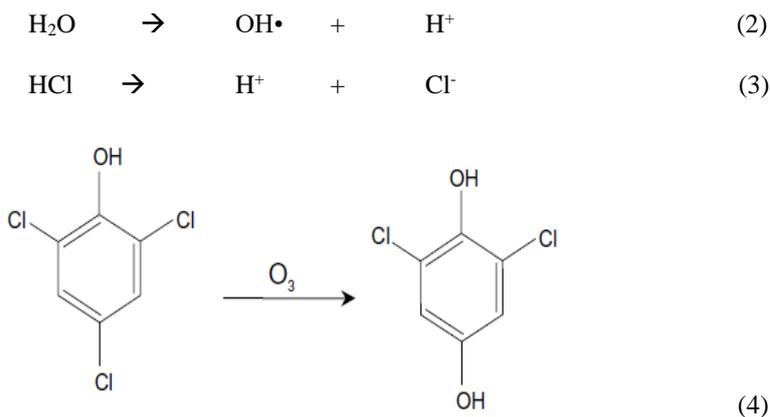
Concentration (ppm)	Rate Constant, $k$ ( $\text{min}^{-1}$ )	Regression Correlation, $R^2$
10	0.0947	0.9718
20	0.0383	0.9977
30	0.0279	0.9880
40	0.0262	0.9977
50	0.0207	0.9975
pH	Rate Constant, $k$ ( $\text{min}^{-1}$ )	Regression Correlation, $R^2$
4	0.0242	0.9797
7	0.0413	0.9946
10	0.0452	0.9964

From Table 4, all the experiments with different initial concentrations and pH values were well fitted to first-order reaction kinetics. The highest precision was obtained at 20 ppm and 40 ppm as these points had the highest regression correlation value of 0.9977. From the table above, the rate constant decreased with the increase in initial solution concentration. This indicates that the degradation rate of 2,4,6-TCP with ozonation decreases with higher initial concentrations of 2,4,6-TCP [42].

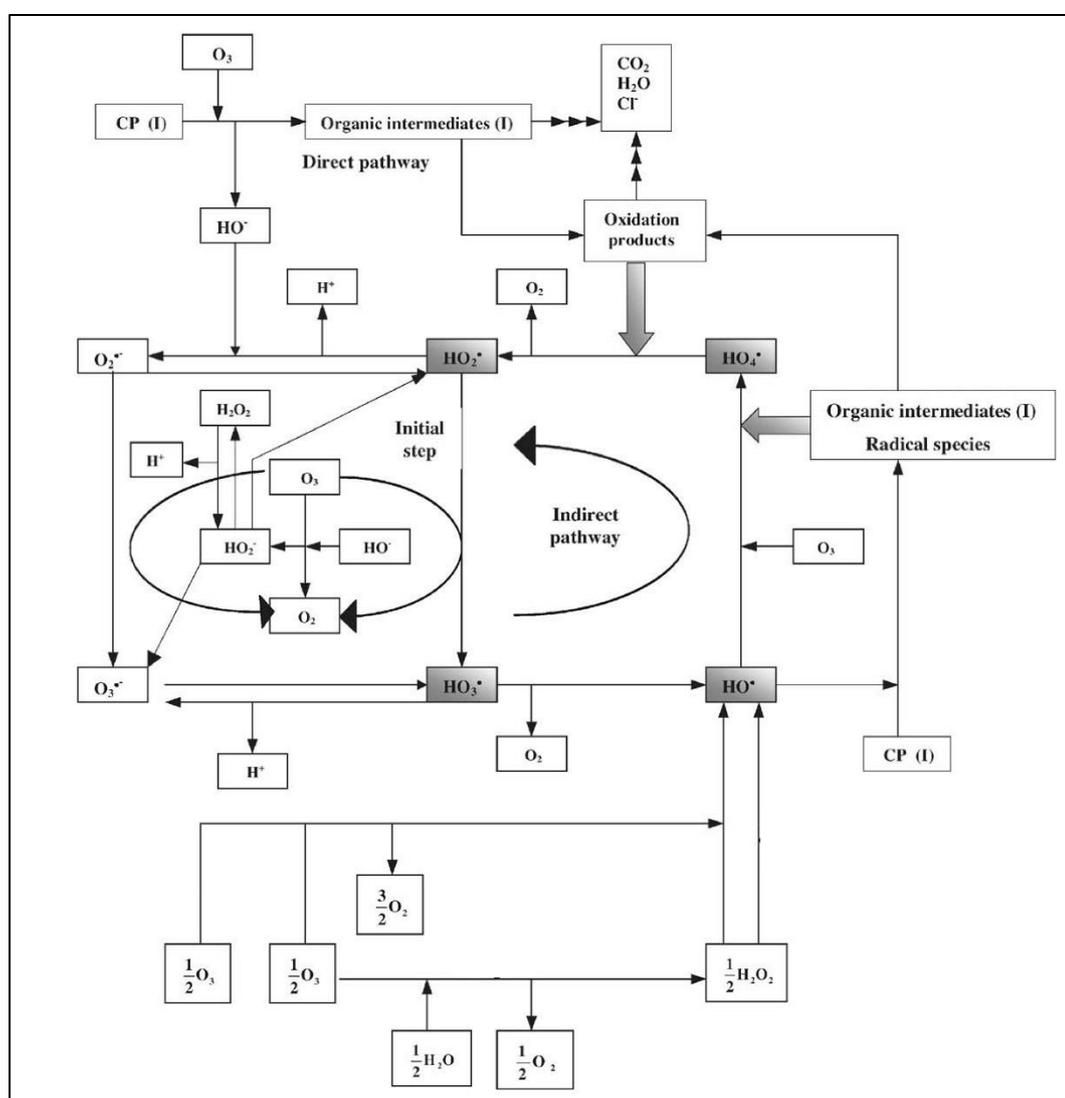
The rate constant increased with higher pH [47] owing to the greater reactivity of the dissociated TCP and the contribution of ozone radical oxidation. This is partly explained by the much lower reactivity of undissociated 2,4,6-TCP with molecular ozone at a lower pH (pH 4) than in its substantially dissociated state at pH 7, and partly by the effect of hydroxyl radical-reactions in alkaline conditions (pH 10). The

latter effect is predominant at high pH levels and a previous study has shown a linear increase in pseudo-first-order reaction rates with pH levels in the range of  $4 < \text{pH} < 10$  [39].

The initial step of the degradation pathway of 2,4,6-TCP by ozonation is dechlorination [10,16]. Graham and co-workers suggested one specific mechanism whereby a hydroxyl group replaces one chlorine atom to form 2,6-dichloro-benzo-1,4-quinone (DCQ), as showed in Figure 6. Based on this reaction scheme, one chlorine in the TCP is substituted by a hydroxyl group to produce a DCQ intermediate, HCl and  $\text{Cl}^\cdot$ . However, it is more likely that there is further dechlorination, and substitution occurs under favourable conditions, such as at a high initial solution pH, high initial solution concentration and longer contact time between ozone and TCP. Among the chlorinated phenols, the degradation rate increases with increasing chlorine substitution [26].



**Figure 6.** Ozone reaction scheme of TCP and the formation of a DCQ intermediate and proton [16,26]



**Figure 7.** General reaction scheme for ozonation of chlorophenols (CPs) (modified from [43])

However, complete dechlorination as shown in Figure 6 is not always achieved, indicating the presence of intermediates such as chlorinated aliphatic products [21,49]. These in turn may react with ozone to form

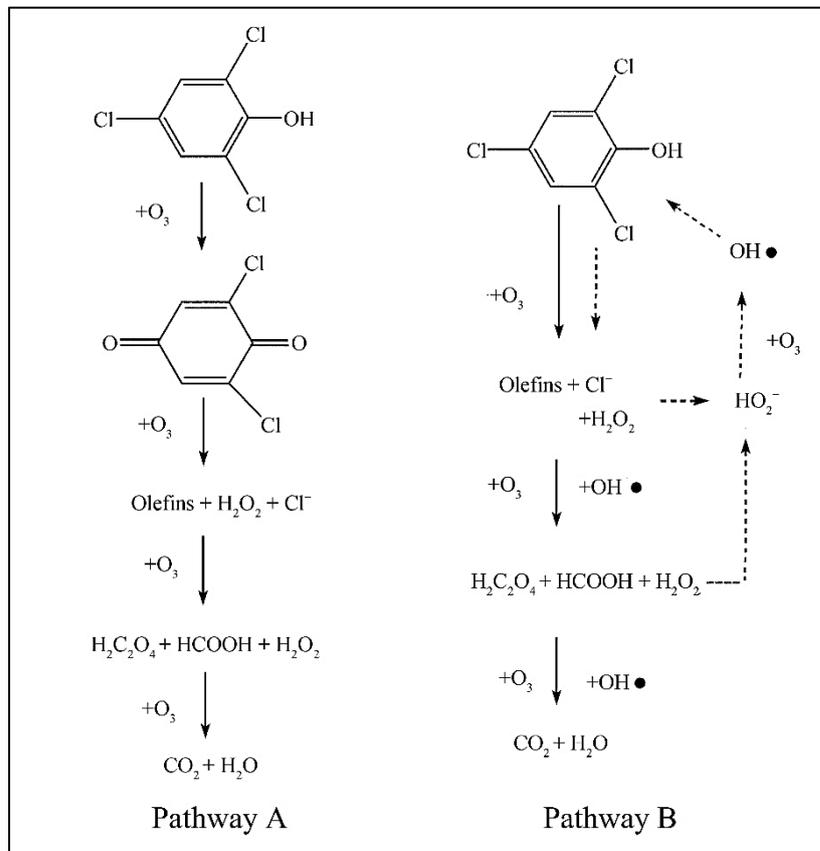
organic acids, such as formic acid and acetic glycolic acids [50], thereby reducing the solution pH. It can be seen that the degradation of TCP produces chloride ions as one of its major products [43]. The number of

chloride ions produced during TCP degradation was found to be in the range of 1.5 and 1.9 per degraded molecule of TCP, with the number in this range systematically increasing with the extent of TCP degraded. Since this is an average value for the reaction, it shows that dechlorination is a major reaction mechanism. It is noted that the reaction rates between the ozone and trichlorophenol depend on the amount of chlorine atoms in a molecule and the position of the chlorine atom substitution [51]. Pi and Wang reported that there are other oxidation end products besides chlorine atoms, such as formic acid, oxalic acid and hydrogen peroxide [16]. The presence of unsaturated acids confirmed the cleavage of the aromatic ring. These findings are further confirmed by the remaining high percentage of COD in this study.

Ozone reacts with the target pollutant, 2,4,6-TCP, either directly or through the formation of hydroxyl radicals (indirect pathway) as shown in Figure 7. Besides hydroxyl radicals, other reactive radical oxidative species (ROS) such as hydroperoxyl radicals, hydrogen peroxide, superoxide radicals, hydrogen trioxyl radicals and so forth are also generated during the chain reaction [2,43]. In the degradation of 2,4,6-TCP by ozonation, the direct pathway of ozonation is also important. Ozone not only reacts with the primary molecule of 2,4,6-TCP but also with the intermediate organic compound formed during ozonation.

The degradation by-products after ozonation treatment can be characterized in terms of their chemical structure, biodegradability and toxicity. Pi and Wang proposed two reaction pathways namely a direct pathway and an indirect pathway for the ozonation of 2,4,6-TCP, as shown in Figure 8. 2,4,6-TCP molecules were first oxidized by molecular ozone to chlorinated quinone, which is later degraded to formic acid and oxalic acid. The complete mineralization of 2,4,6-TCP by ozonation into  $\text{CO}_2$  and inorganic end products has been reported to be obtained only after a long reaction time. One of the end products, oxalic acid, is an ozone-resistant compound [16].

In this study, 20 ppm of 2,4,6-TCP at pH 10 was used for COD and  $\text{BOD}_5$  analyses. The  $\text{BOD}_5$  of 2,4,6-TCP decreased about 26.67% after ozonation treatment. The percentage removal of COD was only 42.10 % as shown in Table 5. Evaluation of  $\text{BOD}_5/\text{COD}$  ratios showed some enhancement in biodegradability of the effluent treated by ozonation. The ratio showed that the biodegradability of the organic pollutants had improved [52]. The same enhancement in biodegradability after ozonation treatment of 2,4-dichlorophenol was also obtained by Contreras and co-workers [49]. This showed that ozonation can serve as a pre-treatment or post-treatment process that can be combined with conventional treatment methods such as biodegradation and filtration processes.



**Figure 8.** Pathway A: Direct molecular ozone reaction, Pathway B: Indirect pathway with a hydroxyl radical reaction. (modified from [16])

**Table 5.** Analyses of BOD<sub>5</sub> and COD

Parameter	Before Ozonation Treatment	After Ozonation Treatment
Chemical Oxygen Demand (COD), mg/ L	19	11
Biological Oxygen Demand (BOD <sub>5</sub> ), mg/ L	30	22
BOD <sub>5</sub> /COD ratios	1.58	2

Ozonation had a significant role in reducing soluble COD and chlorophenol removal. The higher pH of wastewater will result in a better pollutant removal rate in terms of UV-Vis since this experiment was carried out under alkaline conditions of pH 10 using ozone. In contrast, the COD result obtained in this study also indicates that only partial mineralization of 2,4,6-TCP can be achieved by ozonation alone after a reaction time of 30 minutes. The ozonation of 2,4,6-TCP in alkaline conditions achieved 75% whereas COD was reduced only by 42% in the same period. The decrease of 2,4,6-TCP in the spectrum was faster but the reduction of COD was much slower during degradation. Indirect and direct reaction pathways of ozonation with 2,4,6-TCP lead to the formation of low molecular mass acids such as formic acid, oxalic acid and hydrogen peroxide besides chlorine atoms [16], which contributed to the COD value. To determine the mineralization performance of the target pollutant by ozonation, both UV-Vis analysis and the chemical oxygen demand (COD) should be evaluated. The decrease of 2,4,6-TCP in the UV-Vis spectrum may not represent the complete degradation of the target pollutant as there are some final oxidation products formed after the ozonation treatment [16]. Thus, it is important to characterize the degradation by-products after ozonation in terms of their chemical structure, toxicity and biodegradability [2].

In this study, the ozonation process did not achieve complete mineralization of 2,4,6-TCP, as shown in the COD analysis and UV-vis spectra. The complete mineralization of recalcitrant organic matter by ozonation into CO<sub>2</sub> has been reported to be achieved only after long reaction times [2,53,54]. Different approaches have been discussed in the literature on how to overcome the limitations of degradation process using solely ozonation. The application of ozonation alone often encounters the challenges of limited mass transfer of ozone, short life time of generated ozone and excessive energy consumption of ozone production [2]. The optimization of ozone-based systems such as catalytic ozonation are the future direction for the better performance of wastewater treatment [55]. Various catalysts such as alumina-supported nickel oxides [56], zinc oxides [57,58], cerium-vanadium oxide [59], β-FeOOH nanorods [60], biochar [61], nickel ferrite [62], and FeMgO/CNT [63] are being used for the catalytic ozonation degradation of phenols, 2,4,6-

TCP or chlorophenols.

Catalytic ozonation is a promising method for the removal of phenols and chlorophenols in wastewater. However, inconsistent mechanisms of catalytic ozonation were reported by different research groups and the detailed catalytic ozonation mechanism is still undefined [64]. The important parameters involved in catalytic ozonation such as pH, role of active species, active catalyst centre and utilization efficiency of ozone gas should be taken into account when conducting experimental research in order to have a better understanding of the catalytic ozonation mechanism [2]. Furthermore, most of the current studies were conducted using simulated wastewater on a laboratory scale. Hence, further studies should focus on the application of catalytic ozonation in real wastewater treatment systems. Such wastewater solutions will contain more than one organic compound and further analysis would be required.

Furthermore, a combination of ozonation and other methods such as biodegradation, filtration or other advanced oxidation methods should be investigated in order to achieve complete degradation of this toxic organic contaminant. Barik and Gogate reported that the hybrid treatment method of hydrodynamic cavitation (HC) and peroxone process (HC+O<sub>3</sub>+H<sub>2</sub>O<sub>2</sub>) was the most efficient approach for complete mineralization of 2,4,6-TCP [65]. However, undesirable and hazardous by-products may be formed due to the incomplete degradation of the target pollutants. Therefore, Bourgin and co-workers studied the full scale application of biological activated carbon (BAC) as the post treatment method for ozonation in order to eliminate the hazardous oxidation by-products such as bromate and N-nitrosodimethylamine (NDMA) [66]. Aside from treatment efficiency and compliance with environmental regulations, other important factors such as energy consumption analysis will also need to be considered during the selection of the best combined method for wastewater treatment.

## CONCLUSION

This project was conducted to study the potential of ozonation treatment for the degradation of 2,4,6-TCP in aqueous solution. Various operational parameters were found to affect the effectiveness of ozonation on the degradation of 2,4,6-TCP. The results also

indicated that the degree of degradation was influenced by various factors such as the initial 2,4,6-TCP concentration, initial 2,4,6-TCP pH value and the contact time between ozone and 2,4,6-trichlorophenol. The results of this study showed that the degradation rate increased with contact time. It was also shown that the initial concentration was proportional to the degradation rate and vice versa. Furthermore, a higher pH showed a higher degradation rate. In this study, only the 10 ppm 2,4,6-TCP solution yielded a 100 % degradation efficiency, as the contact time carried out for all experiments was only 30 minutes. The findings proved that the degradation of 2,4,6-TCP by the 30-minute ozonation treatment was effective at lower initial concentrations and under alkaline conditions. As such, the further optimization of ozone-based systems such as catalytic ozonation and the combination of ozonation with other methods are suggested in order to completely remove hazardous pollutants in wastewater treatment.

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SUPPLEMENTARY SECTION

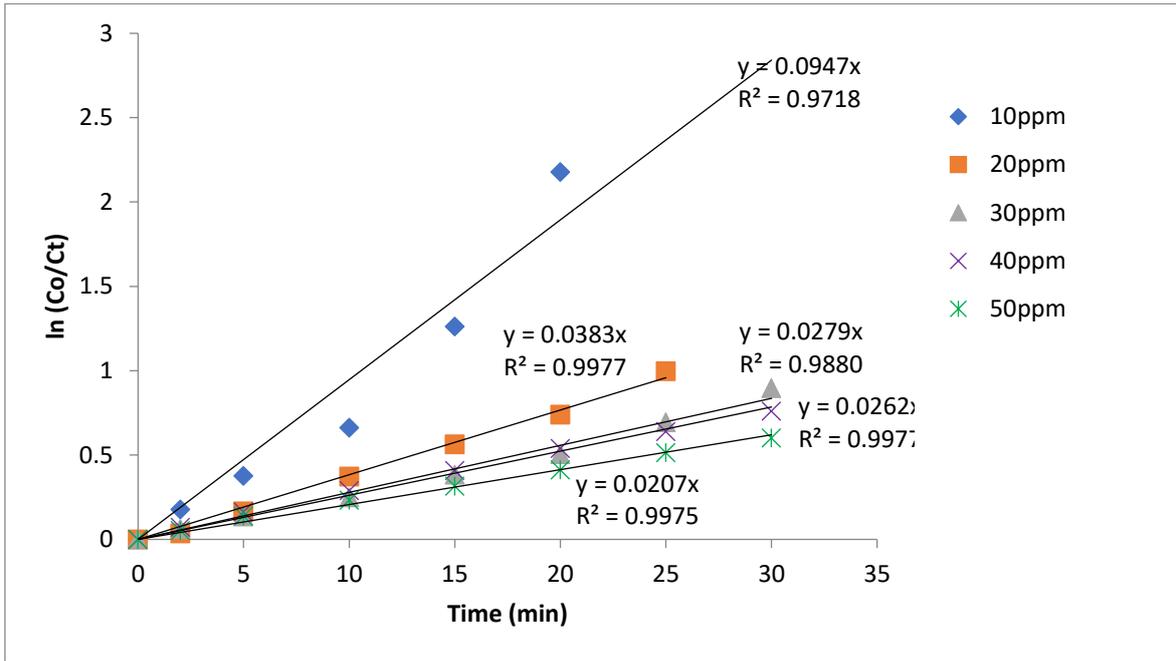


Figure S1. Kinetics Reactions at Different Initial Concentrations of 2,4,6-TCP

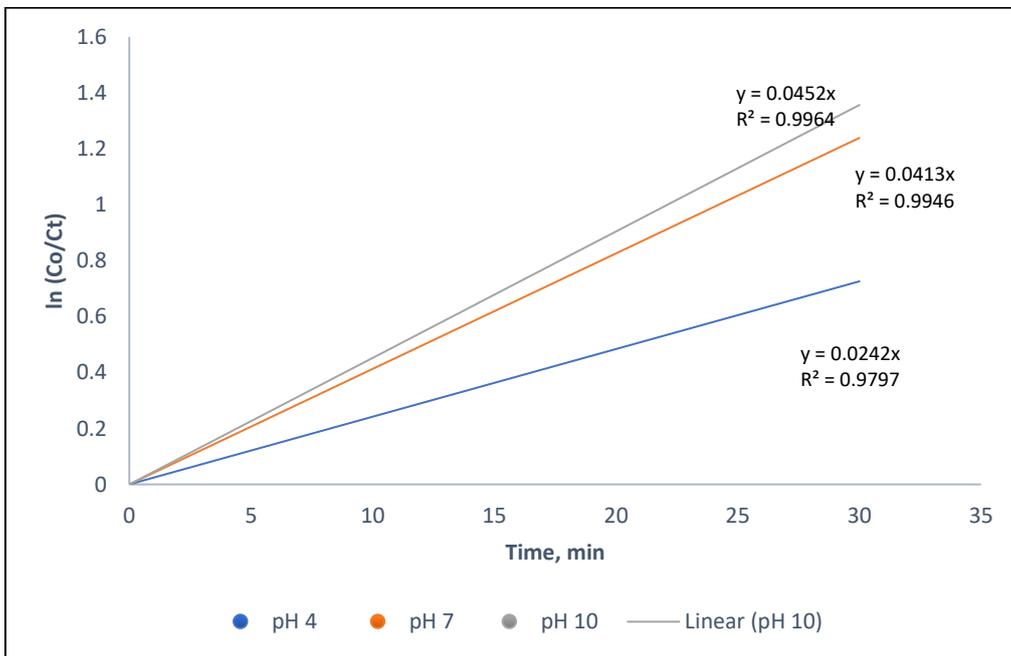


Figure S2. Kinetics Reactions at Different Initial pH values of 2,4,6-TCP