



## Oxidation and Removal of Organic Pollutants from Wastewater Using Photocatalyst

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### الملخص

تعتبر المركبات العضوية الموجودة في الماء ملوثات سامة وضارة للغاية بالبيئة. لذلك؛ بحثت هذه الدراسة في قدرة عملية الأكسدة باستخدام الضوء وثاني أكسيد التيتانيوم ( $TiO_2$ ) كمحفز ضوئي من أجل تحلل وإزالة أحد هذه الملوث العضوية. تم استخدام ثنائي كلورو الفينول (2,4 DCP) كنموذج ملوث بسبب سميته. كما تقدم الدراسة الحالية آلية ونموذج حركي لأكسدة 2,4 DCP و المركب الوسيط الرئيسي الناتج من عملية الأكسدة وهو رابع كلوروفينول (4-CP) واللذان تم الحصول عليهما بناءً على النتائج المعملية. و من أجل الحصول على مزيد من التفاصيل حول مسار التفاعل الضوئي والنموذج الحركي، تم إجراء مجموعة من التجارب باستخدام تراكيز مختلفة من ثاني أكسيد التيتانيوم. كانت أفضل قيمة فعالة ومثلى لتركيز ثاني أكسيد التيتانيوم  $1.5 \text{ mg/L}$ . هناك توافق واضح بين النموذج المستخدم والنتائج المعملية المتحصل عليها. كذلك تم اقتراح آلية ومسار التفاعل للتحلل الضوئي لـ 2,4 DCP.

الكلمات المفتاحية: الأكسدة، ثنائي كلورو الفينول، الآلية، النمذجة الحركية

### Abstract

Organic compounds presented in water have been considered as toxic pollutants and extremely harmful to the environment. Therefore; this study has investigated the ability of an oxidation process using the light and titanium dioxide ( $TiO_2$ ) as a photocatalyst in order to degrade a pollutant. 2,4-Dichlorophenol (2,4 DCP) was taken as a pollutant model due to its toxicity. The present study also reports a mechanism and kinetic model of 2,4 DCP oxidation and its main



intermediate 4-chlorophenol (4-CP) based on the experimental results. In order to obtain more details about the photocatalytic reaction pathway and the kinetic model, set of experiments were carried out using various  $\text{TiO}_2$  doses. The best effective and optimum value of  $\text{TiO}_2$  concentration was 1.5 mg/L. The kinetic model provides a very good fit of the experimental data. The reaction mechanism for the photocatalytic degradation of 2,4 DCP is proposed.

**Keywords:** Oxidation; 2, 4 Dichlorophenol ; Mechanism; Kinetic modelling

### 1. Introduction

It is well known that chlorophenols (CPs) are categorised as a particular group of priority toxic compounds listed by United States Environmental Protection Agency (USEPA). These contaminants are extremely toxic and are not easily biodegradable [1,2]. CPs are generated through many manufactures activities such as petroleum refineries, the bleaching of paper pulp with chlorine, water disinfection and excessive use of pesticides and herbicides [3,4].

Among these pollutant compounds, 2,4 DCP has been recognised as a threat to human health by both European Union and USEPA [5]. In recent years, photocatalytic degradation processes have been widely studied as an effective method to treat wastewater due to its ability to destroy lots of organic and inorganic contaminants at ambient temperature and pressure [6,7]. Normally, the photocatalytic degradation process under optimum conditions (catalyst loading, pH, hydrogen peroxide concentration and light intensity) can mineralize organic pollutants to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [8]. Several photocatalysts are used in this process including titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide ( $\text{ZnO}$ ). Titanium dioxide ( $\text{TiO}_2$ ) has been intensively used in photocatalysis processes of water and wastewater treatment due to some features including safety, resistance to photo corrosion, catalytic



efficiency and cost, as well as titanium dioxide has ability to absorb radiation at wavelengths below 400 nm, meaning the potential to use sunlight as light source [8]. The mechanism and kinetic models of 2,4 DCP degradation have been investigated by many researchers [9,10]. The first step in the photocatalytic degradation of 2,4 DCP is the cleavage of the C–Cl bond producing phenol (4 CP) which later reacts with •OH radicals to form hydroquinone (HQ). However, the •OH might react with 4-CP to form 4-chlorocatechol (4cCat) [11,12]. The role of hydroxyl radicals in the photocatalytic degradation of 4-CP have been widely discussed in the literatures. Most of the studies have concluded that the reaction mechanism for the photocatalytic degradation of 4-CP is very complicated and consequently an approach to study the kinetic assuming the photocatalytic reaction follows a pseudo-first-order kinetics was widely applied [13]. Moreover, the previous studies have mainly two kinds of kinetic models including the linear model according to first-order kinetics and the Langmuir–Hinshelwood (L–H) nonlinear model associated with adsorption processes of the photocatalytic pollutant on the catalyst surface [14–17].

Most of the kinetic reaction models reported in the literature deal with a single reactant chemical species. These proposed kinetic models for the photocatalytic degradation of organic compounds have been mainly obtained depending on the initial rates method. This method does not consider the chemical intermediates species formed during the photo-conversion process. Furthermore, when values of the initial rates are small, only a few experimental points will be considered as well as neglecting the intermediate species [18]. Nonetheless, there are some researchers who have tried to propose several kinetic models including multi chemical species and suggesting the degradation mechanisms of these models [19,20]. They



have used the L–H equation to estimate the values of the kinetic reaction constants for each of the chemical intermediate species. However, these proposed models do not consider the intermediates formation and degradation as well the adsorption constants for all components were not measured experimentally. Therefore, the aim of this work is to propose a pathway for the degradation mechanism and develop a kinetic model for the solar-photocatalytic oxidation of 4-CP including the main intermediates (HQ and 4cCat) formed during the degradation process. This study helps to understand the complex reaction pathways of 4-CP by identifying most of the intermediates formed during the degradation. The developed model predicts the concentrations of 4-CP and its formed intermediates for a wide range of 4-CP initial concentration (25–100 ppm). To give the kinetic model more accuracy and minimise the number of variables, the adsorption rate constants of 4-CP and its intermediates are measured experimentally. This model is developed and validated using experimental data and MATLAB software.

## 2. Materials and methods

### 2.1. Materials

2,4-Dichlorophenol (2,4-DCP, 99%), 4-CP (98%), and Titanium dioxide (TiO<sub>2</sub>-P25, 99.7% anatase) all these chemicals were used as received without further purification. Hydrochloric acid (HCl, 32%) was used to adjust the pH of the reacting mixture. All solutions were prepared with distilled water.

### 2.2 2,4 DCP Oxidation

All experiments were carried out in slurry batch reactor. A 1 L Pyrex glass beaker was employed as a reactor to hold 1 L suspension solution, equipped with a magnetic stirrer. About 0.5, 1, and 1.5 g/L of TiO<sub>2</sub> were used for all oxidation experiments. The pH values of the solutions were monitored using a pH meter (LP 100). 100 ppm of 2,4



DCP was used as initial concentration for all experiments. The suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between 2,4 DCP and TiO<sub>2</sub>. Then, the suspensions were exposed to the solar light for 120 min. At specific time intervals (20 min), 5 mL was withdrawn and filtered by membrane filters to separate the catalyst particles for HPLC analysis.

### **2.3 Intermediate Oxidation**

In order to obtain more information about the photocatalytic reaction scheme, a separate set of experiments were performed using the intermediate (4-CP) as the model reactants. These experiments were performed under the same conditions (photocatalyst loading and light intensity) used in 2,4 DCP photocatalytic degradation experiments. The results of these oxidation experiments used to determine the reaction steps for each intermediate and how it behaved as a model reactant. From these results, the mechanism of the photocatalytic degradation of 2,4 DCP and its intermediate has been proposed.

### **2.5. HPLC analysis**

2,4 DCP and different intermediates were identified and qualified by HPLC analysis. Detection of photoproducts was done at 280 nm, using a Varian Prostar 210 chromatograph with UV–vis detector and a C18 reverse phase column (25 cm × 4.6 mm × 5 μm). The mobile phase was a mixture of acetonitrile, acetic acid and water delivered in the ratio of 0.1 (v/v) with a flow rate of 1 mL min<sup>-1</sup>. The temperature of the column was kept at 25°C throughout all the analysis. Injection volume for all samples was 5 μL. The identification of the intermediates by HPLC was performed by the comparison of the retention time of the peak in the discharged sample with that in the standard sample. The concentrations of compounds were calculated by



using the equations derived from the calibration measurements for authentic samples.

### 3. Results and Discussion

#### 3.1. Adsorption isotherms of 2,4 DCP and its intermediate on TiO<sub>2</sub> photocatalyst

Experimental measurements of the adsorption constants of 2,4 DCP and 4-CP on TiO<sub>2</sub> were performed. After measuring C<sub>e</sub> for all cases, Q<sub>e</sub> can be determined using Eq. (1) [21]:

$$Q_e = \frac{(C_0 - C_e)V}{M_{cat}} \quad 1$$

where C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentrations of the adsorbate, respectively (mg/L). V is the total volume of the solution (L) and M<sub>cat</sub> is the mass of the TiO<sub>2</sub> catalyst. The Langmuir isotherm model, Eq. (2), can be used in this manner to calculate the adsorption constants for 2,4 DCP and its intermediate [22].

$$Q_e = \frac{Q_{max} K_i C_e}{(1 + K_i C_e)} \quad 2$$

where Q<sub>e</sub> (mg/g<sub>cat</sub>) and C<sub>e</sub> (mg/L) are the amount of compound per unit weight and the concentration in the liquid phase at equilibrium, respectively. Q<sub>max</sub> (mg/g<sub>cat</sub>) is the maximum organic compound adsorbed and K<sub>i</sub> (L mg<sup>-1</sup>) is the adsorption constant of component i. To calculate K<sub>i</sub>, Eq. (2) has to be rearranged to linear form as in the following equation:

$$\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{Q_{max} K_i C_e} \quad 3$$

From the slope and the intercept of Eq. (3), the adsorption constant for each component can be obtained when experimental data of C<sub>e</sub> and Q<sub>e</sub> are available. Figs. 1–2 show the linear regressions of Langmuir isotherm for 2,4 DCP and 4-CP respectively.



Table 1 summaries the adsorption constants ( $K_i$ ) and the maximum organic adsorption ( $Q_{max}$ ) for the investigated components. One can notice that the adsorption constant of 2,4 DCP is higher than that of 4-CP which might be due to the high amount of 2,4 DCP adsorbed on the  $TiO_2$  powder to form a monolayer [23].

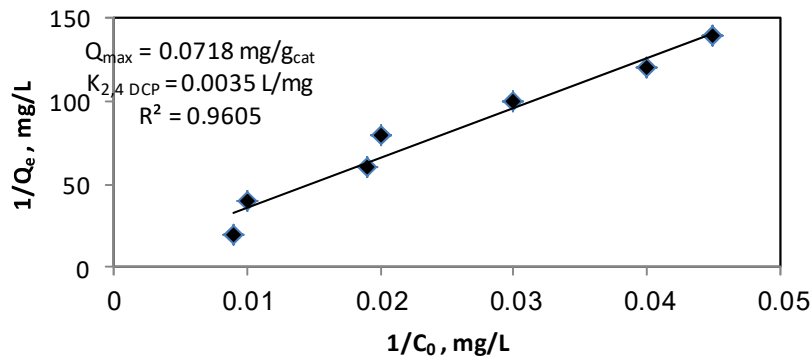


Figure 1 Linear regression for Langmuir isotherm: adsorption of 2,4 DCP on  $TiO_2$

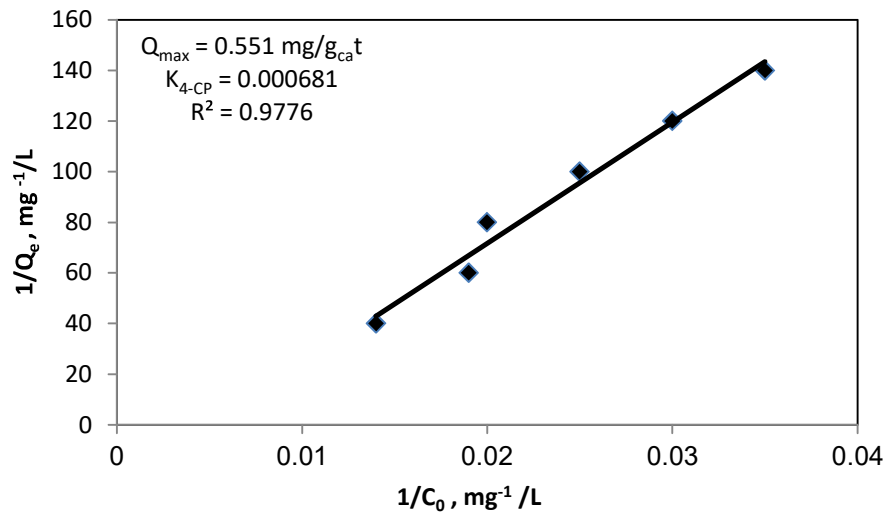


Figure 2 Linear regression for Langmuir isotherm: adsorption of 4-CP on  $\text{TiO}_2$

Table 1 Adsorption for different components on  $\text{TiO}_2$

Component	Maximum organic adsorbed, $Q_{\text{max}}$ ( $\text{mg/g}_{\text{cat}}$ )	Adsorption constant, $K_i$
2,4 DCP	0.0718	0.0035
4-CP	0.551	0.000681

### 3.2. Oxidation of 2,4 DCP

Figure 3 shows a typical experimental results for the solar photocatalytic degradation of 2,4 DCP and its main detected intermediate at different concentrations (0.5, 1.0, 1.5 mg/L) of  $\text{TiO}_2$ . It should be mentioned that 4-CP was the major aromatic intermediate detected during 2,4 DCP photocatalytic degradation on  $\text{TiO}_2$ . During 120 min solar and UV degradation of 2,4 DCP, 4-CP was slightly





increased. In this case, dechlorination might occur on 2,4 DCP to form 4-CP. The degradation efficiencies of 100 ppm initial concentration of 2,4 DCP was determined.

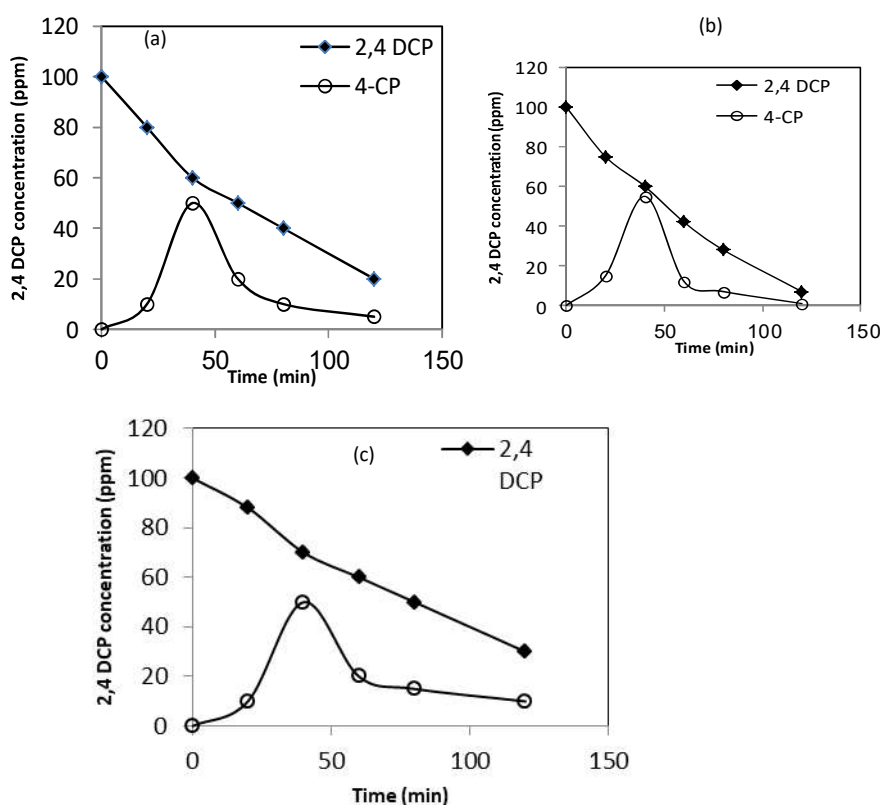


Figure 3 Concentration profiles of 2,4 DCP and its intermediate at several TiO<sub>2</sub> doses, (a) 0.5 mg/L (b) 1 mg/L (c) 1.5 mg/L

### 3.3. Oxidation of the major intermediate 4-CP

Photocatalytic oxidation experiments were conducted using the main intermediate found during the photocatalytic degradation of 2,4 DCP as the model reactant. These experiments are necessary to get more details about the behavior of the intermediate compound. During



120 min photocatalytic degradation of 4-CP, a small amount of 4-CP was observed at the first 60 min then it was rapidly degraded. During the course of photo irradiation (120 min), the 2,4 DCP concentration significantly decreased with increasing 4-CP concentration which might be due to direct attack of  $\cdot\text{OH}$  radical on  $\text{Cl}^-$  atom. Further irradiation degrades 4-CP to either  $\text{CO}_2$  and  $\text{CH}_4$ .

### 3.4. The reaction mechanism and pathway

The proposed reaction mechanism was developed to involve all chemical species observed during the solar photocatalytic degradation of 2,4 DCP. Three intermediate (4-CP, 4cCat and Ph) were detected when degrading 2,4 DCP. However, the detected 4cCat and Ph concentrations were very small. Therefore, it was neglected in the kinetic model of this study. During the course of solar irradiation (150 min), the 2,4 DCP concentration significantly decreased with increasing 4-CP concentration which might be due to direct attack of  $\cdot\text{OH}$  radical on  $\text{Cl}^-$  atom Fig. 4.

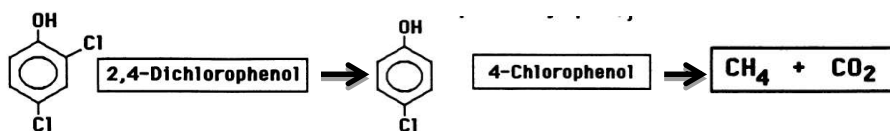


Figure 4 Proposed pathways of 2,4 DCP photocatalytic degradation

### 3.5. Kinetic modelling

Kinetic studies of phenolic compounds on  $\text{TiO}_2$  photocatalyst which deal with a single compound have been investigated in many studies. However, it has been well known that during photocatalytic degradation of organic compounds, some intermediate compounds are formed [24,25]. Therefore, there is a need to develop a model including all chemical species that might be formed during photocatalytic degradation of phenolic compounds. In this respect, a kinetic model for the oxidation of 2,4 DCP and its main intermediate (4-CP) has been developed considering all these chemical species



normally formed during the oxidation. In photocatalytic degradation processes, there is an interaction between chemical species and the photocatalyst surface leading to absorb these species on the surface of  $\text{TiO}_2$  [26]. Thus, it is well accepted that the rates of formation and disappearance of all components can be modelled using L–H equation (Eq. (4)) which considers the adsorption of the chemicals on the catalyst surface and the kinetic reaction constants. The general form of this equation for the system is given as [27].

$$r_i = \frac{dC_i}{dt} = \frac{k_i C_i}{1 + \sum_{i=1}^n K_i C_i} \quad 4$$

where  $r_i$  is the reaction rate of component  $i$  in  $\text{mg}/(\text{L min})$ ,  $k_i$  is the kinetic reaction constant for component  $i$  in  $\text{min}^{-1}$ ,  $K_i$  is the adsorption constant for each of the species participating in the reaction  $\text{L}/\text{mg}$ ,  $n$  denotes the number of participant in the reaction and  $C$  the species concentration  $\text{mg}/\text{L}$ . Applying Eq. (4) for each of the observed components (2,4 DCP and 4-CP) results in two differential equations describing the photocatalytic degradation of 2,4 DCP and its intermediate.

$$\frac{dC_{2,4\text{ DCP}}}{dt} = \frac{-(k_{2,4\text{ DCP}-4\text{ CP}})C_{4\text{ -CP}}}{1 + K_{2,4\text{ DCP}}C_{2,4\text{ DCP}} + K_{4\text{ -CP}}C_{4\text{ -CP}}} \quad 5$$

Equation 5 represents the contribution of various steps of the model and involve the unknown reaction rate constants for each component that can be estimated by fitting the model to the experimental data. The above equation cannot be solved analytically; therefore, for estimating the reaction rate constant two built-in MATLAB subroutines were used. After estimating the best parameter  $K = 0.0053 \text{ min}^{-1}$  the mathematical model can be applied to predict the behavior of the oxidation of 2,4 DCP.

Figure 5 presents the experimental concentration profiles of 2,4 DCP and its intermediate and the estimated profiles for different initial



concentrations. The optimization was performed with an initial concentration of 2,4 DCP 100 mg/L. It can be seen that the kinetic model predicts very well the experimental data for a wide range of initial concentrations.

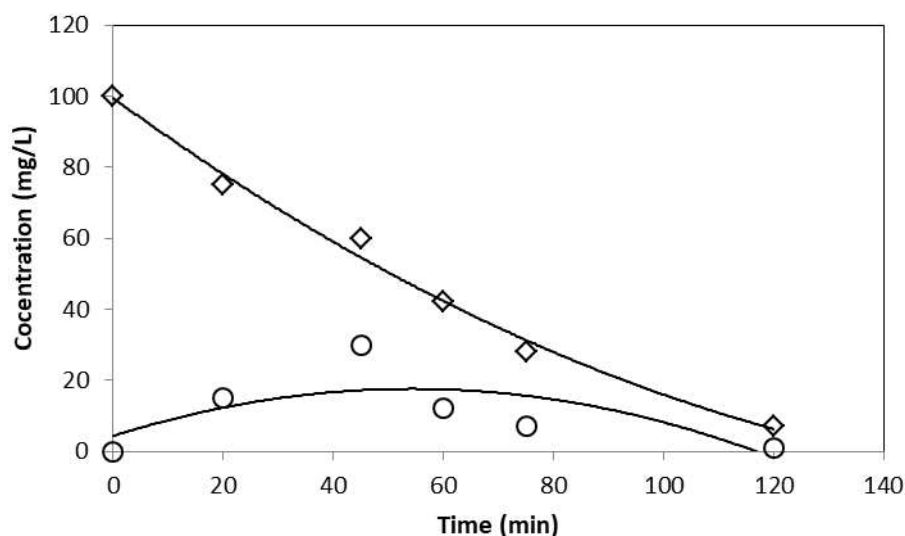


Figure 5 Experimental and estimated concentration profiles for oxidation of 2,4 DCP and using 1 g/L  $\text{TiO}_2$  : ( $\diamond$ ) 2,4 DCP, ( $\circ$ ) 4-CP

#### 4. Conclusion

Three aromatic intermediate compound was identified in the solar oxidation of 2,4 DCP namely 4-CP, 4cCat and Ph using  $\text{TiO}_2$  as a photocatalyst. The reaction pathway for the photocatalytic oxidation of 2,4 DCP is reported including all observed chemical species. This proposed mechanism based on the experimental results obtained for the oxidation of 2,4 DCP and its intermediates individually. However, the 4cCat and Ph compounds were detected in small amounts; therefore, they were neglected from the proposed kinetic model. All the adsorption constants of 2,4 DCP and its major intermediate was determined experimentally. The best effective and optimum value of



TiO<sub>2</sub> concentration was 1.5 mg/L. Furthermore; reaction kinetic model was developed to predict the rate of reaction of 2,4 DCP and its main aromatic intermediate. The proposed model provides very good fit of the experimental data and works very well for a wide range of 2,4 DCP initial concentrations.

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