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Solar photocatalytic degradation of 4-chlorophenol: mechanism and kinetic modelling

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ABSTRACT

The present study reports a mechanism and kinetic model of solar photocatalytic degradation of 4-chlorophenol (4-CP) and its intermediates based on the experimental results. Three intermediate compounds hydroquinone (HQ), 4-chlorocatechol (4cCat) and phenol were found during the solar degradation of different 4-CP concentrations using 0.5 g/L TiO_2 as a photocatalyst. In order to obtain more details about the photocatalytic reaction pathway and the kinetic model, set of experiments were carried out using the major intermediates (HQ and 4cCat) as model reactants. To minimise the number of variables and give more accuracy to the kinetic model, the adsorption constants of 4-CP and its intermediates were obtained experimentally. The reaction mechanism for the photocatalytic degradation of 4-CP is proposed. The proposed model predicts well the concentrations of 4-CP and its by-products during the solar photocatalytic degradation at different initial concentrations. The model provides a very good fit of the experimental data and works for a wide range of 4-CP initial concentrations (25–100 mg/L).

Keywords: Solar-photocatalytic degradation; 4-Chlorophenol; Intermediates; 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, 4-CP 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 mineralise

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organic pollutants to CO_2 and H_2O [8]. Several photocatalysts are used in this process including titanium dioxide (TiO_2) and zinc oxide (ZnO). Titanium dioxide (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 4-CP degradation have been investigated by many researchers [9,10]. The first step in the photocatalytic degradation of 4-CP is the cleavage of the C–Cl bond producing phenol (Ph) which later reacts with $^{\bullet}OH$ radicals to form hydroquinone (HQ). However, the $^{\bullet}OH$ 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

4-Chlorophenol (4-CP, 99%), HQ (98%), 4cCat (99%), Ph (99%) and Titanium dioxide (TiO_2-P25, 99.7% anatase) were purchased from Sigma-Aldrich. All 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 deionised and ultra-pure water.

2.2. 4-CP photocatalytic degradation

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 g/L of TiO_2 was used for all oxidation experiments. The experiments were conducted using Solar Simulator (Sun 2000). The light intensity of Solar Simulator was 1,000 mW/cm^2. The pH values of the solutions were monitored using a pH meter (SP-701LI 120). In order to investigate the effect of initial concentration, different 4-CP concentrations (25, 50, 75 and 100 mg/L) were used. The suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between 4-CP and TiO_2. Then, the suspensions were exposed to the solar light for 180 min. At specific time intervals (30 min), 5 mL was withdrawn and filtered by PTFE 0.45-μm membrane filters to separate the catalyst particles for HPLC analysis.

2.3. Intermediates photocatalytic degradation

In order to obtain more information about the photocatalytic reaction scheme, a separate set of experiments were performed using the intermediates (HQ and 4cCat) as the model reactants. These experiments were performed under the same conditions (photocatalyst loading and light intensity) used in 4-CP 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 4-CP and its intermediates has been proposed.

2.4. Adsorption experiments of 4-CP and its intermediates

In order to determine the adsorption constants of 4-CP and its intermediates experimentally, set of dark experiments were conducted using TiO_2 as photocatalyst. These experiments were conducted separately in a 1 L Pyrex glass beaker for each compound using the same initial concentration (25, 50, 75 and 100 mg/L). After adding 0.5 g/L of TiO_2, the reacting solution was left running for 60 min in order to reach adsorption equilibrium that might be at 45 min as in previous studies. However, in this study, 15 min were added to make sure that the adsorption equilibrium was achieved. Then, a sample was taken for measuring the equilibrium concentration (C_e) that will be used to calculate the adsorption capacity (Q_e).

2.5. HPLC analysis

4-CP and different intermediates were identified and qualified by HPLC analysis. Detection of photoproducts was done at 265 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^{-1}. 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 4-CP and its intermediates on TiO_2 photocatalyst

Experimental measurements of the adsorption constants of 4-CP, HQ and 4cCat on TiO_2 were performed. After measuring C_e for all cases, Q_e can be determined using Eq. (1) [21]:

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

where C_0 and C_e are the initial and equilibrium concentrations of the adsorbate, respectively (mg/L). V is the total volume of the solution (L) and M_{cat} is the mass of the TiO_2 catalyst. The Langmuir isotherm model, Eq. (2), can be used in this manner to calculate the adsorption constants for 4-CP and its intermediates [22].

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

where Q_e (mg/g_{cat}) and C_e (mg/L) are the amount of compound per unit weight and the concentration in the liquid phase at equilibrium, respectively. $Q_{\max}$ (mg/g_{cat}) is the maximum organic compound adsorbed and K_i (L mg^{-1}) is the adsorption constant of component i. To calculate K_i, Eq. (2) has to be rearranged to linear form as in the following equation:

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

From the slope and the intercept of Eq. (3), the adsorption constant for each component can be obtained when experimental data of C_e and Q_e are available. Figs. 1–3 show the linear regressions of Langmuir isotherm for 4-CP, HQ and 4cCat, respectively.

Table 1 summarises the adsorption constants (K_i) and the maximum organic adsorption ($Q_{\max}$) for the investigated components. One can notice that the adsorption constant of 4-CP is higher than that of HQ and 4cCat which might be due to the high amount of

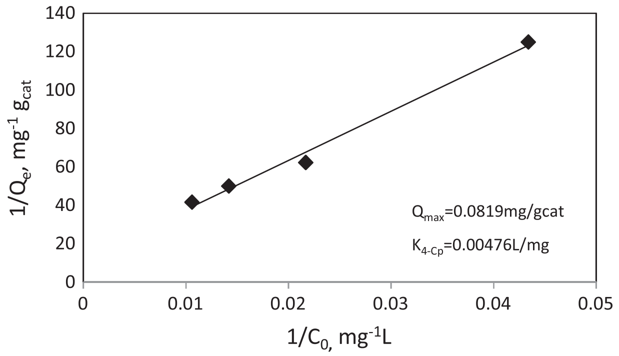

Fig. 1. Linear regression for Langmuir isotherm: adsorption of 4-CP on TiO_2.

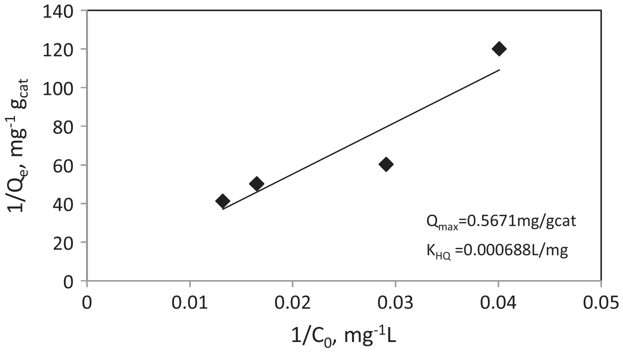

Fig. 2. Linear regression for Langmuir isotherm: adsorption of HQ on TiO_2.

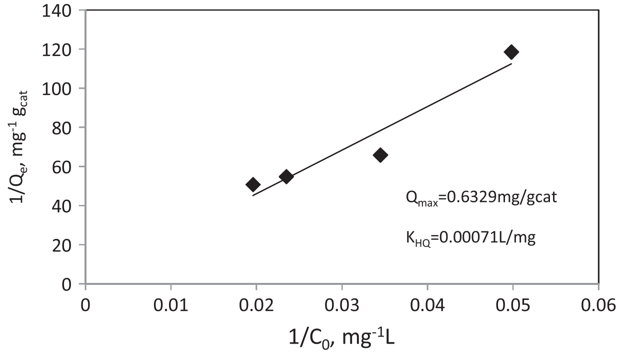

Fig. 3. Linear regression for Langmuir isotherm: adsorption of 4cCat on TiO_2.

Table 1
Adsorption constants for different components on TiO_2

Component	Maximum organic compound adsorbed, Q_{max} (mg/g_{cat})	Adsorption constant, K_i (L/mg)
4-CP	0.0819	0.004760
HQ	0.5671	0.000688
4cCat	0.6329	0.000710

4-CP adsorbed on the TiO_2 powder to form a monolayer [23].

3.2. *Photocatalytic degradation of 4-CP*

Fig. 4 shows a typical experimental results for the solar photocatalytic degradation of 4-CP and its main detected intermediates at different initial 4-CP concentrations (50, 75 and 100 mg/L) and 0.5 g/L TiO_2. All of these compounds were identified in previous studies [9,24]. It should be mentioned that both HQ and 4cCat were the two major aromatic intermediates detected during 4-CP photocatalytic degradation on TiO_2. During 180 min solar degradation of 4-CP, HQ was slightly increased which might be due to the production of HQ from Ph and 4-CP degradation at the same time. In this case, dechlorination might occur on 4-CP to form Ph and then an OH radical adds onto the Ph ring at para-position, leading to the production of HQ [25]. Yang et al. [5] pointed out that the HQ concentration starts decreasing after 180 min when using UV/TiO_2 to degrade 4-CP compound which, is in agreement with our results. Ph was also detected but at low concentration. Therefore, the Ph compound was not included as an intermediate in the proposed kinetic model.

The degradation efficiencies of different 4-CP initial concentrations were also determined. Fig. 5 shows the degradation efficiency of 4-CP at 50, 75 and 100 mg/L, respectively. It is clear that the degradation efficiency decreases with increasing the initial concentration. This result can be clarified by the fact that, at high initial 4-CP concentration, the amount of 4-CP adsorbed on the TiO_2 surface increases leading to decrease the active sites and $^{\bullet}OH$ radical formation [26].

3.3. *Photocatalytic degradation of the major intermediates HQ and 4cCat*

Photocatalytic oxidation experiments were conducted using the main intermediates found during the solar photocatalytic degradation of 4-CP as the model reactants. These experiments are necessary to get more details about the kinetic behaviour of these intermediates and also to measure their adsorption constants experimentally. During 180 min photocatalytic degradation of HQ, a small amount of benzoquinone (BQ) was observed at the first 60 min then it was rapidly degraded Fig. 6.

However, for 4cCat there was no significant intermediates were detected, Fig. 7. The 4cCat as an intermediate might convert to hydroxyhydroquinone [27]. Prakash et al. [28] used 4cCat as a model reactant (pollutant) without intermediate investigations; therefore, there are no clear investigations for solar photocatalytic degradation of 4cCat yet.

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 4-CP. Three intermediate (HQ, 4cCat and Ph) were detected when

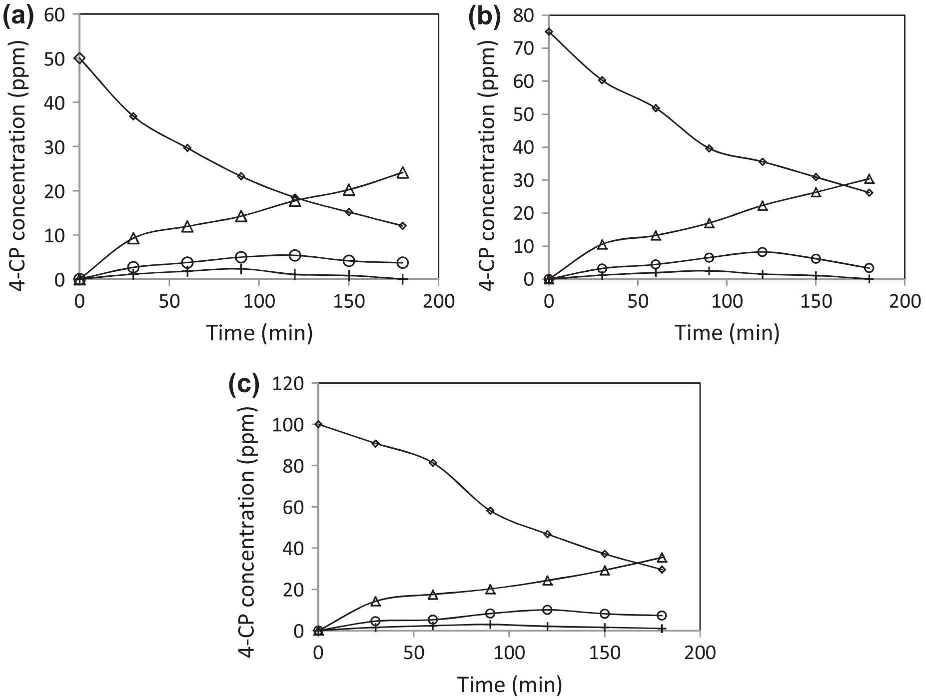

Fig. 4. Concentration profiles of 4-CP and its intermediates at several initial concentrations (a) 50, (b) 75 and (c) 100 mg/L and 0.5 g/L TiO_2: (◊) 4-CP, (△) HQ, (○) 4cCat and (+) Ph.

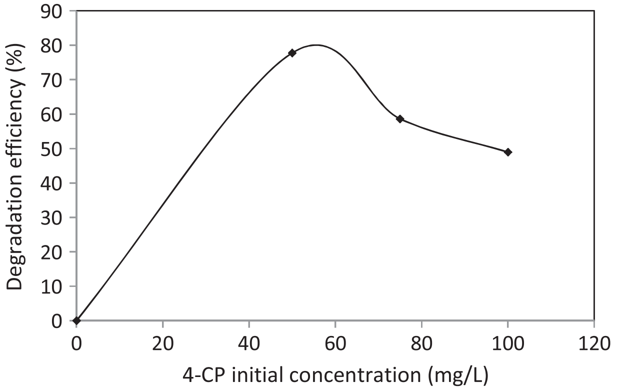

Fig. 5. Effect of the 4-CP initial concentration on the degradation efficiency.

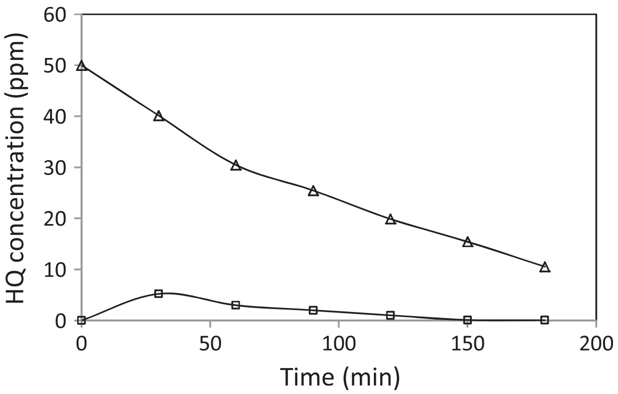

Fig. 6. Concentration profiles of HQ photoconversion and its intermediate (0.5 g/L TiO_2, 1,000 mW/cm^2). (△) HQ and (□) BQ.

degrading 4-CP. However, the detected Ph concentration was very small and might be quickly converted to HQ. Therefore, it was neglected in the kinetic model of this study. During the course of solar irradiation (180 min), the 4-CP concentration significantly decreased with increasing HQ concentration which might be due to direct attack of $^{\bullet}OH$ radical on Cl^- atom. Further solar irradiation degrades HQ to either CO_2 and H_2O or BQ that also converts to the final products. However, hydroxyl radical might react with 4-CP and produce 4cCat, Fig. 8. These findings supporting other investigations [9,24,29,30].

Regarding the kinetic modelling of photocatalytic degradation of 4-CP, several assumptions have to be taken into account as follows: (a) the photocatalytic reactions occur on the catalyst surface; therefore, the rates of formation and disappearance of all components can be modelled using a Langmuir–Hinshelwood (L–H) equation; (b) all observed chemical species

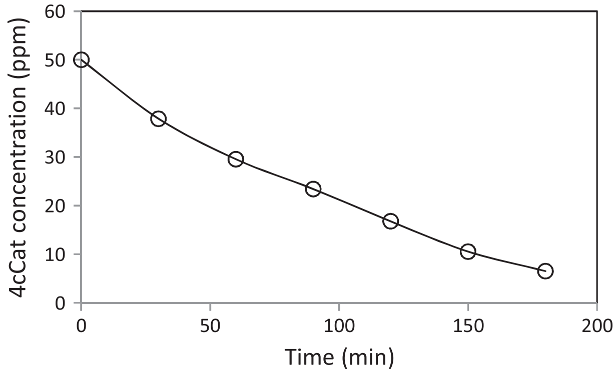

Fig. 7. The concentration profile of 4cCat photoconversion on TiO_2.

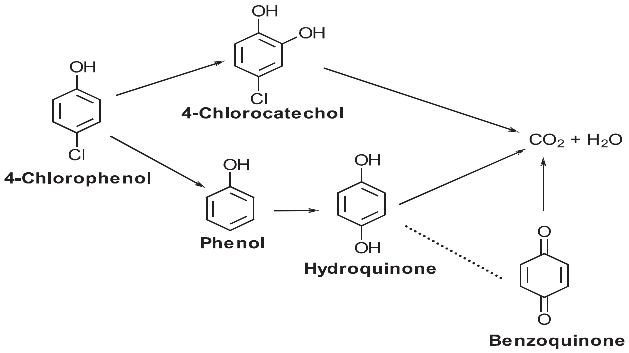

Fig. 8. Proposed pathways of 4-CP photocatalytic degradation.

adsorb on the photocatalyst surface; (c) carbon dioxide does not adsorb on the photocatalyst surface and (d) there is no different behaviour for all chemical species when they are modelled either as a model pollutant or as an intermediate [14,22,31]. Additionally, in this modelling, the reaction rate constants forming HQ ($k_{4-\mathrm{CP-HQ}}$) and 4cCat ($k_{4-\mathrm{CP-4cCat}}$) as intermediates from the oxidation of 4-CP were assumed to be equal. However, the reaction rate constants of their degradations and mineralisation ($k_{\mathrm{HQ-CO_2}}$ and $k_{\mathrm{4cCat-CO_2}}$) are different, Fig. 8.

3.5. Kinetic modelling

Kinetic studies of phenolic compounds on 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 [14,32]. 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 4-CP and its main intermediates (HQ and 4cCat) 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 TiO_2 [33]. 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 [34].

$$r_i = \frac{\mathrm{d}C_i}{\mathrm{d}t} = \frac{k_i C_i}{1 + \sum_{i=1}^{n} K_i C_i} \qquad (4)$$

where r_i is the reaction rate of component i in mg/(L min), k_i is the kinetic reaction constant for component i in min^{-1}, K_i is the adsorption constant for each of the species participating in the reaction L/mg, n denotes the number of participant in the reaction and C the species concentration mg/L.

Applying Eq. (4) for each of the observed components (4-CP, HQ and 4cCat) results in three differential equations describing the photocatalytic degradation of 4-CP and its intermediates.

For 4-CP,

$$\frac{\mathrm{d}C_{4-\mathrm{CP}}}{\mathrm{d}t} = \frac{-\left(k_{4-\mathrm{CP-HQ}} + k_{4-\mathrm{CP-4cCat}}\right)C_{4-\mathrm{CP}}}{1 + K_{4-\mathrm{CP}}C_{4-\mathrm{CP}} + K_{\mathrm{HQ}}C_{\mathrm{HQ}} + K_{\mathrm{4cCat}}C_{\mathrm{4cCat}}} \qquad (5)$$

Assuming $k_{4-\mathrm{CP}} = k_{4-\mathrm{CP-HQ}} = k_{4-\mathrm{CP-4cCat}}$

$$\frac{\mathrm{d}C_{4-\mathrm{CP}}}{\mathrm{d}t} = \frac{-2k_{4-\mathrm{CP}}C_{4-\mathrm{CP}}}{1 + K_{4-\mathrm{CP}}C_{4-\mathrm{CP}} + K_{\mathrm{HQ}}C_{\mathrm{HQ}} + K_{\mathrm{4cCat}}C_{\mathrm{4cCat}}} \qquad (6)$$

Similar equations can be written for each intermediate. For HQ and 4cCat are as follows:

$$\frac{\mathrm{d}C_{\mathrm{HQ}}}{\mathrm{d}t} = \frac{\left(k_{4-\mathrm{CP-HQ}}C_{4-\mathrm{CP}} - k_{\mathrm{HQ-CO_2}}C_{\mathrm{HQ}}\right)}{1 + K_{\mathrm{HQ}}C_{\mathrm{HQ}} + K_{4-\mathrm{CP}}C_{4-\mathrm{CP}} + K_{\mathrm{4cCat}}C_{\mathrm{4cCat}}} \qquad (7)$$

or

$$\frac{\mathrm{d}C_{\mathrm{HQ}}}{\mathrm{d}t} = \frac{\left(k_{4-\mathrm{CP}}C_{4-\mathrm{CP}} - k_{\mathrm{HQ-CO_2}}C_{\mathrm{HQ}}\right)}{1 + K_{\mathrm{HQ}}C_{\mathrm{HQ}} + K_{4-\mathrm{CP}}C_{4-\mathrm{CP}} + K_{\mathrm{4cCat}}C_{\mathrm{4cCat}}} \qquad (8)$$

and for 4cCat:

$$\frac{\mathrm{d}C_{4\mathrm{cCat}}}{\mathrm{d}t} = \frac{(k_{4-\mathrm{CP}-4\mathrm{cCat}}C_{4-\mathrm{CP}} - k_{4\mathrm{cCat}-\mathrm{CO}_2}C_{4\mathrm{cCat}})}{1 + K_{4\mathrm{cCat}}C_{4\mathrm{cCat}} + K_{4-\mathrm{CP}}C_{4-\mathrm{CP}} + K_{\mathrm{HQ}}C_{\mathrm{HQ}}} \tag{9}$$

or

$$\frac{\mathrm{d}C_{4\mathrm{cCat}}}{\mathrm{d}t} = \frac{(k_{4-\mathrm{CP}}C_{4-\mathrm{CP}} - k_{4\mathrm{cCat}-\mathrm{CO}_2}C_{4\mathrm{cCat}})}{1 + K_{4\mathrm{cCat}}C_{4\mathrm{cCat}} + K_{4-\mathrm{CP}}C_{4-\mathrm{CP}} + K_{\mathrm{HQ}}C_{\mathrm{HQ}}} \tag{10}$$

Eqs. (6), (8) and (10) represent 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 equations cannot be solved analytically; therefore, for estimating the reaction rate constants two built-in MATLAB subroutines were used: *lsqcurvefit* for the minimisation of the objective function and *ode45* for the numerical integration of the differential equations. After estimating the best parameters, the mathematical model can be applied to predict the behaviour of the photocatalytic oxidation of 4-CP.

The proposed model that involves two major intermediates (HQ and 4cCat) was based on the degradation mechanism depicted in Fig. 8. However, the step of forming Ph in this degradation pathway was dropped due to its low concentration and the fast degradation. Additionally, some assumptions have been applied in order to use the L–H equation (Eq. (4)) and minimise the unknown variables. Furthermore, the adsorption constants of 4-CP, HQ and 4cCat were experimentally determined in order to provide the kinetic model more accuracy. Three ordinary differential equations (Eqs. (6), (8) and (10)) for describing the proposed degradation mechanism were developed for 4-CP, HQ and 4cCat, respectively. These ordinary differential equations cannot be solved analytically; therefore, MATLAB software was used to solve these equations and estimate the reaction rate constants for all components involved in the developed model. Table 2 summarises the estimated

Table 2
Estimated adsorption and reaction rate constants for the photocatalytic oxidation of 4-CP, HQ and 4cCat

Chemical species	Measured adsorption constant K_i (L/mg)	Estimated reaction rate constant k_i (min^{-1})
4-CP	0.004760	0.0055
HQ	0.000688	0.00034
4cCat	0.000710	0.03251

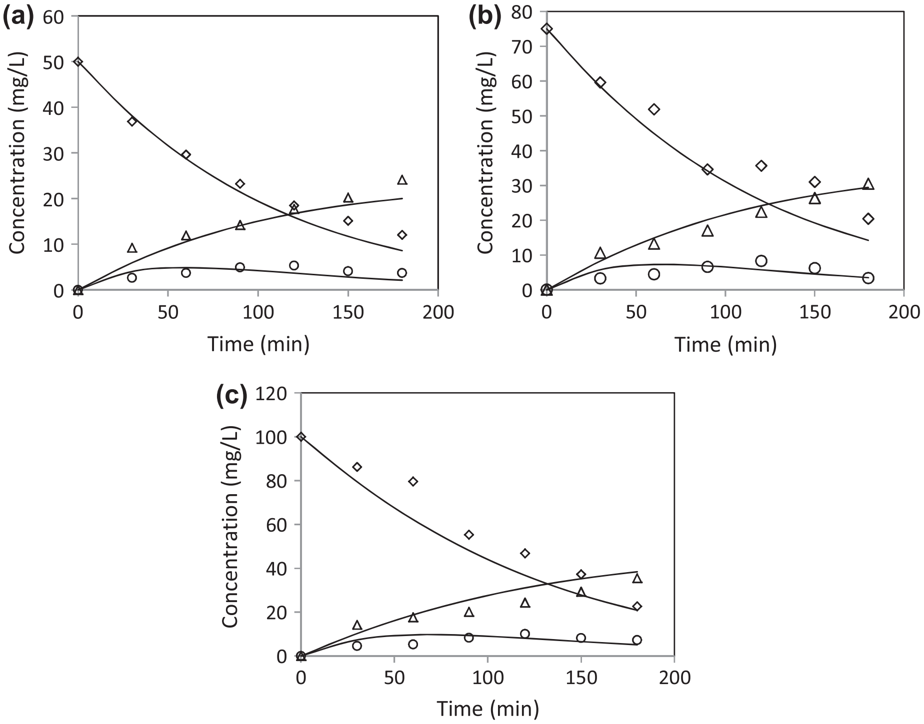

Fig. 9. Experimental and estimated concentration profiles for photocatalytic degradation of 4-CP and 0.5 g/L TiO_2 catalyst: (◊) 4-CP, (△) HQ, (○) 4cCat and (−) model for (a) 50, (b) 75 and (c) 100 mg/L 4-CP initial concentration.

reaction rate constants and measured adsorption constants for 4-CP, HQ and 4cCat, respectively.

Fig. 9 presents the experimental concentration profiles of 4-CP and its intermediates and the estimated profiles for different initial concentrations. The optimisation was performed with three different initial concentrations of 4-CP (50, 75 and 100 ppm). It can be seen that the kinetic model predicts very well the experimental data for a wide range of initial concentrations.

4. Conclusion

Three aromatic intermediate compounds were identified in the solar degradation of 4-CP namely HQ, 4cCat and Ph using TiO_2 as a photocatalyst. The reaction pathway for the photocatalytic oxidation of 4-CP is reported including all observed chemical species. This proposed mechanism based on the experimental results obtained for the oxidation of 4-CP and its intermediates individually. However, the Ph compound was detected in small amounts; therefore, it was neglected from the proposed kinetic model. All the adsorption constants of 4-CP and its major intermediates were determined experimentally. The reaction kinetic model is developed to predict the rate of reaction of 4-CP and its main aromatic intermediates. The proposed model provides very good fit of the experimental data and works very well for a wide range of 4-CP initial concentrations (50–100 mg/L).

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