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Treatment of *o*-Cresol/4-chlorophenol binary mixtures in aqueous solutions by TiO_2 photocatalysis under UV irradiation

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ABSTRACT

Photocatalytic degradation of single and binary mixtures of *o*-cresol and 4-chlorophenol (4-CP) over TiO_2 suspensions under UV irradiation was studied and the mixture effect was discussed. The effects of operating parameters such as initial reactant concentration (0.16–1.04 mM), solution pH (4.50–9.35), and UV light intensity (20–100 W) on the degradation were investigated. It was shown that the degradation of single or binary mixtures of reactants in aqueous solutions could be described by the pseudo-first-order kinetics according to the Langmuir–Hinshelwood model. When the second reactant was in excess, the degradation rates of *o*-cresol and 4-CP in binary mixture system were slower than those in single systems. At a fixed *o*-cresol concentration of 0.45 mM, for example, the apparent first-order rate constant k_{app} for *o*-cresol degradation was 0.323, 0.275, and 0.220 h^{-1} when 0.15, 0.30, and 0.45 mM of 4-CP was present, respectively.

Keywords: Photocatalytic degradation; *o*-Cresol; 4-Chlorophenol; TiO_2; Binary mixtures; UV irradiation

1. Introduction

Many techniques are available to treat or remove organic pollutants from industrial effluents. They include chemical oxidation, biological digestion, thermal treatment, activated carbon adsorption, and advanced oxidation processes (AOPs) [1]. Among the AOPs, photocatalytic degradation that uses semiconductors as photocatalysts (e.g. TiO_2, ZnO, CdS, etc.) provides a promising method for the elimination of organic pollutants in water [2]. Photocatalytic processes have many advantages including complete and rapid degradation of organic pollutants, water, and mineral acids without producing polycyclic byproducts as well as the use of highly active catalysts that is readily adapted to specially designed reactor systems [1,3]. Particularly, the use of TiO_2 for the purpose of photodegradation has been of great interest due to its nontoxic nature, photochemical stability, and low cost when UV light is used as the source of irradiation.

Phenol and its derivatives such as *o*-cresol and 4-chlorophenol (4-CP) are some of the most refractory contaminants, which are often present in the environment because they are commonly used as raw materials in petrochemical and chemical industries [2,4]. These contaminants have been designated as the

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priority pollutants by the United States Environmental Protection Agency due to their harmful effect to organisms even at low concentrations [5]. Generally, the wastewaters discharged from a refinery contain more than one type of phenolic compounds. In other words, pollutants in nature commonly exist as mixtures, in which the photodegradation rate of one reactant may be repressed by the presence of other compounds [1,6,7]. For example, Wang et al. [1] have indicated that the degradation of single 2-chlorophenol and 2-nitrophenol by TiO_2/UV is faster than that in binary mixtures. The same illustrations were also reported in the systems containing two compounds, such as phenol, guaiacol, 2-chlorophenol, and catechol [6]. Chiou et al. [7] have mentioned that the degradation rates of phenol and m-nitrophenol in binary mixtures are smaller than those in single systems.

Most of photodegradation studies have been conducted with respect to single reactant systems including phenol, *o*-cresol, and 4-CP in contrast to their mixtures. That is, the effect of the presence of the second or more reactants on the degradation was rarely studied. For example, the kinetics and the effect of operating parameters on the degradation of single phenol and 4-CP using aqueous suspensions of several photocatalysts have been reported [2,8]. Moreover, the degradation of single phenolic compounds such as *o*-cresol and 4-CP has been studied and compared [9–12]. The aim of this work was to investigate the effect of the presence of the second reactant on photdegradation of *o*-cresol and 4-CP over P-25 TiO_2 suspensions under UV irradiation. Experiments were conducted for both single and binary mixture systems. The influences of operating parameters including the initial reactant concentration (0.16–1.04 mM), solution pH (4.50–9.35), UV light intensity (20 and 100 W), and the absence and presence of H_2O_2 on their degradation were examined.

2. Materials and methods

2.1. Materials and reagents

o-Cresol (98%) and 4-CP (99%) were obtained from Alfa Aesar (UK). The P-25 TiO_2, supplied by Degussa, Japan, is mostly in the anatase form (70% anatase and 30% rutile) with a BET surface area of 53.3 m^2/g and an average particle size of 50 nm, as verified by FESEM (JSM-6701F, UK). The chemicals NaOH and HCl were purchased from J.T. Backer (USA), methanol was from Merck (Germany), and hydrogen peroxide solution (30% w/v) was from Sigma-Aldrich (Germany). The UV light sources used were a water-cooled 20 W low-pressure UV lamp (UVL20PH-6, SEN Japan) and 100 W high-pressure mercury lamp (HL100CH-5, SEN Japan). All chemicals were used as received by the suppliers without further purification.

2.2. Photodegradation experiments

All of the degradation experiments were carried out in a batch photoreactor, as shown in Fig. 1. This system consisted of a cylindrical 1.0 L Pyrex-glass cell (10 cm inside diameter and 10 cm height). A 100 W high-pressure mercury lamp was located in the center of the reactor within a 5 cm diameter double-walled cooling tube. The lamp and tube were immersed in the reactor vessel, and the light path was 80 mm.

The photoreactor was filled with 0.8 L of an aqueous solution containing *o*-cresol, 4-CP, or their mixture, to which P-25 TiO_2 powders (1 g/L) were added. The pH of the suspension was measured using a digital pH meter (Horiba F-23, Japan) by adding 0.1 M NaOH or HCl. The suspension was kept uniform through agitation with a magnetic stirrer (100 rpm). The temperature of the photoreactor was maintained at 25 ± 1°C by a water-cooling jacket (Eyela, NCB-2,600, Japan). The time at which the UV lamp was turned on was considered zero or the beginning of the experiment. The whole system was automatically maintained a constant voltage by a voltage stabilizer (input 140 V, output 110 V).

Photodegradation experiments were performed for 3 h and the liquid samples (1 mL) were collected at every 0.5 h time interval. The samples were filtered through a 0.45 μm syringe filter (Millipore) to remove any TiO_2 particles and were then stored in brown glass bottles (1 mL). The concentrations of *o*-cresol and 4-CP were analyzed by HPLC (Jasco, Japan). The column used was a Merck LiChroCART® 250–4.6 (250 mm length, 4.6 mm diameter), packed with Purospher® STAR RP-18 end-capped (5 μm). A mixture of methanol (60%, v/v) and deionized water was used as the mobile phase at 1.0 mL/min. An aliquot of the sample (10 μL) was injected using the autosampler on the HPLC for analysis at 280 nm. Two separate peaks for *o*-cresol and 4-CP appeared at the residence time between 7.2 and 8.7 min (1.5 min of appearance), and between 9.3 and 10.1 min (0.83 min of appearance), respectively.

All of the solutions were prepared with deionized water here. Each experiment was performed at least in triplicate under identical conditions. The degradation efficiency of the reactant in was calculated by:

$$\text{Degradation efficiency } (\%) = 100 \times \left[1 - \left(\frac{C}{C_0}\right)\right] \qquad (1)$$

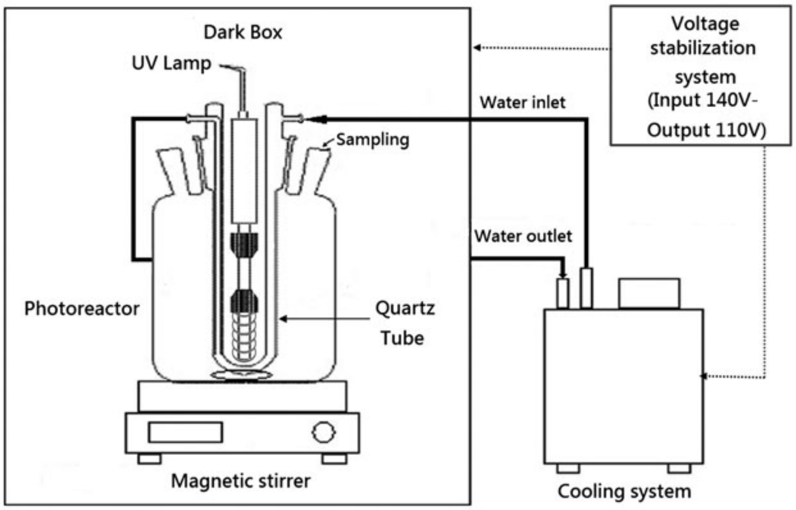

Fig. 1. Schematic diagram of the experimental setup for photocatalytic degradation (Nguyen and Juang, 2014).

where C_0 is initial concentration of the compound and C is concentration of the compound after photoirradiaton for a given time t.

3. Results and discussion

3.1. Effect of solution pH on photodegradation

The pH of the suspension is a key parameter affecting heterogeneous reactions involving semiconductor particles [6,7]. In this study, the degradation of *o*-cresol and 4-CP at different initial pH values (4.50, 7.46, and 9.35) in the TiO_2/UV system was compared. It is seen from Fig. 2 that the degradation of *o*-cresol at pH 4.50 is 64% within 3 h. The performance of the TiO_2/UV system exerts no remarkable pH effect on *o*-cresol removal percentage between pH 7.46 (81%) and pH 9.35 (84%) after 3 h.

On the other hand, the amount of 4-CP degraded gradually increases with increasing pH from 4.50 to 9.35. For example, the degradation efficiency of 4-CP reaches 80, 88, and 95% after 3 h at pH 4.50, 7.46, and 9.35, respectively. Clearly, the degradation of *o*-cresol and 4-CP is more effective in neutral and weakly alkaline media. Such results are consistent with those reported in previous studies [11,13].

The surface functional groups of TiO_2 in water strongly depend on pH according to:

$$TiOH + H^+ \rightarrow TiOH_2^+ \qquad (2)$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \qquad (3)$$

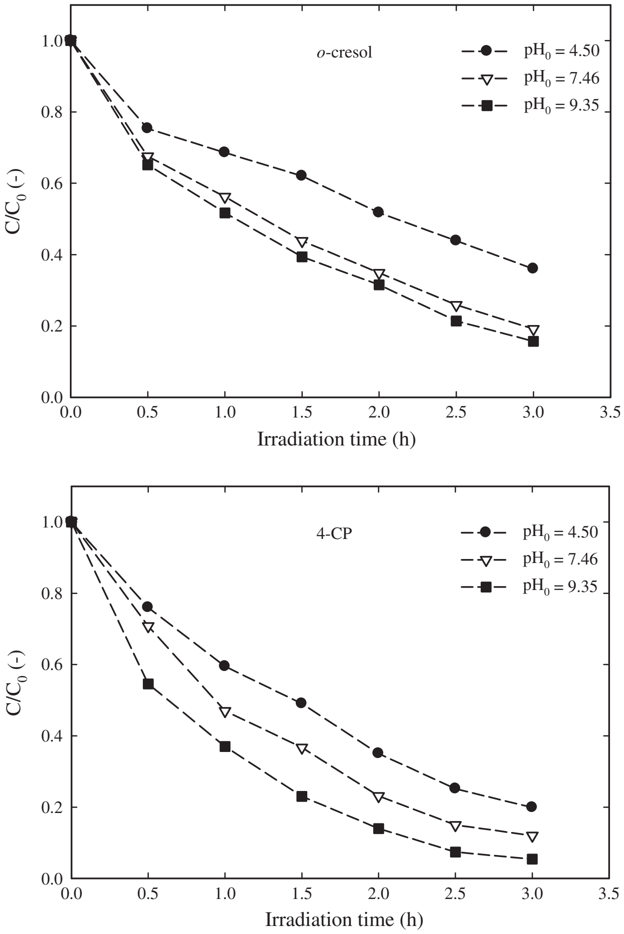

Fig. 2. Effect of the initial pH on the removal of single *o*-cresol and 4-CP using TiO_2/UV at 25˚C (100 W UV, C_0 = 0.52 mM, 1 g/L TiO_2) (Nguyen and Juang, 2014).

where $TiOH_2^+$, TiOH, and TiO^- are the positive, neutral, and negative hydroxyl groups, respectively [7]. One of the key factors determining the distribution of TiO_2 surface functional groups is the point of zero charge (pHpzc) of TiO_2. While $TiOH_2^+$ plays the role when pH < pHpzc, TiO^- is the predominant species at pH > pHpzc. The reactant primarily exists in molecular state when pH is lower than its pK_a but exists as ions at pH greater than its pK_a. The pHpzc of Degussa P-25 TiO_2 is between 6.25 and 6.60 [1,14], and the p*K*a value of *o*-cresol and 4-CP is 10.2 and 9.2, respectively [15,16]. In neutral to weak alkaline media, TiO^- is the predominant species for TiO_2 particles and phenols are primary present in molecular state. Both of them may combine by hydrogen bonding easily, hence increasing the amount of adsorption and enhancing the decomposition rate [13,17].

As to *o*-cresol and 4-CP, the present results show good decomposition effect even under acidic conditions. The formation mechanism of free radicals, which is instead of surface adsorption mechanism, is maybe the rate-limiting step. Hydroxyl radicals are generated by the reactions of light-excited holes with H_2O/OH^- [18]. When TiO_2 is irradiated with light of an energy that exceeds TiO_2 band-gap, an electron from the valance band promotes to the conduction band and leaves an electronic vacancy or hole (h^+) in the valance band. Hence, the act of photo-excitation generates an electron-hole pair [18]:

$$TiO_2 \xrightarrow{h\nu} h^+ + e^- \quad (4)$$

The highly oxidative h^+ ($E^0 = 2.8$ V) directly reacts with the surface-sorbed organic molecules or indirectly oxidizes the organic compounds via formation of OH• radicals according to the following reactions [18]:

$$H_2O + h^+ \rightarrow {}^{\cdot}OH + H^+ \quad (5)$$

$$OH^- + h^+ \rightarrow {}^{\cdot}OH \quad (6)$$

The photo-generated electrons are trapped most often by molecular oxygen but effective electron acceptor such as $S_2O_8^{2-}$ and H_2O_2 can also be used [19]:

$$O_2 + e^- \rightarrow {}^{\cdot}O_2^- \quad (7)$$

The other sources might come from hydrogen peroxide which can be summarized as follows [20]:

$$^{\cdot}O_2^- + H^+ \rightarrow {}^{\cdot}HO_2 (pK_a = 4.88) \quad (8)$$

$$^{\cdot}HO_2 + {}^{\cdot}HO_2 \rightarrow H_2O_2 + O_2 \quad (9)$$

$$^{\cdot}O_2^- + {}^{\cdot}HO_2 \rightarrow HO_2^- + O_2 \quad (10)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad (11)$$

$$H_2O_2 + e^- \rightarrow {}^{\cdot}OH + OH^- \quad (12)$$

$$H_2O_2 + {}^{\cdot}O_2^- \rightarrow {}^{\cdot}OH + OH^- + O_2 \quad (13)$$

$$H_2O_2 \xrightarrow{h\nu} 2 \cdot {}^{\cdot}OH \quad (14)$$

Eqs. (7)–(14) shows that the amount of HO_2 increases when the pH is lower than the pK_a (4.88) of HO_2 and thus, enhancing the sequential reactions and the .OH production. It is hence considered that the OH formation is beneficial to increase the reaction rate [13]. In this study, the effect of pH on *o*-cresol and 4-CP photodegradation decreased as follows: 9.35 > 7.46 > 4.50.

3.2. Effect of the initial concentration on photodegradation

The effect of initial concentrations of single *o*-cresol and 4-CP (0.16–1.04 mM) on the rate of degradation is shown in Fig. 3. The initial rate was calculated from the degradation pattern in the first 0.5 h of irradiation. At initial concentrations of 0.16 and 0.25 mM, approximately 98% and 96% of *o*-cresol was removed within 1.5 h, respectively. The total amount of *o*-cresol degraded increases under the conditions studied. However, at higher concentrations, the increment of rate decreases, suggesting a reduction in the order of the reaction as the substrate concentration increases [21]. The degradation may be also controlled by the limited number of surface sites on TiO_2 particles [7]. For example, when the initial concentration increases from 0.52 to 1.04 mM, only 83 to 57% of *o*-cresol, respectively, is removed within 3 h. Under identical ranges as above, approximately 96, 98, and 97% of 4-CP is removed within 0.5, 1.5, and 2.5 h at the initial concentrations of 0.16, 0.25, and 0.52 mM, respectively. However, with increasing initial concentrations from 0.78 to 1.04 mM, the degradation of 4-CP within 3 h decreases from 83 to 57%.

Yesodharan et al. [22] have reported a reduction of the reaction order at higher reactant concentrations in TiO_2 photocatalysis. At low reactant concentrations, the number of catalytic sites is not the limiting factor of the degradation rate, which is proportional to the reactant concentration, in accordance with the appar-

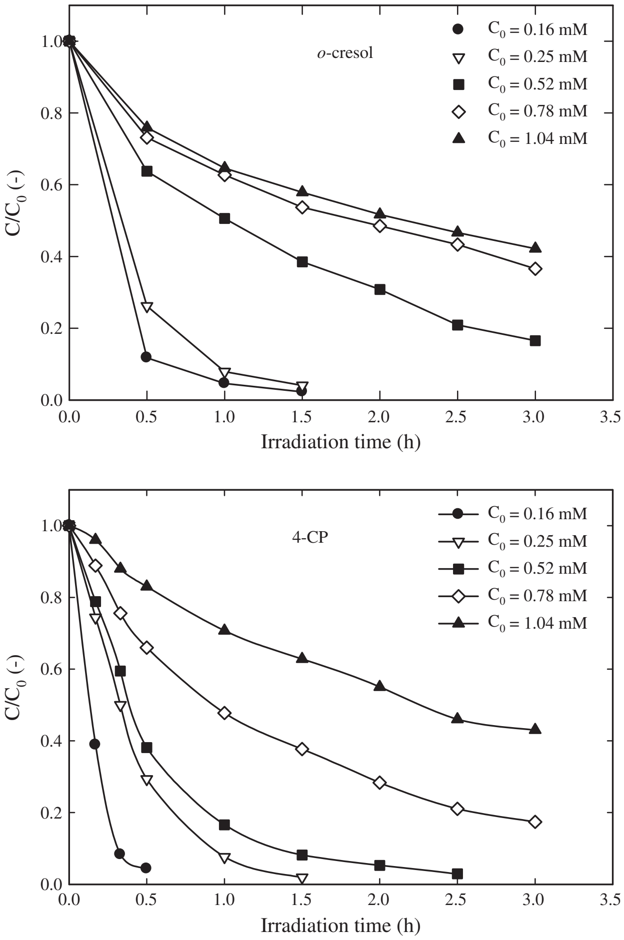

Fig. 3. Effect of the initial concentrations of single *o*-cresol and 4-CP on its removal under 100 W UV light at 25℃ (1 g/L TiO_2, initial pH 7.46) (Nguyen and Juang, 2014).

ent first-order kinetics. At high concentrations, all catalytic sites of the semiconductor surface are occupied and the zero-order kinetics can be applied. In the case of *o*-cresol and 4-CP, the degraded products including intermediates are expected to remain strongly absorbed on the hydroxylated surface of the catalyst through hydrogen bonding [23]. The effective number of active sites available for the adsorption of *o*-cresol and 4-CP is reduced, leading to the reduction in degradation rate at higher reactant concentrations [21]. In comparison with previous studies [23–25], the present results reveal that the degradation is promising at lower reactant concentrations.

As mentioned above, the pK_a value of *o*-cresol and 4-CP is 10.2 and 9.2, respectively. The presence of -CH3 group for *o*-cresol decreases the pK_a value, making it less acidic than 4-CP [15,16]. In addition, the removal of 4-CP is more effective under acidic conditions [9]. Therefore, the degradation of 4-CP is better than that of *o*-cresol.

In this study, the HPLC graphs for *o*-cresol and 4-CP analysis show many undefined peaks. They can be the degraded intermediates which may affect degradation rate. Some intermediates such as methylhydroquinone, 2-methylresorcinol, and 2,5-dihydroxybenzaldehyde were reported during the photodegradation of *o*-cresol [11,13]. In addition to many minor intermediates, the major intermediates of benzoquinone, 4-chlorocatechol, catechol, and hydroquinone were reported during the photodegradation of 4-CP [3,26,27].

3.3. Photodegradation kinetics of o-cresol and 4-CP

The Langmuir–Hinshelwood model was initially used to describe gas–solid reactions [8,9]. Specifically, it is used to describe the kinetics of photocatalytic reactions incorporating aqueous organic compounds [24,28,29]. In this model, the reaction rate (r) is proportional to the fraction of surface covered by the reactant (θ). Considering the Langmuir adsorption equation for surface coverage, we have

$$r = \frac{-dC}{dt} = k_r\theta = \frac{k_r K_{ad} C}{1 + K_{ad} C} \tag{15}$$

where k_r is the intrinsic rate constant (mM/h), which involves several factors like the efficient photon flow, O_2 layer, catalyst's mass, etc. [21], and K_{ad} is the Langmuir adsorption constant (mM^{-1}).

For highly diluted solution ($C < 10^{-3}$ mM in this case) [29], the relationship $K_{ad}C << 1$ is valid; the reaction is essentially an apparent first-order reaction:

$$r = \frac{-dC}{dt} = k_r K_{ad} C = k_{app} C \tag{16}$$

where k_{app} is the apparent first-order rate constant (min^{-1}). After integration, we have,

$$\ln\left(\frac{C}{C_0}\right) = -k_{app} t \tag{17}$$

Fig. 4 shows the variations of the concentrations of single *o*-cresol and 4-CP with time using UV/TiO_2 at 25℃ (1 g/L TiO_2, initial pH 7.46). The concentration-time curves reveal two distinct stages: the initial (sharp) stage ($t < 0.5$ h) and the final (gradual) stage ($t > 0.5$ h). The apparent rate constants are defined during these two stages while following the pseudo-

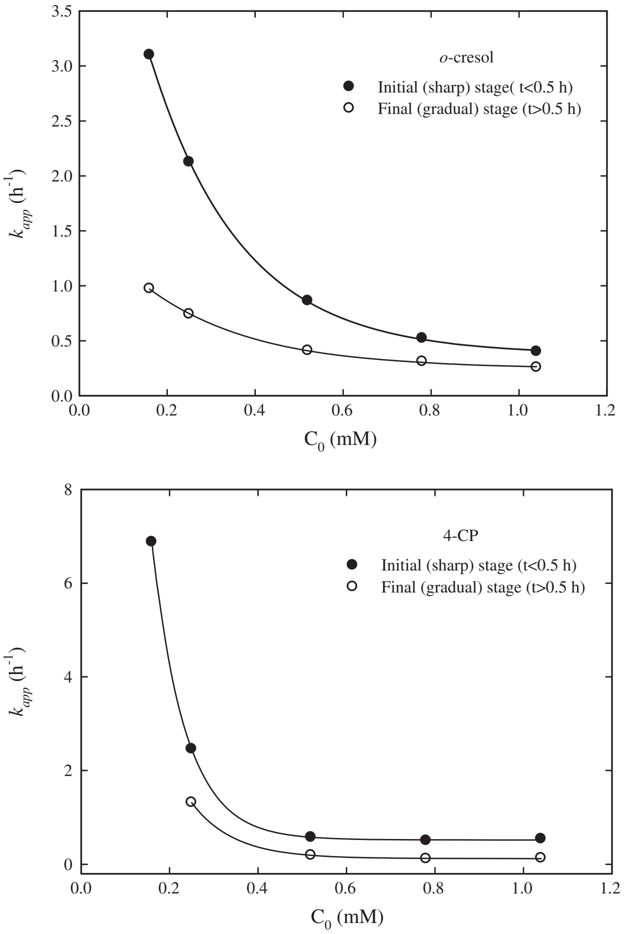

Fig. 4. Effect of the initial concentrations of single *o*-cresol and 4-CP on the apparent rate constant at 25℃ using TiO$_2$/UV (100 W UV, 1 g/L TiO$_2$, initial pH 7.46) (Nguyen and Juang, 2014).

first-order kinetics according to the Langmuir–Hinshelwood model.

When a threshold coverage on the TiO$_2$ surface reaches due to the adsorption of intermediates in the initial stage, the intermediates do not yet occupy the surface of TiO$_2$ (i.e. before 0.5 h of the process). This explains the transition. After a short initial period, the intermediates begin to occupy surface sites, reducing the degradation rate [7]. The values of k_{app} for single *o*-cresol are 3.11, 2.13, 0.86, 0.52, and 0.40 h^{-1} at initial reactant concentrations of 0.16, 0.25, 0.52, 0.78, and 1.04 mM, respectively, whereas those for single 4-CP are 6.88, 2.46, 0.57, 0.50, and 0.47 h^{-1}, respectively.

Table 1 shows the apparent rate constant k_{app} (h^{-1}) for the degradation of single *o*-cresol and 4-CP at different initial pH values by TiO2/UV system. Under the conditions of initial concentration 0.52 mM, 1 g/L TiO$_2$, and 100 W UV irradiation, a more remarkable increase in k_{app} with increasing pH for 4-CP degradation is found in contrast to *o*-cresol degradation.

Table 1
The apparent rate constant k_{app} (h^{-1}) for the degradation of single reactant at different initial pH values by TiO$_2$/UV process (C$_0$ = 0.52 mM, 1 g/L TiO$_2$, 100 W UV irradiation)

	pH		
Compound	4.50	7.46	9.35
o-Cresol	0.32	0.53	0.59
4-CP	0.54	0.98	1.21

3.4. Effect of UV light intensity on photodegradation

To obtain faster degradation, particularly in wastewater treatment, the higher light intensity is suggested to provide more active sites on TiO$_2$ surface with sufficient photon energy [30]. The effect of UV light intensity (20–100 W) on *o*-cresol and 4-CP degradation was studied using 1.0 g/L TiO$_2$ with or without H$_2$O$_2$ (0.2 mM). Fig. 5 shows the results obtained at pH 7.46 when the initial concentration of *o*-cresol and 4-CP was 0.52 mM. It is observed that all of the reactions follow the pseudo-first-order kinetics [17].

The degradation rate constants of *o*-cresol and 4-CP are 0.15 and 0.17 h^{-1}, respectively, by 20 W UV/TiO$_2$ process. They are 0.57 and 1.04 h^{-1}, respectively, by 100 W UV/TiO$_2$ process. These rate constants are lower than the corresponding ones in the UV/H2O2/TiO$_2$ system (0.42 and 0.41 h^{-1}; 0.94 and 1.82 h^{-1}, respectively), as shown in Table 2. A light intensity of 100 W significantly affects *o*-cresol and 4-CP degradation rate, enhancing 3.8- and 6.2-fold (UV/TiO$_2$ system) as well as 2.3- and 4.5-fold (UV/H$_2$O$_2$/TiO$_2$ system) relative to the case of 20 W, respectively. Specifically, the degradation was enhanced with increasing light intensity [30]. The addition of H$_2$O$_2$ enhances the degradation of *o*-cresol and 4-CP by making more H$_2$O$_2$ available to undergo photodissociation.

In addition, the colors of *o*-cresol and 4-CP solutions changed from white (color of TiO$_2$ particles) to white-light yellow after 0.5 h of degradation. After 3 h, the color of solution became white-lemon yellow. No previous studies have mentioned color change of the solution during or after degradation of *o*-cresol and 4-CP. However, addition of H$_2$O$_2$ or the existence of some intermediates as stated in Section 3.2 during the degradation process possibly explains this discrepancy.

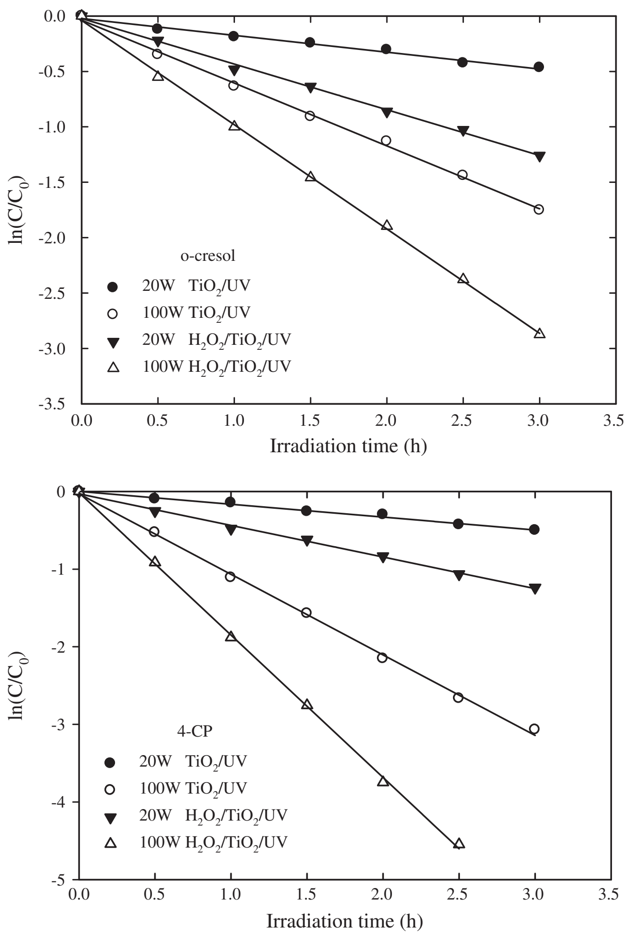

Fig. 5. Degradation rates of single *o*-cresol and 4-CP conducted at 25˚C under different UV light intensities (C_0 = 0.52 mM, 1 g/L TiO_2, 2.0 mM H_2O_2, initial pH 7.46) (Nguyen and Juang, 2014).

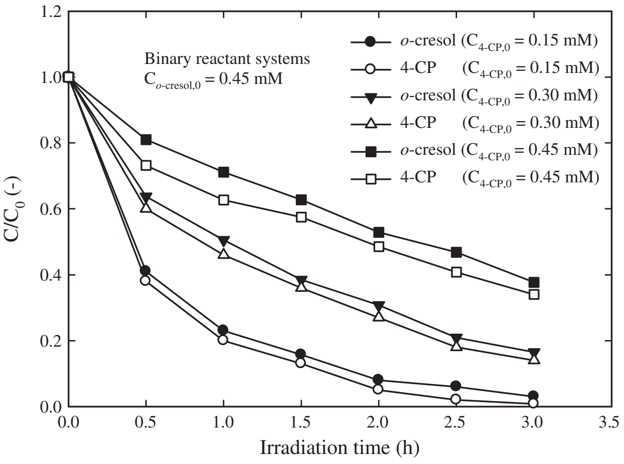

Fig. 6. Time changes of the residual concentrations of binary mixtures of *o*-cresol and 4-CP at pH 7.46 (the initial *o*-cresol concentration was fixed at 0.45 mM, 1 g/L TiO_2) (Nguyen and Juang, 2014).

3.5. Photodegradation of binary mixtures

Degradation of binary mixtures of *o*-cresol and 4-CP was examined at different initial concentration ratios α ($=C_{o\text{-cresol},0}/C_{4\text{-CP},0}$). Fig. 6 shows the results obtained at pH 7.46 as $C_{o\text{-cresol},0}$ is fixed at 0.45 mM. The percentage of unreacted *o*-cresol and 4-CP within 3 h is 37.7% and 34%, respectively, when $\alpha = 1$. It is found that 3% of *o*-cresol and 1% of 4-CP remain unreacted in solution within 3 h when $\alpha = 3$. It is found that the pseudo-first-order kinetics according to the Langmuir–Hinshelwood model is still applicable for the degradation rate of each reactant in binary mixture systems. The apparent rate constants are 0.220 h^{-1} for *o*-cresol and 0.208 h^{-1} for 4-CP at $\alpha = 1$ as well as 0.323 h^{-1} for *o*-cresol and 0.330 h^{-1} for 4-CP at $\alpha = 3$, as shown in Table 3.

Fig. 7 shows the results obtained at pH 7.46 when $C_{4\text{-CP},0}$ is fixed at 0.30 mM. When $\alpha = 2/3$, 16.5% of *o*-cresol and 14.0% of 4-CP are unreacted within 3 h. At $\alpha = 1/3$, the percentage of unreacted *o*-cresol and 4-CP is 38.3 and 35.0%, respectively, within 3 h. Table 3 shows the apparent rate constants are 0.275 h^{-1} for *o*-cresol and 0.293 h^{-1} for 4-CP at $\alpha = 2/3$ as well as 0.206 h^{-1} for *o*-cresol and 0.227 h^{-1} for 4-CP at $\alpha = 1/3$.

Evidently, the degradation of *o*-cresol and 4-CP in binary mixture systems is slower than that in single systems, particularly when the second reactant is in excess (i.e. mole fraction larger than 0.5). The values of k_{app} for *o*-cresol degradation at a fixed *o*-cresol concentration of 0.45 mM are 0.323, 0.275, and 0.220 h-1 when 0.15, 0.30, and 0.45 mM of 4-CP are present, respectively. Compared to the single systems, 4-CP

Table 2
The apparent rate constants k_{app} (h^{-1}) for the degradation of single *o*-cresol and 4-CP under different UV light intensities by TiO_2/UV and H_2O_2/TiO_2/UV (C_0 = 0.52 mM, 1 g/L TiO_2, 2.0 mM H_2O_2, pH 7.46)

	20 W UV		100 W UV	
Compound	TiO_2/UV	H_2O_2/TiO_2/UV	TiO_2/UV	H_2O_2/TiO_2/UV
o-Cresol	0.15	0.42	0.57	0.94
4-CP	0.17	0.41	1.04	1.82

Table 3
The apparent first-order rate constants k_{app} (h^{-1}) for the degradation of binary mixtures at different initial concentrations under 100 W UV irradiation

		k_{app} (h^{-1})				k_{app} (h^{-1})	
$C_{o\text{-cresol},0}$ (mM)	$C_{4\text{-CP},0}$ (mM)	*o*-Cresol	4-CP	$C_{o\text{-cresol},0}$ (mM)	$C_{4\text{-CP},0}$ (mM)	*o*-Cresol	4-CP
0.45	0	1.05[a]	—	0	0.30	—	1.46[a]
0.45	0.45	0.220	0.208	0.30	0.30	0.320	0.331
0.45	0.30	0.278	0.285	0.45	0.30	0.275	0.293
0.45	0.15	0.323	0.330	0.90	0.30	0.206	0.227

[a]Note: Estimated from the results of Fig. 4 by interpolation.

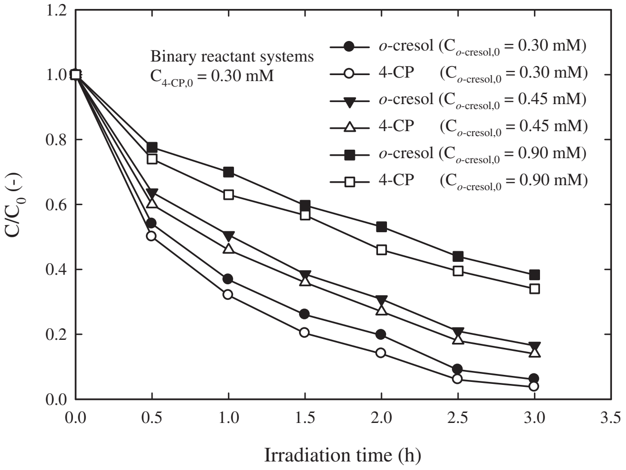

Fig. 7. Time changes of the residual concentrations of binary mixtures of *o*-cresol and 4-CP at pH 7.46 (the initial 4-CP concentration was fixed at 0.30 mM, 1 g/L TiO_2) (Nguyen and Juang, 2014).

shows a faster degradation than *o*-cresol in binary mixture systems. In this case, pH 7.46 is higher than pH_{zpc} of the Degussa P-25 TiO_2 (6.25–6.60) [1,14], so the catalyst surface is negatively charged. This will repulse the approach of chloride ions that are released during 4-CP degradation to the surface, and retard their adsorption. Another reason may come from the competition between chloride ions with oxygen electrons, which hence reduces the formation of O_2^- free radicals then blocks the chain reaction for hydroxyl free radicals [1,20]. The undefined intermediates, which may be present during the degradation of binary mixtures of *o*-cresol and 4-CP, are also considered as a hypothesis to slower the degradation.

4. Conclusions

Photodegradation of single and binary mixtures of *o*-cresol and 4-CP was examined. The degradation rate increased at low reactant concentrations or with increasing UV light intensity. The effect of pH on *o*-cresol and 4-CP degradation decreased in the order: 9.35 > 7.46 > 4.50. The degradation of *o*-cresol and 4-CP in single system was faster than that in binary mixture system when the second reactant was in excess. The degradation kinetics of phenolic compounds in this work highlighted the applicability of the pseudo-first-order kinetics based on the Langmuir–Hinshelwood model. Finally, the hypothesis of the undefined intermediates which may be present during the degradation of *o*-cresol and 4-CP in single and binary mixture systems should be further examined to clarify this argument.

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