Effect of Operating Parameters and Kinetic Study on Photocatalytic Degradation of o-Cresol in Synthetic Wastewater with Irradiated Titanium Dioxide

Anh-Thu Nguyen, and Ruey-Shin Juang

Abstract—In this study, the photocatalytic degradation of o-cresol in synthetic wastewater using ultraviolet irradiation, TiO_2 as photocatalyst and hydrogene peroxide was studied. Photodegradation of four oxidation systems of direct photolysis, H_2O_2/UV, TiO_2/UV, and H_2O_2/TiO_2/UV was compared in a photoreactor with high-pressure mercury lamp irradiation. The effects of such parameters as catalyst loading (0-3 g/L), the initial o-cresol, solution pH (3.5-10.5), added H_2O_2 concentration (2-45 mM), and UV light intensity on photodegradation were investigated in detail. The initial rate of removal from UV alone to H_2O_2/TiO_2/UV process is 0.57×10^{-3} to 7.02×10^{-3} mM/min, respectively. Finally, the photodegradation of o-cresol was described by the Langmuir-Hinshelwood model and followed the pseudo-first-order kinetics.

Keywords—Photocatalytic degradation, o-cresol, titanium dioxide TiO_2, H_2O_2, UV light, Langmuir-Hinshelwood.

I. INTRODUCTION

CURRENTLY, TiO_2 semiconductor photocatalysis has become increasingly promising technique in environment remediation, due to its optical and electronic properties, low cost, case of availability, high stability, and non-toxicity [1], [2].

Phenolic compounds such as o-cresol are widely used in manufacturing products, for examples, herbicides, pharmaceuticals, and cresol-based resin [3]. O-cresol has been listed as one of the priority pollutants in the USA-EPA list [4]. The water solubility of o-cresol is above 24 at 25^0C [5]. Therefore, in the scheme of pollution abatement, the effective elimination of this organic compound becomes an essential requirement.

Photocatalytic degradation of different toxic organic compounds is an attractive technique for the complete destruction of undesirable contaminants in liquid phase by using artificial light [6].

In the present work, the photochemical oxidation of o-cresol in aqueous solution in a batch reactor using ultraviolet irradiation, titanium dioxide, hydrogen peroxide was studied.

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To obtain this target, the photodegradation of o-cresol was compared using different irradiation systems such as UV alone, H_2O_2/UV, TiO_2/UV, and H_2O_2/TiO_2/UV. Effects of TiO_2 catalyst loading, the pH, concentration of H_2O_2, initial o-cresol, and UV intensity on photodegradation rate were also evaluated. Moreover, the photodegradation of o-cresol in aqueous solution satisfactorily was described by the Langmuir-Hinshelwood model and followed the pseudo-first-order kinetics.

II. EXPERIMENTAL SECTION

A. Reagent

The organic compound o-cresol was purchased from Alfa Aesar, Britain. Other chemicals including NaOH, and HCl were offered from J.T. Backer, USA, methanol from Merck, Germany, and hydrogen peroxide solution (30% w/v) from Sigma-Aldrich, Germany. Photocatalyst TiO_2 (P-25, ca. 70% anatase and 30% rutile), offered from Degussa, Japan, has a BET specific surface area of 53.33 m^2/g and an average particle size of 50 nm measured by FESEM (JSM-6701F, UK) as shown in Fig. 1. The light source used was a water-cooled 20 W low-pressure UV lamp (UVL20PH-6, SEN Japan) and 100 W high-pressure mercury lamp (HL100CH-5, SEN Japan).

B. Experimental Setup

All experiments were performed in a batch photoreactor, as shown in Fig. 2. It consisted of a cylindrical Pyrex-glass cell (1.0 L capacity) with an inner diameter and height of 10 cm and 10 cm, respectively. A 100-W high-pressure mercury lamp was located in the reactor center within a 50 mm diameter double-wall cooling tube. The lamp and tube were immersed in the reactor cell with a light path of 80 mm.

C. Photodegradation Process

The reactor was filled with 0.8 L of the aqueous solution containing o-cresol, to which Degussa TiO_2 P-25 powder was added (1 g/L). The suspended solution was kept uniform by agitation with a magnetic stirrer (100 rpm). The pH value of solution was adjusted by the addition of 0.1 M NaOH or HCl that was monitored by a digital pH meter (Horiba F-23, Japan). The temperature of the photoreactor was kept constant at 25 ± 1^oC by a water-cooling jacket (Eyela, NCB-2600, Japan). The time at which the UV lamp was turned on was considered time zero or the beginning of the experiment.

D. Analytical Methods

Experiments were performed for 180 min. The liquid samples (1 mL) were taken at preset time intervals (every 30 min). The samples were filtered through a 0.45 µm syringe filter (Millipore) to remove TiO_2 particles before being stored in a brown glass bottle for analysis of compound concentration by HPLC (Jasco, Japan). The column employed was the Merck LiChroCART® 250-4.6 (250 mm length, 4.6 mm diameter), packed with Purospher® STAR RP-18 endcapped (5 µm).

A mixture of methanol (60%, v/v) and deionized water was used as the mobile phase at flow rate of 1.0 mL/min. An aliquot of the sample (10 µL) was injected by auto-sampling of HPLC (Jasco, Japan) and analyzed at a wavelength of 280 nm.

Each experiment was duplicated at least under identical conditions. All solutions were prepared with deionized and doubly distilled water throughout this study.
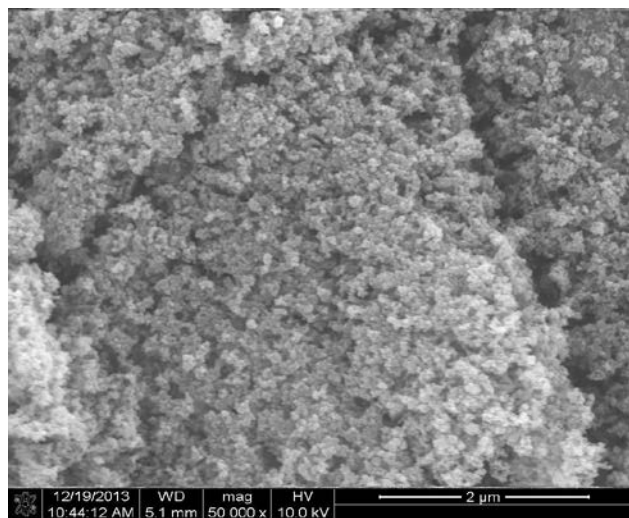

Fig. 1 The FESEM picture of TiO_2 P-25 particles

III. RESULTS AND DISCUSSION

A. Effect of operating parameters on o-cresol photodegradation

Aqueous solutions of *o*-cresol were irradiated under various reaction conditions using direct photolysis (UV alone), H_2O_2/UV, TiO_2/UV, and H_2O_2/ TiO_2/UV processes. Fig. 3 shows the change in degree of degradation versus irradiation time of aqueous solution of *o*-cresol. Direct photolysis of *o*-cresol with 100-W UV lamp alone leads to a negligible phenol removal only 12 % within 180 min. About 57% of *o*-cresol is degraded when 2.0 mM H_2O_2 is added. When the solution is treated with 1 g/L TiO_2 under UV irradiation, the obtained removal is 73%. Besides, the combination of two processes (H_2O_2/TiO_2/UV) improves phenol removal up to 96%. The results of percentage removal of photodegradation are calculated as follows:

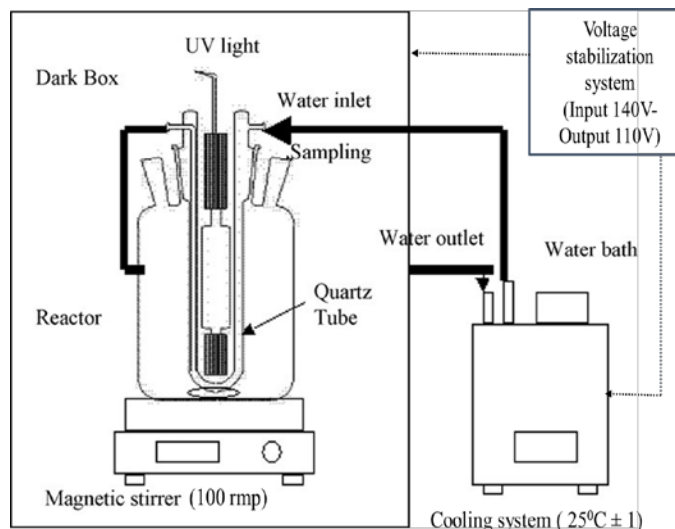$$\text{Removal } \% = 100*[(C_0 - C)/C_0] \qquad (1)$$

Fig. 2 Schematic diagram of the experimental set-up for the photoreactor

Where C_0 is initial concentration of compound, C is concentration of compound after photo-irradiation (Eq. (1)).
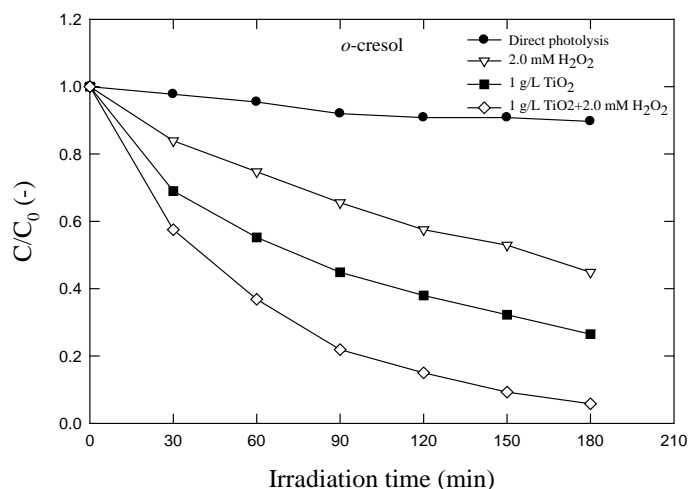

Fig. 3 Effect of various oxidation process on *o*-cresol removal using UV light-100 W at 25^0C ($C_0 = 0.45$ mM, 1 g/L TiO_2, 2.0 mM H_2O_2)

Although the Langmuir-Hinshelwood model is developed to describe gas-liquid reactions, it is widely used for liquid-solid reactions. In other words, it is used to describe the kinetics of photocatalytic reactions of aquatic organics [7].

The Langmuir-Hinshelwood model basically relates the degradation rate (*r*) and the concentration of organic compound (*C*), as shown in Eq. (2), where k_r is the intrinsic rate constant and K_{ad} is the adsorption equilibrium constant. When the adsorption is relatively weak or the concentration of organic compound is low, the Eq. (2) can be simplified to the first-order kinetics with an apparent rate constant k_{app} (Eq. (3)).

$$r = -\frac{dC}{dt} = \frac{k_r K_{ad} C}{1 + K_{ad} C} \qquad (2)$$

$$\ln\left(\frac{C}{C_0}\right) = -k_r K_{ad} t = -k_{app} t \qquad (3)$$

A plot of $-\ln(C/C_0)$ versus reaction time t yields a straight line, and the slope is the apparent rate constant.

TABLE 1
PSEUDO-FIRST-ORDER KINETICS CONSTANTS (K_{APP}), CORRELATION COEFFICIENT (R^2) AND INITIAL RATE (R_0) FOR O-CRESOL USING VARIOUS OXIDATION METHODS UNDER IRRADIATION OF 100-W UV ($C_0 = 0.45$ MM, 1 G/L TIO$_2$, 2.0 MM H$_2$O$_2$)

System	k_{app} (min^{-1})	R^2	r_0 (mM/min)
Direct photolysis	1.1×10^{-3}	0.971	0.57×10^{-3}
H$_2$O$_2$/UV	3.7×10^{-3}	0.995	1.92×10^{-3}
TiO$_2$/UV	6.3×10^{-3}	0.994	3.28×10^{-3}
H$_2$O$_2$/ TiO$_2$/UV	13.5×10^{-3}	0.999	7.02×10^{-3}

B. Effect of photocatalysis loading of TiO$_2$ on o-cresol photodegradation.

The amount of catalyst added to solution is one of important parameters in suspended photodegradation processes [8]. In order to evaluate the effect of TiO$_2$ dosage on photodegradation of o-cresol, different dosages of TiO$_2$ P-25 (0-3.0 g/L) were used to mix with solution of 0.45 mM o-cresol.

Fig. 4 shows the effect of dosage TiO$_2$ catalyst on o-cresol removal using UV light-100 W at 25^0C ± 1 ($C_{phenol,0} = 0.45$ mM, pH 7.5). It is found that the removal of direct photolysis is lowest with 12%. When the dosage of TiO$_2$ increases from 0.5 to 3.0 g/L, the photodegradation of o-cresol increases from 60% to 85%. It also shows that there is no significant difference of degradation between 2.0 g/L (83%) and 3.0 g/L (85%) of added TiO$_2$ dosage. On the other hand, compared to the other dosages of TiO$_2$, 1.0 g/L also gives the high removal for o-cresol degradation with 74%. Therefore, we decided to use 1.0 g/L TiO$_2$ for the other experiments in this study.

C. Effect of initial o-cresol concentration on photodegradation

Fig. 5 shows the photodegradation of o-cresol at different initial concentration from 0.14 to 0.91 mM on the removal using TiO$_2$/UV at 25^0C ± 1 (1g/L TiO$_2$, initial pH 7.5).

At initial concentration from 0.14 to 0.23 mM, about 96% to 98% concentration is removed for o-cresol within 90 min. It is recognized that the total amount of o-cresol degraded increases under the condition studied. However, with an increase in concentration C_0 of compound, the fraction of unreacted compound (C/C_0) increases. Therefore, it is revealed that photocatalytic oxidation is rather promising at low organic pollutants concentrations [8].

On the other hand, at a high o-cresol concentration, the active sites may be covered by o-cresol and its intermediates that cause reduced generation of e$^-$-h$^+$, which reduces photocatalytic degradation efficiency [9]. The other presumption is that as the initial o-cresol concentration increases but the light intensity, illumination time and the mass of photocatalyst are constant, hence, the $^\bullet$OH and O$_2^{2-}$ species formed on the surface of photocalyst are constant, then the relative of the $^\bullet$OH and O$_2^{2-}$ for attacking o-cresol decreases and the photodegradation decreases [10]. Another factor may be from the competition between absorbed compounds and H$_2$O molecules for photodegraded h$^+$ which is responsible for the reduction on photodegradation rate [11, 12].
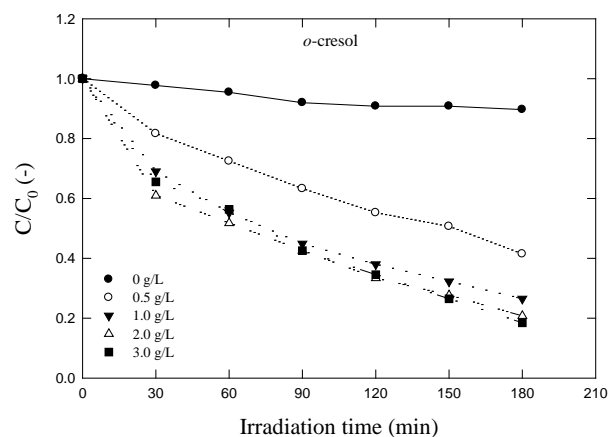

Fig. 4 Effect of dosage TiO$_2$ catalyst on o-cresol removal using UV light-100 W at 25^0C ($C_0 = 0.45$ mM, pH 7.5)
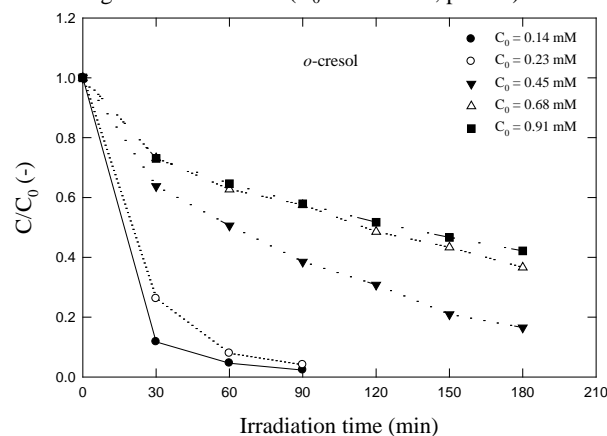

Fig. 5 Effect of the initial o-cresol concentration on the removal using TiO$_2$/UV at 25^0C (1 g/L TiO$_2$, initial pH 7.5)

D. Effect of pH on o-cresol photodegradation

Another parameter of some import in reaction involving semiconductor particle surfaces in heterogeneous media is the pH of the suspensions, as it indicates the surface of characteristics of the catalyst. The zero zeta potential for the TiO$_2$ material used here occurs at pH 5.6 [13]. The semiconductor particle surface is positively charged at more acidic pH, while at pH > 5.6 the surface is negatively charged as in Eqs. (4) and (5).

$$\text{TiOH} + \text{H}^+ \rightarrow \text{TiOH}_2^+ \tag{4}$$
$$\text{TiOH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O} \tag{5}$$

This is important consequences on the adsorption/desorption properties of particle surface of the catalyst, as well as on the photoadsorption/photodesorption features of such surfaces [10]. The influence, hence, that pH changes may have on interfacial electron transfer kinetics (photoreduction and photooxidations) is obviously [13, 14].

Fig. 6 shows the photodegradation of o-cresol at three different pH values (3.5, 7.5 and 10.5) in the TiO$_2$/UV system. Clearly, the degradation is fastest at pH 10.5 in alkaline media where the phenoxide species is present (pK_a of o-cresol is 10.316) and slowest at pH 3.5.
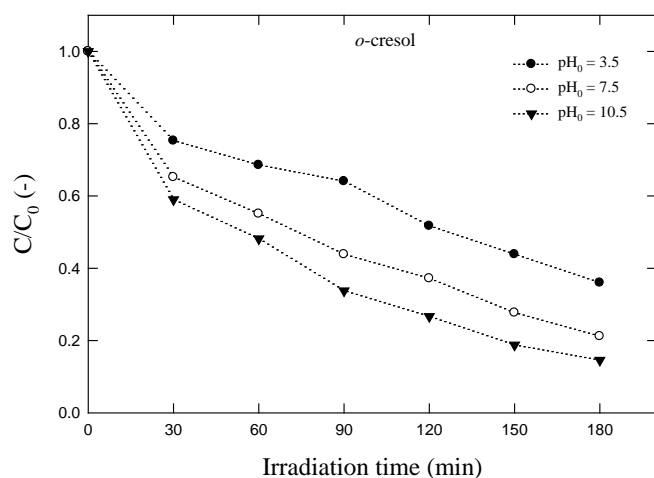
Fig. 6 Effect of the initial solution pH on o-cresol removal using TiO$_2$/UV at 25^{0}C (C$_0$=0.45 mM, 1 g/L TiO$_2$)
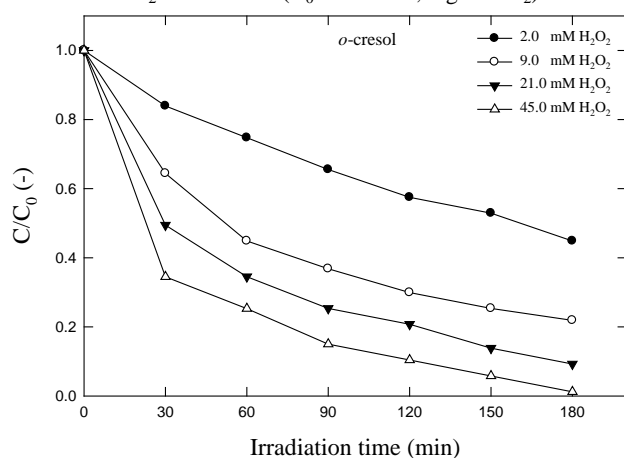

Fig. 7 Effect of the initial H$_2$O$_2$ concentration on o-cresol removal using H$_2$O$_2$/UV process at 25^{0}C (C$_0$ = 0.45 mM, initial pH 7.5)

E. Effect of added H$_2$O$_2$ concentration on o-cresol photodegradation

Aiming at having a deeper insight into the effective reactivity of $^\bullet$OH radicals and avoiding the detrimental light scattering effect due to the presence of semiconductor particles such as TiO$_2$ in this study, o-cresol were investigated in aqueous solution initially containing different amounts of hydrogen peroxide (H$_2$O$_2$/UV).

Fig. 7 shows the effect of added H$_2$O$_2$ concentration (2.0 - 45.0 mM) on o-cresol photodegradation at pH 7.5 using H$_2$O$_2$/UV system. It is found that the degradation increases with increasing H$_2$O$_2$ concentration. The addition of H$_2$O$_2$ from 2.0 to 45.0 mM leads to an increase in removal efficiency from 55% to 94% within 180 min. Besides, it is found that the color of o-cresol solution changed from no color to the light yellow after 180 min of photodegradation. This case might be explained that there was an appearance of some undefined intermediates in photodegradation reaction process.

F. Effect of UV light intensity on o-cresol photodegradation

The effect of UV light intensity (20-100 W) on o-cresol photodegradation was examined in the presence of 1.0 g/L TiO$_2$ with or without H$_2$O$_2$. Fig. 8 shows the results obtained at pH

7.5 when the initial concentration of o-cresol was fixed at 0.45 mM. It is also indicated that all the reactions followed the pseudo-first-order kinetics.
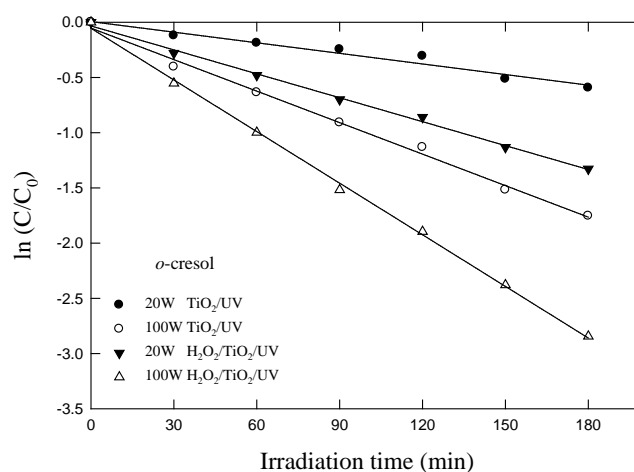

Fig. 8. Rate of o-cresol degradation at 25^{0}C and different UV light intensities (C$_0$=0.45 mM, 1 g/L TiO$_2$, 2.0 mM H$_2$O$_2$ initial pH 7.5)

TABLE 2
THE DEGRADATION RATE CONSTANTS OF O-CRESOL AT DIFFERENT UV LIGHT INTENSITIES (20W-100W) WITH TWO OXIDATION PROCESSES OF TiO$_2$/UV AND H$_2$O$_2$/TiO$_2$/UV (1 G/L TiO$_2$, 2.0 MM H$_2$O$_2$)

Rate constant	20 W		100 W	
	TiO$_2$/ UV	H$_2$O$_2$/TiO$_2$/UV	TiO$_2$/ UV	H$_2$O$_2$/TiO$_2$/UV
k_{app} (min^{-1})	3.2 x 10^{-3}	7.2 x 10^{-3}	9.5 x 10^{-3}	15.6 x 10^{-3}

The degradation rate constants with a light intensity of 20 and 100 W in the UV/ TiO$_2$ process are 3.2 x 10^{-3} and 7.2 x 10^{-3} min^{-1}, respectively, which are much less than the corresponding constants in the UV/H$_2$O$_2$/ TiO$_2$ system (9.5 x 10^{-3} and 15.6 x 10^{-3} min^{-1}, respectively), as shown in Table 2. Hence, it is found that UV light intensity has a positive effect on o-cresol removal rate.

G. Photodegradation kinetics of o-cresol

Fig. 9 shows the apparent rate constants of single o-cresol degradation in these two stages that follows a pseudo-first-order kinetics. The possible reason for leading to such transition is the threshold coverage of TiO$_2$ surface due to the adsorption of reaction intermediates, then the surface of TiO$_2$ is not yet occupied by the intermediates in the initial stage (i.e., before 30 min). After that short period, the intermediates start to occupy the surface sites, thus, decreasing the photodegradation rate of the reactant [15]. Table 3 shows the apparent rate constants k_{app} (h^{-1}) of o-cresol at different initial concentration.

The Langmuir-Hinshelwood model or pseudo-first-order kinetics are applied to study the photodegradation kinetics of o-cresol. The concentration versus time curves reveal two distinct stages: the initial (sharp) stage (t<0.5h) and the final (gradual) stage (t>0.5h).
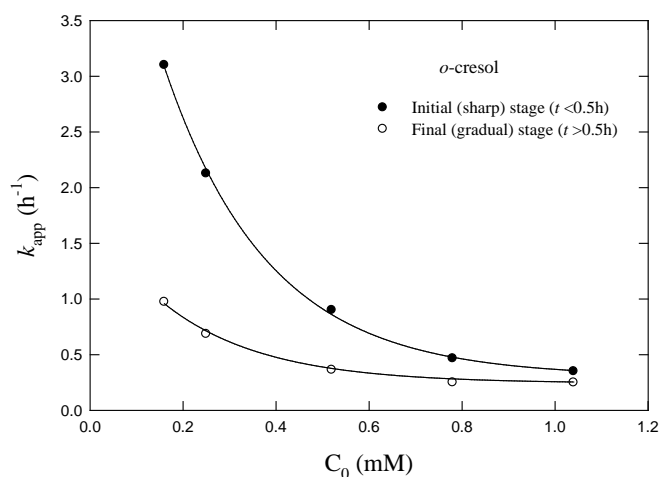
Fig. 9. Effect of the initial *o*-cresol concentration on apparent rate constant at 25^0C by using TiO_2/UV (C_0=0.45 mM, 1 g/L TiO_2)

TABLE 3
THE APPARENT RATE CONSTANTS K_{app} (H^{-1}) OF *O*-CRESOL AT DIFFERENT INITIAL CONCENTRATION

Rate constant	Initial concentration C_0 (mM)				
	0.14	0.23	0.45	0.68	0.91
k_{app} (h^{-1})	2.710	2.528	0.573	0.412	0.298

IV. Conclusions

The various experimental oxidation systems that can influence the overall rate of photodegradation of *o*-cresol have been examined in detail. The combination of UV light, TiO_2, and H_2O_2 could enhance the efficiency of *o*-cresol degradation. The optimal pH for photodegradation of *o*-cresol could be obtained at 7.5. The Langmuir- Hinshelwood model could describe the photodegradation in single system. The apparent rate constants of *o*-cresol at different initial concentration (0.14, 0.23. 045, 0.68, and 0.91 mM) are 2.710, 2.528, 0.573, 0.412, and 0.298 h^{-1}, respectively. It shows that the photocatalytic oxidation is rather promising at low organic pollutants concentrations.

References

[1] H.W. Chen, Y. Ku, Y.L. Kuo, "Effect of Pt/TiO_2 characteristics on temporal behavior of *o*-cresol decomposition by visible light-induced photocatalysis," *Water Research*, vol. 41, pp. 2069-2078, April 2007. http://dx.doi.org/10.1016/j.watres.2007.02.021

[2] C.M. Gomez, G. Del Angel, F. Tzompantzi, R. Gomez, L.M. Torres-Martinez, "Photocatalytic degradation of p-cresol on Pt/γAl_2O_3-TiO_2 mixed oxides: Effect of oxidizing and reducing pre-treatments," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 236, pp. 21-25, March 2012. http://dx.doi.org/10.1016/j.jphotochem.2012.03.016

[3] N. Shivaraman, R. Pandey, "Characterization and biodegradation of phenolic wastewater," *Journal of Indian Association for Environmental Management*, 27, pp. 12-15, 2000.

[4] M. Callahan, M. Slimak, N. Gabel, I. May, C. Fowler, J. Freed, P. Jennings, R. Durfree, F. Whitmore, B. MESTRI, "Water-related environmental fate of 129 priority pollutants. Volume 1: Introduction and technical background, metals and inorganics, pesticides and PCBs [Final Report], 1979.

[5] E. Copper, "On the relations of Phenol and Meta-Cresol to Proteins; A Contribution to our knowledge of the Mechanism of Disinfection," *Biochemical Journal*, 6(4), pp. 362-387, 1912.

[6] H.Q. Zhan, H. Tian, "Photocatlytic Degradation of Acid Azo Dyes in Aqueous TiO_2 Suspension I. The Effect of Substituents," *Dyes and Pigments*, vol. 37, pp. 231-239, 1998. http://dx.doi.org/10.1016/S0143-7208(97)00060-0

[7] T.R.N. Kutty, S. Ahuja, "Retarding effect of surface hydroxylation on titanium (IV) oxide photocatalyst in the degradation of phenol," *Mater. Res. Bull.*, 30, pp. 233-241, 1995. http://dx.doi.org/10.1016/0025-5408(94)00129-4

[8] C.H. Chiou, C.Y. Wu, R.S. Juang, "Influence of operating parameters on photocatalytic degradation of phenol in UV/TiO_2 process," *Chemical Engineering Journal*, vol. 139, pp. 322-329, 2008. http://dx.doi.org/10.1016/j.cej.2007.08.002

[9] I.K. Konstantinou, T.A. Albanis, "TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review," *Applied Catalysis B: Environment*, 49(1), pp. 1-14, 2004. http://dx.doi.org/10.1016/j.apcatb.2003.11.010

[10] S. Lathasree, A. Rao, B. SivaSankar, V. Sadasivam, K. Rengaraj, "Heterogeneous photocatalytic mineralization of phenols in aqueous solutions," *Journal of Molecular Catalysis A: Chemical*, 223(1-2), pp. 101-105, 2004. http://dx.doi.org/10.1016/j.molcata.2003.08.032

[11] U.I. Gaya, A.H. Abdullah, "Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 9(1), pp. 1-12, 2008. http://dx.doi.org/10.1016/j.jphotochemrev.2007.12.003

[12] Y. Abdollahi, "Photodegradation of o-cresol by ZnO under UV irradiation," *International Journal of Chemistry*, 2, ISSN 2306-6415, 2012.

[13] R. Terzian, N. Serpone, C. Minero, E. Pelizzetti, "Photocatalyzed Mineralization of Cresols in Aqueous Media with Irradiated Titania", *Journal of Catalysis*, vol. 128, pp. 352-365, 1991. http://dx.doi.org/10.1016/0021-9517(91)90294-E

[14] M. Gratzel, "Heterogeneous Photochemical Electron Transfer", *CRC*, Boca Raton, FL, pp. 125, 1989.

[15] C.H. Chiou, C.Y. Wu, R.S. Juang, "Photocatalytic Degradation of phenol and *m*-nitrophenol using irradiated TiO_2 in aqueous solution," *Separation and Purification Technology*, 62, pp. 559-564, March 2008.