PHOTOCATALYTIC DEGRADATION OF MULTIPLE CHLOROPHENOLS AS SIMULATED ENVIRONMENTAL POLLUTANTS IN $TiO_2/H_3PW_{12}O_{40}$/AG COMPOSITE FILM SYSTEM

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Abstract. Photocatalytic degradation of chlorophenols (CPs) has been attracting an increasing attention lately. In the paper, $TiO_2/H_3PW_{12}O_{40}$/Ag composite film was prepared by sol-gel method with programmed heating hydrothermal technology and spin coating technique to treat CPs. Direct photolysis of five CPs was performed according to the pseudo-first-order kinetics model, in which the photolysis rate of PCP was faster than that of the others under the simulated solar light. The results of mineralization indicated that the aromatic ring in PCP was difficult to be broken down via direct photolysis. By $TiO_2/H_3PW_{12}O_{40}$/Ag composite film, photocatalytic degradation efficiency elevated due to the enhancement of the quantum efficiency and visible-light absorption in comparison with direct photolysis as well as other reaction systems ($TiO_2/H_3PW_{12}O_{40}$ film and TiO_2 film), and the mineralization of PCP increased to 75.70%. The initial degradation rate (r_0) was in the following order as PCP (0.158 $mg \cdot L^{-1} \cdot min^{-1}$) > 4-CP (0.144 $mg \cdot L^{-1} \cdot min^{-1}$) > 2,4-DCP (0.014 $mg \cdot L^{-1} \cdot min^{-1}$) > 2,4,6-TCP (0.047 $mg \cdot L^{-1} \cdot min^{-1}$) > 2-CP (0.038 $mg \cdot L^{-1} \cdot min^{-1}$), confirming $TiO_2/H_3PW_{12}O_{40}$/Ag composite film as new catalyst to be more effective at removing for CPs.
Keywords: *direct photolysis, kinetics model, chlorine substituent, mineralization degree, degradation path*

Introduction

Chlorophenols (CPs) possess 19 homologues including mono-, di-, tri-, tetra-, and penta-chlorinated phenols, which have been widely used as pesticides, herbicides, fungicides, acaricides, and mold inhibitors (Olaniran et al., 2011; Garba et al., 2019; Yang et al., 2018; Guo et al., 2016). The position and quantity of chlorine substituent in CPs are closely correlated to their toxicity, e.g. ortho-substituted homologues are generally of lower toxicity than meta- and para-ones, and polychlorinated CPs are ascribed to increase hazardous effect for the organisms (Devillers et al., 1986; Du et al., 2016; Yu et al., 2019; Ge et al., 2017). CPs have been listed as priority pollutants by US EPA because of their adverse environmental effects, consequently, the disposal is currently one of the most serious environmental issues (Descorme et al., 2017). Photocatalytic degradation of CPs has been attracting an increasing attention lately, and numerous semiconductors have been investigated (Ku et al., 1996; Li et al., 2011; Gaya et al., 2009; Han et al., 2018; Al-Fahdi et al., 2019). TiO_2 is the most studied photocatalyst, however, the disadvantages including low quantum yield (approximately 0.14 at 365 nm) (Emeline et al., 2006), the limited solar light utilization (Meng et al., 2018), hindered its practical application.

In our previous work, an efficient plasmonic $TiO_2/H_3PW_{12}O_{40}$/Ag composite film was fabricated with an enhanced solar light photocatalytic activity due to the combined actions

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of electrons-trapping via $H_3PW_{12}O_{40}$, visible-response induced by Ag, and Schottky-junction formed between TiO_2 and Ag (Lu et al., 2017). It has been documented that the chlorine positions in chlorophenol homologues act an important role in its photo-degradation kinetics (Hugül et al., 2000; Czaplicka et al., 2006). It is well known that ·OH is a very strong activator as well as ortho- and para-directing in electrophilic aromatic substitution (Antonaraki et al., 2002). Therefore, ·OH radical that was confirmed as the main role in $TiO_2/H_3PW_{12}O_{40}$/Ag reaction system (Lu et al., 2017) can directly attack the electron-rich positions in CPs molecules with a rapid degradation rate.

The current study is aimed to compare the removal efficiency and rate between direct photolysis and photocatalytic degradation of mono-, di-, tri- and penta-chlorophenols in TiO_2, $TiO_2/H_3PW_{12}O_{40}$, and $TiO_2/H_3PW_{12}O_{40}$/Ag systems. Moreover, the influence of chlorine substituent position and quantity on photocatalytic degradation in $TiO_2/H_3PW_{12}O_{40}$/Ag system was intensively investigated. The speculation of degradation path accompanied by mineralization degree analysis was discussed. This work would provide necessary information on the development of photocatalysis technique in practical application towards CPs wastewater treatment.

Material and methods

Reagents

The titanium tetraisopropoxide (TTIP, 98%) was purchased from Sigma-Aldrich Corporation. $H_3PW_{12}O_{40}$ (guaranteed reagent, GR), isopropanol (analytical purity, AR), $AgNO_3$ (AR), 2-CP (AR), 4-CP (AR), 2,4-CP (AR), 2,4,6-CP (AR) and PCP (AR) were purchased from China Pharmaceutical Group. Other chemicals were of reagent grade and applied without further purification. Double distilled water was utilized throughout the experimental procedures.

Catalyst preparation

The combining process of sol-gel-hydrothermal route and temperature programming was employed to fabricate $TiO_2/H_3PW_{12}O_{40}$/Ag composite film, which has been described in our previous study (Lu et al., 2017). The as-prepared film was confirmed with anatase phase TiO_2, the intact saturation Keggin structure, and metallic Ag inserted into the pore structures of $TiO_2/H_3PW_{12}O_{40}$, which enhanced the quantum efficiency, visible-light absorption and further improving in the photocatalytic performance.

Direct photolysis and photocatalytic experiment

2-chlorophenol (CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), and pentachlorophenol (PCP) were selected as the targets, the corresponding molecular structures and detection conditions were listed in *Table 1*. The photocatalytic degradation of CPs was conducted in a home-made quartz photoreactor (*Fig. 1*) under the simulated solar light provided by a PLS-SXE300 Xe lamp (300 W, Beijing Trustech Co. Ltd., China) placing *ca*. 15 cm above the reactor. The lamp was equipped with cut filters to match solar light with wavelength of 320-780 nm, as well as light intensity of 200 mW/cm^2 measured by a radiometer (OPHIR, Newport, USA) (Lu et al., 2012). In the photocatalytic system, 2 pieces of coated films (Ag-$TiO_2/H_3PW_{12}O_{40}$ composite film, $TiO_2/H_3PW_{12}O_{40}$ composite film, or TiO_2 film) with a weight of *ca.* 5.0 mg were submerged in CPs solution (100 ml; 5 $mg \cdot L^{-1}$). Prior to

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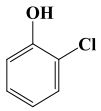
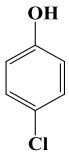
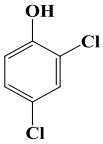
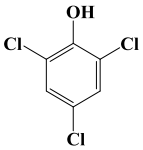
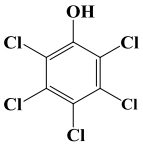
irradiation, the films were maintained in dark for 30 min to reach adsorption-desorption equilibrium of CPs. After irradiation, 2 mL CPs solution was sampled and analyzed at 30 min intervals. The experiments were carried out in triplicate. Direct photolysis were conducted in the same conditions without catalyst.

Table 1. *Molecular structures and detection conditions of CPs*

CPs	Molecular structures	Detection conditions HPLC equipped with Waters 2489 UV/visible detector and symmetry C18 (4.6 × 250 mm, particle size 5 μm)
2-CP		Mobile phase of acetonitrile (40%) and H_2O (60%, containing 0.1% acetic acid) at a flow rate of 0.7 ml·min^{-1} with a detection wavelength of 254 nm
4-CP		Mobile phase of acetonitrile (50%) and H_2O (50%, containing 1% acetic acid) at a flow rate of 1.0 ml·min^{-1} with a detection wavelength of 254 nm
2,4-DCP		Mobile phase of methyl alcohol (80%) and H_2O (20%) at a flow rate of 1.0 ml·min^{-1} with a detection wavelength of 284 nm
2,4,6-TCP		Mobile phase of methyl alcohol (80%) and H_2O (20%, containing 0.3% phosphoric acid) at a flow rate of 1.0 ml·min^{-1} with a detection wavelength of 210 nm
PCP		Mobile phase of methyl alcohol (90%) and H_2O (10%, containing 2.0% acetic acid) at a flow rate of 0.7 ml·min^{-1} with a detection wavelength of 254 nm

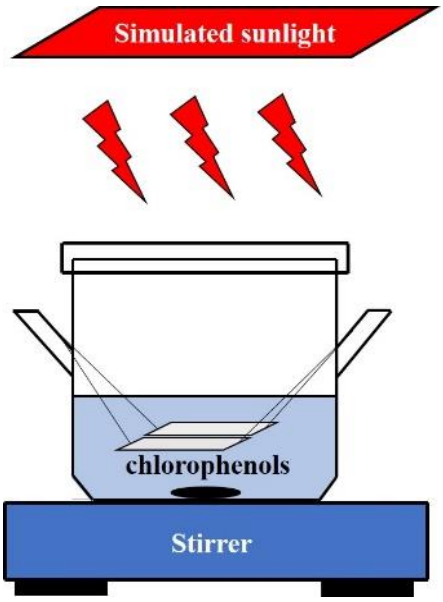


Figure 1. *Self-constructed quartz photoreactor*

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Kinetics

Direct photolysis and photocatalytic degradation kinetics was accorded to simplified pseudo-first-order kinetics (Eq. 1) when the initial concentration of target compound was low.

$$ln\ (C_0/C_t) = K_{app} \cdot t + b \quad \text{(Eq.1)}$$

$$r_0 = K_{app} \cdot C_0 \quad \text{(Eq.2)}$$

in which K_{app} is the apparent constant; C_0 and C are initial and process concentration of the target compound, respectively; t is the reaction time; b is the intercept, R value was obtained by fitting with the least square method.

Statistical analysis

Statistical analysis and linear regression were conducted using SPSS 23.0 statistical software (SPSS Inc., Chicago, USA). The differences of K_{app} and r_0 were tested by one-way ANOVA, in which the comparisons were considered statistically significant, when $P < 0.05$.

Results

Direct photolysis and photocatalytic degradation

The direct photolysis of CPs under UV light was usually studied in many previous reports (Pandiyan et al., 2002; Hong et al., 2000); however, UV light only was around 4-5 percent in sunlight. In the current study, solar simulating irradiation was selected as light source, which was more similar to that of the practical proceeded under the natural sunlight. The results (*Fig. 2*) showed that PCP represented the highest direct photolysis rate as 90.95% after 240 min irradiation, followed by 4-CP (66.05%), 2,4-DCP (50.41%), 2,4,6-TCP (43.02%), and 2-CP (5.11%), which concluded most CPs could be direct photodegraded quickly except 2-CP.

In photocatalytic degradation system, the removal efficiency of CPs was increased obviously after adding the catalysts relative to direct photolysis (*Fig. 3*). By $TiO_2/H_3PW_{12}O_{40}$/Ag film, after 120 min irradiation, the photocatalytic degradation efficiency of 2-CP, 4-CP, 2,4-CP, 2,4,6-TCP, and PCP was 48.49%, 89.89%, 94.57%, 75.15%, and 90.50%, respectively. The degradation efficiency integrally elevated when irradiation time extended to 240 min, 4-CP, 2,4-CP and PCP was hardly completely degraded, while 90.22% of 2,4,6-TCP and 82.40% of 2-CP was degraded. All the values were higher than the attained degradation efficiency in $TiO_2/H_3PW_{12}O_{40}$ or TiO_2 film reaction systems.

Kinetics

By direct photolysis (*Fig. 4* and *Table 2*), the values of initial react rate (r_0) were in order as PCP (0.051 $mg \cdot L^{-1} \cdot min^{-1}$) > 4-CP (0.021 $mg \cdot L^{-1} \cdot min^{-1}$) > 2,4-DCP (0.014 $mg \cdot L^{-1} \cdot min^{-1}$) > 2,4,6-TCP (0.011 $mg \cdot L^{-1} \cdot min^{-1}$) > 2-CP (0.001 $mg \cdot L^{-1} \cdot min^{-1}$).

By photocatalytic degradation (*Fig. 5* and *Table 3*), kinetic study was conducted by selecting TiO_2 film, $TiO_2/H_3PW_{12}O_{40}$ film and $TiO_2/H_3PW_{12}O_{40}$/Ag film as the catalyst.

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In $TiO_2/H_3PW_{12}O_{40}$/Ag composite film system, the values of initial react rate (r_0) were in order as PCP (0.158 $mg \cdot L^{-1} \cdot min^{-1}$) > 4-CP (0.144 $mg \cdot L^{-1} \cdot min^{-1}$) > 2,4-DCP (0.014 $mg \cdot L^{-1} \cdot min^{-1}$) > 2,4,6-TCP (0.047 $mg \cdot L^{-1} \cdot min^{-1}$) > 2-CP (0.038 $mg \cdot L^{-1} \cdot min^{-1}$), which was faster than that of $TiO_2/H_3PW_{12}O_{40}$ or TiO_2 film.

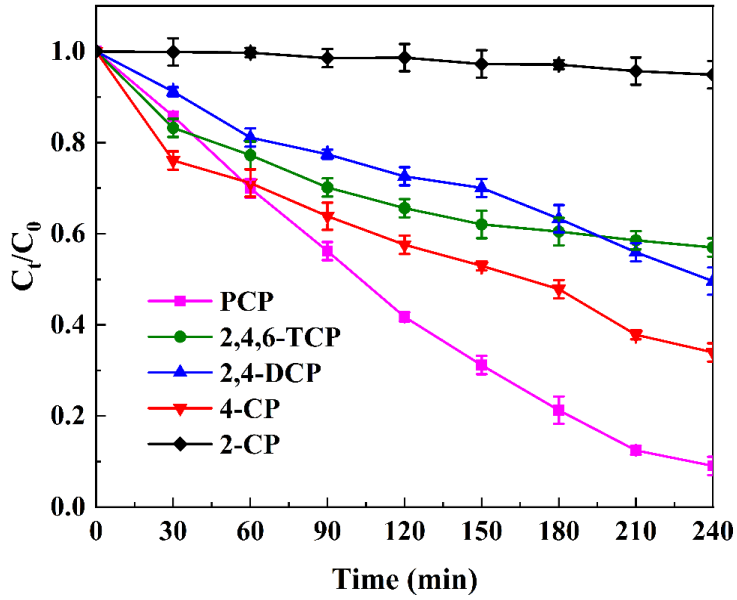

Figure 2. *Direct photolysis of CPs*

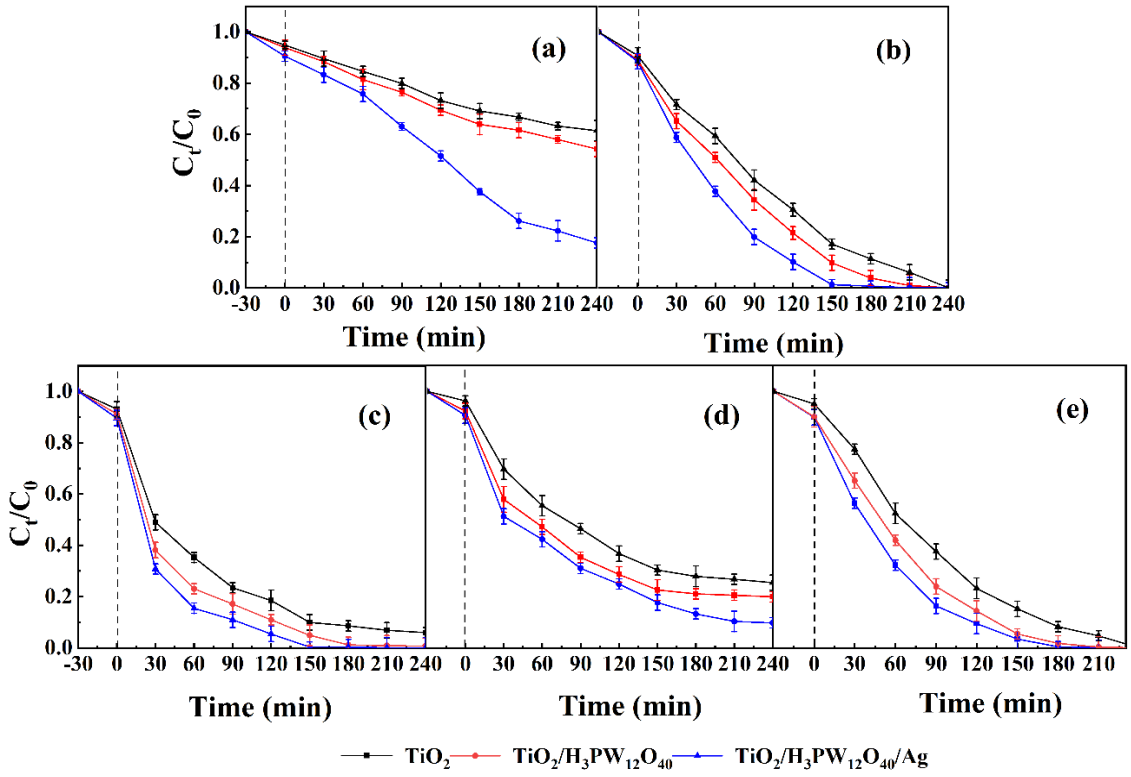

Figure 3. *Photocatalytic degradation of CPs by $TiO_2/H_3PW_{12}O_{40}$/Ag film, $TiO_2/H_3PW_{12}O_{40}$ film and TiO_2 film (a) 2-CP; (b) 4-CP; (c) 2,4-DCP; (d) 2,4,6-TCP; (e) PCP*

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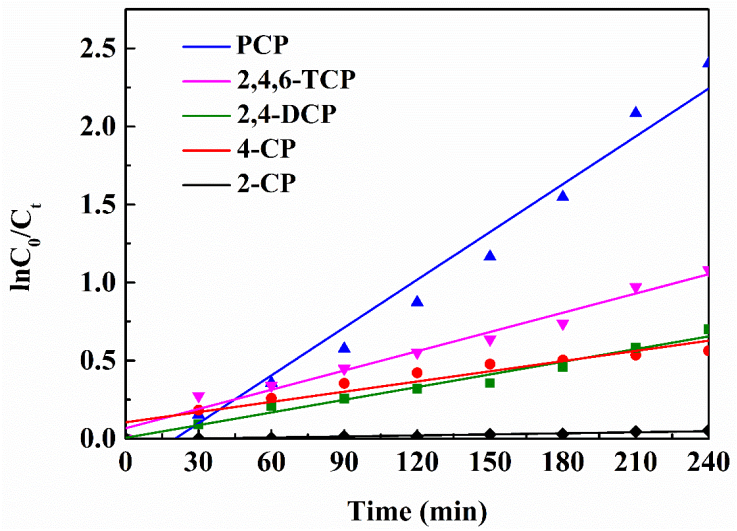

Figure 4. *Direct photolysis kinetics*

Table 2. *Direct photolysis kinetics*

CPs	Kinetic equation $ln(C_0/C) = K_{app}t$	Apparent constant K_{app} (min^{-1})	Initial rate r_0 ($mg \cdot L^{-1} \cdot min^{-1}$)	R
2-CP	y = 0.0002x – 0.0064	0.0002	0.001	0.9708
4-CP	y = 0.0041x + 0.0670	0.0041	0.021	0.9882
2,4-DCP	y = 0.0027x + 0.0058	0.0027	0.014	0.9895
2,4,6-TCP	y = 0.0022x + 0.1051	0.0022	0.011	0.9548
PCP	y = 0.0102x – 0.2070	0.0102	0.051	0.9855

Table 3. *Photocatalytic degradation kinetics*

Films	CPs	Kinetic equation $ln(C_0/C) = K_{app}t$	Apparent constant K_{app} (min^{-1})	Initial rate r_0 ($mg \cdot L^{-1} \cdot min^{-1}$)	R
TiO_2	2-CP	y = 0.0020x + 0.0410	0.0020	0.010	0.9892
	4-CP	y = 0.0129x – 0.0291	0.0129	0.065	0.9952
	2,4-DCP	y = 0.0116x + 0.2938	0.0116	0.058	0.9928
	2,4,6-TCP	y = 0.0056x + 0.1989	0.0056	0.028	0.9653
	PCP	y = 0.0146x-0.1851	0.0146	0.073	0.9928
$TiO_2/H_3PW_{12}O_{40}$	2-CP	y = 0.0025x + 0.0424	0.0025	0.013	0.9927
	4-CP	y = 0.0253x – 0.5083	0.0253	0.127	0.9695
	2,4-DCP	y = 0.0212x + 0.0697	0.0212	0.106	0.9841
	2,4,6-TCP	y = 0.0065x + 0.3175	0.0065	0.033	0.9454
	PCP	y = 0.0253x – 0.5083	0.0253	0.127	0.9695
$TiO_2/H_3PW_{12}O_{40}$/Ag	2-CP	y = 0.0075x – 0.1095	0.0075	0.038	0.9900
	4-CP	y = 0.0287x – 0.4627	0.0287	0.144	0.9665
	2,4-DCP	y = 0.0340x – 0.2204	0.0340	0.170	0.9828
	2,4,6-TCP	y = 0.0094x + 0.2502	0.0094	0.047	0.9862
	PCP	y = 0.0315x – 0.6207	0.0315	0.158	0.9657

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Mineralization degree

The mineralization of PCP (20 $mg \cdot L^{-1}$) was evaluated by monitoring the changes of TOC in both direct photolysis and $TiO_2/H_3PW_{12}O_{40}$/Ag photocatalytic degradation system. Even though degradation rate of PCP was faster than that of other CPs in the two reaction systems, the mineralization degree of PCP was approximately 25.70% in direct photolysis, whereas it reached 75.70% in the photocatalytic reaction after 720 min (*Fig. 6*).

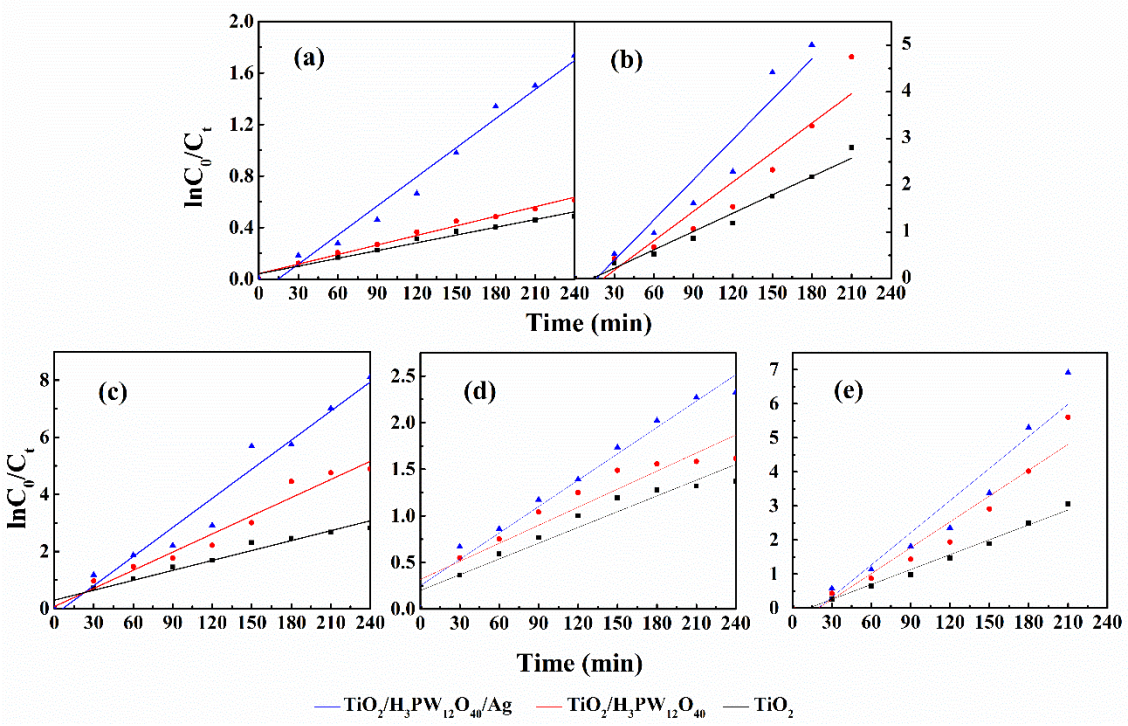

Figure 5. *Photocatalytic degradation kinetics*

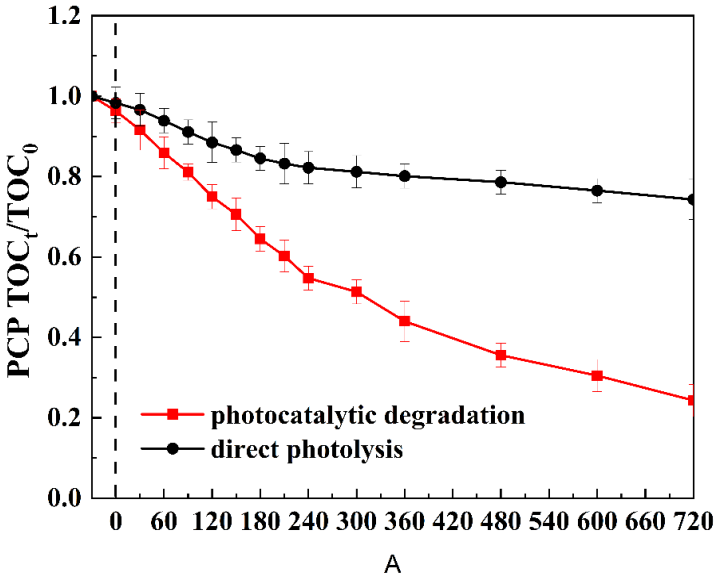

Figure 6. *TOC evolution of CPs*

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Discussion

Based on the results of direct photolysis and photocatalytic degradation, it could be concluded as follow: firstly, all position was full by chlorine atoms in PCP molecule resulting in electron density decreased on the ring due to the electron withdrawing properties of Cl atoms, making the ring less favorable to electrophilic attack, so increased degradation rate (Kim et al., 2003); secondly, degradation of 2-CP was retarded due to the formation of intramolecular hydrogen bonding between OH and Cl (Yang et al., 2014); thirdly, the degradation rate order of 4-CP > 2,4-DCP > 2,4,6-TCP was attributed to the fact that the more chlorine substituent in *meta*- position, the stronger passivation generated among them (Sundstrom et al., 1989). Therefore, the direct photolysis and photocatalytic degradation was mainly controlled by the position and quantity of substituted chlorine atoms in CPs, which were in agreement with other reports (Ko et al., 2007; Yuan et al., 2005).

As-prepared $TiO_2/H_3PW_{12}O_{40}$/Ag film showed the excellent photocatalytic property, the results showed that K_{app} of as-prepared $TiO_2/H_3PW_{12}O_{40}$/Ag reaction system increased significantly in comparison with TiO_2 system ($P < 0.05$). Because $TiO_2/H_3PW_{12}O_{40}$/Ag reaction system delayed the recombination of holes and electrons pairs efficiently owing to the synergistic effects between the Keggin unit and TiO_2 and the generation of Schottky junction at the interface between Ag and TiO_2, meanwhile expanded the absorption of visible-light due to SPR effect (Lu et al., 2017). It is worth noting that only a limited amount of *ca*. 5.0 mg $TiO_2/H_3PW_{12}O_{40}$/Ag was used in the current system, the degradation rate under simulated solar light was considerable in comparison with that in other studies (*Table 4*) even if their experimental conditions showed more advantages including of strong ultraviolet as light source or large catalyst amount.

Table 4. *Photocatalytic degradation dynamics in other reports*

CPs	Co ($mg \cdot L^{-1}$)	Catalyst	Lamp	Initial rate r_0 ($mg \cdot L^{-1} \cdot min^{-1}$)	Reference
2-CP	10	TiO_2 ($2\ g \cdot L^{-1}$)	15 W black flue fluorescent	0.047	Ku et al., 1996
4-CP	20	TiO_2/AC-PC ($2.5\ g \cdot L^{-1}$)	125 W Hg lamp	6.733	Herrmann et al., 2002
2,4-DCP	20	TiO_2 ($0.1\ g \cdot L^{-1}$)	125 W Hg lamp	0.569	Jardim et al., 1997
2,4,6-TCP	100	α-Fe_2O_3 ($1.5\ g \cdot L^{-1}$)	Solar simulator	0.231	Bandara et al., 2001
PCP	170	TiO_2 ($0.1\ g \cdot L^{-1}$)	125 W Hg lamp	0.789	Jardim et al., 1997

In the mineralization study, the photon energy of simulated solar light can only destroy Cl-C of PCP molecule successively till producing the mono-chlorinated phenol but not powerful enough to break down the aromatic ring (Skurlatov et al., 1997). In photocatalytic degradation system, the complex effect of dichlorination, hydroxylation and ring-cleavage functioned in the removal of chlorophenols (Tang et al., 1996). The specific degradation path was shown in *Figure 7*.

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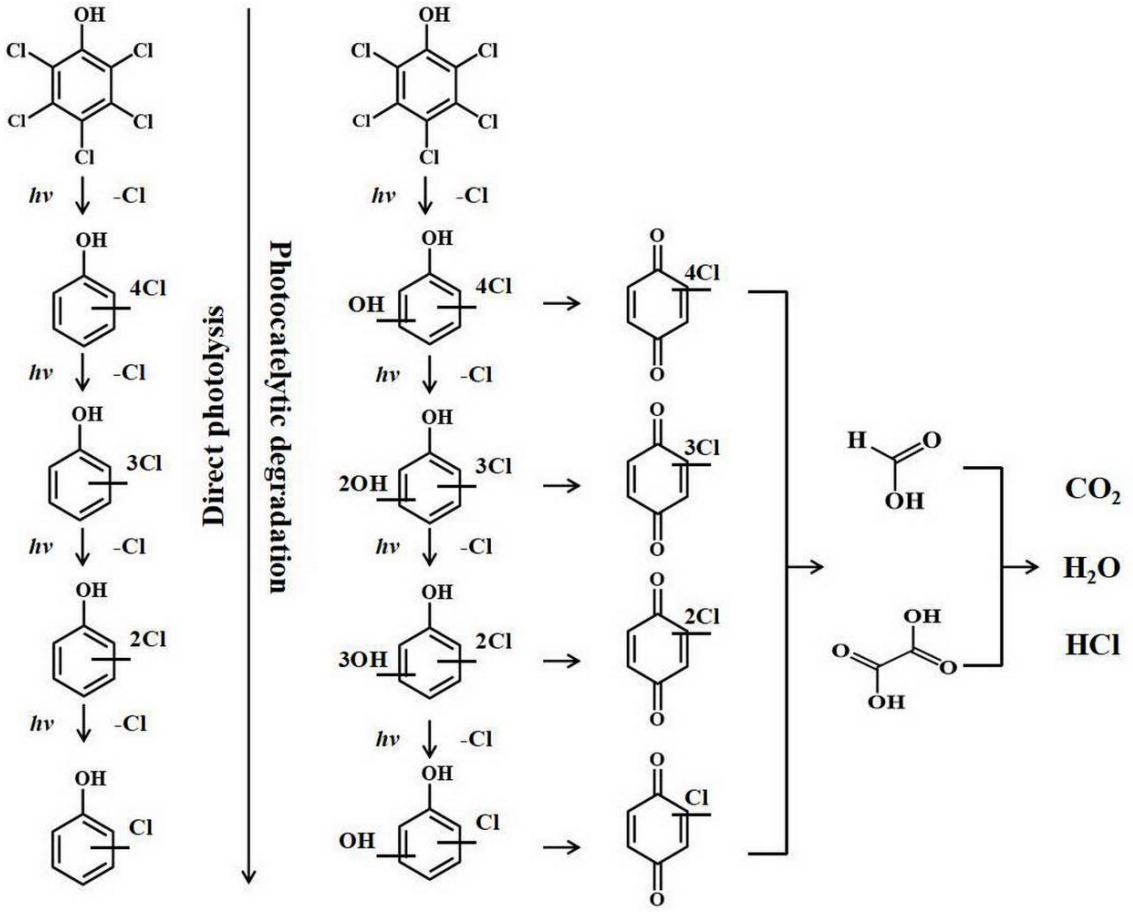

Figure 7. *Possible reaction pathway during photocatalytic degradation of PCP*

Conclusion

$TiO_2/H_3PW_{12}O_{40}$/Ag composite film as new photocatalyst represented an excellent removal efficiency towards CPs under the simulated sunlight relative to others photocatalytic system. The values of initial react rate (r_0) were in the order as PCP (0.158 $mg \cdot L^{-1} \cdot min^{-1}$) > 4-CP (0.144 $mg \cdot L^{-1} \cdot min^{-1}$) > 2,4-DCP (0.014 $mg \cdot L^{-1} \cdot min^{-1}$) > 2,4,6-TCP (0.047 $mg \cdot L^{-1} \cdot min^{-1}$) > 2-CP (0.038 $mg \cdot L^{-1} \cdot min^{-1}$) in the current system, which was related with chlorine substituent position and quantity in CPs molecules. Therein, PCP was highest degradation rate due to the decreased electron cloud density by full chlorine substituents in the phenolic ring, and 75.70% PCP (20 $mg \cdot L^{-1}$) could be mineralized after 720 min irradiation due to ·OH attack. This work will provide necessary information on the development of photocatalysis technique for chlorophenols wastewater treatment in practical application. Moreover, it can be predicted that other noble metal (Pt, Cu, et al) modified $TiO_2/H_3PW_{12}O_{40}$ will also show excellent photocatalytic performance, and the photoelectrocatalytic study of $TiO_2/H_3PW_{12}O_{40}$/Ag composite film is expected.

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