

Article Optimization of Degradation Kinetics towards O-CP in H₃PW₁₂O₄₀/TiO₂ Photoelectrocatalytic System

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Abstract: Kinetics is crucial for photoelectrocatalytic degradation of organic contaminants. A 12-tungstophosphoric acid/titania (H₃PW₁₂O₄₀/TiO₂) composite film was prepared by the sol-gel-hydrothermal route to investigate the optimal conditions and degradation kinetics of o-chlorophenol (o-CP). The photoelectrocatalytic degradation efficiency of o-CP was 96.6% after 180 min under optimum conditions (impressed voltage: 0.5 V, solution pH: 6.3, and initial concentration: $5 \text{ mg} \cdot \text{L}^{-1}$), and the apparent kinetics constant (*K'*) was a 6.0-fold increase compared to the photocatalytic system. Furthermore, the photoeletrocatalytic reaction rate of o-CP by H₃PW₁₂O₄₀/TiO₂ and TiO₂ film was 0.090 and 0.020 mg \cdot L⁻¹ · min⁻¹, respectively, and a higher apparent quantum yield ($\Phi = 32.14\%$) of H₃PW₁₂O₄₀/TiO₂ composite film was attained compared to TiO₂ film ($\Phi = 10.00\%$), owing to the fact that more photo-generated carriers were produced and effectively separated. Intermediate products identified during o-CP degradation by liquid chromatography-mass spectrometer (LC-MS) were 2-Chlorohydroquinone (CHQ), catechol (CT), and hydroxyl-hydroquinone (H-HQ). The H₃PW₁₂O₄₀/TiO₂ photoelectrocatalytic system exhibited outstanding potential for the removal of chlorinated organic contaminants in wastewater.

Keywords: degradation kinetic; photoelectrocatalytic system; $H_3PW_{12}O_{40}/TiO_2$ composite film; o-chlorophenol; impressed voltage

1. Introduction

As the most promising and widespread semiconducting material in photocatalysis and photoelectrocatalysis [1–3], TiO₂ is a remarkably stable photoactive material, which can be incorporated and immobilized in a photocatalytic system [4–7]. Consequently, an electrical potential can be directly applied to a conductive support, leading to a synergistic effect between the photocatalytic and electrocatalytic process. However, the photoexcitation and quantum efficiency is limited due to the wide band gap (3.2 eV for anatase) [8]. Due to their unoccupied W 5d orbit, polyoxometallates (POMs) can trap the photoelectron on the surface of TiO₂, which effectively restrains the recombination of the electrons and holes [9,10]. Moreover, high light harvesting efficiency can be attained through the hybridization of Ti 3d and W 5d orbits [11,12]. POMs–TiO₂ composite catalyst showed excellent photocatalytic activity towards various organic contaminants, including dyes and endocrine disrupters [13–16]. However, its photoeletrocatalytic activity was not exploited.

Kinetics is crucial for the degradation of organic contaminants in the reaction system [17,18]. Degradation kinetics can reveal the maximum catalytic capability of a heterogeneous reaction system, identify the limiting steps, and optimize the degradation rate of organic compounds [19,20]. Furthermore, the photo-generated electrons and holes of semiconductors can facilitate the degradation reactions based on the formation of radicals [21–23] in addition to the factors of impressed voltage, pH, and initial concentration of the targeted organic compound. The study of the separation



of photo-generated electrons and holes is attracting increasing attention, with investigations of quantum efficiency, carrier density, and so on [24–28], that may further reveal in-depth information on photocatalytic and photoelectrocatalytic reaction mechanisms.

Thus, in the current study, o-CP, listed as a priority pollutant by the United States Environmental Protection Agency (US EPA), was selected to reveal the kinetics of photoelectrocatalytic degradation in the POMs-TiO₂ system. In addition, the intermediate products were determined and the degradation path was studied. This study could provide essential information on the photoeletrocatalytic degradation of chloro-organic contaminants in wastewater.

2. Material and Methods

2.1. Catalyst Preparation

As a typical POMs, $H_3PW_{12}O_{40}$ was employed to prepare the $H_3PW_{12}O_{40}/\text{TiO}_2$ composite film by the easily-operated sol-gel-hydrothermal route. First, 2 mL titanium tetraisopropoxide (TTIP) was dissolved in 6 mL isopropanol and 0.03 mmol $H_3PW_{12}O_{40}$ was dissolved with 1.6 mL isopropanol under ultrasonic for 10 min. The resulting $H_3PW_{12}O_{40}$ solution was then dropped into the TTIP solution. An adequate acetic acid solution was added to slow down the hydrolysis rate of TTIP, and 2 mol·L⁻¹ HCl was used to adjust the solution to pH 2–3. Stirring was continued until a white transparent sol was obtained. The sol was heated to 200 °C at a rate of 2 °C·min⁻¹ in a Teflon-lined autoclave (Jinan Henghua Technology Co., LT, China, 316-type steel material 8mm lined with Teflon 8 mm). The resulting hydrogel was spin-coated on conductive glass (50 mm × 15 mm × 1 mm) and aged 7 days. The composite film obtained was denoted as $H_3PW_{12}O_{40}/\text{TiO}_2$ and pure TiO₂ film was prepared by using the current method in the absence of $H_3PW_{12}O_{40}$ for comparison.

2.2. Photoelectrocatalytic Degradation

A PLS-SXE300 Xe lamp (300 W, Beijing Trusttech Co. Ltd., Beijing, China) with an IR-cut filter to remove most of IR irradiation (780–1100 nm), produced light that matched well with natural solar light, with the wavelength ranging from 320 to 780 nm and light intensity of 200 mW/cm², as measured by a PD300-1Wradiometer (OPHIR, Newport, RI, USA). An CHI700E electrochemical workstation (Shanghai Chenhua Instrument Co. LTD, China) was used to provide an electric field in the reaction system and $H_3PW_{12}O_{40}/TiO_2$, Pt wire, and Ag/AgCl were employed as working electrode, counter electrode, and reference electrode, respectively. Photoluminescence spectra were recorded with a HR800 instrument (Jobin-Yvon, Paris, France) in macroscopic configuration with a 325 nm line of He-Cd laser. The immobilized composite film (ca. 4.5 mg) was immersed in a self-designed quartz reactor with o-CP aqueous solution (100 mL). The photoelectrocatalytic reaction system (Figure 1) consisted of light source, electrochemical workstation, quartz reactor, and o-CP aqueous solution.

The adsorption–desorption equilibrium experiment was carried out prior to irradiation and power-up and the o-CP solution was stirred in the dark for 30 min to ensure the o-CP molecules contacted adequately with the catalyst. During the photoelectrocatalysis reaction, fixed amounts of o-CP solution was taken out at given intervals of reaction time, and analyzed by high performance liquid chromatograph (HPLC) equipped with a Waters 2489 UV/visible detector (Shanghai Dexiang Technology Co., LTD, China) and symmetry C18 (4.6×250 mm, particle size 5 µm), using a mobile phase of acetonitrile (40%) and H₂O (60%, containing 0.1% acetic acid) at a flow rate of 0.7 mL·min⁻¹ and wavelength of 254 nm.



Figure 1. Photoelectrocatalytic reaction system.

3. Results and Discussion

3.1. Optimization of Photoelectrocatalytic Degradation Kinetics

The influence of impressed voltage (U = 0.3 V, 0.5 V, 0.8 V, and 1.0 V) on the photoelectrocatalytic degradation towards o-CP in the H₃PW₁₂O₄₀/TiO₂ system is shown in Figure 2a. After 180 min, the degradation efficiency reached 96.6% under 0.5 V which was comparably higher than that under 0.3 V (89.4%), 0.8 V (94.3%), and 1.0 V (87.3%). This was mainly attributed to the maximum amounts of photo-generated electrons in the case of the fixed light intensity (200 mW/cm²) and catalyst amount (ca. 4.5 mg) [29], and the degradation efficiency increased as voltage increased. However, the excess voltage may have caused the reallocation of the space charge layer and the Hector–Helmholtz layer, which would reduce the number of photogenerated carriers [30].

As illustrated in Figure 2b, the degradation efficiency achieved the maximum value (96.6%) at pH = 6.3 (its natural condition), due to the highest adsorption capacity of o-CP (11.2%) onto the composite film. Additionally, the photocatalytic activity of TiO₂ also peaked at 6.2 (pHpzc) [31]. The degradation efficiency decreased in both alkaline conditions (79.70% at pH = 8.1 and 73.80% at pH = 10.0) and acid condition (78.3% at pH = 4.2).

The degradation efficiency was 86.3%, 96.6%, 77.3%, 69.4%, and 64.0% with initial concentrations of 2.5 mg·L⁻¹, 5.0 mg·L⁻¹, 10.0 mg·L⁻¹, 15.0 mg·L⁻¹, and 20.0 mg·L⁻¹, respectively (Figure 2c). With a fixed catalyst amount, the highest efficiency was achieved when initial o-CP concentration was 5 mg·L⁻¹, due to the ratio of catalytic active sites to substrate molecules [32].



Figure 2. The influence of impressed voltage (**a**), pH (**b**), and initial concentration (**c**) on the photoelectrocatalytic performance of $H_3PW_{12}O_{40}/TiO_2$ film towards o-chlorophenol (o-CP) degradation.

3.2. The Photoelectrocatalytic Degradation Kinetics

Photoelectrocatalytic degradation kinetics is well described by the Langmuir–Hinshelwood (L-H)-type kinetic model (Equation (1)) assuming the rate is controlled by Langmuir-type adsorption [33].

$$r = -dC_t/dt = k_r K_a C_t/(1 + K_a C_t)$$
⁽¹⁾

where *r* is reaction rate, C_t is the process concentration of the target compound, *t* is the reaction time, k_r is rate constant, and K_a is the apparent adsorption equilibrium constant.

When the concentration is very low, and K_aC_t is much lower than 1, the above equation can be simplified as:

$$r \approx k_r K_a C_t \text{ i.e., } -dC_t/dt = k_r K_a C_t$$
⁽²⁾

Thus,

$$\ln(C_0/C_t) = k_r K_a C_t = K't \tag{3}$$

where K' is the apparent reaction constant and C_0 is the initial concentration.

The kinetics under different conditions are described and summarized in Figure 3 and Table 1. K' and r reached 0.018 min⁻¹ and 0.090 mg·L⁻¹·min⁻¹, respectively, in the H₃PW₁₂O₄₀/TiO₂ photoelectrocatalytic reaction system under optimal conditions (impressed voltage: 0.5 V, solution pH: 6.3, and initial concentration: 5 mg·L⁻¹). This was an excellent result, with a limited catalyst amount (ca. 4.5 mg) compared with related, photocatalytic research (Table 2). The degradation rate (r) of o-CP in the photoelectrocatalytic system had the greatest effect on the variation of the impressed voltage, which was 0.055 mg·L⁻¹·min⁻¹ (0.3 V), 0.090 mg·L⁻¹·min⁻¹ (0.5 V), 0.071 mg·L⁻¹·min⁻¹ (0.8 V), and 0.035 mg·L⁻¹·min⁻¹ (1.0 V), indicating that this factor may exert an essential influence on the kinetics. Compared with the photocatalytic system (degradation efficiency of o-CP was 33.7%), the efficiency increased significantly to 96.6% with optimum impressed voltage (Figure 4), and K' was enhanced by 6.0-fold in the H₃PW₁₂O₄₀/TiO₂ photoeletrocatalytic system (Figure 5 and Table 3).



Figure 3. The influence of impressed voltage (**a**), pH (**b**), and initial concentration (**c**) on the kinetics of o-CP degradation.

Influence Factor	Conditions	Initial Rate r ₀ (mg·L ⁻¹ ·min ⁻¹)	Apparent Constant <i>K'</i> (min ⁻¹)	Kinetics Equations $ln(C_0/C) = K't$	<i>R</i> ²
	0.3 V	0.055	0.011	y = 0.011x	0.991
Improceed voltage	0.5 V	0.090	0.018	y = 0.018x	0.991
impressed voltage	0.8 V	0.071	0.014	y = 0.014	0.983
	1.0 V	0.035	0.008	y = 0.007x	0.973
	pH = 4.2	0.045	0.009	y = 0.009x	0.982
Solution nH	pH = 6.3	0.090	0.018	y = 0.018x	0.991
Solution p11	pH = 8.1	0.045	0.009	y = 0.009x	0.996
	pH = 10.0	0.055	0.011	y = 0.011x	0.995
	$2.5 \text{ mg} \cdot \text{L}^{-1}$	0.028	0.011	y = 0.010x	0.988
	$5.0 \text{ mg} \cdot \text{L}^{-1}$	0.090	0.018	y = 0.018x	0.991
Initial concentration	$10.0 \text{ mg} \cdot \text{L}^{-1}$	0.090	0.009	y = 0.009x	0.987
	$15.0 \text{ mg} \cdot \text{L}^{-1}$	0.120	0.008	y = 0.008x	0.977
	$20.0 \text{ mg} \cdot \text{L}^{-1}$	0.120	0.006	y = 0.006x	0.977

Table 1. The kinetics equations of o-CP photoelectrocatalytic degradation.

 Table 2. Comparison of degradation dynamics under various systems.

Pollution Concentration	Catalyst	Lamp	Reaction Rate	References
$5 \text{ mg} \cdot \text{L}^{-1}$	$H_3PW_{12}O_{40}/TiO_2$ ca. 0.045 g·L ⁻¹	300 W Xenon lamp	$0.087 \text{ mg} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$	Our work
$5 \text{ mg} \cdot \text{L}^{-1}$	ZnO-ZnS@Polyaniline $0.5 \text{ g} \cdot \text{L}^{-1}$	104 W White visible light lamp	$0.008 \text{ mg} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$	[34]
$10 \text{ mg} \cdot \text{L}^{-1}$	TiO_2 2 g·L ⁻¹	1000 W Xenon lamp	$0.478 \text{ mg} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$	[35]

Table 3. The kinetics equations of o-CP degradation.

Conditions	Initial Rate r (mg·L ⁻¹ ·min ⁻¹)	Apparent Constant K'(min ⁻¹)	Kinetics Equations $ln(C_0/C) = K't$	<i>R</i> ²
Photocatalytic degradation	0.015	0.003	y = 0.003x	0.993
Photoelectrocatalytic degradation	0.090	0.018	y = 0.018x	0.991
TiO ₂ film	0.020	0.004	y = 0.004x	0.975
$H_3PW_{12}O_{40}/TiO_2$ composite film	0.090	0.018	y = 0.018x	0.991



Figure 4. The degradation efficiency of o-CP in photocatalytic and photoeletrocatalytic systems.



Figure 5. The reaction kinetics of o-CP in photocatalytic and photoeletrocatalytic systems.

3.3. The Kinetics of $H_3PW_{12}O_{40}/TiO_2$ Composite Film and TiO₂ Film in the Photoeletrocatalytic System

In the photoeletrocatalytic system, *r* of o-CP by H₃PW₁₂O₄₀/TiO₂ and TiO₂ film was 0.090 and 0.020 mg·L⁻¹·min⁻¹, respectively (Figure 6, Figure 7, and Table 3). The apparent quantum yield (Φ) was directly derived from *r* to the effective photon flux (I_0) under 420 nm illumination: Φ (%) = 100 × *r*/ I_0 [36]. A higher apparent quantum yield (Φ = 32.14%) of H₃PW₁₂O₄₀/TiO₂ composite film was attained in comparison with TiO₂ film (Φ = 10.00%) under optimal conditions (Table 4).



Figure 6. The degradation efficiency of o-CP by $H_3PW_{12}O_{40}/TiO_2$ and TiO_2 film in the photoeletrocatalytic system.

Table 4. The apparent quantum yield (Φ) of photoelectrocatalytic degradation.

Catalyst Type	$I_0 \text{ (mW/cm}^2)$	$r (\text{mg} \cdot \text{L}^{-1} \cdot \text{min}^{-1})$	Φ
TiO ₂ film	20	0.020	10.00%
H ₃ PW ₁₂ O ₄₀ /TiO ₂ composite film	28	0.090	32.14%



Figure 7. The reaction kinetics of o-CP by H₃PW₁₂O₄₀/TiO₂ and TiO₂ film in the photoeletrocatalytic system.

As-prepared $H_3PW_{12}O_{40}/TiO_2$ composite film showed an excellent photoeletrocatalytic property because more photo-generated carriers were produced and separated efficiently based on the capability of accepting electrons of $H_3PW_{12}O_{40}$. This was confirmed by the higher photocurrent intensity (6.2 µA) than that of TiO₂ film (3.0 µA), together with excellent stability of recycling (Figure 8) in the photocurrent response experiment, and the considerably lower photoluminescence (PL) intensity of the broad emission (with a wavelength range of 350–800 nm) in the TiO₂/H₃PW₁₂O₄₀ system compared with that of the TiO₂ system (Figure 9). Furthermore, Mott–Schottky plots (Figure 10) of both the TiO₂ film and TiO₂/H₃PW₁₂O₄₀ composite film showed a positive slope, thus their carrier densities can be estimated by the following equation:

$$N_{d} = (2/e_{0}\varepsilon\varepsilon_{0})[d(1/C^{2})/dV]^{-1}$$
(4)

where N_d , e_0 , ε , ε_{0} , and $d(1/C^2)/dV$ represent the carrier density, electron charge, the dielectric coefficient (about 170), the permittivity of vacuum, and the straight slope obtained from the plot, respectively [37]. Consequently, the carrier density of $H_3PW_{12}O_{40}/TiO_2$ composite film was 5.92×10^{22} cm⁻¹ which was higher than that of TiO₂ film (4.86×10^{22}).



Figure 8. Photocurrent density of H₃PW₁₂O₄₀/TiO₂ composite film and TiO₂ film.



Figure 9. Photoluminescence (PL) spectra of TiO_2 film and $TiO_2/H_3PW_{12}O_{40}$ composite film.



Figure 10. Mott–Schottky plots of TiO₂ film and TiO₂/H₃PW₁₂O₄₀ composite film.

3.4. The Photoelectrocatalytic Degradation Path

Under the attack of OH which was the primary radical in the $TiO_2/H_3PW_{12}O_{40}$ system [14], the intermediate products including 2-chlorohydroquinone (CHQ), catechol (CT), and hydroxyl-hydroquinone (H-HQ) were identified by LC-MS (Table 5). Furthermore, the parent and intermediate species underwent a ring-opening reaction and were finally mineralized. The possible photoelectrocatalytic degradation pathways of o-CP were as follows (Figure 11).

	m/z	Structure
o-CP	126.8	OH CI
ain intermediate products	142.8	
	108.3	он он он
	124.3	ОН

Table 5. The structure of o-CP and the main intermediate products.



Figure 11. The possible photocatalytic degradation pathways of o-CP by $H_3PW_{12}O_{40}/TiO_2$ composite film.

4. Conclusions

The as-prepared $H_3PW_{12}O_{40}/TiO_2$ photoeletrocatalytic system showed an outstanding potential for o-CP degradation with an efficiency of 96.6% after 180 min under optimum conditions, and K' was enhanced 6.0-fold compared with the photocatalytic system. Meanwhile, more photo-generated carriers were produced and separated efficiently in $H_3PW_{12}O_{40}/TiO_2$ composite film compared with TiO₂ film in the photoeletrocatalytic system. It is worth noting that the catalyst amount and the impressed voltage were only ca. 4.5 mg and 0.5 V, respectively, which together were an excellent property, indicating that this technique is more environmentally-friendly and energy-efficient and has great advantages over other techniques. It could be also be applied in the treatment of organochlorine wastewater.

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