

Study on the Photocatalytic Degradation of Monochlorophenol Pollutants by Titanium Dioxide in Aqueous Solutions

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1. Introduction

In recent years, the use of photocatalytic reaction to degrade non-biodegradable organic substances, especially the removal of toxic substances, is gradually being taken seriously. Using semi-conductors as the light-emitting sources for heterogeneous photocatalysis of organic substances in water not only completely degrades the organic substances into low molecular weight chemical compounds such as carbon dioxide and water, but also saves treatment costs because it is not necessary to add special chemicals. This is a controlled treatment method worth studying further⁽¹⁾. With increasing maturity in the treatment technology of toxic substances, lots of research results indicated that effects on the treatment of chlorophenol pollutants are excellent. Davis et al⁽²⁾ used natural light/CdS, Matthews⁽³⁾, D'Ollveira⁽⁴⁾ et al used UV/TiO₂ heterogeneous photocatalytic methods to study its feasibility in removing chlorophenols. The results were excellent. This research used batch experiment method using a especially made glass reactor to study the photocatalytic degradation of a single chlorophenol existing independently and co-existing in organic substances. Under a single reactant existence, the main research content is in changing the concentration of the substance and in constructing a kinetic model. Under the existence of two or more reactants, the solid weight of titanium dioxide is changed to study the competitive reactions of all substances.

2. Methodology

The photocatalytic reaction facilities for this research include a self-constructed 17-cm diameter round glass reactor (with acrylic water circulating layer) with a 27-cm height and 5 liters in capacity, UV light sources (TL-33, UVP Inc, Made in England), stirrer (N-04407-00, Cole-Parmer, Made in U.S.A.), constant temperature water circulating bath (TU-16A, Techne, Made in U.S.A.), acid-base controller (pH/ORP controller 3675, Jenco, Made in Taiwan). The TiO₂ used is anatase type (Janssen Chimica, Made in Belgium) with average 0.79 μ m diameter, the specific surface area is 15.2 m²/g. The concentrations of single chlorophenols in this research were measured with the HPLC (Hitachi, Made in Japan).

3. Conclusion and Discussion

Figure 1 is the change relational diagram of the five initial concentrations of 3-chlorophenol with respect to time. The reaction for the highest concentration $38 \times 10^{-5} \text{M}$ was conducted for 2 hours and was reduced to $18 \times 10^{-5} \text{M}$. The $3.8 \times 10^{-5} \text{M}$ and $1.9 \times 10^{-5} \text{M}$ concentrations separately conducted at 80 minutes and 40 minutes were observed to be completely removed. From the figure we can see that the slopes of the curves of reactants with greater initial concentrations are more consistent and the reaction slowed down when the residual concentration is reduced during the reaction period.

The TiO_2 photocatalytic reaction complied with the Langmuir-Hinshelwood model⁽³⁾⁽⁴⁾. Table 1 shows the pseudo-reaction rate constant (K') values of single chlorophenols under different control factors using this model. In this research, the reactants must first be formed into intermediate products before it can achieve complete degradation. During their formation, these intermediate products will compete with the original reactants. Their degradation and adsorption rates are different from the original reactants. This should be viewed as a new reactant that will gradually affect the whole system. That is why the K' values deduced from the experiment data cannot properly describe the photocatalytic reaction of single chlorophenols, they can only be viewed as the overall parameters for the whole system.

Figure 2 is the change relational diagram of 2-chlorophenol and 3-chlorophenol residual rates and time under the co-existence state. After 2 hours of reaction, the residual rates all reached about 15%. By observing the figure, we know that the concentration change curves of the two reactants are almost overlapped, similar to the reaction of the same products. Using the integral differential method, the pseudo-reaction rate constants of 2-chlorophenol and 3-chlorophenol computed are $14 \times 10^{-5} \text{M}$ are 0.017095 and 0.015143. The average pseudo-reaction rate constant computed for this experiment is 0.01561 with a difference of only 0.00041 with the average value of 0.01612 computed with the integral differential method. They are almost equal, indicating that 2-chlorophenol and 3-chlorophenol in the co-existence state can be viewed as a new substance.

Figure 3 is the change relational diagram of single chlorophenol residual rates and time under the co-existence state. After 2 hours of reaction, the residual rates of the three kinds of chlorophenols are reduced to about 20%. The trends and forms of the three are very similar. To ascertain the competitive position of single chlorophenol in the co-existence state, the TiO_2 amount was reduced to 0.05 g/L. The results are as shown in Figure 4. Superior and inferior groups can be differentiated since the start of the reaction period. Since the amount of TiO_2 is extremely small, the reactions of 3-chlorophenol and 4-chlorophenol are progressing almost on an overlapped curve. After 2 hours of reaction, the residual rates reached about 80%, while 2-chlorophenol was reduced to about 60%. This indicated that 2-chlorophenol actually occupied a superior position under the single chlorophenol co-existence state and has the fastest reaction rate in the competitive reaction of the three. This result is completely the same as the single reactant existence state.

4. Conclusion

Using TiO_2 with near-ultraviolet photocatalytic reaction has excellent effect on the treatment of single chlorophenol pollutants. Pollutants with concentrations smaller than $7 \times 10^{-5} \text{M}$ can be completely degraded in 2 hours. This experiment proved that the photocatalytic reaction of single chlorophenols followed the progress of the Langmuir-Hinshelwood Kinetic Model. When two kinds of single chlorophenols co-exist, they can be viewed as a new substance. Its pseudo-reaction rate constant can be deduced excellently through double the concentration of a single substance. When TiO_2 is reduced to a certain extent, the photocatalytic reactions of single chlorophenols become competitive. The ascending orders of superiority are 4-chlorophenol, 3-chlorophenol and 2-chlorophenol.

5. References

- 1) Gratzel M. (1983): Energy Resources through Photochemistry and Catalysis, Academic Press Inc.
- 2) Davis A. P., and C. P. Huang (1990): The Removal of Substituted Phenols by Photocatalytic Oxidation Process with Cadmium Sulfide. Water research 24 (5), pp. 543- 550.
- 3) Matthews R. W. (1987): Photooxidation of Organic Impurities in Water Using Thin Film of Titanium Dioxide. J. Phys. Chem. 91, pp. 3328-3333.
- 4) D'Ollveira J., G. Al-Sayyed, and P. Pichat (1990): Photodegradation of 2- and 3-chlorophenol in TiO_2 Aqueous Suspensions. ES & T 24, pp. 990-996.

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Table 1 The K' Values Obtained by Using the Langmuir- Hinshelwood Model

control factors	variables	2-chlorophenol	3-chlorophenol	4-chlorophenol
reactant concentration ($\times 10^{-5} \text{M}$)	38	0.00751	0.00346	0.00296
	15	0.01415	0.01216	0.01124
	7	0.03771	0.04503	0.06135
	3.8	0.06236	0.06896	0.10690
light intensity ($\mu\text{W}/\text{cm}^2$)	1.9	0.07857	0.09484	0.11880
	4.55	0.07980	0.07020	0.09959
	2.95	0.06236	0.06896	0.10690
	1.39	0.05273	0.04396	0.04498
	0.87	0.02554	0.04396	0.05972
pH value	0.39	0.01718	0.02279	0.06173
	2	0.06198	0.04918	0.07417
	4	0.06236	0.06896	0.10690
	5.5	0.04621	0.07606	0.12300
	7	0.03363	0.05837	0.09613
	8.5	0.01884	0.01055	0.02596
	10	0.00565	0.09798	0.02092

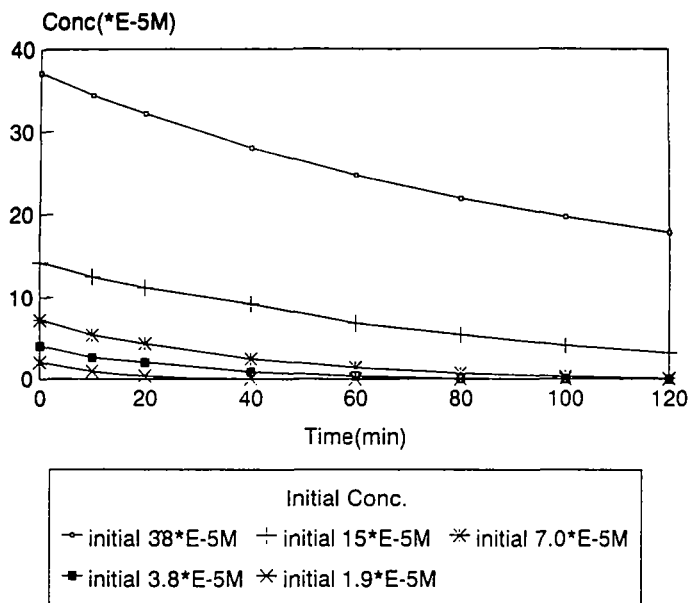


Figure 1 The Change Diagram of 3-chlorophenols with Different Initial Concentrations with Respect to Time (Light Intensity is 2.95 mW/cm², pH=4)

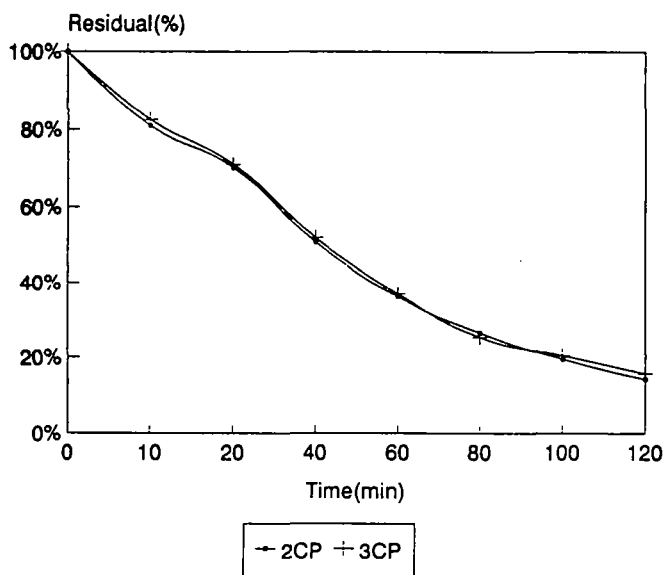


Figure 2 Residual Rates and Time Relational Diagram of 2-chlorophenol and 3-Chlorophenol under Co-existent Reaction (Initial concentrations are all $7.0 \times 10^{-5}M$)

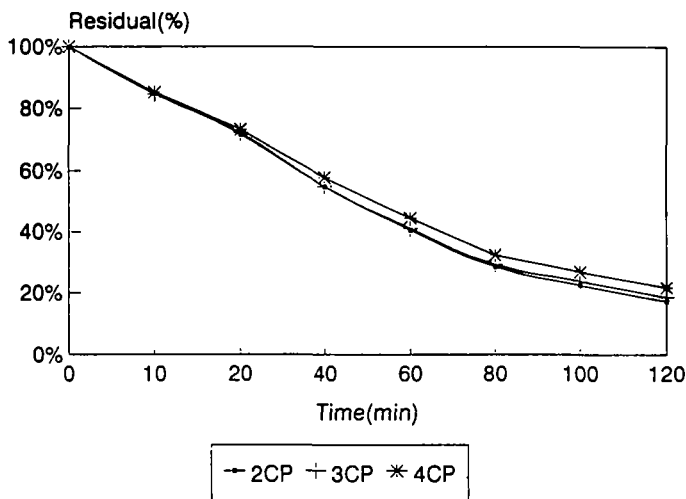


Figure 3 Residual Rates and Time Relational Diagram of 3 Single Chlorophenols under Co-existent Reaction (TiO₂ amount = 10 g/L, initial concentrations are all 7.0 x 10⁻³M)

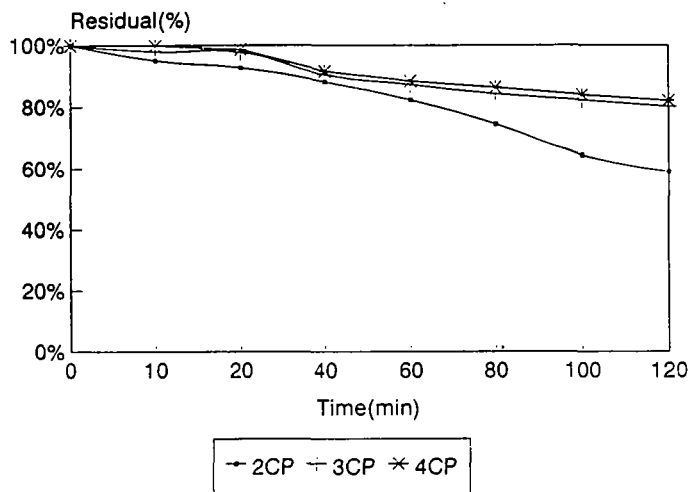


Figure 4 Residual Rates and Time Relational Diagram of 3 Single Chlorophenols under Co-existent Reaction (TiO₂ amount = 0.05 g/L, initial concentrations are all 7.0 x 10⁻³M)