

Photocatalytic degradation of phenol in aqueous solution using TiO_2/Ti thin film photocatalyst^①

FAN Cairmei(樊彩梅)¹, SUN Yarping(孙彦平)¹, MIN Yanqin(闵延琴)¹,
HAO Xiaogang(郝晓刚)¹, LI Xinjun(李新军)², LI Fangbai(李芳柏)³

(1. Department of Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China;

(2. Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510070, China;

3. Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-Environment and Soil Sciences, Guangzhou 510650, China)

Abstract: In order to clarify the respective role of the UV light, catalyst, external bias as well as their combined effects on the photodegradation process and to clarify the photocatalytic mechanism under different experimental conditions, a series of experiments were conducted in a shallow pond photoreactor with an effective volume of 100 mL using TiO_2/Ti thin film prepared by anodization as photocatalyst. A 300W UV lamp ($E_{\text{max}} = 365 \text{ nm}$) was used as side light source. The effect of light intensity on photocatalysis was also conducted. The results show that photocatalytic oxidation is an effective method for phenol removal from waters. The degradation rate can be improved by applying an anodic bias to the TiO_2/Ti film electrode, phenol can not be decomposed under only 365 nm UV light irradiation even in the presence of hydrogen peroxide. In the range of our research, the phenol removal rate can be described in terms of pseudo-first order kinetics.

Key words: phenol; TiO_2/Ti film; photocatalysis

CLC number: X 703.1; O 625

Document code: A

1 INTRODUCTION

Heterogeneous photocatalysis has been widely investigated as an alternative method for degradation of organic pollutants in recent 20 years. TiO_2 is the most investigated photocatalyst up to date because it is often used in the treatment of pollutant chemicals, based on its remarkable activity, chemical stability, and also on its non-toxic properties.

Phenol or phenolic compounds exist widely in daily life and in industrial wastewater originating from coke ovens, petroleum manufacture or paint stripping operations, and have become common pollutants in water bodies. Eleven phenolic compounds have been listed by USEPA as priority pollutants due to their stability and bio-accumulation^[1]. Shanxi is one of the coal-producing provinces of China and has heavily polluted water from coal industry, so choosing phenol as a model pollutant to study the photodegradation process is of a particular interest.

In this paper a TiO_2/Ti film prepared by anodization in sulfuric acid solution was used as photocatalyst. Many studies have been reported about the relations between fixed- TiO_2 crystallographic struc-

ture and surface properties and the effect of these properties on the photocatalytic properties^[2-7]. However, this study just aims to clarify the respective role of the UV light, catalyst, external bias as well as their combined effects on the photodegradation process, and to clarify the photocatalytic mechanism under different experimental conditions. This study may provide valuable information leading to a better understanding of the photocatalytic degradation performance.

2 EXPERIMENTAL

2.1 Material

Titanium foil (0.127 mm thick, 99.7% in purity) and copper foil (0.127 mm thick, 99% in purity) were purchased from Aldrich. Phenol chemical was analytic grade and was used without any further purification. All of the other chemicals used were of the reagent grade.

2.2 Preparation of titanium dioxide films

Before making titanium dioxide film, the foil was cleaned by using acetone and a subsequent rinse

① **Foundation item:** Project(29776032, 20006011) supported by the National Natural Science Foundation of China; project(20001013) by the Natural Science Foundation of Shanxi Province; project(010873) by the Natural Science Foundation of Guangdong Province

Received date: 2002 - 05 - 24; **Accepted date:** 2002 - 10 - 08

Correspondence: FAN Cairmei, PhD; Tel: + 86-351-6018193; E-mail: Fanem@163.com

in distilled water. The thin films of titanium dioxide for the photocatalytic studies were prepared by anodic oxidation of titanium foil in sulfuric acid solution using an electrophoresis power supply (self-made). A same size copper foil in size of 60 mm × 10 mm was used as cathode. The film growth was under combined galvanostatic/potentiostatic control, that is, the anodization was undertaken at a constant current density of 280 mA/cm² until the cell voltage reached a specified value 210 V and then the potential was maintained until the current had dropped down to a steady-state value. The freshly generated titanium dioxide film electrode was then washed by distilled water and dried in an oven at 100 °C for 1 h. By X-ray diffraction detection an anatase crystalline form of titanium dioxide was obtained under this experimental condition.

2.3 Photoreactor and light source

A batch photoreactor system was used, as shown in Fig. 1, which consists of a shallow pond glass reactor, a 300W UV high pressure Hg-lamp ($E_{\max} = 365$ nm made by Shanghai Yaming Lamp Plant) and a potentiostat (EG&G pare Model 363). The lamp was placed at the top of the reactor as the side light source to provide UV radiation and can be adjusted for different light intensity. A cutoff filter (self-made) was utilized in the road of light to remove wavelengths below 300 nm and guarantee only > 300 nm irradiation. The photoreactor has an effective volume of 100 mL, in which TiO₂/Ti film as photocatalyst was just placed under the surface of solution. During the photocatalytic reaction the phenol solution was aerated by bubbling air and irradiated by UV light. At different irradiation time intervals, the samples of phenol solution were drawn and analyzed for determining the concentration of phenol and COD.

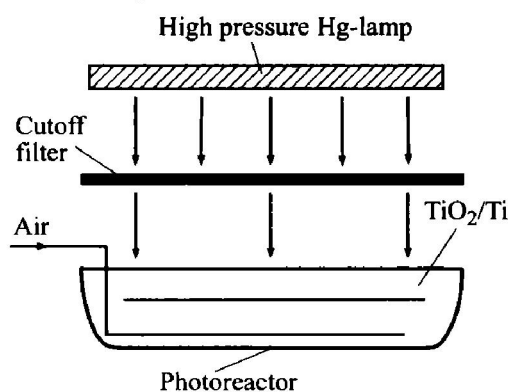


Fig. 1 Scheme of photoreactor system

2.4 Degradation of phenol

Photooxidation tests of phenol included four sets for different objectives. The first set of photodegradation tests was carried out under UV irradiation for 3.0 h with an initial content of 100 mg/L and differ-

ent treating processes of UV, CA (catalysis), PC (photocatalysis) and PEC (photoelectrocatalysis) to determine the degree of phenol degradation, in order to clarify the respective role of UV, catalyst, external bias, light cutoff filter as well as their combined effect played in the photocatalytic process. The second set of photooxidation tests was performed to determine the mineralization of phenol. The third set of photooxidation tests was designed to measure the degradation of phenol under different light intensity. The last set of photooxidation tests was carried out to investigate the photodegradation of phenol affected by hydrogen peroxide under the same experimental condition in three different processes of UV + H₂O₂, PC + H₂O₂ and UV + without filter + H₂O₂, and to clarify the photodegradation mechanism.

2.5 Analytical methods

Phenol samples were withdrawn at desired time interval during reaction for analysis. The concentration of phenol in the solution was analyzed by a UV-VIS spectrophotometer (Shanghai Third Analytic Instrument Plant) at 510 nm by 4-aminantipyryr method. COD concentration in water samples was measured by a COD instrument HH-5 (Jiangsu Electroanalytic Instrument Plant) with results expressed in mg/L.

3 RESULTS AND DISCUSSION

3.1 Degradation of phenol

Fig. 2 shows the plots of remaining rate vs time for phenol degradation under different experimental conditions. This set of experiments included five tests with the same initial phenol content of 100 mg/L, $I = 2.57$ mW/cm² and same initial pH of 7.0, but with different treating processes of adsorption, photolysis without cutoff filter, photolysis, photocatalysis and photoelectrocatalysis with cutoff filter to clarify the role of catalyst, UV light, light filter, electrical bias as well as their combined effect, respectively, in the process of phenol degradation. It may be important to compare these processes for better understanding the photooxidation performance.

Test 1 (adsorption process) was conducted in a dark condition without UV irradiation. The experimental results demonstrate that a little degradation of phenol occurs during the first half hour due to the adsorption of phenol on the surface of TiO₂/Ti film and a recovery of phenol in the solution due to the desorption of the film at the later stage.

Test 2 (direct photolysis) was performed with a light intensity of 2.57 mW/cm² without a cutoff filter in the absence of TiO₂/Ti film catalyst representing the direct UV oxidation. The degradation rate of 21.4% of phenol in solution was achieved after irradiation for 3.0 h. It may arise from photodegradation

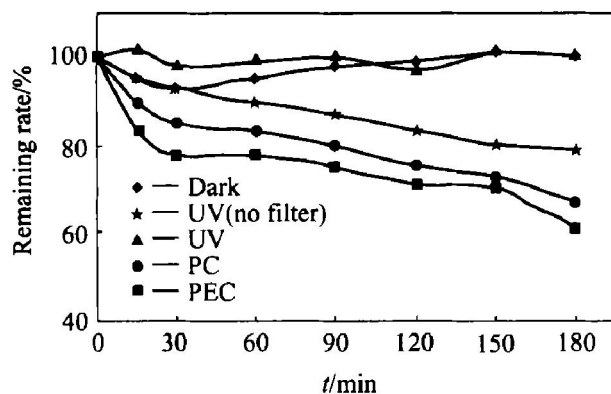


Fig. 2 Plots of remaining rate vs time for phenol degradation

excited by a slight far-UV light owing to the light spectra of the high pressure Hg-lamp with wavelengths below 300 nm and phenol molecules absorbing the UV light at $E_{\max} = 275$ nm. This is in conformity with Draper's first law of optical chemical reaction.

Test 3(photolysis) was carried out with a light intensity of 2.57 mW/cm^2 using a cutoff filter in the absence of TiO_2/Ti film catalyst representing the UV oxidation. The results show that almost no degradation of phenol in aqueous solution is achieved after irradiation for 3.0 h. This means that this kind of light can not decompose phenol. On the other hand, this also proves that the cutoff filter is very effective. That is, the degradation of phenol at this condition is not affected by light below 300 nm wavelengths, so the degradation of phenol in the following tests was performed under irradiation of > 300 nm wavelengths, mainly at $E_{\max} = 365$ nm.

Test 4(photocatalysis) was then carried out with UV light ($I = 2.57 \text{ mW/cm}^2$) combined with TiO_2 photocatalyst representing the PC oxidation. The experimental results demonstrate that the degradation of phenol in the PC oxidation achieves a better performance for phenol oxidation, which means that the combined efforts achieved a higher reaction rate. Therefore it can be inferred that the degradation of phenol resulted from photocatalytic oxidation, UV light and photocatalyst is two indispensable elements for PC process under 365 nm irradiation.

Test 5(photoelectrocatalysis) was executed under UV irradiation ($I = 2.57 \text{ mW/cm}^2$) using the TiO_2/Ti film as a working electrode and a copper foil as a counter electrode, in which the two electrodes were placed in parallel and connected to the potentiostat with applying 0.5 V electrical bias representing the PEC oxidation process. Several studies^[8-10] indicated that the externally applied anodic bias greatly improves the efficiency of charge separation by driving the photogenerated electrons via the external circuit to the counter electrode, thus enhances the reaction rate in the PEC degradation process. In our cas-

es, the experimental results demonstrate that the reaction rate of phenol degradation in the PEC process is faster than that in the PC process, but it does not express very distinct improvement, although it achieves the best performance compared with the other processes.

3.2 Mineralization of phenol

In order to study the mineralization of phenol, the COD concentration was also monitored against the reaction time and compared with the variation of phenol concentration as shown in Fig. 3. This photocatalytic experiments were conducted under the initial phenol content of 100 mg/L, $\text{pH} = 7$, $I = 2.57 \text{ mW/cm}^2$. The phenol concentration and COD concentration were reduced slowly during the reaction period, but the former was reduced faster than the latter. After 6.0 h reaction, the phenol removal was 61.2% and the COD removal was 50.5%, which indicates the reaction has only achieved an incomplete mineralization of phenol, and a longer irradiation time is needed for phenol to complete mineralization.

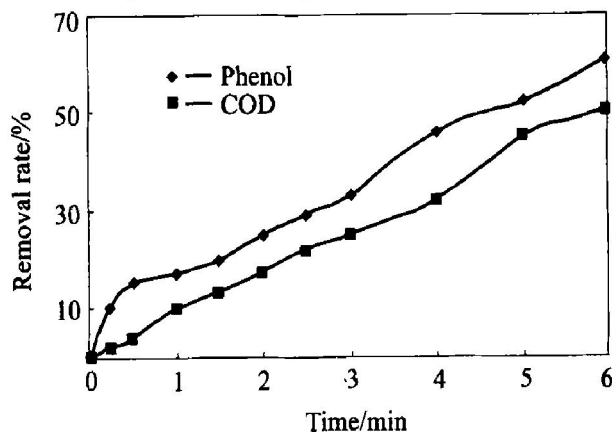


Fig. 3 Plots of removal rate vs time for phenol degradation

The photocatalytic partial oxidation can be also detected via detecting the products of partial oxidation. In our previous study^[11] of phenol degradation in a channel reactor, aromatic intermediate products, such as catechol, hydroquinone and benzoquinone were detected quantitatively in the course of the photoelectrochemical degradation of phenol, among them catechol is the main phenolic intermediate.

3.3 Effect of light intensity

The intensity of incident light is one of the major factors in the photocatalytic process. This set of tests was conducted under different light intensities of 0.78, 1.29, 2.57 and 4.43 mW/cm^2 by changing the vertical distance between light source and photoreactor. The experimental results show that the phenol removal increases with the increasing of light intensity as shown in Fig. 4. The reason is that for certain

light source, the higher light intensity leads to the more photon received by catalyst and then the more photogenerated e^- and h^+ as well as the more $\bullet OH$ radicals. The linear relationship between $-\ln(\rho/\rho_0)$ and irradiation time means that the degradation of phenol follows the pseudo first-order kinetics. When the light intensity is higher than 5.0 mW/cm^2 , it will warm up the reaction solution, leading to the volatilization of phenol. So in our experiment the light intensity was controlled below 5.0 mW/cm^2 .

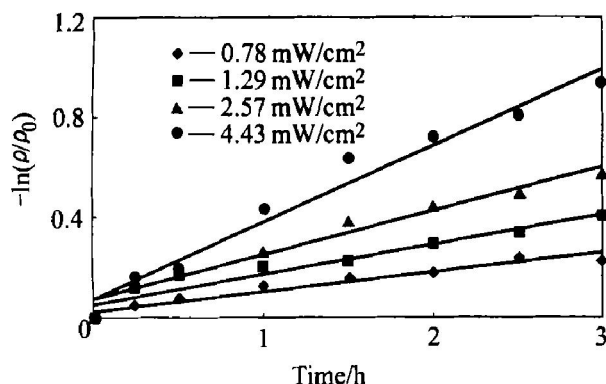


Fig. 4 Effect of light intensity on photocatalysis

3.4 Effect of H_2O_2

A set of photodegradation tests was designed to investigate the photodegradation of phenol affected by peroxide hydrogen at the same experimental conditions $\rho_0 = 100 \text{ mg/L}$, $pH = 7$, $I = 2.57 \text{ mW/cm}^2$ in three different processes of $UV + H_2O_2$, $PC + H_2O_2$ and $UV + \text{without filter} + H_2O_2$. The experimental results are illustrated in Fig. 5, in which the data of UV and PC process are also expressed for comparison.

It is well known that the $UV + H_2O_2$ process is a homogeneous AOP and has been proven to be effective in treating waters containing a number of aliphatic and aromatic compounds^[12]. Generally, the effectiveness of homogeneous light-driven oxir

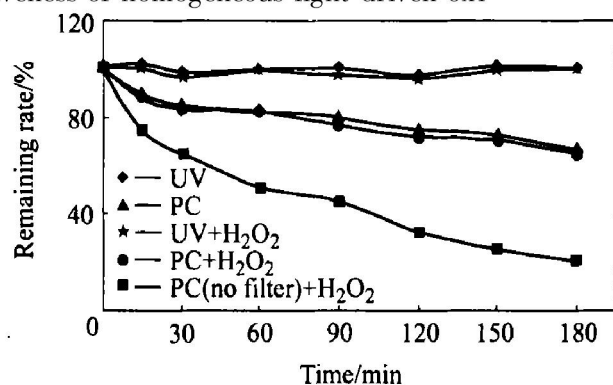


Fig. 5 Effect of H_2O_2 on degradation of phenol

ation processes is associated with very reactive species—hydroxyl free radicals, which are generated in the reaction mixture by the direct photolysis of H_2O_2 under UV irradiation: $H_2O_2 + h\nu \rightarrow 2\bullet OH$, the

hydroxyl radicals attach organic compounds relatively non-selectively^[13, 14]. Therefore the key factor to obtain hydroxyl radicals is closely connected with the light source. As shown in Fig. 5, there is almost no distinction between $UV + H_2O_2$ and UV process, indicating that homogeneous reaction does not take place in the process of $UV + H_2O_2$, and the same situation is obtained in the process of $PC + H_2O_2$. But on the other hand it can be deduced that the formation of hydroxyl free radicals in the PC process is supplied by the reaction of positive holes with water and OH^- on the surface of titanium dioxide. In the process of $PC + H_2O_2$ without a filter the degradation of phenol is significantly enhanced, which means that the production of hydroxyl radicals from hydrogen peroxide requires a large dissociation energy in order to cleave the $O-O$ bond, that is to say, short wave UV energy is necessary to lead to useful radical yields.

4 CONCLUSIONS

1) The photocatalytic oxidation is an effective method for degradation phenol in water using TiO_2/Ti thin film as photocatalyst. The removal rates of phenol depend on the external bias, light source, light intensity and other factors. The applied anodic bias can improve the efficiency of charge separation and hence enhance the reaction rate of photodegradation process, but the improvement does not exhibit ideal performance.

2) There is almost no disappearance of phenol in aqueous solution in the photolytic process under irradiation of $> 300 \text{ nm}$ wavelengths, even in the presence of peroxide hydrogen. But in the process of $PC + H_2O_2$ without cutting off the $< 300 \text{ nm}$ wavelength lights the degradation of phenol is significantly enhanced, meaning that short wave UV energy is necessary to lead to useful hydroxyl radical yields. In our experimental range the phenol removal increases with the increasing of light intensity.

REFERENCES

- [1] Kieth L H. EPA's priority pollutants: what they come from where they're going? [J]. AICHE Symp Ser Water, 1980, 77(209): 249.
- [2] Dumitriu D, Bally A R, Ballif C, et al. Photocatalytic degradation of phenol by TiO_2 thin films prepared by sputtering [J]. Applied Catalysis: Environmental, 2000, 25: 83-92.
- [3] LI X Z, LIU H L, YUE P T, et al. Photoelectrocatalytic oxidation of rose bengal in aqueous solution using a Ti/TiO_2 mesh electrode [J]. Environ Sci Technol, 2000, 34(20): 4401-4406.
- [4] LI X Z, LI F B, FAN C M, et al. Photoelectrocatalytic degradation of humic acid in aqueous solution using a Ti/TiO_2 mesh photoelectrode [J]. Water Res, 2001, 36

- (9): 2213 - 2222.
- [5] LI X Z, FAN C M, SUN Y P. The enhancement of photocatalytic oxidation of humic acid in TiO_2 suspension by increasing cation strength [J]. *Chemo Sphere*, 2002, 48(4): 453 - 460.
- [6] LI F B, WANG L Y, LI X J, et al. Preparation and properties of innovative Ti/ TiO_2 mesh photoelectrode for methyl orange photoelectrocatalytic oxidation [J]. *The Chinese Journal of Nonferrous Metals*, 2001, 11(6): 977 - 981. (in Chinese)
- [7] Vinodgopal K, Hotchandani S, Kamat P V. Electrochemically assisted photocatalysis: TiO_2 particulate film electrodes for photocatalytic degradation of 4-chlorophenol [J]. *J Phys Chem*, 1993, 97(26): 9040 - 9044.
- [8] Kesselman J M, Lewis N S. Photoelectrochemical degradation of 4-chlorocatechol at TiO_2 electrodes: Comparison between sorption and photoreactivity [J]. *Environ Sci Technol*, 1997, 31(8): 2298 - 2305.
- [9] Hidaka H, Kazukiko T S, Zhao J, et al. Photoelectrochemical decomposition of amino acids on a TiO_2 /OTE particulate film electrode [J]. *J Photochem Photobiol*, 1997, 109: 165 - 170.
- [10] Vinodgopal K, Stafford U, Gray A K, et al. Electrochemically assisted photocatalysis—2. The role of oxygen and reaction intermediates in the degradation of 4-chlorophenol on immobilized TiO_2 particulate films [J]. *J Phys Chem*, 1994, 98(27): 6797 - 6803.
- [11] FAN C M, SUN Y P. Photoelectrocatalytic destruction of phenol using TiO_2 thin film and the distribution of reaction products [J]. *Journal of Taiyuan University of Technology*, 2000, 31(5): 525 - 528. (in Chinese)
- [12] Beltrán F J, Ovejero G, Acedo B. Oxidation of atrazine in water by UV light radiation combined with H_2O_2 [J]. *Wat Res*, 1993, 27(6): 1015 - 1021.
- [13] Buxton G V, Greenstock C L, Helman W P, et al. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution [J]. *J Phys Chem Ref Data*, 1988, 17(2): 513 - 886.
- [14] KU Y, WANG L S, SHEN Y S. Decomposition of EDTA in aqueous solution by UV/ H_2O_2 process [J]. *J Hazard Mat*, 1998, 60: 41 - 45.

(Edited by YUAN Sai-qian)