

Interactive Oxidation of Photocatalysis and Electrocatalysis for Degradation of Phenol in a Photoreactor

FAN Cai-mei (樊彩梅)¹, WANG Yan (王艳)^{1,2}, LIANG Zhen-hai (梁镇海)¹,
WANG Yun-fang (王韵芳)¹, HAO Xiao-gang (郝晓刚)¹, SUN Yan-ping (孙彦平)¹

(1. College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan, Shanxi 030024, China;
2. College of Chemistry and Bioengineering, Taiyuan University of Science and Technology, Taiyuan, Shanxi 030021, China)

Abstract: TiO₂/C particles as photocatalyst were prepared by dipping TiO₂ suspension solution with activated carbon and were applied in the photocatalytic–electrocatalytic degradation of phenol, the Ti/SnO₂+Sb₂O₃/PbO₂ electrode and oxygen diffusion electrode were used as anode and cathode respectively, and a 250 W ultraviolet lamp (365 nm) as side light source. The SEM results of TiO₂/C and Ti/SnO₂+Sb₂O₃/PbO₂ anode indicated that the TiO₂ on carbon particles was uniform and PbO₂ film on the surface of anode was in cauliflower form, the XRD result of oxygen diffusion electrode showed that only crystalline graphite was found. The influential parameters of degradation process such as applied cell voltage (*E*), initial concentration of phenol (*C*₀), amount of TiO₂ catalyst and air flow rate (*v*) were discussed. Under the following experimental conditions of *C*₀=50 mg/L, pH=6, *E*=2 V, TiO₂ 0.98 mg/mL, *v*=382.2 mL/min, and light intensity *I*=10.5 mW/cm², phenol could be entirely degraded, and about 89% of total organic carbon (TOC) was removed after 3 h degradation.

Key words: interactive oxidation; photocatalysis and electrocatalysis; TiO₂/C; phenol

CLC No.: X703.1; O644.11

Document Code: A

Article ID: 1009-606X(2009)05-0916-06

1 INTRODUCTION

Over the last few decades, heterogeneous photocatalytic process particularly with TiO₂ as photocatalyst had attracted considerable attention due to its high photocatalytic activity and inexpensive cost^[1], but because the slurry photocatalytic process was too difficult to separate the photocatalyst from solution in practical application, several studies were reported using immobilized TiO₂ in a fluidized bed photocatalytic process^[2-7]. On the other hand, due to the high recombination between photogenerated electrons and holes was a major limiting factor controlling the photocatalytic efficiency, many researchers applied a bias to a immobilized TiO₂ anode to decrease the recombination rate of photogenerated electron–hole pairs, and the efficiency of photocatalytic process had indeed been improved^[8-12]. Generally the photocatalysis–electrocatalysis was that TiO₂ powder was immobilized on some electric materials as photoelectrode, for instance Ti/TiO₂, Ti mesh/TiO₂ electrodes. In practice such immobilized TiO₂ photocatalysis–electrocatalysis can solve the separation problem of catalyst from solution, but the reaction area is obviously declined, compared with the slurry

photocatalytic process. Hence exploration of a novel photocatalytic–electrocatalytic system is essential for increasing the degradation efficiency.

In this study, we designed to take advantage of the combination function of photocatalysis and electrocatalysis to solve the separation problem and enhance the removal of organic pollutants from water. So TiO₂ was immobilized on activated carbon as photocatalyst, Ti/SnO₂+Sb₂O₃/PbO₂ electrode was used as electrochemical anode, oxygen electrode, which was made of acetylene black, and graphite was used as electrochemical cathode. This novel oxidation process was expected to improve the degradation efficiency of organic pollutants effectively. The reasons for such consideration may be listed as follows: (1) TiO₂/C photocatalyst can give ·OH under UV irradiation and adsorb organic pollutants; (2) the Ti/SnO₂+Sb₂O₃/PbO₂ electrode can produce ·OH electrochemically; (3) oxygen diffusion electrode can produce H₂O₂ under suitable reaction conditions, and the H₂O₂ can be converted into ·OH; (4) the quick movement of TiO₂/C particles in photoreactor can eliminate the mass transfer infection, and make the concentration of solution and ·OH radicals uniform. Therefore, the present work is very significant.

Received date: 2009-02-09; **Accepted date:** 2009-05-12

Foundation item: Supported by the National Natural Science Foundation of China (No. 20476070, 20876104); Project of Shanxi Province Science and Technology Programs (No. 20090311082)

Biography: FAN Cai-mei (1961–), female, native of Yongji City, Shanxi Province, Ph. D., professor, engaged in the study of photoelectrocatalytic degradation of organics, Tel: 0351-6018193, E-mail: fancm@163.com.

2 EXPERIMENTAL

2.1 Materials

Degussa P25 titanium dioxide was used, which is a mixture of anatase and rutile with mean size of 30 nm and specific surface area of 50 m²/g. Analytic grade activated carbon with particle size of 2.1~3.0 mm was used as the support of photocatalyst. Phenol chemical was analytic grade and used without any further purification. All of the other chemicals used were of the reagent grade.

2.2 Preparation of TiO₂/C Particles

Activated carbon particles were rinsed with distilled water, then the cleaned activated carbon particles were put into deionized water and seethed for 2 h at 100 °C. After being washed with deionized water and filtrated, the material was dried at 105 °C for 2 h, and then used for support of TiO₂. TiO₂ powder was distributed evenly in deionized water with reference to certain concentration and stirred vigorously, then the processed activated carbon particles were immersed in TiO₂ suspension solution for 4 h and the mixture was agitated all the time. Finally TiO₂/C was placed in an oven for heat treatment at programably controlled temperature to 180 °C for 2 h.

2.3 Preparation of Oxygen Diffusion Electrode and Ti/SnO₂+Sb₂O₃/PbO₂

Self-made oxygen diffusion electrode was composed of stainless steel mesh and paste of acetylene black and graphite. Firstly stainless steel mesh was cut into an 8 cm×1 cm rectangle and treated in the acetone, 0.05 mol/L H₂SO₄ and deionized water one by one. Then acetylene black and graphite were mixed at the mass ratio of 1:1, and were agitated in the presence of appropriate ethanol solution and some 60% polytetrafluoroethene (PTFE). Then the mixture underwent 10 min ultrasonic vibration. With the evaporation of ethanol, the mixture changed into paste, then the paste was coated on the stainless steel mesh and pressed in certain pressure into about 1.0 mm slice. Finally, the mixture was annealed in the muffle oven for 30 min at 360 °C.

Ti/SnO₂+Sb₂O₃/PbO₂ anode electrode was prepared by the combined method of thermal decomposition and electro-deposition, the detailed preparation procedures can be found in Ref.[13]. The sheet size of anode was 8 cm×1 cm.

2.4 Procedures of Photocatalytic–Electrocatalytic Degradation

Figure 1 shows a schematic diagram of the batch

scale experimental reactor system. The photoreactor system consists of a cylindrical quartz glass reactor, a 250 W high-pressure mercury lamp (Institute of Electric Light Source, Beijing), a potentiostat (MODEL363, England) and electrodes. The UV lamp (365 nm wavelength) used as the side light source was positioned by the cylindrical reactor, the UV lamp was surrounded by a circulating water jacket in case the temperature of reaction solution was warmed up. The photoreactor had an effective volume (V) of 100 mL, in which a Ti/SnO₂+Sb₂O₃/PbO₂ electrode as anode and an oxygen electrode as cathode were placed in parallel and connected with the potentiostat, meanwhile TiO₂/C particles as photocatalyst was just placed in the solution of phenol. During the reaction the phenol solution was irradiated by UV light and aerated by mini-type air pump to provide air and keep TiO₂/C in a fluidized state. At different irradiation time intervals, the samples of phenol solution were drawn and analyzed by 4-amionantipyrine using 721 spectrophotometer (Shanghai Third Analytic Instrument Plant) and multi N/C 3000 TOC analyzer (Analytik Jena AG).

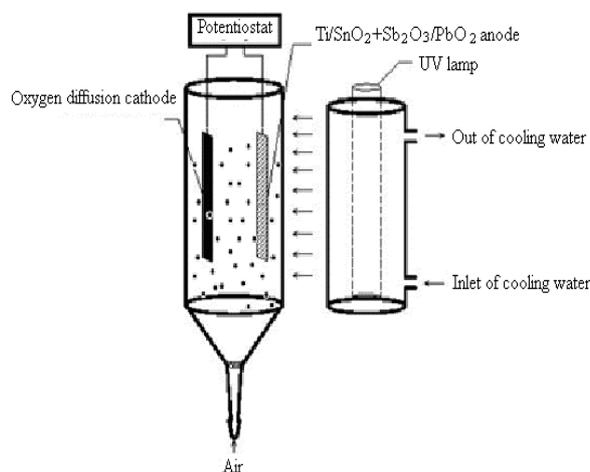


Fig.1 Schematic diagram of photoreaction system

2.5 Characterization of Electrodes

Morphology of TiO₂/C catalyst particles was observed by LEO 438VP SEM, surface structure of Ti/SnO₂+Sb₂O₃/PbO₂ was analyzed by AMHAY-IOOOB SEM, and crystal phase of oxygen diffusion electrode was investigated by Rigaku, D/max-2500 XRD.

3 RESULTS AND DISCUSSION

3.1 Characterization of the Immobilized TiO₂/C and Electrodes

Figure 2 shows the SEM micrograph of

immobilized TiO_2/C . From the figure, it can be seen that the surface of TiO_2/C is rather rough and the material on the surface shows some aggregated particulates but relatively uniform. There are some cracks on the surface, which can exactly help the immobilized TiO_2/C have a better adsorption between catalyst and contaminants all the time, and improve transfer velocity of interface electric charge, consequently the photocatalytic degradation rate may be increased.

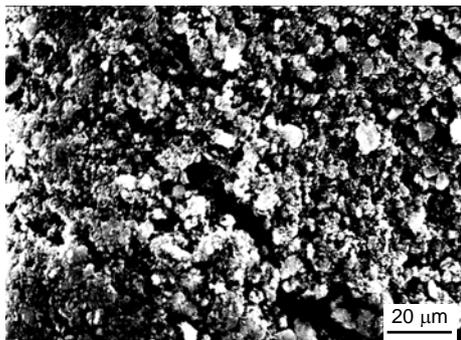


Fig.2 SEM micrograph of immobilized TiO_2/C

The SEM photograph of $\text{Ti}/\text{SnO}_2+\text{Sb}_2\text{O}_3/\text{PbO}_2$ electrode surface is given in Fig.3. The photograph shows that the distribution of PbO_2 is regular in cauliflower form, which expresses a dimensional porous electrocatalyst, thus it possesses larger reaction area to improve reaction rate.

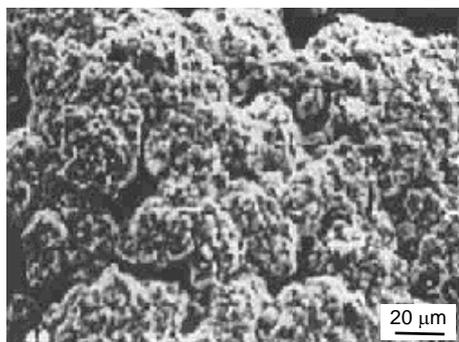


Fig.3 SEM micrograph of $\text{Ti}/\text{SnO}_2+\text{Sb}_2\text{O}_3/\text{PbO}_2$ electrode surface

The XRD patterns of graphite and oxygen diffusion electrode are shown in Fig.4. It can be seen that the spectra of graphite and oxygen diffusion electrode are identical basically, which indicates that only crystalline graphite existed in oxygen diffusion electrode. The diffraction peak of graphite was stronger than oxygen diffusion electrode, but the peak breadth of oxygen diffusion electrode became wider, the particle size of graphite slice was possibly changed during the preparation of oxygen diffusion electrode.

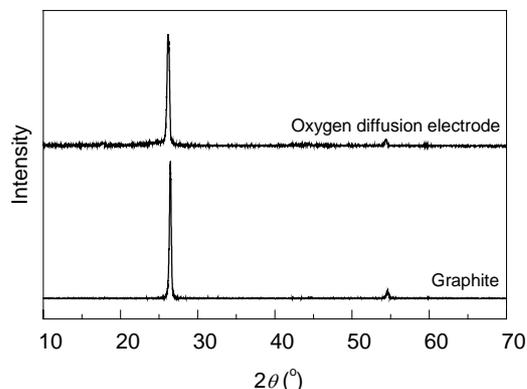


Fig.4 XRD patterns of graphite and oxygen diffusion electrode

3.2 The Photocatalytic–Electrocatalytic Process and Reaction Kinetic in Photoreactor

In order to clarify the effects of UV light, photocatalyst, electrochemistry as well as their combination function on removal rate of phenol, four experimental processes of adsorption, electrocatalysis, photocatalysis and photocatalysis–electrocatalysis were designed, the results were shown in Fig.5. Here C was the concentration of phenol in solution at reaction time t , and C_0 the initial phenol concentration in solution at reaction time $t=0$. The experimental conditions were $C_0=50$ mg/L, $V=100$ mL, pH 6, applied cell voltage $E=2$ V, light intensity $I=10.5$ mW/cm², wavelength $\lambda=365$ nm, amount of TiO_2 catalyst 0.98 mg/mL, and air flow rate $v=382.2$ mL/min.

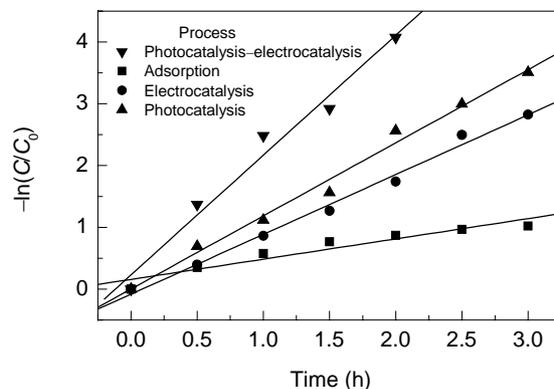


Fig.5 Phenol remaining rate vs. time of different processes

Adsorption process was conducted in a dark condition without UV irradiation and electricity, electrocatalysis process was carried out under 2.0 V cell voltage in the absence of TiO_2/C catalyst particules and UV irradiation, while photocatalysis was carried out with UV irradiation combined with TiO_2/C photocatalyst, photocatalysis–electrocatalysis was executed under UV irradiation in the presence of TiO_2/C

particales, oxygen electrode and $\text{Ti}/\text{SnO}_2+\text{Sb}_2\text{O}_3/\text{PbO}_2$ electrode. The experimental results indicated that the degradation rate of phenol could achieve 43.75%, 57.81%, 67.30% and 91.64% respectively for adsorption, electrocatalysis, photocatalysis and photocatalysis–electrocatalysis after 1.0 h reaction. These demonstrated that photocatalytic–electrocatalytic process was more efficient than adsorption, photocatalysis and electrocatalysis, it should be attributed to the synergetic effect between photocatalysis and electrocatalysis in this reactor, and the adsorption also played an important role in the degradation process.

It was well known that the photocatalytic degradation of organic pollutant in water fit to apparent first-order kinetic equation at low concentration^[14,15]. From Fig.6, it can be seen that both photocatalysis and electrocatalysis and photocatalysis–electrocatalysis all showed to obey apparent first-order kinetic equation in our experiments, moreover, the apparent rate constant K could attain 0.0340 min^{-1} for photocatalytic–electrocatalytic process, while the apparent rate constants for the processes of adsorption, electrocatalysis and photocatalysis were 0.00570, 0.0157, 0.0195 min^{-1} , respectively. Clearly, the combined process of photocatalysis and electrocatalysis was an effective process for phenol removal from water.

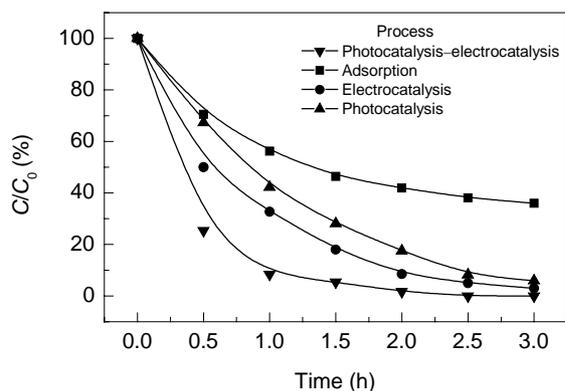


Fig.6 Reaction kinetics of different processes

3.3 Effect of Initial Concentration of Phenol

To understand the effect of initial concentration of phenol on photocatalytic–electrocatalytic degradation, three experiments under different initial concentration was proceeded in comparison of the TOC removal rate due to the fast disappearance of phenol in solution. The experimental conditions were $V=100 \text{ mL}$, $\text{pH}=6$, $E=2 \text{ V}$, $I=10.5 \text{ mW/cm}^2$, $\lambda=365 \text{ nm}$, $\text{TiO}_2 \text{ } 0.98 \text{ mg/mL}$, and $v=382.2 \text{ mL/min}$. The results are shown in Fig.7 (TOC and TOC_0 are the total organic carbon concentration of

phenol in solution at reaction time t , and $t=0$), it can be seen that the mineralization efficiency decreased with increase of phenol content. The 50 and 100 mg/L of phenol in photocatalysis–electrocatalysis only led to TOC reduction of 88.77% and 74.65% after 3.0 h degradation, while the 20 mg/L of phenol obtained a higher TOC reduction 97.42% after the same reaction time. This showed that the phenol at high concentration was comparatively difficult to mineralize completely in photocatalysis–electrocatalysis process, in other words, the photocatalysis–electrocatalysis fit to deal with organic micropollutants in water.

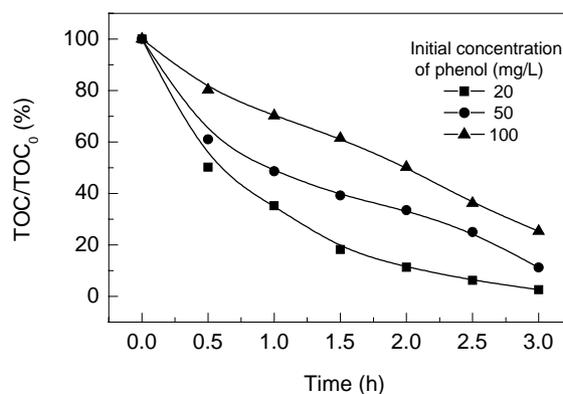


Fig.7 Effect of initial concentration of phenol on degradation

3.4 Effect of Applied Cell Voltage

The cell voltage is a key parameter for the electrode reactions. To evaluate photocatalysis–electrocatalysis efficiency at different cell voltages on mineralization of phenol, 4 tests were conducted for comparison of the TOC remaining rate under different cell voltages of 1, 2, 3 and 4 V respectively. The experimental conditions were $C_0=50 \text{ mg/L}$, $V=100 \text{ mL}$, $\text{pH}=6$, $I=10.5 \text{ mW/cm}^2$, $\lambda=365 \text{ nm}$, $\text{TiO}_2 \text{ } 0.98 \text{ mg/mL}$,

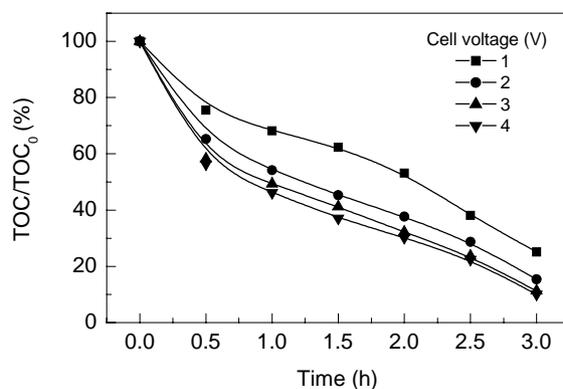


Fig.8 Effect of cell voltage on photocatalytic–electrocatalytic degradation of phenol

and $v=382.2$ mL/min. The effect of applied cell voltage on the mineralization of phenol in photocatalytic–electrocatalytic process is shown in Fig.8. The mineralization rate of organic pollutants increased with the cell voltage increasing from 1 to 4 V, but when the cell voltage was higher than 2 V, the improvement of TOC removal did not change obviously, this means that a proper little bias is suitable for photocatalysis–electrocatalysis reaction, otherwise the by-reaction such as oxygen evolution on anode would happen, thus 2 V applied cell voltage was suitable for this photocatalysis–electrocatalysis process.

3.5 Effect of Immobilized TiO₂ Catalyst Amount

The effect of amount of immobilized TiO₂ catalyst on the mineralization of phenol in photocatalytic–electrocatalytic process is shown in Fig.9. When the amount of immobilized TiO₂ catalyst was less than 1 mg/mL, the mineralization rate of phenol increased with the increase of amount of TiO₂, while the amount of immobilized TiO₂ was more than 1 mg/mL, the mineralization rate of phenol decreased. This phenomenon may be that smaller TiO₂ could form uniform thin film on the surface of activated carbon and absorb UV light sufficiently to produce photogenerated holes and electrons on the semi-conductor surface, while the amount of immobilized TiO₂ was higher, part of TiO₂ particles aggregated together and could not absorb UV light effectively, moreover this would influence the adsorption ability of activated carbon for organics. Thus 0.98 mg/mL TiO₂ was employed in our present experiments.

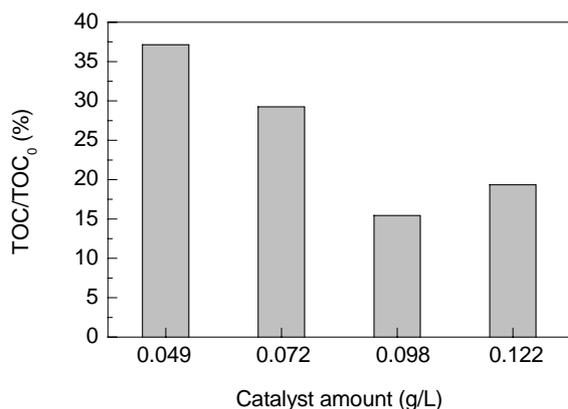


Fig.9 Effect of catalyst amount on degradation of phenol

3.6 Effect of Airflow

It was well known that molecular oxygen could not only capture photogenerated electrons, but also improve the mass transfer efficiency in photocatalytic process. Thus, it was essential to investigate the effect of airflow

on the photocatalysis–electrocatalysis degradation of phenol solution. The experimental conditions were $C_0=50$ mg/L, $V=100$ mL, $E=2$ V, $\text{pH}=6$, $I=10.5$ mW/cm², $\lambda=365$ nm, and TiO₂ 0.98 mg/mL. From Fig.10, it can be seen that photocatalytic–electrocatalytic degradation of phenol fitted well for the apparent first-order kinetic equation, but the rate constant did not increase constantly with the increase of airflow. The degradation rate constant of phenol gradually increased to 0.0258 min⁻¹ with the increase of airflow until 382.2 L/min. However, when the airflow was 410.4 L/min, the rate constant decreased to 0.0169 min⁻¹, this result makes us feel little puzzled. Maybe the air velocity of 410.4 L/min was too fast to the reaction on the TiO₂/C photocatalytic particles and oxygen diffusion electrode, leading to the decrease in the removal rate of phenol from water, therefore choosing a right airflow value was crucial.

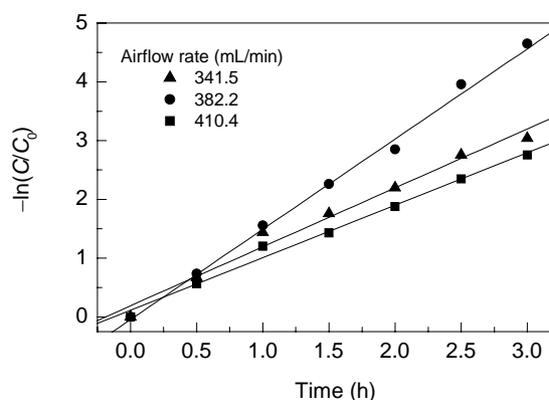


Fig.10 Effect of airflow rate on photocatalytic–electrocatalytic degradation of phenol

4 CONCLUSIONS

(1) The SEM micrograph of prepared TiO₂/C and Ti/SnO₂+Sb₂O₃/PbO₂ electrode showed their surfaces were rough and well-distributed, and the XRD patterns of oxygen electrode showed only crystalline graphite existed.

(2) The present results of photocatalytic–electrocatalytic degradation of phenol showed that phenol could be entirely degraded and about 89% TOC was removed after 3 h degradation under the following experimental conditions of initial concentration of phenol 50 mg/L, effective volume of photoreactor 100 mL, pH 6, applied cell voltage 2 V, amount of TiO₂ catalyst 0.98 mg/mL, air flow rate 382.2 mL/min, and light intensity 10.5 mW/cm². The adsorption played an important role in the degradation process.

(3) The combined process of photocatalysis with

TiO₂/C as photocatalyst and electrocatalysis with PbO₂ catalytic anode and oxygen diffusion cathode was an efficient process for the enhanced removal of organic pollutants from water in a photoreactor.

REFERENCES:

- [1] Lim T H, Kim S D. Photocatalytic Degradation of Trichloroethylene (TCE) over TiO₂/Silica Gel in a Circulating Fluidized Bed (CFB) Photoreactor [J]. *Chem. Eng. Process.*, 2005, 44(2): 327–334.
- [2] Roberto L P, Rodolfo J B, José L G, et al. Design of Fluidized Bed Photoreactors: Optical Properties of Photocatalytic Composites of Titania CVD-coated onto Quartz Sand [J]. *Chem. Eng. Sci.*, 2005, 60(10): 2785–2794.
- [3] Karches M, Morstein M, Von Rohr P R, et al. Plasma-CVD-coated Glass Beads as Photocatalyst for Water Decontamination [J]. *Catal. Today*, 2002, 72(3/4): 267–279.
- [4] Lim T H, Kim S D. Trichloroethylene (TCE) Degradation by Photocatalysis in Annular Flow and Annulus Fluidized Bed Photoreactors [J]. *Chemosphere*, 2004, 54(3): 305–312.
- [5] Kanki T, Hamasaki S, Sano N, et al. Water Purification in a Fluidized Bed Photocatalytic Reactor Using TiO₂-coated Ceramic Particles [J]. *Chem. Eng. J.*, 2005, 108(1/2): 155–160.
- [6] Lee D K, Kim S C, Cho I C, et al. Photocatalytic Oxidation of Microcystin-LR in a Fluidized Bed Reactor Having TiO₂-coated Activated Carbon [J]. *Sep. Purif. Technol.*, 2004, 34(1/3): 59–66.
- [7] Nam W, Kim J, Han G. Photocatalytic Oxidation of Methyl Orange in a Three-phase Fluidized Bed Reactor [J]. *Chemosphere*, 2002, 47(9): 1019–1024.
- [8] Waldner G, Pourmodjib M, Bauer R, et al. Photoelectrocatalytic Degradation of 4-Chlorophenol and Oxalic Acid on Titanium Dioxide Electrodes [J]. *Chemosphere*, 2003, 50(8): 989–998.
- [9] Leng W H, Zhang Z, Zhang J Q. Photoelectrocatalytic Degradation of Aniline over Rutile TiO₂/Ti Electrode Thermally Formed at 600 °C [J]. *J. Mol. Catal. A: Chem.*, 2003, 206(1/2): 239–252.
- [10] Zanoni M V B, Sene J J, Anderson M A. Photoelectrocatalytic Degradation of Remazol Brilliant Orange 3R on Titanium Dioxide Thin-film Electrodes [J]. *J. Photochem. Photobiol. A: Chem.*, 2003, 157(1): 55–63.
- [11] Quan X, Chen S, Su J, et al. Synergetic Degradation of 2,4-D by Integrated Photo- and Electrochemical Catalysis on a Pt Doped TiO₂/Ti Electrode [J]. *Sep. Purif. Technol.*, 2004, 34(1/3): 73–79.
- [12] Fan C M, Guo X D, Liang Z H, et al. Preparation and Photoelectrocatalytic Properties of TiO₂ Thin Film Electrode [J]. *Rare Metal Mater. Eng.*, 2005, 34(3): 409–412 (in Chinese).
- [13] Liang Z H, Sun Y P. Properties of Ti/SnO₂-Sb₂O₃+MnO₂/PbO₂ Anode [J]. *J. Inorg. Mater.*, 2001, 16(1): 183–187.
- [14] Matthews R W. Kinetics of Photocatalytic Oxidation of Organic Solutes over Titanium Dioxide [J]. *J. Catal.*, 1988, 111(2): 264–272.
- [15] Chen P H, Jeng C H. Kinetics of Photocatalytic Oxidation of Trace Organic Compounds over Titanium Dioxide [J]. *Environ. Int.*, 1998, 24(8): 871–879.