Degradation of 2,4-dichlorophenol with a novel TiO$_2$/Ti-Fe-graphite felt photoelectrocatalytic oxidation process

ZHAO Bao-xiu[1,2], LI Xiang-zhong[2], WANG Peng[1,*]

1. School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China. E-mail: zhaobaoxiuhit@163.com
2. Department of Civil and Structural Engineering, The Hong Kong Polytechnic of University, Hunghom, Kowloon, Hong Kong, China

Abstract

Degradation of 2,4-dichlorophenol (2,4-DCP) was studied in a novel three-electrode photoelectrocatalytic (PEC) integrative oxidation process, and the factors influencing the degradation rate, such as applied current, flow speed of O$_2$, pH, adscititious voltage and initial 2,4-DCP concentration were investigated and optimized. H$_2$O$_2$ was produced nearby cathode and Fe^{2+} continuously generated from Fe anode in solution when current and O$_2$ were applied, so, main reactions, H$_2$O$_2$-assisted TiO$_2$ PEC oxidation and E-Fenton reaction, occurred during degradation of 2,4-DCP in this integrative system. The degradation ratio of 2,4-DCP was 93% in this integrative oxidation process, while it was only 31% in E-Fenton process and 46% in H$_2$O$_2$-assisted TiO$_2$ PEC process. So, it revealed that the degradation of 2,4-DCP was improved greatly by photoelectrical cooperation effect. By the investigation of pH, it showed that this integrative process could work well in a wide pH range from pH 3 to pH 9.

Key words: 2,4-dicholrophenol; TiO$_2$; photoelectrocatalytic; hydrogen peroxide; E-Fenton

Introduction

2,4-Dichlorophenol (2,4-DCP), as a kind of interme-diator of chloro-pesticides, has dreadful toxicity and disturbing to human and animal's endocrine system, has caused researchers' attention (Topalov *et al.*, 2000; Zhang *et al.*, 2005). At present, some processes and methods have been offered and designed to degrade 2,4-DCP for water or wastewater treatments, like microbe methods, physical and chemical methods. However, because of high toxicity and low endurable concentration, it is difficult to completely degrade 2,4-DCP to match the standard environmental permit. Presently, advanced oxidation processes (AOPs) have been developed and investigated. AOPs have been considered as very promising alternative processes to conventional processes in water or wastewater treatment for their high degradation efficiency to oxide organic contaminants by the generation of hydroxyl radicals (HO·) which has powerful oxidation ability.

TiO$_2$, as a photocatalyst, has been studied for its high catalytic efficiency, no toxicity and stable chemical per-formance. However, it is difficult for TiO$_2$ powder to disperse and be recycled in aqueous solution, TiO$_2$ is mostly coated on some carriers before use (Fernandez *et al.*, 2004; Egerton *et al.*, 2006). When it is irradiated by photon whose energy exceeded 3.2 eV, holes that

have powerful oxidation ability and electrons that have reduction ability are both generated on the surface of TiO$_2$, but recombination of holes and electrons occurs at the same time, reducing the catalytic performance of TiO$_2$. In order to enhance TiO$_2$ catalytic ability, it is modified by adulterating metal ions or some metal oxides to restrict or reduce the recombination efficiency (Bauer *et al.*, 1999; Zhao *et al.*, 2001; Li *et al.*, 2002; Li and Li, 2003). There are some reports on the catalytic application of TiO$_2$ (Leng *et al.*, 2000; Lee *et al.*, 2003). However, reports about the association degradation of organic with TiO$_2$ and others processes are mostly simple. There are some reports (Chen *et al.*, 2003; Zhang *et al.*, 2003; He *et al.*, 2003; Wang *et al.*, 2004; Chen *et al.*, 2004; Sônia *et al.*, 2005; Li *et al.*, 2006; An *et al.*, 2005; Ji *et al.*, 2006) on PEC combination processes, but reagents in these processes are needed to cast outside of reactor.

To increase organic degradation and save running cost, TiO$_2$/Ti-Fe-graphite felt PEC oxidation process was designed and studied in this article. This integrative oxidation process was made up by the association of TiO$_2$/UV/Fenton/H$_2$O$_2$/Electrical energy, and it is interest-ing that all reagents were generated by reactor, avoiding casting outside. As have been known, Fenton reaction has high oxidation for HO· generation through decomposition H$_2$O$_2$ by ferrous in an acidic environment, and TiO$_2$ pho-tocatalytic reaction has the best performance in a neutral environment because its equipotential point is about 6.5. Considering achieving high degradation efficiency, a novel

(TiO$_2$/Ti-Fe)-GF PEC integrative process was designed. In this integrative system, H$_2$O$_2$-assisted TiO$_2$ PEC oxidation and E-Fenton reaction occur in one reactor and their hybrid degradation and mineralization to organic were greatly improved. Furthermore, H$_2$O$_2$ and ferrous are generated simultaneously in solution, avoiding casting reagents outside and saving running cost.

1 Materials and methods

1.1 Materials for electrode and reagents

2,4-DCP (analytical grade) purchased from ALDUICH company (USA) and works as model pollutant; TiO$_2$/Ti electrode was prepared by our research group and was cut into 10 mm × 50 mm size before use; graphite Felt, from the National Specialty Products of USA, was cut into the same size as TiO$_2$/Ti anode. A piece of rectangle stainless steel sheet which has the same size as TiO$_2$/Ti was performed passivation pretreatment before use. H$_3$PO$_4$, NaH$_2$PO$_4$ and Na$_2$HPO$_4$ (all analytical grade) were used to collocate buffer solution; Na$_2$SO$_4$ (analytical grade) was used as support electrolyte; water used in this experiment was distilled water.

1.2 Preparation of TiO$_2$/Ti electrode and its characterization

TiO$_2$/Ti thin film electrode was prepared in the mixture solution of 1.5 mol/L H$_3$PO$_4$ and 0.3 mol/L HF using low-voltage anodic oxidation method. An electrical current was applied by an electrophoresis power supply (EPS 600, Pharmacia Biotech). The whole anodic oxidation process was conducted through galvanostatic-potentiostatic stage. Detailed preparation process and its structural characterization were reported by our previous research work (Xie and Li, 2006).

1.3 Analysis methods

2,4-DCP concentration was determined by the high performance liquid chromatography (Finnigan TSP HPLC P4000) which is equipped with a reversed column (RESTEK Pinnacle II, d-C18, 4.6 mm×250 mm ID), an UV detector (UV-6000LP) and an automatic sampler (AS3000). The mobile phase composes of acetonitrile, water and acetic acid (69:30:1); its flow rate was set at 0.85 ml/min and the retained time was kept at 5.0 min. The main absorption wavelength of 2,4-DCP is 286 nm. pH value was measured by pH meter (Thermo Orion 720).

1.4 Three-electrode PEC reactor and experiment procedure

Experimental device is shown in Fig.1. TiO$_2$/Ti electrode was used as one anode and Fe flake was used as another anode; GF was used as cathode and reference electrode was saturated calomel electrode (SCE). To control the current distribution, a variable resistor was jointed with Fe electrode. Oxygen (O$_2$) was supplied nearby cathode and its flow rate was kept at a certain value; an UV-A (8 W) lamp was set outside of the reactor.
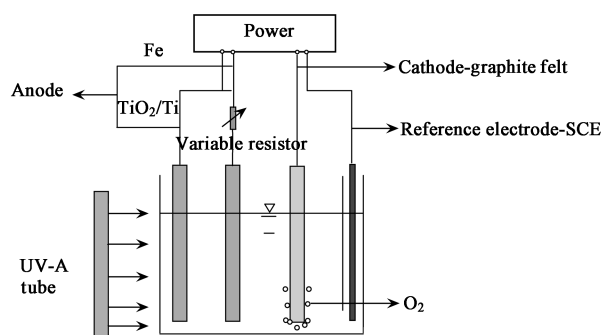

Fig. 1 PEC reactor of the TiO$_2$/Ti-Fe-GF integrative system. SCE: Saturated calomel electrode.

Prepare 15 mg/L 2,4-DCP aqueous solution containing 0.02 mol/L Na$_2$SO$_4$ used as support electrolyte and connect reactor as Fig.1. Before all electrodes get adsorption equilibrium in 2,4-DCP aqueous solution, put 50 ml 2,4-DCP solution into the quartz reactor and start reaction. After the experiment started, 0.5 ml sample was withdrawn from the middle part of the quartz reactor at perselected time intervals.

2 Results and discussion

2.1 Three-electrode PEC reactor

In this integrative reactor, the design of three-functional-electrode was novel. Anode was made up by TiO$_2$/Ti electrode conducting TiO$_2$ PEC reaction and Fe electrode conducting E-Fenton reaction, and GF as a carrier to generate H$_2$O$_2$ was used as cathode, so PEC oxidation reaction under UV-A irradiation and electrical current was realized in one reactor, which showed that all oxides were produced by system itself, avoiding casting reagents outside. Another unique design was that a rheostat was linked with Fe, which could control the current distribution to the two anodes and protect TiO$_2$ electrode. E-Fenton demands high current to degrade organic, and TiO$_2$ only needs low current to conduct PEC reaction. In summary, this design of PEC oxidation reactor not only increased degradation of 2,4-DCP, but decreased running cost.

2.2 Effect of current on 2,4-DCP degradation

In order to study the effect of current on 2,4-DCP degradation and single anodic oxidation contribution to degradation, two sets of experiment were conducted. The first was performed in the Fe-GF electrolysis system, in which Fe was used as anode and GF was used as cathode. The second was monitored in TiO$_2$/Ti-GF electrolysis system and TiO$_2$/Ti was acted as anode. To avoid the generation of H$_2$O$_2$ in solution, nitrogen (N$_2$) was supplied for 30 min before reaction start until the whole reaction ended. Considering saving energy and protect TiO$_2$/Ti electrode, two experiments were conducted under low current, instead of high current of conventional electrolysis process.

From Fig.2a, it can be seen that 2,4-DCP degradation increased only from 2.5% of 0.5 mA to 7.5% of 8.0 mA after 120 min reaction, and from Fig.2b, degradation
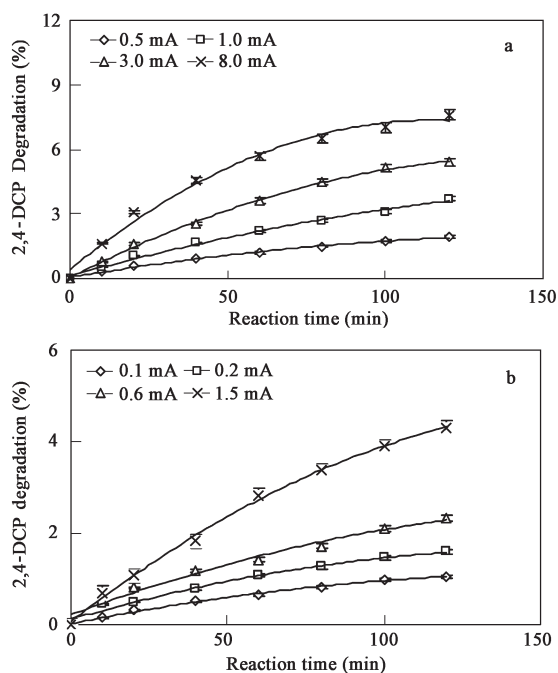
Fig. 2 Effect of current on 2,4-DCP degradation in Fe-GF electrolysis system (a) and TiO_2/Ti-GF electrolysis system (b). Conditions: initial 2,4-DCP concentration is 15 mg/L; bubbling N_2; without UVA irradiation and pH buffer.

enhanced just from 1.1% of 0.1 mA to 4.2% of 1.5 mA at the same reaction time. It proved that anodic oxidation was not dominant during 2,4-DCP degradation using low current. So, 0.2 mA current applied on TiO_2/Ti anode was selected and 3.0 mA current was applied on Fe. Then the total current was 3.2 mA and it was adopted in the following experiments.

2.3 Effect of O_2 and its flow speed on 2,4-DCP degradation

Fig.3 shows that supplying O_2 increased 2,4-DCP degradation greatly. The reason is that in the presence of O_2, O_2 reacted with electrons to generate H_2O_2 which was involved in H_2O_2-assisted TiO_2 PEC oxidation and E-Fenton reaction. In the two reactions, HO· was produced greatly. Furthermore, H_2O_2 as a electron-trapper could improve TiO_2 PC efficiency, so O_2 played an important role during 2,4-DCP degradation. Corresponding reactions

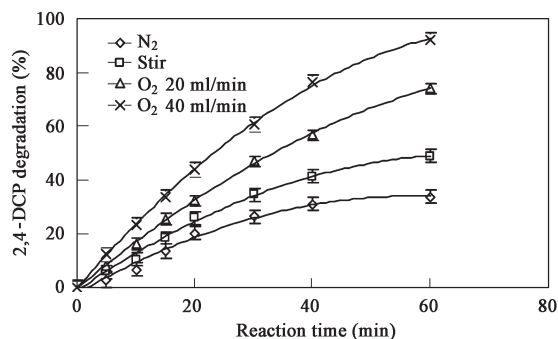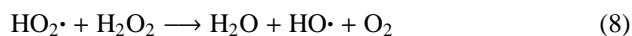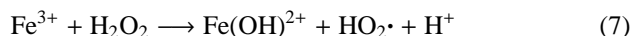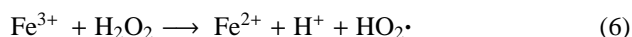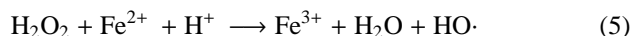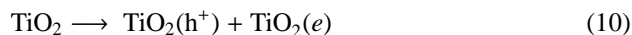Fig. 3 Degradation of 2,4-DCP under various atmosphere in integrative process. Conditions: initial 2,4-DCP concentration is 15 mg/L; bubbling N_2; with UVA irradiation and pH without control.

were as follows:

$$Fe \longrightarrow Fe^{2+} + 2e \tag{1}$$

$$O_2 + 2e + 2H^+ \longrightarrow H_2O_2 \tag{2}$$

$$H_2O_2 + e \longrightarrow HO· + HO^- \tag{3}$$

$$H_2O_2 \xrightarrow{hv} 2HO· \tag{4}$$

$$H_2O_2 + Fe^{2+} + H^+ \longrightarrow Fe^{3+} + H_2O + HO· \tag{5}$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^+ + HO_2· \tag{6}$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe(OH)^{2+} + HO_2· + H^+ \tag{7}$$

$$HO_2· + H_2O_2 \longrightarrow H_2O + HO· + O_2 \tag{8}$$

$$HO· + 2,4\text{-DCP} \longrightarrow \text{intermediates} \tag{9}$$

However, in the nitrogen atmosphere, only TiO_2 PC reaction occurred and involved reactions were as follows:

$$TiO_2 \longrightarrow TiO_2(h^+) + TiO_2(e) \tag{10}$$

$$h^+ + H_2O \longrightarrow HO· + H^+ \tag{11}$$

$$HO· + 2,4\text{-DCP} \longrightarrow \text{intermediates} \tag{12}$$

So, the concentration of HO· was lower greatly than that in the oxygen atmosphere. On the other hand, degradation enhanced with the increase of O_2 flow speed shown from this figure. The reason was probably that higher flow could boost dissolution of O_2 and improve degradation speed. Considering of degradation time, O_2 flow speed was adopted 40 ml/min in following experiments.

2.4 Effect of pH on 2,4-DCP degradation

In this integrative process, two main reactions were influenced greatly by pH, H_2O_2-assisted TiO_2 PEC reaction and E-Fenton reaction. Three sets experiments were carried out respectively to study the effect of pH on 2,4-DCP degradation. The first was set in H_2O_2-assisted TiO_2 PEC process; the second was conducted in E-Fenton process and the last was in integrative process.

From Fig.4, it can be seen that the optimal pH was 3 in E-Fenton reaction system and it was fit for the best pH of classical Fenton reaction. Degradation increased firstly and then decreased and the best pH was 7 in H_2O_2-assisted TiO_2 PEC system, because the equipotential
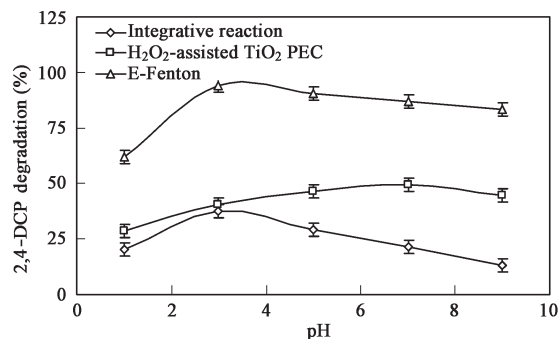

Fig. 4 Effect of pH buffered with H_3PO_4-NaH_2PO_4-Na_2HPO_4 solution on 15 mg/L 2,4-DCP degradation in E-Fenton (applied current is 3.0 mA, supplying O_2 nearby GF and without UVA irradiation); H_2O_2-assisted TiO_2 PEC (applied current is 0.2 mA, supplying O_2 nearby GF and with UVA irradiation) and integrative process (applied current is 3.2 mA, supplying O_2 nearby GF and with UVA irradiation).

point of TiO$_2$ was about 6.5 and nearby this point, TiO$_2$ surface was at neutral state which did good for TiO$_2$ to absorb active groups (Candal *et al.*, 1998). TiO$_2$ surface took on positive before equipotential point and negative after equipotential point, so, before equipotential point, the probability for OH$^-$ combined with holes was slight, reducing the concentration of HO·, and after equipotential point, generated H$_2$O$_2$ concentration was slight, reducing TiO$_2$ PC performance because the proper environment for H$_2$O$_2$ generation was acidic.

In the integrative process, degradation trend appeared the similar trend as E-Fenton; however, its change was not obvious when pH exceeded 3. It displayed that E-Fenton and H$_2$O$_2$-assisted TiO$_2$ PEC reaction produced an effect of pH buffer. On basis of the above results it can be concluded that integrative process worked well in a wide pH range which has a significant application foreground in some practical wastewater treatment. Furthermore, H$_2$O$_2$-assisted TiO$_2$ PEC reaction was superior to E-Fenton at any pH value (Fig.4), which showed that H$_2$O$_2$-assisted TiO$_2$ PEC reaction was dominant in integrative process during of 2,4-DCP degradation.

2.5 Effect of adscititious voltage on 2,4-DCP degradation

In integrative process, adscititious voltage has two effects, one is that it provides energy to start E-Fenton and H$_2$O$_2$-assisted TiO$_2$ PEC reaction, the other is that it drives the decomposition of electron and hole of TiO$_2$ surface increasing TiO$_2$ PC efficiency. To demonstrate its effect, experiment of adscititious voltage effect on 2,4-DCP degradation was performed under the same experimental conditions and results are shown in Fig.5.
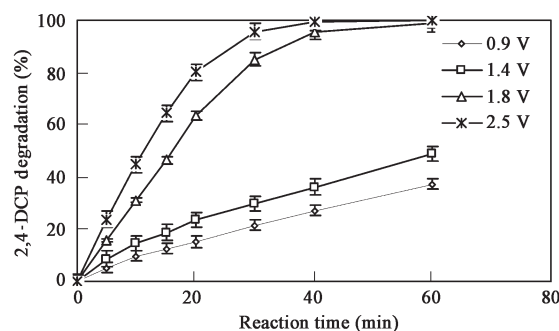

Fig. 5 Effect of adscititious voltage on 2,4-DCP degradation in integrative process without N$_2$ buffer.

It can be clearly seen that 2,4-DCP degradation was improved with the enhancement of adscititious voltage. This is likely that adscititious anodic voltage made energy belt bend of TiO$_2$ increase, restraining the composition of electrons and holes, and boosting the concentration of holes. However, considering TiO$_2$/Ti electrode life, thickness of charge layer caused by applied voltage should not exceed electrode's thickness, otherwise electrode would be destroyed and eroded. That is to say that applied voltage should not exceed electrode's critical break voltage. What important was that a degradation break appeared when

voltage increased from 1.4–1.8 V as shown in Fig.5, the degradation ratio almost reached 100% of 1.8 V from 38% of 1.4 V only after 40 min. It was probably that electrons and holes were effectively separated when voltage exceeded a certain voltage in the range of 1.4–1.8 V. It should be noticed that the degradation ratio was not prominent and their degradation difference was not obviously in the range of 0.9–1.4 V, which proved the existing of exciting voltage. In addition, only slight degradation difference appeared between 1.8 V and 2.5 V. The reason was that TiO$_2$ exerted fully its PC efficiency under this condition and by-reaction consuming HO· occurred with the increase of voltage. It suggested that H$_2$O$_2$-assisted TiO$_2$ PEC reaction acted as an important role during 2,4-DCP degradation and it further certificated there indeed existed an exciting voltage in the range of 1.4–1.8 V.

2.6 Effect of initial 2,4-DCP concentration on its degradation

To study the effect of 2,4-DCP concentration in integrative process, series of concentration experiments were carried out. Fig.6 shows that degradation ratio decreased with the increase of 2,4-DCP initial concentration. The reason is that the intermediates concentration increased with the enhancement of organic initial concentration, which restrained organic from adsorbing on TiO$_2$ surface and transferring in solution, so, degradation ratio decreased. However, degradation capability increased with enhancement of organic initial concentration because the increase of organic concentration could enhance its quantity per volume, which improved contact chance with oxidative groups and increased degradation capability.
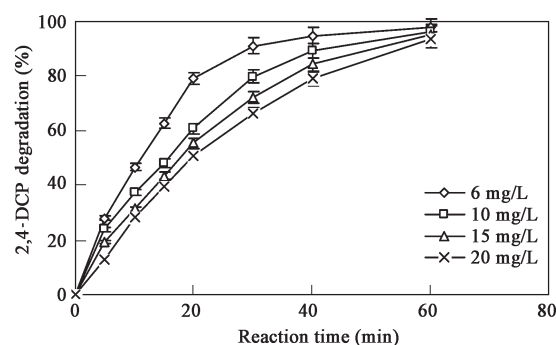

Fig. 6 Effect of initial 2,4-DCP concentration on its degradation in integrative process without N$_2$ buffer.

2.7 Reaction kinetics of PEC integrative process

On the basis of the results, two main reactions, H$_2$O$_2$-assisted TiO$_2$ PEC and E-Fenton, had dominant contribution to 2,4-DCP degradation. The kinetics of integrative, H$_2$O$_2$-assisted TiO$_2$ PEC and E-Fenton's reaction was studied. It could be seen that the three processes all abided pseudo first-order kinetics, the corresponding kinetics parameters are listed in Table 1. Under low O$_2$ flow rate and absorption equilibrium, degradation of TiO$_2$ PEC reaction only occurred on its surface, so, ln(C_0/C) versus reaction time took on a satisfying linearity. In solution,

Reaction process	Kinetics equation	Rate constant ($\times 10^{-2}$ min^{-1})	Relation coefficient (R^2)	Degradation (%)
E-Fenton	$\ln(C_0/C)=0.0061t+0.0492$	0.61	0.9377	31.6
TiO$_2$ PEC	$\ln(C_0/C)=0.0105t+0.0131$	1.05	0.9953	45.7
Integrative	$\ln(C_0/C)=0.0411t+0.0112$	4.11	0.9941	93.2

main reaction was the classical Fenton reaction and it also followed the pseudo first-order kinetics. So, the whole integrative reaction abided first-order kinetics. From Table 1, the constant of E-Fenton was 0.61×10^{-2} min^{-1} and 1.05×10^{-2} min^{-1} of H$_2$O$_2$-assisted-TiO$_2$ PEC oxidation, compared with 4.11×10^{-2} min^{-1} of integrative process, then a clear conclusion was gotten that the combination of E-Fenton and H$_2$O$_2$-assisted TiO$_2$ PEC oxidation could boost the degradation of 2,4-DCP.

3 Conclusions

A novel three-electrode PEC oxidation process was designed and some important factors were studied. In this integrative process, H$_2$O$_2$ conducting H$_2$O$_2$-assisted TiO$_2$ PEC and ferrous conducting E-Fenton were produced by process itself, avoiding casting outside and saving running cost. The application of adscititious electric field and the supply of O$_2$ nearby cathode in solution both boosted the decomposition of electrons and holes and accelerated TiO$_2$ PC performance. At last, degradation kinetics of integrative process was studied and the result proved that the processes abided by pseudo first-order reaction.

References

An T C, Li G Y, Zhu X H *et al*., 2005. Photoelectrocatalytic degradation of oxalic acid in aqueous phase with a novel three-dimensional electrode-hollow quarz tube photoelectrocatalytic reator[J]. Appl Catal A, 279: 247–256.

Bauer R, Waldner G, Fallmann H *et al*., 1999. The photo-fenton reaction and the TiO$_2$/UV process for waste water treatment-novel developments[J]. Catal Today, 53: 131–144.

Candal R J, Zeltner W A, Anderson M A, 1998. TiO$_2$ mediated photoelectrocatalytic purification of water[J]. Advan Oxid Technol, 3: 270–276.

Chen J S, Liu M C, Zhang L *et al*., 2003. Application of nano TiO$_2$ towards polluted water treatment combined with electro-photochemical method[J]. Water Res, 37: 3815–3820.

Chen J S, Liu M C, Zhang J D *et al*., 2004. Photocatalytic degradation of organic wastes by electrochemically assisted TiO$_2$ photocatalytic system[J]. J Environ Management, 70: 43–47.

Egerton T A, Janus M, Morawski A W, 2006. New TiO$_2$/C sol-gel electrodes for photoelectrocatalytic degradation of sodium oxalate[J]. Chemosphere, 63: 1203–1208.

Fernandez J, Kiwi J, Baeza J *et al*., 2004. Orange II photocataly-sis on immobilised TiO$_2$ effect of the pH and H$_2$O$_2$[J]. Appl Catal B: Environ, 48: 205–211.

He C, Xiong Y, Chen J *et al*., 2003. Photoelectrochemical performance of Ag-TiO$_2$/ITO film and photoelectrocatalytic activity towards the oxidation of organic pollutants[J]. J Photochem and Photobio A, 157: 71–79.

Ji M, Jin L N, Fu J F *et al*., 2006. Potential bias on the photoelectrocatalytic degradation of fulvic acid[J]. Environ Chem, 25: 145–148.

Lee J M, Kim M S, Hwang B, 2003. Photodegradation of acid red 114 dissolved using a photo-Fenton process with TiO$_2$[J]. Dyes Pigments, 56(1): 59–67.

Leng W H, Cheng S A, Liu H *et al*., 2000. Photocatalytic degradation of aniline in water on immobilized titanium[J]. Acta Scientiae Circums Tantiae, 20: 499–503.

Li X Z, Liu H L, Li F B *et al*., 2002. Photoelectrocatalytic oxidation of rhodamine B in aqueous solution using Ti/TiO$_2$ mesh photoelectrodes[J]. Environ Sci Heal A, 37: 55–69.

Li X Z, Li F B, 2003. Photocatalytic oxidation using a new catalyst-TiO$_2$ microsphere for water and wastewater treatment[J]. Environ Sci Technol, 35: 3989–3994.

Li J Q, Li L P, Zheng L *et al*., 2006. Photoelectrocatalytic degradation of rhodamine B using Ti/TiO$_2$ electrode prepared by laser calcination method[J]. Electrochimica Acta, 51: 4942–4949.

Sôonia M A J, Jeosadaqu J S, Ariovaldo O F, 2005. Photoelectrocatalytic treatment of *p*-nitrophenol using Ti/TiO$_2$ thin-film electrode[J]. J Photochem and Photobio A: Chem, 174: 71–75.

Topalov A, Molnar-Gabor D, Kosanic M *et al*., 2000. Photomineralization of the herbicide mecoprop dissolved in water sensitized by TiO$_2$[J]. Water Res, 34: 1473–1478.

Xie Y B, Li X Z, 2006. Interactive oxidation of photoelectrocatalysis and electro-Fenton for azo dye degradation using TiO$_2$-Ti mesh and reticulated vitreous carbon electrodes[J]. Mater Chem Phy, 95: 39–50.

Wang H Y, Jiang Z P, Y G *et al*., 2004. Study of photoelectrocatalytic oxidation of benzoic acid[J]. J Environ Sci, 25: 25–29.

Zhang J F, Liu H, Sun Y Y *et al*., 2005. Responses of the antioxidant defenses of the Goldfish *Carassius auratus* exposed to 2,4-dichlorophenol[J]. Environ Toxicol and Pharmacol, 19: 185–190.

Zhang W B, An T C, Xiao X M *et al*., 2003. Photoelectrocatalytic degradation of reactive brilliant orange K-R in a new continuous flow photoelectrocatalytic reactor[J]. Appl Catal A, 255: 221–229.

Zhao W K, Niu X Y, He F *et al*., 2001. Preparation of TiO$_2$/SiO$_2$ and its photocatalytic activity for degradation of dye X-3 B in aqueous solution[J]. Chinese Journal of Catal, 22: 171–174.