

# Kinetics of photoelectrocatalytic degradation of humic acid using $B_2O_3 \cdot TiO_2/Ti$ photoelectrode

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**Abstract:** An innovative photoelectrode,  $B_2O_3 \cdot TiO_2/Ti$  electrode, was prepared by galvanostatic anodisation. The morphology and crystalline texture of the  $B_2O_3 \cdot TiO_2$  film on electrode were examined by atomic force microscopy (AFM) and X-ray diffraction respectively. The examination results indicated that the anatase was the dominant component. The kinetics of photoelectrocatalytic (PEC) degradation of humic acid (HA) was investigated; the results demonstrated that effects from strongness to weakness on the photoelectrocatalytic degraded rate of humic acid: power of UV-lamp, area of  $TiO_2$  film, bias, original concentration of humic acid solution. The optimum conditions were power of UV-lamp 125 W, area of  $TiO_2$  film 42.0 cm<sup>2</sup>, bias 1.4 V, original concentration of humic acid solution 5 mg/L in this PEC reaction system.

**Keywords:**  $TiO_2$ ; photoelectrocatalytic degradation; humic acid; kinetics

## Introduction

Eighty percent of organic substances in the source water is from crude humic acid that is a crude organic compound created by rotting and decomposing in natural cycle, the higher content of humic acid is, the worse quality of the water is, not only can it cause chrominance, offensive odor, corrosion and sediment in water distribution piping, but also is one of the mostly precursor substances of byproducts which are generated in routine chloride disinfections at present (Stephen, 2000; Yoshimi, 2000; Tang, 1994). Most of these byproducts have been proved to be a potential carcinogen by experiments. So the control of byproducts in chloride disinfections is one of the most important projects in the drinking water treatment in the world (Wang, 2000; Zeng, 2003; Jia, 1997). The main way of controlling formation of byproducts in chloride disinfections is to remove the precursor substances of DBPs, i.e. the natural organic matters of humic acid category.

There are some reports on treating these organic compounds by  $TiO_2$  photocatalytic oxidation (Li, 1994; 2002; Matthews, 1990), the signal  $TiO_2$  catalysts that were prepared by deposit or sol-gel method usually were used and had low activity.

In this paper, composite  $B_2O_3 \cdot TiO_2/Ti$  electrode as catalyst was prepared by electrochemical method and was used to remove humic acid in aqueous solution by photoelectrocatalytic oxidation, the kinetics of photoelectrocatalytic degradation of humic acid was researched systemally, some experimental bases were provided for accelerating the practical application of  $TiO_2$  photocatalytic oxidation technology in water treatment.

## 1 Experiment

### 1.1 Materials

Comprised  $B_2O_3 \cdot TiO_2/Ti$  catalyst (home-made); humic acid solution was confected using biochemical humic acid reagent (Shanghai Biochemical Reagent Factory), its concentration is 20 mg/L; other chemicals (Tianjin Tianhe Chemical Reagent Factory) were of analytical reagent grade and used without further purification. Doubly distilled water was used throughout this study.

### 1.2 Experimental installation and equipment

The photoelectrocatalytic reactor system is shown in Fig.

1. The main components were the cylinder quartz cell with the effective volume of 300 ml, in which a  $B_2O_3 \cdot TiO_2/Ti$  was as anode and Pt wire was as the work-electrode, the 125 W high-pressure mercury lamp was positioned inside the cylindrical vessel surrounded by a circulating water jacket to control temperature. Air was supplied to the system, then the potentiostat was opened and a certain bias between an anode and a cathode was exerted.

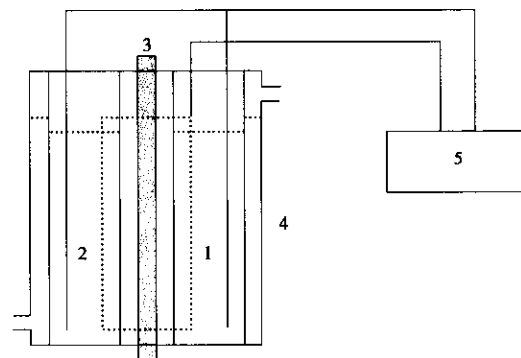


Fig. 1 Photoelectrocatalytic reaction system

1.  $TiO_2/Ti$  photo anode; 2. Pt cathode; 3. UV lamp; 4. reactor; 5. potentiostat

The change of absorbency of humic acid is determined by 752 UV raster spectrophotometer (Gaomi Analysis Instrument of Shandong); PHS-3C acidity instrument (Xiaoshan Analysis Instrument Factory) and 65-1 comprise electrode (Shanghai Electric and Phonic Instrument Factory) are used to determine the pH of solution; DC potentiostat (Shanghai Sanke Electric Implement Ltd.) is used to adjust outside bias voltage, The morphology and crystalline texture of the catalyst on film were examined by Atomic Force Microscopy (USA DI D-3100-AFM-CONTACT) and X-ray Diffraction (Japan XRD-6000X) respectively.

### 1.3 Procedure

#### 1.3.1 Preparation of catalyst

Titanium plate was cut to be rectangle (25 mm × 10 mm × 0.5 mm), and cleaned in the mixed acid of both HF and  $HNO_3$  (concentration ratio is 1:1). The film  $B_2O_3 \cdot TiO_2/Ti$  electrode was made in mixed solution of both  $H_2SO_4$  (0.75 mol/L) and  $H_3BO_3$  (0.5 g/L) by anodisation of titanium, in which the titanium and copper plate were used as an anode

and as a cathode respectively. The XRD spectra and AFM graph of  $B_2O_3 \cdot TiO_2/Ti$  electrode prepared by anodisation are shown in Fig.2 and Fig.3 respectively.

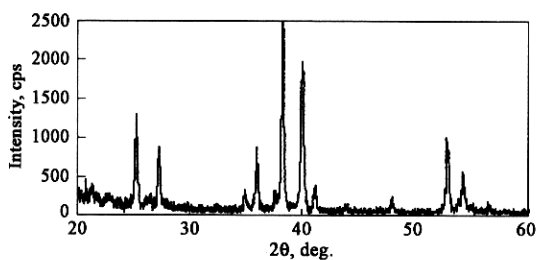


Fig.2 XRD spectra of  $B_2O_3 \cdot TiO_2/Ti$  electrodes prepared by anodisation

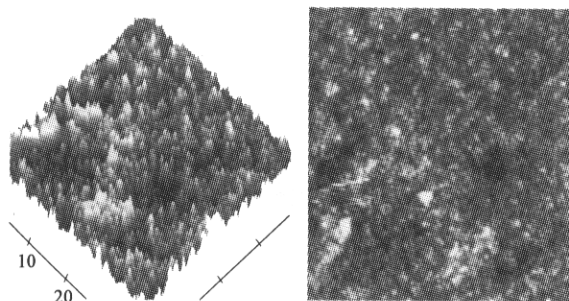


Fig.3 AFM graph of  $B_2O_3 \cdot TiO_2$  electrodes prepared by anodisation

The diffraction angles ( $2\theta$ ) of 25.28, 37.82, and 47.64 shown in Fig.2 belonged to the (101), (004), (200) diffraction peaks of the sharp anatase titanium respectively, at the same time the diffraction peaks of  $Ti_2B_5$  could be detected in the diffraction angles of 25.6, 34.7, 35.3, 36.9, 38.9, 48.1, and 53.2, but their diffraction peaks were not obvious because the content of  $Ti_2B_5$  was little. Both three-dimensional microscopy and the morphology of the  $B_2O_3 \cdot TiO_2/Ti$  film, detected by AFM, showed that the surface of compound film is in order, and there were a lot of micropores and chinks on the surface. The particles tend to be more spherical. The diameters of micropores are between 14–16 nm.

### 1.3.2 Photoelectrocatalytic oxidation reaction

250 ml humic acid solution was put into photo-reactor system. All of initial concentration of humic acid solution was 20 mg/L without special explanation, 125 W high-pressure mercury lamp, at initial pH value of 3.18, the  $B_2O_3 \cdot TiO_2/Ti$  photoelectrode area of 7  $cm^2$ . Air was supplied continuously to the photo-reactor system and the reaction lasted 2 h. The samples were analyzed at a certain interval of time.

## 2 Results and discussion

### 2.1 Effect of pH on PEC degradation rate of HA

In order to study the effect of pH on the PEC oxidation of HA, photodegradation efficiencies of HA were investigated in the same ultraviolet light power but at different pH values of 3.18, 4.76, 6.02, 8.15 and 10.11 respectively, without applying electrical bias. The experimental results are shown in Fig.4.

Fig.4 indicates that the PEC degradation rate of HA was faster in acidic solution than that in the alkaline solution, and this value increased as the initial pH decreased.

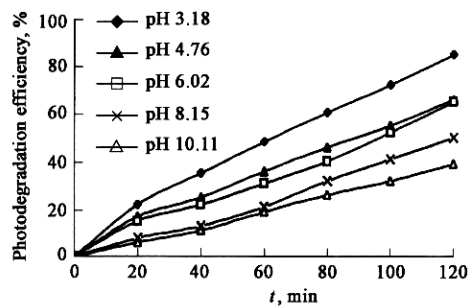


Fig.4 Effect of pH on photo-degradation of HA

The adsorption behavior of  $B_2O_3 \cdot TiO_2/Ti$  photocatalyst surface plays an important role in this type of PEC oxidation reaction, because the photocatalytic process mainly occurs on the photocatalyst surface, but not in bulk solution (Kamat, 1989; Zuo, 2001). When the pH of solution changes, it can change the surface electrification character of catalyst, effect on the adsorption behavior of organic compound, and effect on the photocatalytic degradation of organic compound for the reason that the pH dose not match the spot of equal voltage.

Among the function groups of humic acid, hydroxyl and phenol-hydroxyl are more active, and present negative charges in the aqueous solution. The positive charge on the catalyst increases when the pH decreases. The electrostatic attraction between the HA molecule with negative charge and catalyst with positive charge leads to the increase of both HA adsorption amount on the surface of  $TiO_2$  catalyst and degradation rate HA; when the pH increases, the negative charge on the surface of the catalyst increases, the HA molecule adsorption on the surface of  $TiO_2$  catalyst is affected by the repulsion between the HA and catalyst, and this suppresses the photodegradation process. As a result, the PEC degradation rate on the  $B_2O_3 \cdot TiO_2/Ti$  photocatalyst surface decreases as the pH increases. The initial pH of the solution in the following experiments is 3.8 without special explanation.

### 2.2 The kinetics of the PEC degradation of HA

Several experimental results indicated that the rate of photocatalytic degradation of various organic contaminants over illuminated  $TiO_2$  fitted the Langmuir-Hinshwood kinetics. When the initial concentration of organic contaminants was very small, the Langmuir-Hinshwood rate form reduced to the apparent first-order kinetics form, i.e.

$$\ln(C_0/C) = kt. \quad (1)$$

The first-order kinetic constant  $k$  is mainly related to the key factors, such as area of  $B_2O_3 \cdot TiO_2/Ti$  catalyst ( $A$ ), the UV light power ( $W$ ), electrical bias applied ( $V$ ) and the initial humic acid concentration ( $C_0$ ), under certain pH condition in PEC oxidation process, i.e.

$$k = f(W, C_0, V, A) = m(W)^a (C_0)^b (V)^c (A)^d, \quad (2)$$

where  $m, a, b, c, d$  are constants.

#### 2.2.1 The effects of UV lamp power on PEC degradation rate of HA

The UV lamps of 0 W (dark), 20 W, 40 W, 60 W, and 125 W were used in PC oxidation respectively to research the relationship between light intensity and PC degradation rate of HA at pH 3.18 without bias. The experimental results are shown in Fig.5

The results indicated the higher UV lamp power was,

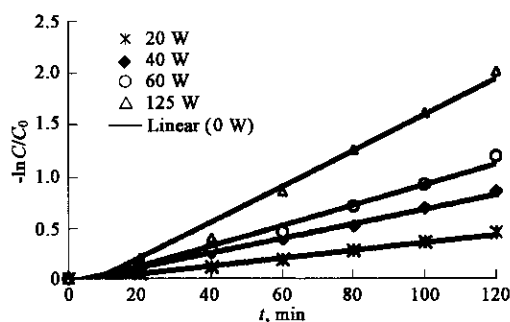


Fig. 5 The kinetic characters of PC degradation of HA at different power of UV lamp

the faster PC degradation of HA was, a good linearity relation between  $\ln(C/C_0)$  and  $t$  was reflected. The data of apparent first-order rate constant ( $k$ ) and regression coefficient square ( $R^2$ ) at varied UV lamp power is listed in Table 1, while the relation between apparent first-order rate constant  $k$  and the power of UV light can be indicated by Equation (3):

$$k = k_1 W^a \quad (3)$$

Where  $k_1$  is the constant.  $k_1$  and  $a$  can be calculated from the data in Table 1, i.e.

$$k = 0.0003 W^{0.8386} \quad (4)$$

Table 1 The kinetic parameters of PC degradation of HA at different power of UV lamp

UV lamp power, W	$k$ , $\text{min}^{-1}$	$R^2$
20	0.0037	0.9895
40	0.007	0.9958
60	0.0099	0.9855
125	0.0172	0.9854

### 2.2.2 The effect of initial concentration of HA on PEC oxidation velocity

The effects of initial concentrations of HA (5, 10, 15, 20 mg/L) on  $k$  in PC degradation of HA are demonstrated in Fig. 6.

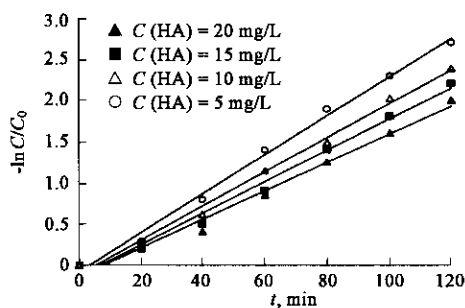


Fig. 6 The kinetic character of PC degradation of HA at different initial concentration of HA

The experimental results in Fig. 6 show that the degradation rate increases and  $k$  decreases when the initial concentration of HA increases. The data of apparent first-order rate constant ( $k$ ) and regression coefficient square ( $R^2$ ) at varied initial concentration of HA are listed in Table 2, while the relation between apparent first-order rate constant  $k$  and the initial concentration of HA can be indicated by Equation (5):

$$k = k_2 C^b \quad (5)$$

where  $k_2$  and  $b$  are constants.  $k_2$  and  $b$  can be calculated from the data in Table 2, i.e.

$$k = 0.0341 C^{-0.2217} \quad (6)$$

Table 2 The kinetic parameters of PC degradation of HA at different initial concentration of HA

$C_0$ (HA), mg/L	$k$ , $\text{min}^{-1}$	$R^2$
5	0.0236	0.9945
10	0.0208	0.9928
15	0.0190	0.9879
20	0.0172	0.9854

### 2.2.3 The effects of bias on the rate of PC degradation of HA

The effects of bias (0, 0.2, 0.6, 1.0, 1.4, 1.8 and 2.0 V) on  $k$  in PC degradation of HA are demonstrated in Fig. 7.

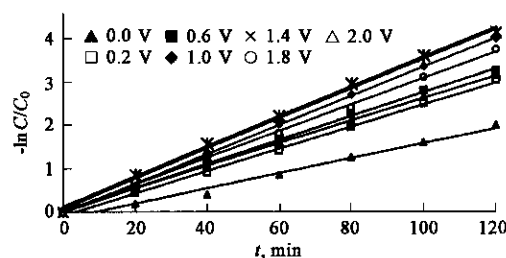


Fig. 7 The kinetic characters of PC degradation of HA at different bias

Experimental results showed that the optimum bias was 1.4 V, while  $k$  rose with rise of bias when bias was lower than 1.4 V, and  $k$  decrease with rise of bias when bias was higher than 1.4 V.  $R^2$  and  $k$  at different outside bias voltage are listed in Table 3.

Table 3 The kinetic parameters of the PC degradation of HA at different bias

Bias, V	$k$ , $\text{min}^{-1}$	$R^2$
0.0	0.0172	0.9854
0.2	0.0225	0.9979
0.6	0.0276	0.9984
1.0	0.0337	0.9996
1.4	0.0345	0.9972
1.8	0.0306	0.9982
2.0	0.0260	0.9994

The relation between  $k$  and bias can be expressed as Equation (7):

$$k = 0.0323 V^{0.2511} \quad (7)$$

### 2.2.4 The effects of the area of $\text{B}_2\text{O}_3 \cdot \text{TiO}_2/\text{Ti}$ catalyst on the rate of PC of HA

The effects of area of  $\text{B}_2\text{O}_3 \cdot \text{TiO}_2/\text{Ti}$  catalyst (0, 7, 14, 28, 42, 56  $\text{cm}^2$ ) on  $k$  in PC degradation of HA are demonstrated in Fig. 8.

Experimental results in Fig. 8 show that the optimum area of catalyst in this PC oxidation system was 42  $\text{cm}^2$ , the efficiency of PC degradation of HA decreased with increase of area of catalyst when the area of catalyst was more than 42  $\text{cm}^2$ , which may be related to the shield effect and hindering transitions of substances in the solution. The data of  $k$  and  $R^2$  using different area catalysts are presented in Table 4.

The relation between the area of catalyst and  $k$  could be got according to the data in Table 4, i.e.

$$k = 0.0528 A^{0.4525} \quad (8)$$

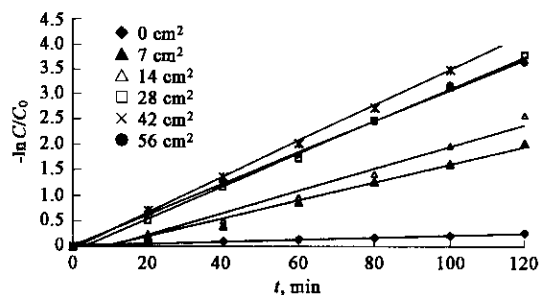


Fig.8 The kinetic characters of PC degradation of HA at different areas of catalyst

Table 4 Kinetic parameter of PC degradation of HA at different area of catalyst

Area of catalyst, $cm^2$	$k$ , $min^{-1}$	$R^2$
0	0.0019	0.9829
7	0.0172	0.9854
14	0.0213	0.9754
28	0.0317	0.9978
42	0.035	0.9986
56	0.0303	0.9982

### 2.2.5 The kinetic model of PEC degradation of HA

The apparent rate constant  $k$  of PEC oxidation of HA could be expressed as Equation (9) according to above experimental results:

$$k = m (W)^{0.8386} (C_0)^{-0.2217} (V)^{0.2511} (A)^{0.4323} \quad (9)$$

The apparent rate constant  $k$  could be detected by experiments when the power of UV lamp, the initial humic acid concentration, the bias, and the area of catalyst determined, the  $k$  was  $0.0343 \text{ min}^{-1}$  in the PEC degradation system of HA when  $W$ ,  $C_0$ ,  $V$  and  $A$  were 125 W, 20 mg/L,  $7 \text{ cm}^2$  and 1.3 V respectively at initial pH 3.18. The  $m$  could be calculated when the detected  $k$  was substituted by  $0.0343 \text{ min}^{-1}$  in Equation (10), the value of  $m$  was 4.83. The apparent rate constant  $k$  of PEC oxidation of HA could be expressed further as Equation (10):

$$k = 4.83 \times 10^{-4} (W)^{0.8386} (C_0)^{-0.2217} (V)^{0.2511} (A)^{0.4323} \quad (10)$$

The Equation (10) shows that the factors of effects from strongness to weakness on the photoelectrocatalytic degraded rate of humic acid were power of UV-lamp, area of  $TiO_2$  film, bias, original concentration of humic acid solution.

The kinetic equation of PEC degradation of HA using  $B_2O_3 \cdot TiO_2/Ti$  as photocatalyst could be expressed as follows:

$$-\ln C/C_0 = 4.83 \times 10^{-4} (W)^{0.8386} (C_0)^{-0.2217} (V)^{0.2511} (A)^{0.4323} t \quad (11)$$

The theoretical data calculated by Equation (11) with the experimental data were compared in order to check the accuracy of Equation (11), the UV lamp power of 125 W, the initial humic acid concentration of 20 mg/L, the area of catalyst of  $7 \text{ cm}^2$ , the initial pH of 3.18 and the bias of 1.0 V were used in the experiment (Fig.9).

The experimental results in Fig.9 showed the theoretical data calculated by Equation (11) tallies with the experimental data basically.

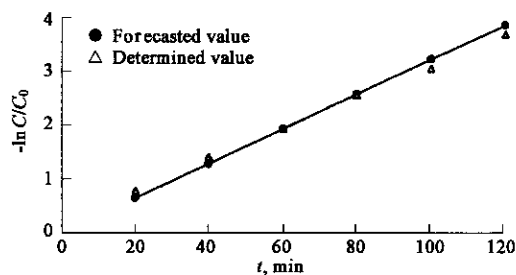


Fig.9 Comparison of the theoretical data with the experimental data

## 3 Conclusions

The pH of solution plays a very important role in the photocatalytic degradation of HA, the degradation of HA in acid solution was faster than that in alkaline solution

In the PEC oxidation system, the kinetic model of PEC degradation of HA could be expressed as  $-\ln C/C_0 = 4.83 \times 10^{-4} (W)^{0.8386} (C_0)^{-0.2217} (V)^{0.2511} (A)^{0.4323} t$ , the factors of effects from strongness to weakness on the photoelectrocatalytic degraded rate of humic acid were power of UV-lamp, area of  $TiO_2$  film, bias, original concentration of humic acid solution. In this PEC reaction system, the optimum conditions were power of UV-lamp 125 W, area of  $TiO_2$  film  $42.0 \text{ cm}^2$ , bias 1.4 V, and original concentration of humic acid solution 5 mg/L.

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