

# Determination of hydroxyl radicals in TiO<sub>2</sub>/Ti photoelectrocatalytic oxidation system using Fe(phen)<sub>3</sub><sup>2+</sup> spectrophotometry

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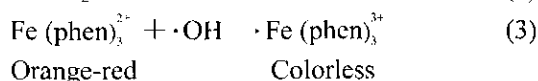
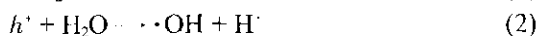
**Abstract:** A new method of determining the cumulate concentration of hydroxyl radicals in the TiO<sub>2</sub>/Ti photoelectrocatalytic (PEC) oxidation system was established by *o*-phenanthroline-Fe(II)(Fe(phen)<sub>3</sub><sup>2+</sup>) spectrophotometry and using anion exchange membrane. Fe(phen)<sub>3</sub><sup>2+</sup> can be oxidized to *o*-phenanthroline-Fe(III)(Fe(phen)<sub>3</sub><sup>3+</sup>) by strong oxidization of hydroxyl radicals ( $\cdot\text{OH}$ ). Then the cumulate concentration of hydroxyl radicals can be calculated through determining the change of the Fe(phen)<sub>3</sub><sup>3+</sup> absorbency at 509 nm. In addition, the research results showed the production rate of hydroxyl radicals was affected obviously by pH of solution, the cumulate concentration of hydroxyl radicals was the largest at nearby the initial pH 6.3 (isoelectric point), and the change direction of pH after illumination tended to nearby isoelectric point.

**Keywords:** TiO<sub>2</sub>/Ti catalyst; photoelectrocatalysis; *o*-phenanthroline-Fe; hydroxyl radical; anion exchange membrane

## Introduction

Semiconductor photocatalytic oxidation applied in the environmental engineering field was paid attention in the past few years (Garraway *et al.*, 1994), especially semiconductor TiO<sub>2</sub> photocatalytic oxidation technique has become research heatpoint in both water and wastewater depth treatment field (Skmerm *et al.*, 2001; James and John, 2004; Maria *et al.*, 2004). The photo-produced hole in the valence band of the irradiated TiO<sub>2</sub> semiconductor has very strong oxidative capability, and can capture the electrons of the water molecule to create hydroxyl radical ( $\cdot\text{OH}$ ) that is one of the strongest oxidants in the water, almost has no selectivity to objects and can mineralize difficult degraded organic contaminants (Matthews, 1988; Linsebigler *et al.*, 1995). Therefore, it is very significant to research the regularity of created hydroxyl radical in TiO<sub>2</sub>/Ti photoelectrocatalytic oxidation system for increasing treatment efficiency of contaminants in wastewater and accelerating the practical application of TiO<sub>2</sub> photocatalytic oxidation technology in water treatment.

Hydroxyl radical has the characters of strong reactive activity, short living time ( $<10^{-4}$  s) and low existing concentration etc. The main methods of hydroxyl radical determination include electron spin resonance (EPR) (Satoshi *et al.*, 2003; Wolfrum *et al.*, 1994), fluorometric method (Yang and Guo, 2001; Tai *et al.*, 2002) and high performance liquid chromatography (HPLC) (Jen *et al.*, 1998) etc., however these methods are difficult to be applied in ordinary laboratory due to expensive reagents, special apparatus and the complex operation. The determination of hydroxyl radical by Fe(phen)<sub>3</sub><sup>2+</sup> spectrophotometry can overcome the shortcomings of above methods, its determination principle is as follows.



Fe(phen)<sub>3</sub><sup>2+</sup> is common oxidation-reduction indicator, its color can reflect acutely the change of the oxidation-reduction state. The strongest absorption peak of Fe(phen)<sub>3</sub><sup>2+</sup> [*o*-phenanthroline-Fe(II)] is at 509 nm, while the absorption of Fe(phen)<sub>3</sub><sup>3+</sup> [*o*-phenanthroline-Fe(III)] at 509 nm is weak enough to be omitted. The amount of Fe(phen)<sub>3</sub><sup>2+</sup> decrease is the amount of hydroxyl radical in the system because Fe(phen)<sub>3</sub><sup>2+</sup> is oxidized into Fe(phen)<sub>3</sub><sup>3+</sup> by hydroxyl radical. So the cumulate concentration of hydroxyl radical can be obtained indirectly using the Fe(phen)<sub>3</sub><sup>2+</sup> spectrophotometer (Jin *et al.*, 1996).

Much investigation showed that the photoelectrocatalytic oxidation can increase the efficiency of photocatalytic oxidation obviously through inhibiting the ineffective recombination between photo produced electrons and photo-produced holes, and has good prospect of research (Kesselman *et al.*, 1997; Dong and Anderson, 1994). Nevertheless the inves-

tigation on both the determination method and the regularity of created hydroxyl radical in TiO<sub>2</sub>/Ti photoelectrocatalytic oxidation system has not been reported so far.

The Fe(phen)<sub>3</sub><sup>3+</sup> oxidized from Fe(phen)<sub>3</sub><sup>2+</sup> in photoelectrocatalytic oxidation system can be reduced again through obtaining electrons in cathode, and which cause interference for determination. The determination method of hydroxyl radical established in the paper can overcome above interference by using anion exchange membrane to inhibit the Fe(phen)<sub>3</sub><sup>3+</sup> capturing electrons from the cathode. The determination principle is showed in Fig. 1.

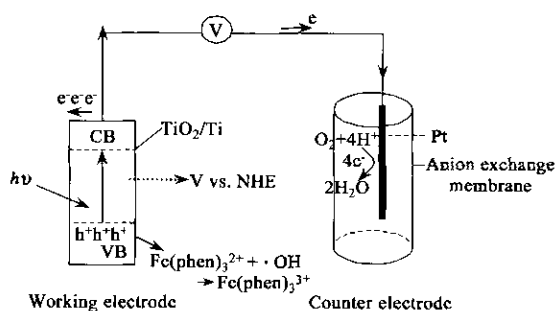


Fig.1 Diagram of both generation and determination principle of hydroxyl radical

## 1 Materials and experiments

### 1.1 Materials

TiO<sub>2</sub>/Ti catalyst was home-made (Liu *et al.*, 2003). Anion exchange membrane was purchased from Zhejiang Xinke Materials Co. 0.2% (m/v) Fe(phen)<sub>3</sub><sup>2+</sup> solution, 1 mol/L ferrous sulfate. All chemicals were of the analytical reagent grade and used without further purification. Doubly distilled water was used throughout this study.

### 1.2 Experiments and equipment

The photoelectrocatalytic reactor system is showed in Fig.2. The main components were the cylinder quartz cell with the size of 25 mm in diameter and 50 mm in height, a 20 W-ultraviolet light source (Jinzhou Optics Equipment Co.), and a potentiostat (Shanghai Sanke Electric Appliance Co.). A Pt wire (40 mm in length with a 0.4-mm diameter). PHS-3C type acidity instrument (Xiaoshan Analysis Equipments Co.) and 65-1 comprise electrode (Shanghai Electro Optic Device Factory).

### 1.3 Methods

Firstly 4 ml solution of the 0.2%(m/v) Fe(phen)<sub>3</sub><sup>2+</sup> was added into 200 ml doubly distilled water as use-solution, then the absorbance value of the use-solution at 509 nm was measured as A<sub>0</sub>.

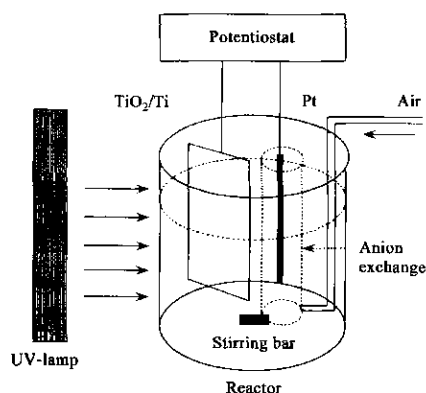


Fig.2 Diagram of reactor for photoelectrocatalytic reaction

Ten milliliter use-solution was taken into the reactor, the bias voltage was applied and the ultraviolet light was turned on, then a certain volume solution was taken out and its absorbance value with the irradiating time were determined as A<sub>t</sub>, so ΔA (the change of absorbance value after UV-light irradiation) = A<sub>0</sub> - A<sub>t</sub>, the cumulated concentration of hydroxyl radical could be calculated through the below equation:

$$[\cdot\text{OH}] = \Delta A / (\epsilon L) \quad (4)$$

In above equation,  $\epsilon = 1.1 \times 10^4 \text{ L}/(\text{mol} \cdot \text{cm})$ ,  $L = 1 \text{ cm}$

## 2 Results and discussion

### 2.1 Determination of hydroxyl radical in TiO<sub>2</sub>/Ti photocatalytic oxidation system

Both 10 ml use-solution and the TiO<sub>2</sub>/Ti film catalyst were put into the reactor, turning on the ultraviolet light, then the samples were taken out and its absorbance value were determined after interval 10 min. The experimental results showed (Fig.3) that the change of [ $\cdot\text{OH}$ ] with irradiating time in TiO<sub>2</sub>/Ti photocatalytic oxidation system could be divided into three stages: (1) when the irradiating time was less than 20 min, the cumulate concentration of hydroxyl radical increased with the irradiating time. The reason might be that hydroxyl radicals were produced continuously with irradiating time and oxidized Fe(phen)<sub>3</sub><sup>2+</sup> into Fe(phen)<sub>3</sub><sup>3+</sup> rapidly, so the cumulate concentration of hydroxyl radical increased rapidly. Meanwhile, both Fe(phen)<sub>3</sub><sup>3+</sup> concentration and electron concentration produced on TiO<sub>2</sub>/Ti film surface by UV-light irradiation also increased rapidly, the reaction that  $\cdot\text{OH}$  oxidize Fe(phen)<sub>3</sub><sup>2+</sup> into Fe(phen)<sub>3</sub><sup>3+</sup> was in dominance; (2) when the irradiating time was between 20 to 30 min, the cumulated concentration of hydroxyl radical decreased slowly. It may related to the reactive enhance of Fe(phen)<sub>3</sub><sup>3+</sup> reduced into Fe

(phen)<sub>3</sub><sup>2+</sup> by photo-generated electrons, when the concentrations of both Fe(phen)<sub>3</sub><sup>3+</sup> and the photo-generated electrons increased with irradiating time, while the increase of Fe(phen)<sub>3</sub><sup>2+</sup> concentration in the solution reflected the decrease of concentration of hydroxyl radical indirectly; (3) when the irradiating time was more than 30 min, the cumulate concentration of hydroxyl radical tended to be stable gradually. It might be related that the reactions between Fe(phen)<sub>3</sub><sup>2+</sup> oxidized into Fe(phen)<sub>3</sub><sup>3+</sup> by ·OH and Fe(phen)<sub>3</sub><sup>3+</sup> reduced into Fe(phen)<sub>3</sub><sup>2+</sup> by the photogenerated electrons tended to be balanced gradually.

Above experimental results showed that the reduction of photo-generated electrons interfered the determination of hydroxyl radical in simple photocatalytic oxidation system using *o*-phenanthroline-Fe(II) spectrophotometry.

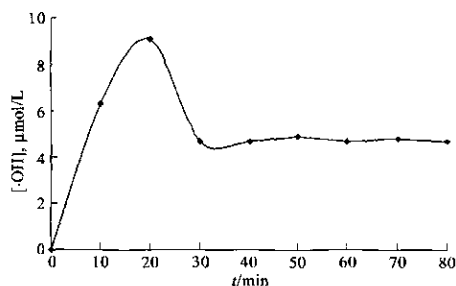


Fig.3 Changes of cumulate concentration of hydroxyl radical with irradiation time

## 2.2 Determination of hydroxyl radical in TiO<sub>2</sub>/Ti photoelectrocatalytic oxidation system

In the paper experimental equipment shown in Fig.2 was used in order to avoid the interference of Fe(phen)<sub>3</sub><sup>3+</sup> reduced into Fe(phen)<sub>3</sub><sup>2+</sup> by the photoproducted electrons, the photo-generated electrons were transferred to cathode by the bias, while the cathode and the anode was separated by anion exchange membrane in photoelectrocatalytic oxidation process. So Fe(phen)<sub>3</sub><sup>3+</sup> could not contact with cathode and could not be reduced.

The effects of bias on creation regularity of hydroxyl radical in photoelectrocatalytic oxidation system are shown in Fig.4.

The experimental results in Fig.4 indicated that: (1) the interference from Fe(phen)<sub>3</sub><sup>3+</sup> reduced into Fe(phen)<sub>3</sub><sup>2+</sup> by photo-generated electrons on determination of hydroxyl radical was overcome positively; (2) the cumulate concentration of hydroxyl radical created by UV-light irradiation could be enhanced effectively with a little bias, it showed that the bias was favorable to photocatalytic oxidation reaction; (3) the increase of the cumulate concentration of hydroxyl radical

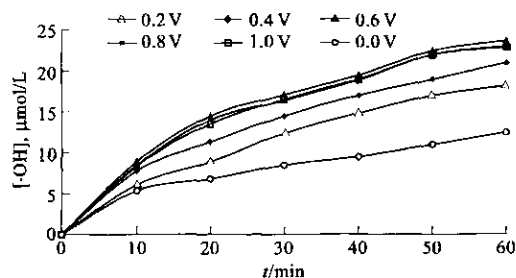


Fig.4 Changes cumulate concentration of hydroxyl radical in TiO<sub>2</sub>/Ti PEC oxidation system as irradiation time

created by UV-light irradiation was not obviously with enhancement of the bias, when the bias was larger than 0.6 V. It showed that the ineffective recombination between photo-generated electrons and photo-generated holes was inhibited effectively when the bias reached 0.6 V; (4) there was not hydroxyl radical in the system without light irradiation.

## 2.3 Effects of pH value on the creation of hydroxyl radical

Both flat band potential and charges on the surface of TiO<sub>2</sub> are affected by solution pH, so the efficiency of hydroxyl radical produced by UV-light irradiation may be affected indirectly by solution pH in photocatalytic oxidation system. The effects of pH on generation regularity of hydroxyl radical were investigated systematically in pH 3—9 because Fe(phen)<sub>3</sub><sup>2+</sup> existed stably in pH 3—9. The pH values of solution before and after irradiation were determined under 0.6 V bias and 20 W UV-light for 60 min, and pH values of solution was adjusted with sulfuric acid and sodium hydroxide solutions. The experimental results are shown in Fig.5.

The experimental results indicated that the efficiency of hydroxyl radicals produced by light irradiation increased with the continuous enhance of pH value when the initial solution pH was less than pH value at TiO<sub>2</sub> equipotential point (pH 6.3; Li and Li, 2001), the efficiency of hydroxyl radicals was maximum at nearby TiO<sub>2</sub> equipotential point, and the efficiency decreased gradually with the continuous enhance of pH value when the initial pH of solution was larger than pH at TiO<sub>2</sub> equipotential point. Compared with the change of pH value before and after UV-light irradiation, it could be found that the pH value of the system always changed towards equipotential point by the assistance of electric field.

Above results might be related to TiO<sub>2</sub> being amphoteric oxidants, there were a lot of hydroxyls on TiO<sub>2</sub> surface because the coordination of water led titanium-hydroxyl bond. There could exist following

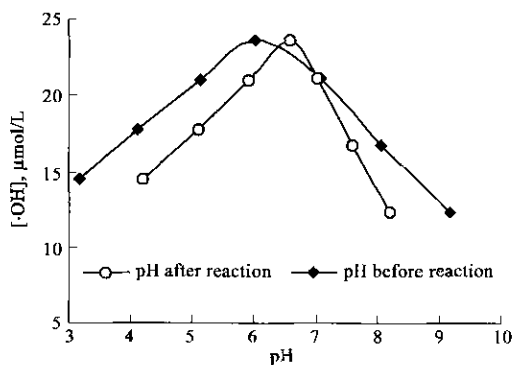
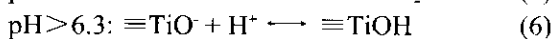
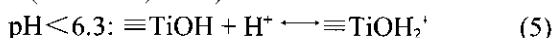


Fig.5 Effects pH value on generation regularity of  $\cdot\text{OH}$  in PEC oxidation system

equilibration between acid and alkali due to titanium-hydroxyl bond at different pH aqueous solution (Fan *et al.*, 2003).



The change of solution pH value affected the existence of  $\text{TiOH}$ ,  $\text{TiOH}_2^+$  and  $\text{TiO}^-$  groups on  $\text{TiO}_2$  surface, and further affected the efficiency of produced  $\cdot\text{OH}$  by UV-light irradiation.

### 3 Conclusions

It was feasible to determine the cumulate concentration of hydroxyl radicals in  $\text{TiO}_2$  PEC oxidation system using  $\text{Fe}(\text{phen})_3^{2+}$  spectrophotometry by the assistance of anion exchange membrane. The efficiency of hydroxyl radicals in PEC oxidation system could be enhanced effectively by the assistance of little bias. The efficiency of hydroxyl radicals in  $\text{TiO}_2/\text{Ti}$  could be affected obviously by pH value of solution, the cumulate concentration of hydroxyl radical produced was maximum at nearby  $\text{TiO}_2$  equipotential point, the pH value of solution after UV-light irradiating always changed towards equipotential point.

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