

Electrically enhanced photodegradation of an azodye (Acid Orange II) using a Pt/TiO₂ film electrode irradiating with an UV lamp

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Abstract: A photoelectrochemical process in the degradation of an azodye (Acid Orange II) on a Pt/TiO₂ film electrode was investigated. By using the glass device and the voltage stabilized source of direct current, decolorization ratios higher than 78% were observed during a period of 5h. Comparing this value with the sum of the decolorization ratios obtained by a sole application of electrochemical (lower than 3%) and photochemical (about 23%) procedures, a significant synergic effect between both processes was observed. The effects of adsorptious voltage and pH value on the decolorization ratios were obvious while the effect of the amount of aeration was minor.

Keywords: photoelectrochemical process; Pt/TiO₂ film electrode; synergic effect

Introduction

The printing and dyeing industry has a high potential environmental impact, principally due to the release of large volumes of wastewater that contain high organic charge and strong coloration. There are many processes to treat wastewater from printing and dyeing industry, but the traditional processes, such as adsorption, flocculation, extraction, activated sludge process etc., can not remove the refractory organic compounds efficiently or lead to secondary pollution.

In recent years, photocatalytic oxidation processes have drawn much attention because research has shown that it could degrade organic pollutants at low or medium concentration with little secondary pollution, and a potential of utilizing solar energy (Wu, 2000). On the other hand, the electrochemical process has also showed high efficiency for color removal and for degradation of recalcitrant pollutants such as cyanide, EDTA and aniline (Chiang, 1995; Pelegrini, 1999). In fact, it is the hydroxyl radicals that carry out the destruction of organic pollutant. Photocatalysis and electrolysis are two ways to produce OH· radicals. In photocatalysis, these radicals are generated upon illumination of aqueous suspensions of a semiconductor with light of sufficient energy (Brillas, 1998). Electron-hole pairs are then photogenerated in the semiconductor, which can migrate to the interface where they react with suitable adsorbed redox species. In aerated aqueous suspensions, the photogenerated electrons promote the reduction of dissolved oxygen (Brillas, 1998):



whereas the photogenerated holes oxidize adsorbed water molecules to give hydroxyl radicals (Brillas, 1998):



The O₂^{·-} formed from Reaction(1) can lead after several steps, to the generation of H₂O₂ (Brillas, 1998):



On the other hand, hydroxyl radicals can be produced by means of two electrochemical processes: anodic oxidation and mediated electrooxidation(Brillas, 1998). The anodic oxidation generate OH[·] radicals at the anode from water oxidation in a process similar to Reaction(2). But in mediated electrooxidation, organics react with electrochemically generated species, such as H₂O₂:



TiO₂ is the most attractive photocatalyst for decreasing pollutants and purifying both water and air (Chih-Cheng, 2000; Rajeshwar, 1995; Chen, 1993; 1994). The suspended TiO₂ is now commonly used but it agglomerates easily and using TiO₂ suspensions for the oxidation of pollutants involves, in addition to costly, discontinuous treatments such as filtration and resuspension of the catalyst, and quite low quantum efficiency is obtained. These disadvantages seriously restrict the appliance and development of photocatalysis. One of the effectual method to overcome those disadvantages is the fixation of the photocatalyst. It has been shown that the photocatalytic activity of titanium(IV) oxide is influenced by surface area, crystal structure(anatase and/or rutile) and density of surface hydroxyl groups(Papp, 1993). Several attempts have been performed to increase its photoefficiency either by noble metal deposition or by ion doping(Matoss, 1998). Research in this field is now making rapid progress. During the past several years previous investigators have modified this density through the photodecomposition of the platinum group metals onto the surface of the titanium(IV) oxide catalyst(Papp, 1993). Surface modification of TiO₂ by the addition of Pt, Pd or RuO₂ has been found to increase the photocatalytic activity of the semiconductor 10—10³ times(Sakata, 1982). We have demonstrated that the photocatalytic activity of TiO₂ is greatly increased by supporting metal or metal oxide catalysts such as Pt or RuO₂ on TiO₂ (Sakata, 1982).

In this work, the photoelectrochemical degradation of an azodye on the Pt/TiO₂ film electrode is reported. The synergy of photocatalysis and electrolysis in the degradation of the azodye and the effects of voltage, quantities of aeration, initial concentration and pH value on the degradation rate in homemade rectangle reactor are systematically studied.

1 Experimental

The Ti sheet (99.60% purity, size = 8.9 cm × 7.7 cm, thickness = 1.0 mm, obtained from the Beijing Steel Academy, China) was burnished by sandpaper, cleaned with distilled water and immersed for 1h in an aqueous solution of 10% HCl. A thin TiO₂ film was obtained by putting the dried slice into the muffle heating to 800℃ and keeping this temperature for 1h. The oxidized film of TiO₂ was determined by X-ray diffraction(XRD). Then the Pt/TiO₂ photocatalyst was prepared by depositing Pt on fixed TiO₂ film by illuminating it in a H₂PtCl₆ solution for 1h. It was examined by X-ray fluorescence(XRF) to determine the amount of Pt(0.0976 wt%).

The acid orange II(obtained from the Fine Chemistry Key Laboratory of the State, Dalian University of Technology) was used as target compound. The photoreactor was made of glass and its size was 9.8 cm × 5.5 cm × 0 cm. The Pt/TiO₂ photoelectrode was applied as anode and the stainless steal(9.0 cm × 9.0 cm) as cathode. The dye solution was illuminated by 300W high pressure mercury lamp (Shanghai Yamjing Lamp Factory, China) with a maximum centered at λ = 365 nm with different supply of voltage on the electrodes and different condition of aeration in the solution. The voltage was provided by the voltage stabilized source of direct current (Shanghai Zhenhua Voltage Regulator Factory, China). The intermittent and batch mode of operation was employed. The 721-spectrophotometer(Shanghai Third Analytic Apparatus Factory, China) and the PHS-3B digital acidity/ionometer(Hangzhou Wanda Apparatus & Instrument Factory, China) were employed to determine the concentration and the pH value of the dye solutions. All experiments were operated at room temperature(25℃). The concentration was 10 mg/L without special

explanations. The decolorization ratio and the load of degradation were defined as:

$$\text{Decolorization ratio} = \frac{C_0 - C}{C_0} \times 100\% , \tag{7}$$

$$\text{Load of degradation} = \frac{(C_0 - C) \cdot l}{T \cdot P \cdot L} \times 100\% , \tag{8}$$

in which C_0 = initial concentration (mg/L); C = concentration at T time (mg/L); l = volume (L); T = time (h); P = power (W); L = lighting intensity (W/m^2).

2 Results and discussion

2.1 The synergic effect of photocatalysis and electrolysis

The aqueous solutions of acid orange II were treated using the processes of photocatalysis, electrolysis and electrochemically assisted photocatalysis. Fig. 1 shows the time-course of acid orange II for these different runs. It can be seen from Fig. 1 that the sole electrolysis without UV-irradiation can be neglected with less than 3% of conversion within 5h. The sole photocatalysis had effect on the degradation of the dye and the decolorization ratios were 23.6%. Nevertheless, a significant degradation of the dye with the decolorization ratios about 78% was observed during a single process of electrochemically assisted photocatalysis. It indicated that the photocatalysis and the electrolysis had synergic effect on the degradation of acid orange II.

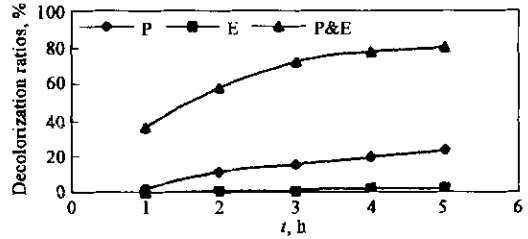


Fig. 1 The synergic effect of photocatalysis and electrolysis P: photocatalysis; E: electrolysis; P&E: electrochemically assisted photocatalysis

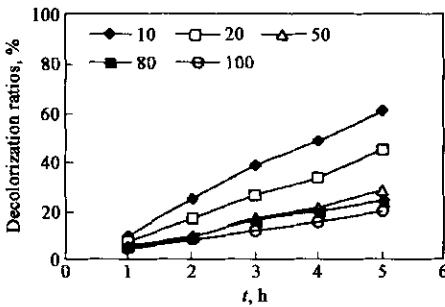


Fig. 2 The effect of concentrations on the decolorization ratios (voltage = 25V; aeration = 0.2 m³/h)

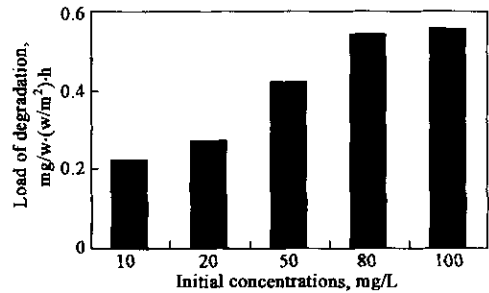


Fig. 3 Load of degradation within 5h (voltage = 25V; aeration = 0.2 m³/h)

2.2 Effect of initial concentration

Fig. 2 shows the time course of photoelectrochemical degradation of acid orange II with different concentrations. The load of degradation under average light intensity of high pressure mercury lamp ($7.3 W/m^2$) during a period of 5h is shown in Fig. 3. It can be seen from Fig. 2 and Fig. 3 that the increase of Acid Orange II initial concentrations had remarkable effect upon the dye removal. The decolorization ratios decreased from 60.6% to 19.6% while the load of degradation increased from 0.22 to 0.55 ($mg/w \cdot (w/m^2) \cdot h$) with the concentration increasing from 10 mg/L to 100 mg/L. The results of kinetic analysis for the reaction of dye removal are given in Table 1. The degradation of dyes is of the apparent first order and the linear coefficients are around 0.99. Obviously, the pseudo rate constant K_{sh} decreased with the increase of

concentrations.

2.3 Effect of adscititious voltage

The recombination between the photogenerated electron-hole pairs can be suppressed and thus the quantum efficiency enhanced by applying an external anodic bias to the Pt/TiO₂ film electrode. Fig.4 shows the effect of adscititious voltage on the degradation by electrochemically assisted photocatalysis. The decolorization ratios of dyes increased gradually from 31.2% to 69.7% with the increase of voltage from 5V to 25V during a period of 5h.

2.4 Effect of pH value

The pH value was adjusted by the aqueous solution of H₂SO₄ and NaOH for investigation of the effect of pH value on degradation. Fig.5 shows the time course of photoelectrochemical degradation of acid orange II with different pH value. The effect of pH value on the degradation of dyes was remarkable. The reaction rate of dyes removal within 5h decreased from 94% to 76% with the increase of the pH value from 2.68 to 8.33. During the whole period of reaction, the decolorization ratios increased quickly during the first hour while slowly after 2h.

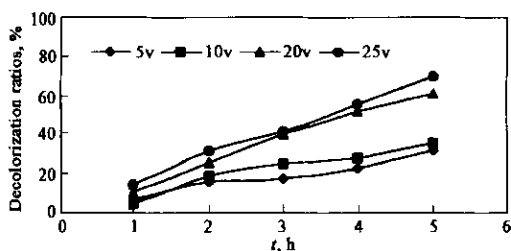


Fig.4 The effect of voltage on the decolorization ratios (amount of aeration = 0.2 m³/h; pH = 5.38)

Table 1 K_{sh} and linear coefficient R^2 for the degradation of dyes at different initial concentrations (voltage = 25V, aeration = 0.2 m³/h, illumination 5h)

Concentration, mg/l.	K_{sh} , h ⁻¹	R^2
10	0.1874	0.9924
20	0.1178	0.9864
50	0.0662	0.9946
80	0.0538	0.9905
100	0.0430	0.9965

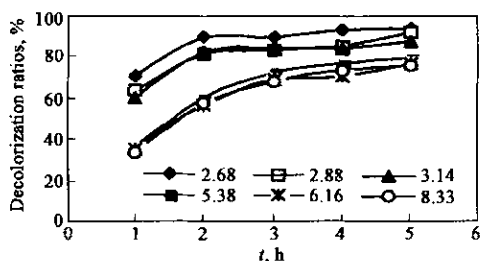


Fig.5 The effect of pH value on the decolorization ratios (voltage = 25V; amount of aeration = 0.2 m³/h)

2.5 Effect of the amount of aeration

In aerated aqueous solutions, the photogenerated electrons promote the reduction of dissolved oxygen whereas the photogenerated holes oxidize adsorbed water molecules to give hydroxyl radicals. Therefore, the different conditions of aeration were investigated. Fig.6 shows that the decolorization ratios changed negligibly with the increase of the amount of aeration. It proved that the effect of the amount of aeration on the decolorization ratios was not obvious.

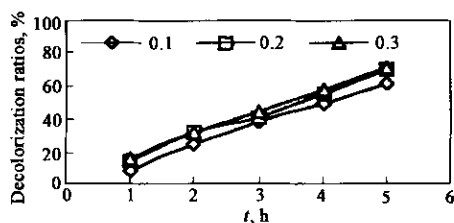


Fig.6 The effect of amount of aeration (m³/h) on the decolorization ratios (voltage = 25V; pH = 5.38)

3 Conclusions

The photocatalysis and the electrolysis have synergic effect in the degradation of the acid orange II. The decolorization ratios under the electrochemically assisted photocatalysis (78%) were much higher than either of that under sole electrolysis and sole photocatalysis.

The degradation of acid orange II is of the apparent first order. The increase of acid orange II initial concentrations had remarkable effect upon the dye removal. The load of degradation increased from 0.22 to

0.55 (mg/w·(w/m²)·h) with the concentrations increasing from 10 mg/L to 100 mg/L.

The effects of adsorbent voltage and pH value on the reaction of dyes removal were obvious. The decolorization ratios increased from 31.2% to 69.7% with the increase of voltage while decreased from 94% to 76% with the increase of pH value during a period of 5h.

The effect of the amount of aeration was not obvious.

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