

A novel photoelectrochemical reactor three dimension electrode-slurry photocatalytic reactor

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Abstract A novel photoelectrochemical reactor, three dimension electrode-slurry photocatalytic reactor, was designed and characterized by the current enhancement and COD removal efficiency. An apparent photoelectrochemical synergic effect was observed for the treatment of dye containing waste water in the reactor.

Keyword Photoelectrochemical; Photocatalytic; Three Dimension Electrode; Reactor.

1. INTRODUCTION

The photoelectrochemical technology with external potential appears to be a research front of photocatalytic degradation of organic pollutants. Many academic interests have been focused on this area in recent years [1-3]. However, The main purpose of electrochemically assisted photocatalysis is just to represent a proof-of-concept that anodic bias on TiO₂ electrode can drive away the photogenerated-electron and -hole in different directions, and reduce their recombination. Therefore, in the most of electrochemically assisted photocatalytic experiments, the applied anodic bias is almost controlled to be lower than the oxidation potential of the investigated organic pollutant so that no direct electrochemical oxidation interferes with the photocatalysis [1-4]. To date, the electro-assisted photocatalysis at higher voltage has scarcely been investigated.

It is worthy of notice that recently the interest in the application of electrochemical oxidation to the wastewater treatment has been increased [5-6]. In particular, the electrochemical technologies based on three dimension electrodes for wastewater treatment have attracted much more attention [6-8] because the electrodes are characterized with large specific surface areas and high performance in comparison to conventional two-dimensional electrode [5-6].

Recently, we have started to investigate a novel hybrid photoelectrochemical technology for organic wastewater treatment based on three dimension electrode and slurry photocatalysis of semiconductor. The aim of the present paper is to report a new-designed reactor, three dimension electrode-slurry photocatalytic reactor, and its characterization of the current enhancement and COD removal efficiency in a wider ranger of voltage.

2. EXPERIMENTAL

2.1 Material

The photocatalyst used was TiO₂ (Degussa P25). The dye, reactive brilliant red X-3B prepared to 1.0 mmol·L⁻¹ (COD: 265.9 ppm). The granulated activated carbon (GAC) was used as the filler of three dimension electrode. It has a surface area of 870.0 m²·g⁻¹, an average particle size of 3.5×5.1 mm and ash content of 8.1%. A CHI650A electrochemical system, which is computerized, was used as a potentiostat.

2.2 Photoelectrochemical Reactor

The experimental set-up is presented in Fig.1. It is an open double-layered reactor (28.0 cm×6.0 cm×10.0 cm) made of polytetrafluoroethylene plate. The stainless steel anode and cathode (main electrode) were equipped across the reactor. 200.0g GAC used as particle electrodes were packed between the two main electrodes situated 26.6 cm apart from each other and the suspension of RBRX containing 1.0g titanium dioxide was added into the reactor. When the compressed air was sparged into the reactor by a micropore plate from the bottom of reactor cell, it

appeared two layers. The upper one was mainly the suspension of TiO_2 with a height of about 1.0 cm, and the lower one was mainly the GAC particle electrode with a packed height of about 1.0 cm. A 500 W high-pressure mercury lamp was located 12.0 cm above the reactor as an illuminant.

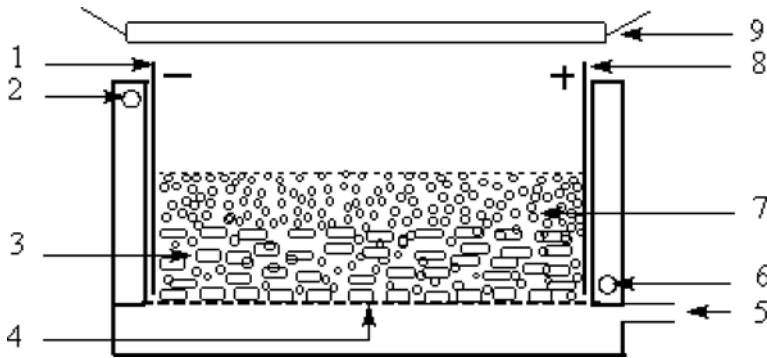


Fig.1 Schematic diagram of three dimension electrode-photocatalytic reactor

1-Cathode; 2--Outlet of recycled water; 3--GAC layer; 4--Micropore plate; 5--Inlet of compressed air; 6--Inlet of recycled water; 7--Titanium dioxide layer; 8--Anode; 9--UV illuminant.

3. RESULTS AND DISCUSSION

3.1 Dependence of Voltage on Current

The photocurrent of the cell is one of major parameters characterizing photoreactor. Thus, it was extensively investigated in the electrochemically assisted photocatalytic process. Kraeutler et al. [9] first recognized that semiconductor particulate in the slurry cell might have similar performance with film electrode in the photoelectrochemical cell. They and other researchers have studied in detail the photocurrent-voltage curves for slurry electrode, and found that the photocurrent is very small and lower than $0.2\mu\text{A}$ [10-11], although the slurry electrode has the great advantage of good mass-transfer. However, the photocurrent of the thin film reactor is much higher than that of the slurry reactor and no less than $25\mu\text{A}$ [12-15].

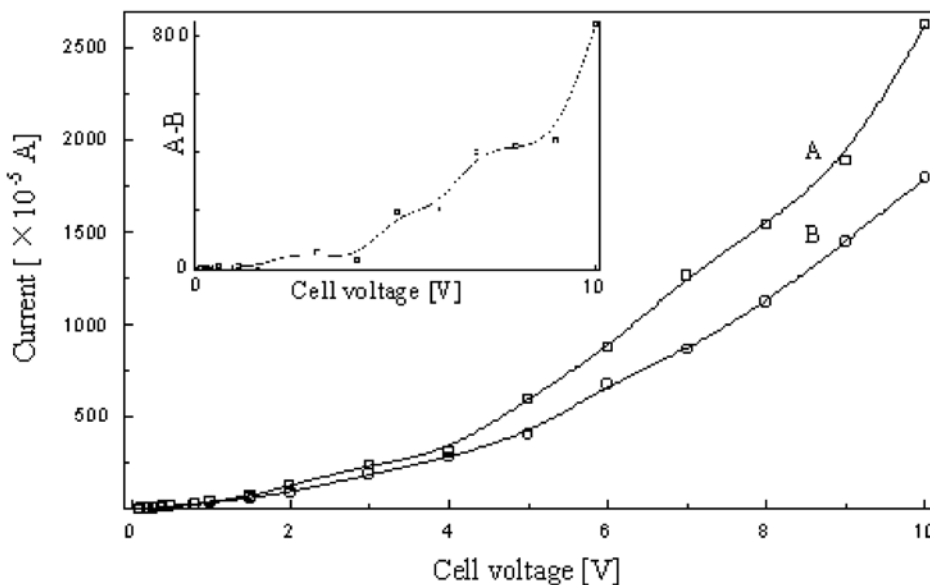


Fig.2 Dependence of voltage on current

A--Current at 10 second in the electrochemical process; B--Current at 10 second in the photoelectrochemical process;

In our experiment, a high photocurrent, about $12.6\mu\text{A}$, was observed in the three dimension electrode-slurry photocatalytic reactor, and it is about 60 folds more than that of the reported slurry reactor [11], although it is lower than that of the above mentioned thin film reactor. This can be considered as an enhancement effect of three dimension electrode to slurry photocatalytic reactor. The enhancement effect can be attributed to that the three dimensional electrode with expanded specific area has a large collecting area of photo-generated electron. It is expected that this kind of reactor may have high treatment efficiency for pollutants because the magnitude of the

photocurrent of the cell is an indicator of the rate of oxidation at the anode [15].

The change of the current with cell voltage in the reactor was also measured and shown in Fig.2. Both current of photoelectrochemical and electrochemical process increased significantly with the increase of applied voltage. Furthermore, the current difference of the photoelectrochemical and the electrochemical process also increased as the increase of the voltage shown in the inset of Fig. 2. This result indicated that the higher the applied voltage, the stronger the ability of capturing photogenerated electron of the anode.

Additionally, it was found that the current of photoelectrochemical process was not only greater than the current of photocatalytic or electrochemical process alone, respectively, but also greater than the sum of both current of photocatalytic and electrochemical process alone. This may be an evidence of a synergic effect between photochemical and electrochemical process in the reactor.

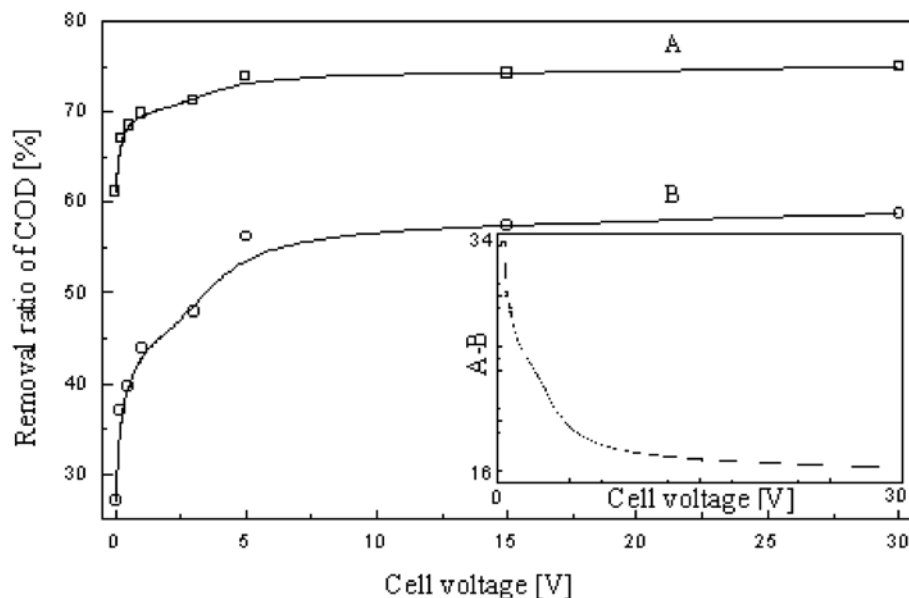


Fig.3 Dependence of voltage on COD removal

A--COD removal in the photoelectrochemical process; B--COD removal in the electrochemical process;

3.2 Dependence of Voltage on COD removal

The effect of applied voltage on the COD removal was conducted and the profile was shown in Fig.3. It is obvious that both COD removal curves in the electrochemical and photoelectrochemical processes increased dramatically with the increase of cell voltage. However, the COD removal of the latter is always higher than that of the former. Furthermore, the difference of their COD removal is also dependent on the applied voltage. It is worth to notice that at the lower voltage, the differences of two curves become greater. It means that there is a more significant synergic effect existing in the photoelectrochemical process at lower voltage than at the higher voltage. The synergic effect at the lower voltage may origin from the reduction of photo-generated electrons and hole, not from other reactions because no any electrochemical reaction occurs at the lower voltage.

The role of potential bias in the photocatalytic degradation of organic pollutants is not only limited to reducing the electron-hole recombination, but also can still have a direct or/and indirect electrochemical oxidation to the organic pollutant. Thus, we could see from the curve B of Fig.3 that the COD removal of electrochemical effect increased dramatically than that of photoelectrochemistry at the high cell voltage. Therefore, it is convenient to control simultaneously the photocatalytic and electrochemical reaction in the reactor under suitable voltage. This conclusion did not conform to the Vinodgopal's view, he believed that it has not been possible to influence a photoreaction in a TiO₂ slurry system with an externally applied potential bias [16].

3.3 Origin of Synergic Effect

It is convinced that oxygen could be changed into the stronger oxidizing agent, H₂O₂, on the electrode by a two-electron reduction of oxygen on carbon electrode [17-18]. The electrogenerated H₂O₂ can be further changed into the OH· radical, in situ, by photolysis reaction in the presence of UV light in the three dimension electrode-photocatalytic reactor [19]. Thus, one of the degradation mechanisms of organic pollutants in the reactor is convinced to be the OH-oxidation besides anodic oxidation. It is also believed that the reaction of the photoelectro-generated OH-radical,

in situ, is an important origin of the above mentioned synergic effect of the COD removal besides the recombining reduction of photogenerated- electron and -hole by anodic bias. Moreover, OH[·] can be generated at the anode surface at the same time of oxygen evolution [20-22]. These agents generated, in situ, can also cause the oxidation of RBRX and its intermediates.

From the above analysis, the degradation of dye can be carried out by many oxidation routines, such as anodic oxidation, the oxidation of electrogenerated H₂O₂ and OH[·], the oxidation of photogenerated hole and OH[·], and the photoelectrochemical synergic effect etc. This is may be a good interpretation of effective destroying of RBRX using the three dimension electrode-slurry photocatalytic reactor.

4. CONCLUSIONS

A new reactor, three dimension electrode-slurry photocatalytic reactor, was designed. It has many advantages, such as not only has high efficiency of packed bed, but also has the advantage of good mass transfer of fluid bed. Thus, the reactor has an apparent characterization of current enhancement and high COD removal efficiency for pollutants.

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