PHOTOELECTROCHEMICAL DEGRADATION OF METHYLENE BLUE WITH NANO TiO$_2$ UNDER HIGH POTENTIAL BIAS

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Abstract. In this work, photoelectrocatalytic degradation of wastewater containing methylene blue (MB) was investigated using a novel photoelectrochemical reactor – a three dimensional electrodes-photocatalytic oxidation reactor in which nano TiO$_2$ was used as photocatalyst. The experimental results are assessed in the terms of decolorization and Chemical Oxygen Demanded (COD) removal efficiencies. The experimental results showed that the three dimensional electrode-photocatalytic reactor could effectively destroy MB within a reaction time of 30 min. It was found that the three dimensional electrode technologies under high potential bias have an apparent enhancement effect on the photocatalytic degradation of MB in water with nanometer TiO$_2$. At a cell voltage of 60.0 V and a concentration of 5 g·l^{-1} TiO$_2$, the decolorization and the COD removal efficiencies in the photoelectrochemical process were increased by 21.8% and 14.1%, respectively, compared to those in the single photocatalytic process.

1. INTRODUCTION

Heterogeneous photocatalytic processes using nanometer semiconductor as a photocatalyst, is a good advanced oxidation technology for organic pollutants [1]. The photocatalytic properties of nano TiO$_2$ for wastewater treatment have been investigated extensively in slurry cells and on immobilized films [2-3]. The appeal of this technology is the prospect of complete mineralization of the pollutants into a harmless compound [4]. Unfortunately, in spite of having numerous approved patents related to this technology, the technical development of a practical water treatment system, even pilot scale level, has not yet been successfully achieved [5]. The high degree of recombination of photogenerated electrons and holes is a major limiting factor controlling the photocatalytic efficiency and impeding the practical application of this technique in the degradation of contaminants in wastewater [2]. Thus, several researchers have recently attempted to increase the photocatalytic efficiency of titanium dioxide using electrochemical methods by applying an external anodic bias to drive the photo-generated electrons [6-9].

However, in most of electrochemically assisted photocatalytic experiments, the applied anodic bias potential is always lower than the oxidation potential of the organic pollutant so that no direct electrochemical oxidation complicates the analysis of photocatalytic efficiency [10]. It is clear that these investigations only effectively represent a proof-of-concept of enhanced effects of external bias on photocatalytic degradation of organic pollutants by reducing the electron-hole recombination [6-9]. Nevertheless, it is worth pointing out that electrochemistry is also a method of removing organic pollutants [11-13]. In other words, potential bias plays an important role in enhancing degradation of organic pollutants not only by both reducing the electron-holes recombination but also by direct electrochemical oxidation at an anodic bias which is higher than the oxidation potential of the organic pollutant. However, there are few reports that discuss this hybrid photoelectrochemical technology at high potential bias [14]. In this work, we investigated mainly the combination of the photocatalysis of nano TiO$_2$ with three-dimensional electrodes under high anodic bias.

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Much attention was paid to probe the enhancement effects of this hybrid technology comparing with photocatalysis and the effect of operating conditions on the photoelectrocatalytic efficiency using methylene blue (MB) as a test pollutant.

2. EXPERIMENTAL

Material. Photocatalyst was nanometer titanium dioxide (Degussa P25), mainly anatase (Ca. 70%) in the shape of non-porous polyhetral particles of Ca. 30 nm mean size with a surface area of 50 m^2g^{-1}. The dye used, methylene blue, was analytic grade reagent, and the dye solutions were prepared with deionized water at a concentration of 1.0 mmol·l^{-1} (Chemical Oxygen Demanded (COD) 508.9 ppm and colorization 47204), except as indicated. Electrocatalyst (EC) was prepared by adding 5.0% MnO_2 in granulated activated carbon (GAC) and used as the filler of the three-dimensional electrode in this experiment. The EC has an average particle size of 4.0·6.2 mm and ash content of 8.1%. Both the main electrodes were made of stainless steel and used after dipped into diluted sulfuric acid for 3 min and then washed with deionized water twice.

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 PVC plate. The stainless steel anode and cathode (main electrode) were situated 26.0 cm apart from each other. 150.0 g of EC were used as particle electrodes and packed between the two main electrodes and suspension of 1.0 g titanium dioxide containing MB was added into the reactor. When compressed air was bubbled into the reactor by a micropore plate from the bottom of reactor, the reactor material separated into two layers. The upper layer is mainly the suspension of TiO_2 with a depth of about 1.0 cm, and the lower layer is mainly the EC 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. The emitting radiation is a continuous spectra in the range of 200 ~ 800 nm with a peak intensity at 365 nm. The intensity of ultraviolet light on the surface of the reaction solution was at the average of 6.64 mW·cm^{-2}.

Procedure. A methylene blue aqueous solution of 80.0 ml 1.0 mmol·l^{-1} was added into the reactor and immersed for 5.0 min. After the post-immersion residual solution was removed, a 200.0 ml solution of MB containing 1.0 g titanium dioxide was fed into the photoelectrochemical reactor each run. The reactor was timed starting when the d. c. power, illu-
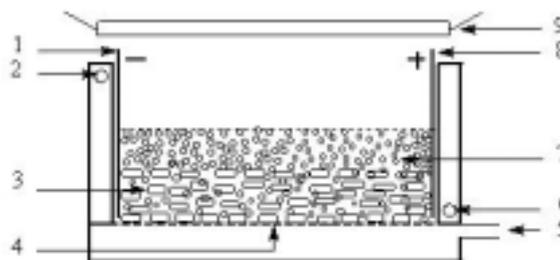

Fig. 1. Schematic of reactor set-up (1- cathode; 2- outlet of recycled water; 3- particle filler electrode; 4- micropore titanium plate; 5- inlet of compressed air; 6- inlet of recycled water; 7- titanium dioxide layer; 8- anode; 9- UV illuminant).

mination and compressed air supply were switched on. Except as indicated, general treating conditions were 30.0 V voltage, 0.6 m^3·h^{-1} airflow, 5.0 g·l^{-1} titanium dioxide and 30 min treatment time. The experimental temperature was kept at 30±2 °C and overheating of the reaction solution was prevented with the use of a cooling fan over the reactor. The post-treatment colloid solutions were separated by centrifuge and filtered through a Millipore membrane for color and COD analysis. Color and decolorization ratios were measured with spectrophotometer methods and calculated according to the literature [15]. COD was measured with potassium dichromate method [16].

3. RESULTS AND DISCUSSION

Bard *et al.* [17-19] first recognized that photoelectrochemical cells and semiconductor powders might behave similarly, thus opening a practical way for photocatalysis. They considered a powder as a miniaturized photoelectrochemical cell in which the "wire" connecting the irradiated semiconductor anode to the counter electrode is infinitely small. Based on these ideas, Bard and his colleagues investigated the characteristics of semiconductor powders as the slurry electrodes. Their results suggested that when an oxidation process scavenged the holes, the photogenerated electrons would build up on the particle surface. The photogenerated electrons are able to be collected at an inert electrode (usually Pt) immersed in the semiconductor powder suspension [17-18, 20-21]. Thus semiconductor powder suspension can behave as electrodes, so-called slurry electrodes, in the same manner as single crystal and polycrystalline semiconductor materials.
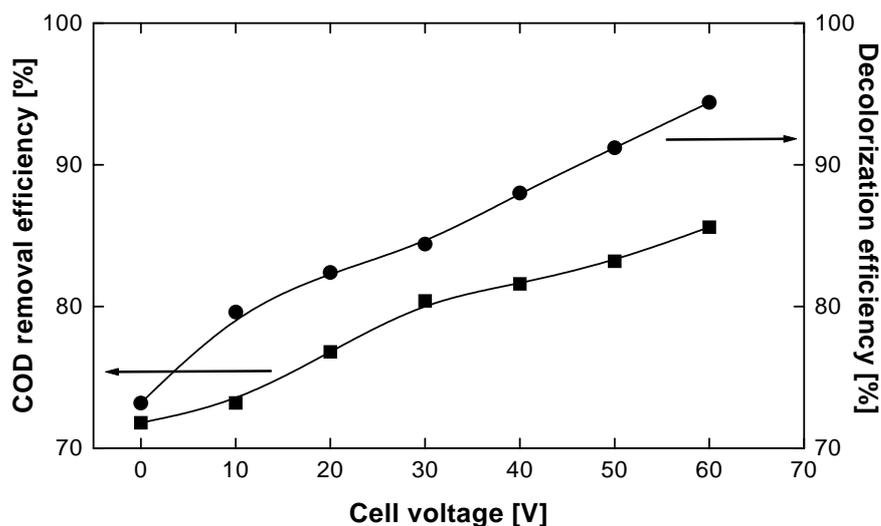
Fig. 2. Effect of cell voltage on decolorization and COD removal efficiencies (concentration of TiO$_2$: 5 g·l^{-1}; initial concentration of MB: 1 mmol l^{-1} and reaction time: 30 min).

Effect of potential bias on photocatalytic reaction. Fujishima and Honda [22] first used a single-crystal rutile TiO$_2$ photoanode for photoelectrocatalytic decomposition of water under the influence of an anodic bias. To increase the photocatalytic efficiency of such semiconductors for degrading undesirable organics in aqueous solution, the anodic bias is also used for nanocrystal semiconductor photocatalysis [6-9]. However, in these electrochemically assisted photocatalytic experiments, the applied anodic bias potential is always lower than the oxidation potential of the organic pollutant so that no direct electrochemical oxidation complicates the photocatalysis [10]. In this paper, we investigated the effect of anode potential bias on the photoelectrochemical degradation of MB at a range of cell voltages from 0.0 to 60.0 V. The decolorization efficiency and COD removal efficiency were shown in Fig. 2. It is easily seen that both the decolorization and the COD removal efficiencies were greatly affected by the applied cell voltage. COD removal efficiency is 71.8% and decolorization efficiency is 72.8% without any cell voltage. This is attributed to photocatalytic degradation of the nano semiconductor and the adsorption of both photo- and electro- catalysts. By increasing of the cell voltage, COD removal and the decolorization efficiencies were substantially improved. The best COD removal of 85.7% with the best decoloization efficiency of 94.6% was obtained at 60.0 V cell voltage. This enhanced effect in the photoelectrochemi-

cal process may be attributed to two factors. First, the external electric field can capture photogenerated electrons, reducing the recombination of these electrons and holes; second, the high anodic bias can result in the electrochemical oxidation of MB. In practice, a 30.0 V cell voltage can be used because the cell voltage is not only in a range of safe voltage (36.0 V), but also gives increase in the treatment efficiency.

Effect of treatment time on photoelectrochemical degradation efficiency. The efficiencies of the decolorization and COD removal at different treatment time are presented in Fig. 3. It is seen that the decolorization efficiency and reduction of COD removal both increased with increasing reaction time. The highest decolorization efficiency of about 94.6% was obtained in the photoelectrochemical process and the highest removal of COD reached 80.4% within 30 min.

From the high decolorization and COD removal efficiencies, we can infer that most of MB was completely mineralized. Additionally, the decolorization efficiencies are always higher than that of COD removal in all the processes. This finding is not surprising, given that many intermediates are involved in oxidative decontamination of MB.

Effect of concentration of nano TiO$_2$. For various photoreactors, the optimal concentration of nano titanium dioxide has to be determined since it strongly depends on the geometry of the photoreactor and the incident flux, and the mean
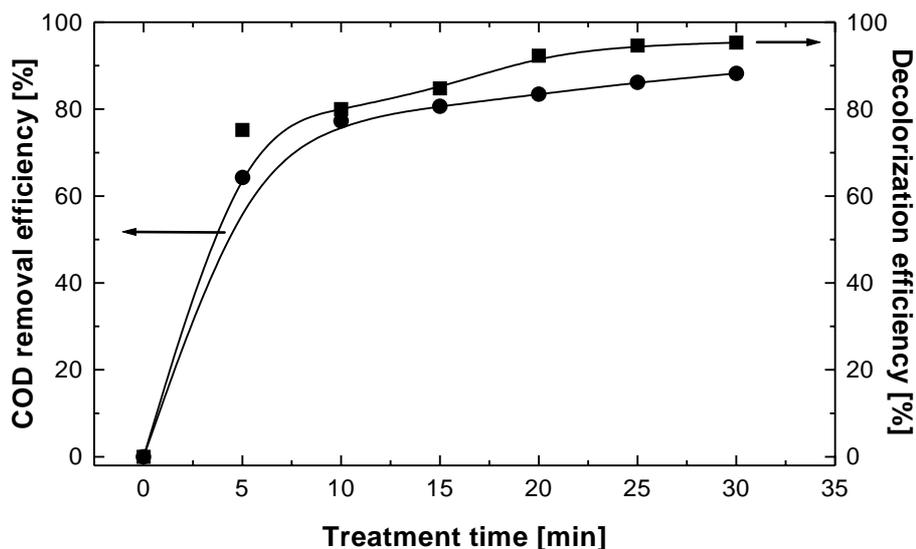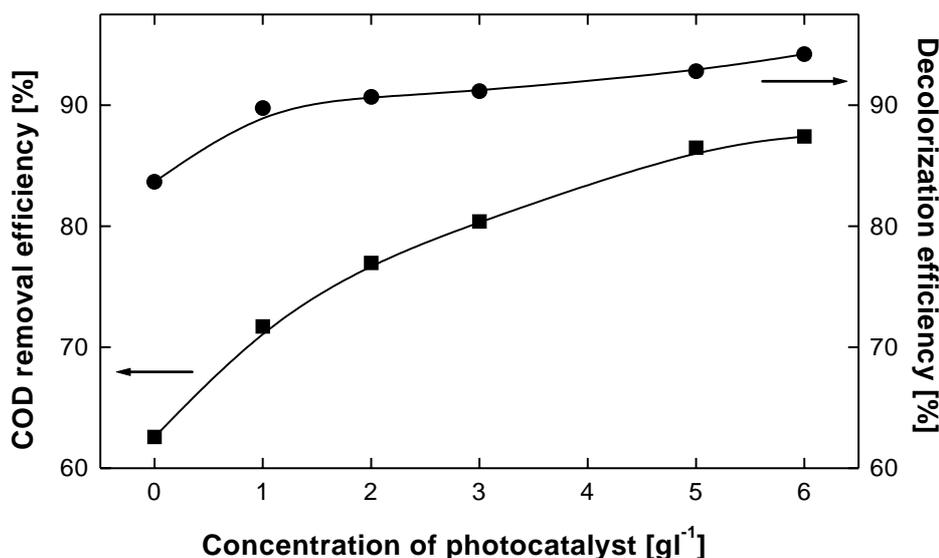
Fig. 3. Effect of treatment time on decolorization and COD removal efficiencies (cell voltage: 30 V; concentration of TiO_2: 5 $g \cdot l^{-1}$ and initial concentration of MB: 1 $mmol \cdot l^{-1}$).

optical pathway [23]. Therefore, the influence of the concentration of TiO_2 material on the reaction rate of photoelectrochemical degradation was studied in a range of 0.0 ~ 6.0 $g \cdot l^{-1}$. The data is shown in Fig. 4. It can be seen that the decolorization and COD removal efficiencies have the similar change trends. They increased rapidly first and then vary slightly with increase in TiO_2 concentration. The results can be interpreted that, at the low TiO_2 concentration, more active sites were presented with TiO_2 increase, leading to an increase in reaction rate. However, at high TiO_2 concentration, the catalytic rates improve

gently because of scattering of ultraviolet light [23]. Therefore, it is essential to select a suitable dosage of TiO_2 in the reactor. From Fig. 4, the desired amount of TiO_2 is 5 $g \cdot l^{-1}$ for this photoreactor.

Effect of initial concentration of MB. The electrochemically assisted photocatalytic degradation was studied by changing the initial concentration of MB solution from 0.25 to 2.00 mM. The profiles of COD and decolorization efficiencies versus the initial concentrations are shown in Fig. 5. It is seen that the initial concentration of MB solution has a

Fig. 4. Effect of concentration of nano TiO_2 on decolorization and COD removal effiencies (cell voltage: 30 V; initial concentration of MB: 1 $mmol \cdot l^{-1}$ and reaction time: 30 min).
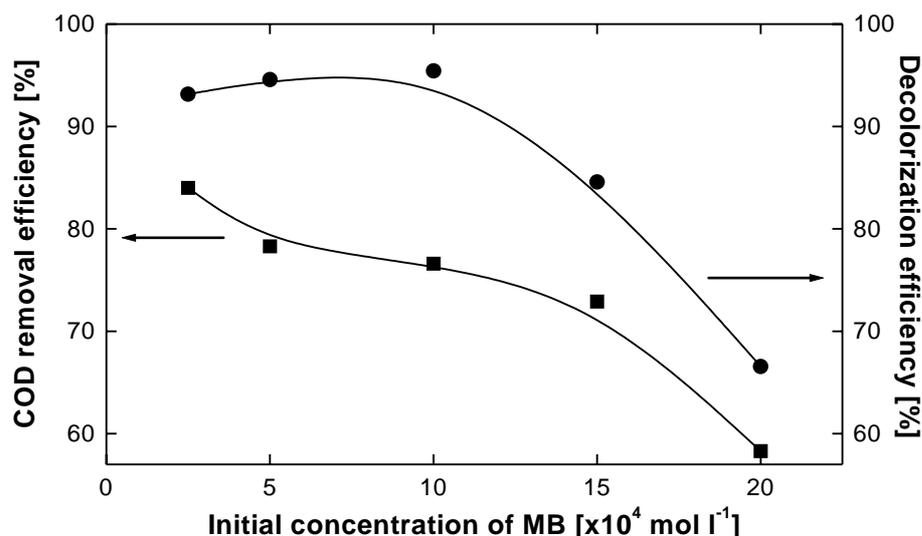
Fig. 5. Effect of initial concentration of MB on decolorization and COD removal effiencies (cell voltage: 30 V; concentration of TiO$_2$: 5 g·l^{-1} and reaction time: 30 min).

significant effect on the decolorization and COD removal efficiency. The removal of COD decreases with increase of initial concentration while the decolorization efficiency just begins to decrease at concentration $>1.00 \times 10^{-3}$ mol·l^{-1}. This decrease is because the transparency of the MB solution reduces dramatically at high concentration, hence the transmission intensity of ultraviolet light reduces and the photosensitization of the photocatalyst is significantly cut down.

4. CONCLUSIONS

The experimental results show that photoeletrochemical technology is a more effective process than a photocatalytic process for degrading MB in water. The optimal experimental efficiencies were obtained at a cell voltage of 30.0 V, a concentration of TiO$_2$ semiconductor of 5.0 g·l^{-1}, an initial concentration of MB of 1 mM and a reaction time of 30.0 min.

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