



Feasibility study of photoelectrochemical degradation of methylene blue with three-dimensional electrode-photocatalytic reactor

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Abstract

The photoelectrochemical degradation of methylene blue in aqueous solution was investigated with three-dimensional electrode-photocatalytic reactor. It was found that the methylene blue could be degraded more efficiently by photoelectrochemical process than by photocatalytic oxidation or electrochemical oxidation alone. The decolorization efficiency and COD reduction were 95% and 87% for a photoelectrochemical process, respectively, while they were only 78% and 68% for a single electrochemical process and 89% and 71% for a single photochemical process. The TOC reduction of the former also reached as high as about 81% within a reaction time of 30.0 min. And these degradation reactions conformed to pseudo-first-order kinetics. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Electrochemical oxidation; Photocatalytic oxidation; Photoelectrochemical degradation; Methylene blue; Wastewater treatment; Three-dimensional electrodes

1. Introduction

Heterogeneous processes using semiconductor catalysts offer a good advanced oxidation technology for organic pollutants and have attracted extensive interest (Ollis, 1985; Hoffmann et al., 1995). Up to now, titanium dioxide in the anatase form is still the most commonly used photocatalyst because it has the reasonable photoactivity (Matthews, 1992) and the advantages of being not toxic, insoluble and comparatively inexpensive. The photocatalytic properties of titanium dioxide particles have been investigated extensively in slurry cell and as immobilized films (Ollis, 1985; Matthews, 1992; Hoffmann et al., 1995; Sopyan et al., 1996). However,

charge recombination between the photogenerated electrons and holes is often a major limiting factor as this impedes charge transfer at the semiconductor–electrolyte surface (Hoffmann et al., 1995).

Recently, several attempts have been made to increase the photocatalytic efficiency of titanium dioxide, such as noble metal deposition (Alberici and Jardim, 1994), ion doping (Navio et al., 1999) and electrochemically assisted method. In the last one, an external anodic bias is applied to drive the photogenerated electrons and holes in different directions so that the charge recombination is decreased (Vinodgopal et al., 1993; Vinodgopal and Kamat, 1996; Kesselman et al., 1997; Byrne et al., 1999).

The electrochemical technology, which is well known as “a clean method of wastewater treatment”, has lots of advantages. Many related investigations have been reported (Brillas et al., 1997, 1998a; Do and Yeh, 1998). In particular, the electrochemical technologies based on three-dimensional electrodes have been attracting much

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more attention (Brown et al., 1994; Rajeshwar et al., 1994; Tissot and Fragniere, 1994; Tennakoon et al., 1996; Bockris and Kim, 1997; Simonsson, 1997; Xiong and Karlsson, 2001). It has been recognized widely that the rate of conversion within an electrochemical reactor can be increased substantially by the use of the three-dimensional electrode with its extensive specific surface area in comparison to conventional two-dimensional electrodes (Bockris and Kim, 1997; Simonsson, 1997). However, as far as we know, the application of the three-dimensional electrodes has not been attempted to photocatalytic degradation yet.

More recently we have set out to study the combination of the three-dimensional electrodes with other technologies such as ultrasound oxidation, biochemical oxidation and photocatalytic oxidation, etc. In the present paper, we will devote to investigate the feasibility of methylene blue degradation using a novel photoelectrochemical reactor, three-dimensional electrode-photocatalytic reactor, and to detect any associative effects between the photocatalysis of powdered titania suspension and three-dimensional electrodes.

2. Experimental

2.1. Material

The photocatalyst used was titanium dioxide (Degussa P25). 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} (COD 508.9 ppm) and pH 6.6 without adjusting the pH of the solution. Water, free of ammonia, was used to determine NH_4^+ . Electrocatalyst (EC) was prepared with the granulated activated carbon (GAC) adding 5% MnO_2 and used as the filler of the three-dimensional electrode in this experiment. The EC has a surface area of $870.0 \text{ m}^2 \text{ g}^{-1}$, an average particle size of $4.0 \times 6.2 \text{ mm}$ and ash content of 8%. Both the main electrodes were made of stainless steel and used after certain disposition treatment.

2.2. Apparatus

Absorption spectra of methylene blue were recorded with a mode UV-PC2501 spectrophotometer (Hitachi, Japan). A 500 W high-pressure mercury lamp was used as an illuminant. The total organic carbon (TOC) reduction was measured with a TOC-5000 total organic carbon analyzer (Shimadzu). An ion chromatography (Metrohm), 732 IC detector, 733 IC separation center, 709 IC pump and 752 pump units, was used for anion analysis, with a 6.1006.100 Metrosep Anion Dual 2 column. A solution containing 2.0 mM NaHCO_3 and 1.3 mM Na_2CO_3 was used as an eluent with the flow

$800.0 \text{ } \mu\text{l min}^{-1}$ and the sampling volume was $1.0 \text{ } \mu\text{l}$. NH_4^+ was analyzed according to the literature (EPA of China, 1989).

2.3. Photoelectrochemical reactor

The experimental set-up is presented in Fig. 1. It is an open double-layered reactor ($28.0 \text{ cm} \times 6.0 \text{ cm} \times 10.0 \text{ cm}$) made of polytetrafluoroethylene plate. The stainless steel anode and cathode (main electrode), situated 26.0 cm apart from each other, were equipped across the reactor. 150.0 g EC used as particle electrodes were packed between the two main electrodes and the suspension of MB containing 1.0 g titanium dioxide was added into the reactor. When compressed air was sparged into the reactor by a micropore plate from the bottom of the reactor cell, the reactor becomes 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 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 radiations of the illuminant are a continuous spectra in the range 200–800 nm with the highest peak at 365 nm. The intensity of ultraviolet light on the surface of reaction solution was achieved at the average of 6.64 mW cm^{-2} .

2.4. Recommended procedure

A methylene blue aqueous solution of $80.0 \text{ ml } 1.0 \text{ mmol l}^{-1}$ was added into the reactor, immersion and adsorption were conducted for 5.0 min before photoelectrochemical degradation. And then, 1.0 g titanium dioxide and 200.0 ml solution of 1.0 mmol l^{-1} methylene blue were added into the reactor after the residual solution for the adsorption was removed. With a

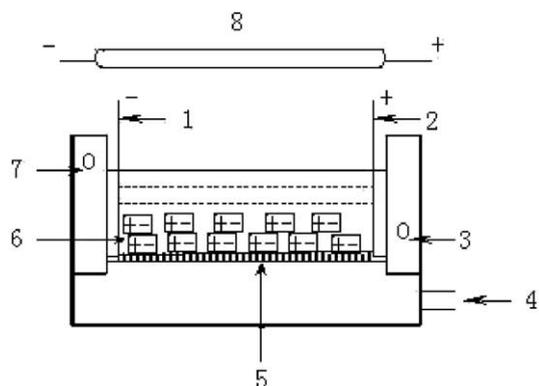


Fig. 1. Schematic of reactor set-up: (1) cathode; (2) anode; (3) inlet of recycled water; (4) inlet of compressed air; (5) micropore plate; (6) particle filler or EC and TiO_2 .

0.6 $\text{lm}^3 \text{h}^{-1}$ sparged air, 30.0 V direct current and illumination, the photoelectrochemical procedure was carried out for 30.0 min in the reactor. 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 colloid solutions were sampled at each 5 min interval, separated with centrifuge and filtered through a Millipore (0.45 μm) membrane for color, degradation kinetics, COD and TOC analyses. Color and decolorization efficiencies were measured with spectrophotometer methods and calculated according to the literature (Zhou, 1988; An et al., 2001). The analytic wavelength selected for optical absorption measurements of methylene blue was 664 nm. COD was measured with potassium dichromate after the filtered sample was digested with a WMX COD microwave digestion system (Huanhai Engineering Company of Shantou, China Patent: 92 1 14210.2).

3. Results and discussion

3.1. Investigation of decolorization

The changes in the UV spectra of MB from 200 to 800 nm were measured and the selected UV spectra for the photoelectrochemical degradation process were shown in Fig. 2. It can be seen from the figure that the MB decreased dramatically as the reaction time increased. According to the reduction of the absorbencies at the visible range, i.e., from 420 to 620 nm, the decolorization efficiencies of the MB solution under various conditions were calculated with the reported method (Zhou, 1988; An et al., 2001) and presented in Fig. 3. Without cell voltage and illumination, about 34% of the color were removed within 30.0 min. The decolorization is due to the adsorption plus air catalytic degradation effect of the EC (Fortuny et al., 1999). For the photocatalytic degradation process alone, a decolorization

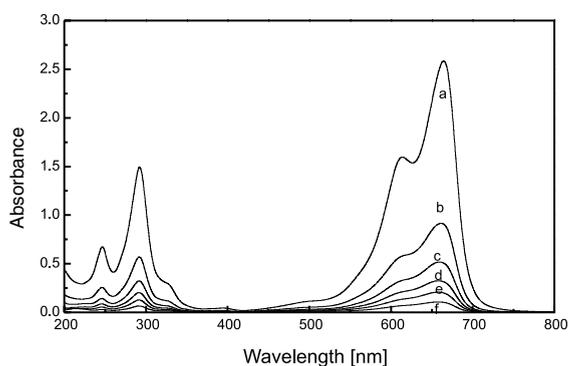


Fig. 2. Change of U-visible spectra of MB: (a) 0.0; (b) 5.0; (c) 10.0; (d) 15.0; (e) 20.0; (f) 30.0 min.

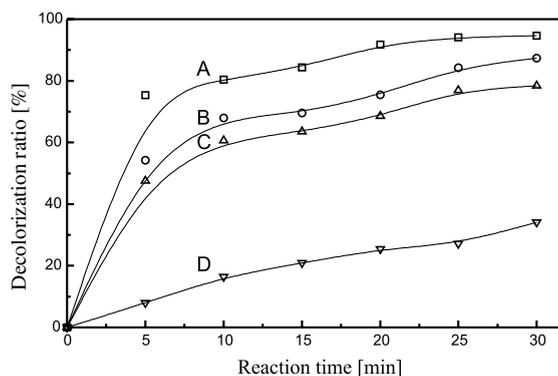


Fig. 3. Decolorization efficiencies of MB in various conditions: (A) illumination and 30 voltage; (B) illumination and no voltage; (C) no illumination and 30 voltage; (D) no illumination and no voltage.

efficiency of 89% was obtained. It is 11% higher than the decolorization efficiency found in a single electrochemical oxidation process. This might be explained by assuming that the photocatalytic degradation was more effective on a blue substrate. However, these decolorization efficiencies are lower than those found in the photoelectrochemical degradation, which are about 95%. The results indicate possibly that there is a somewhat associated effect in the photoelectrochemical process of MB degradation. The associated effect may be due to the fact that the external potential can reduce the recombination of the electron-hole pair.

3.2. Degradation kinetics of MB

The degradation efficiencies were calculated according to the ratios between the absorbency reductions in the process of reaction and the initial absorbency of the investigated solution at maximum wavelength (664 nm). The dependence of the degradation efficiency on reaction time is given in Fig. 4. From curve (A) of Fig. 4, about 32% of MB was removed by absorption plus air catalytic degradation effect of EC (Fortuny et al., 1999) over a reaction time of 30.0 min. However, a degradation efficiency as high as 97% was obtained in the same reaction time for the photoelectrochemical process with the three-dimensional electrode-photocatalytic reactor. By comparing with these values, the lower degradation efficiencies were observed in a single application of the electrocatalytic degradation (81%) or the photocatalytic degradation process (90%).

It is well recognized that photocatalytic degradation of organic pollutants accords with pseudo-first-order kinetics (Matos et al., 1998; An et al., 2000). In this work, pseudo-first-order kinetics was also noticed in the photoelectrochemical degradation process as well as in the electrochemical and photocatalytic processes. Apart

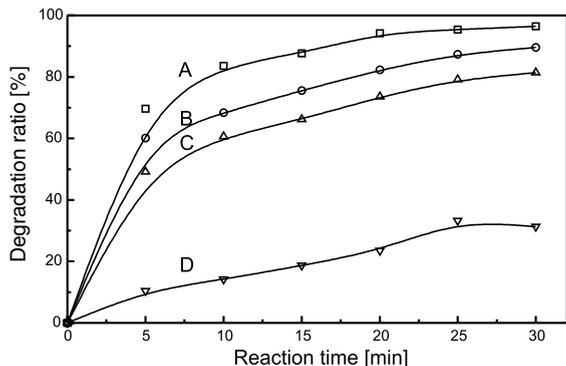


Fig. 4. Degradation efficiencies of MB in various conditions: (A) illumination and 30 voltage; (B) illumination and no voltage; (C) no illumination and 30 voltage; (D) no illumination and no voltage.

from the first sampling time which has large adsorption of solute, the reactions all conform to pseudo-first-order kinetics in the three systems. The kinetic regression equations and parameters were listed in Table 1. It can be seen that the rate constant of degradation kinetics for photoelectrochemical process is apparently greater than that for the electrocatalytic or the photocatalytic process alone.

3.3. Reduction of COD

The efficiencies of COD removal at different reaction times in various conditions are shown in Fig. 5. It can be seen from Fig. 5 that in all three processes, the COD concentration decreased with the increase of reaction time. During the course of 30.0 min, the reduction of the COD concentration in the photoelectrochemical degradation reached 87%, in comparison with 68% in the electrocatalytic and 71% in the photocatalytic procedure. However, a low decrease in the COD, 33%, was found without illumination and applied direct current. Obviously, the COD of the MB solution can be removed more efficiently in the photoelectrochemical degradation than others. The experimental result might be interpreted by assuming that most of the solute was completely mineralized in the photoelectrochemical process.

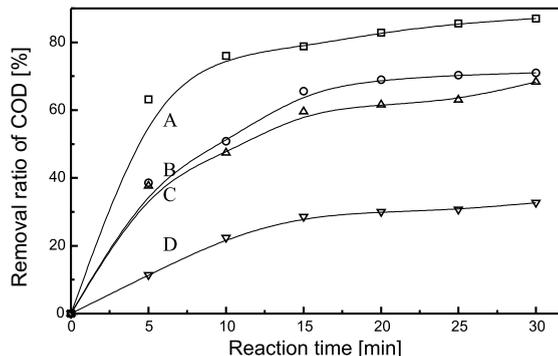


Fig. 5. Removal efficiencies of COD in various conditions: (A) illumination and 30 voltage; (B) illumination and no voltage; (C) no illumination and 30 voltage; (D) no illumination and no voltage.

Comparing Figs. 3–5, it can be seen that the efficiencies of the degradation and decolorization are obviously higher than those of the COD removal. This finding is not surprising, given that many intermediates are involved in the oxidative mineralization of MB.

3.4. TOC analysis

As mentioned above, the solutes were not instantaneously oxidized to CO_2 , the oxidation presumably proceeding via a number of intermediates. Therefore, the decrease of optical absorption at the maximum wavelength of MB is not an infallible indicator of organic solute concentration in the wastewater since the intermediate decomposition products may have not absorption at the selected wavelength of MB. Moreover, the removal of the COD does not also embody completely the mineralization of MB. In consequence, the reduction of the TOC was also presented to test the complete mineralization efficiency of MB in the three-dimensional electrode-photocatalytic reactor. The kinetics of the loss of the TOC in the photoelectrochemical process was recorded and is shown in Fig. 6. From Fig. 6, it can be seen that the loss of the TOC is rapid at the beginning of the experimental run, then followed by a more gradual removal of organic pollutants and does not increase much beyond 30.0 min. The maximum

Table 1
Kinetic equations and parameters of MB degradation in various conditions

Conditions	Kinetic equations	Regression coefficient	Kinetic constant (min^{-1})	Half-life (min)
Illumination and voltage	$A = 3.292 - 0.088t$	0.986	0.088	7.9
Only illumination	$A = 3.535 - 0.056t$	0.998	0.056	12.4
Only voltage	$A = 3.658 - 0.041t$	0.995	0.041	16.9

A denotes the absorbency at 664 nm.

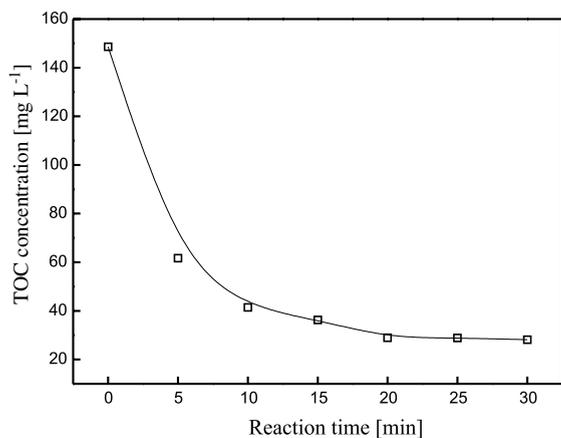


Fig. 6. Reduction kinetics of TOC in the photoelectrochemical process.

Table 2
Ion concentration before and after the degradation

Ions (ppm)	After degradation	Before degradation
Cl ⁻	40.284	31.114
NH ₄ ⁺	13.230	0.000
NO ₃ ⁻	2.694	0.000
SO ₄ ²⁻	25.575	0.000

reduction of the TOC reaches 81% in the photoelectrochemical degradation process. In addition, large amounts of inorganic ions were found in the treated solution using photoelectrochemical degradation process, as shown in Table 2. Thus, we are further convinced that most of the organic pollutants were mineralized completely. The determined concentrations of NH₄⁺ and SO₄²⁻ are lower than the ion concentration calculated from the TOC reduction values. It may be due to the fact that the decreased ions may be adsorbed on the EC and do not release to the reaction solution.

3.5. Dissolving of electrode material

It is well known that electrode material may be dissolved into the solution when it was used as an anode of the electrolytic cell. In order to observe the dissolution condition of the used anode in the photoelectrochemical process, ICP analysis was employed to determine the concentration of various metals in the electrolytic solution after photoelectrochemical degradation lasting 30.0 min. The results found are presented in Table 3. We can observe from these data that the concentrations of various metals were very low in the electrolytic solution. Thus, the soluble reaction (1) at the main anode can be ignored completely in this experiment.

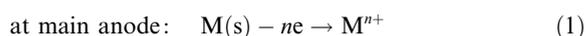


Table 3
Concentration of dissolved metal ions

Metal ions	Concentration (ppm)
Fe	10.900
Mn	5.084
Ni	3.814
Zn	1.768
Cr	0.412
Cu	0.081

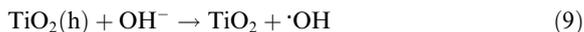
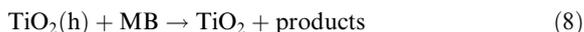
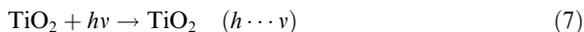
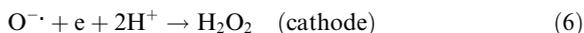
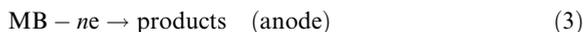
3.6. Reaction mechanisms

The reaction mechanisms for the single application of photocatalytic oxidation have been convincingly studied and reported in the literature (Peterson et al., 1991; Hoffmann et al., 1995). The reaction mechanisms using electrochemical process with GAC electrodes were also studied by many researchers (Tatapudi and Fenton, 1993; Alvarez-Gallbegos and Pletcher, 1999; Pletcher, 1999) and us (Chen and Zhu, 1998). All of them believed that oxygen could be changed into the stronger oxidizing agent, H₂O₂, on the electrode by a two-electron reduction of oxygen. The electrogenerated H₂O₂ can be further changed into the OH radical, in situ, in the presence of transitional metal ions (Brillas et al., 1998b; Chen and Zhu, 1998; Huang, 1991). Thus, the other electrochemical degradation mechanisms of organic pollutants with the three-dimensional electrode are convinced to be the indirect oxidation of the electrogenerated H₂O₂ and ·OH radical besides direct anodic oxidation.

Additionally, it is well known that a large amount of water must be electrolyzed in the reactor with the generation of oxygen and hydrogen at electrodes, besides the direct and indirect electrochemical oxidation of the organic compounds (Brillas et al., 1998b; Pletcher, 1999), when a 30.0 V DC acted across the two main electrodes. The side reaction in the reactor may have occurred, as below:



However, the generated oxygen can be used as a photogenerated electron scavenger, enhancing the photocatalytic efficiency (Vinodgopal et al., 1993). Moreover, ·OH can be generated at the anodic surface at the same time of oxygen evolution (Comninellis and Battisti, 1996; Brillas et al., 1998b; Canizares et al., 1999). These agents originated can also cause the oxidation of MB and its intermediates. Thus, in the paper, the major photoelectrochemical reactions initiating redox processes in the three-dimensional electrode-photocatalytic reactor can be summarized as follows (Peterson et al., 1991; Tatapudi and Fenton, 1993; Vinodgopal et al., 1993; Vinodgopal and Kamat, 1996; Chen and Zhu, 1998; Alvarez-Gallbegos and Pletcher, 1999; Canizares et al., 1999; Pletcher, 1999):



where e and h are the electron and hole, respectively, which are formed within the semiconductor particles after bandgap excitation. From the above-mentioned mechanism, the degradation of MB can be carried out by many oxidation routines, such as anodic oxidation, the oxidation of electrogenerated H_2O_2 and $\cdot\text{OH}$, the oxidation of photogenerated hole and $\cdot\text{OH}$, and the photoelectrochemical synergetic effect, etc. This may be a good interpretation of effective destroying of MB using the three-dimensional electrode-photocatalytic reactor.

4. Conclusions

Comparison with conventional photocatalytic degradation, the photoelectrochemical degradation process is fast, 30.0 min, and of high degradation efficiency of about 96%, removal efficiency of COD about 87% and reduction of TOC about 81%. The degradation of MB in the photoelectrochemical process conformed to pseudo-first-order kinetics, and the kinetics constant is 0.088 when the half-life $t_{1/2}$ is 7.9 min^{-1} .

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