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Photocatalytic degradation of methylene blue in TiO$_2$ aqueous suspensions using microwave powered electrodeless discharge lamps

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Abstract

Photocatalytic degradation of methylene blue (MB) in TiO$_2$ aqueous suspensions using microwave (MW) powered electrodeless discharge lamps (EDLs) was studied. MB of initial concentration 100 mg/l was mainly decomposed in the process of photocatalytic degradation using EDLs (PCD/EDLs) after 15 min of irradiation. The corresponding mineralization efficiency was 45%. The influence of factors as EDLs, solution volume and TiO$_2$ catalyst dosage on the decomposition of MB in the PCD/EDLs process was also investigated. The optimal decomposition efficiency was observed when EDLs-4 (four 10 mm × 50 mm EDLs), solution volume of 50 ml and TiO$_2$ catalyst dosage of 1–4 g/l were used in the study. The PCD/EDLs process was promising in treating MB polluted water.
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Keywords: Microwave; Electrodeless discharge lamp; TiO$_2$; Decomposition; Methylene blue

1. Introduction

The ways of treating waste water have been reported by many papers [1,2]. Among them, advanced oxidation processes (AOPs) have been studied intensively in pollutants degradation in the last decades. AOPs generally involves Fenton, UV/Fenton, UV/H$_2$O$_2$, UV/O$_3$, UV/TiO$_2$ processes, etc. which could generate active agents ($^\bullet$OH, HO$_2$$^-$) and oxidize pollutants effectively [3,4]. Nevertheless, most AOPs are not ideal to be performed in practice since some of them use chemicals (ferric or ferrous salts), which might cause secondary pollution, and some of them use oxidants as ozone and hydrogen peroxide, which are costly. These have challenged scientists to improve the processes, or explore new ways to get better effect.

An interesting method involving electrodeless discharge lamps (EDLs) inside a reaction mixture was firstly proposed by Den Besten and Tracy [5], and later applied in organic photochemistry by Církva and Hájek [6]. EDLs can generate ultraviolet–visible (UV–vis) light when irradiated by electromagnetic field, which is covered by numerous patents and papers [7,8]. The method was excellent for its simultaneous effect of UV–vis and microwave (MW) electromagnetic field, and rea-

sonable photochemical efficiency. Recently, Horikoshi et al. [9,10] applied two quartz cylindrical plasma lamps powered by MW in photocatalytic degradation of environmentally unwanted compounds as rhodamine B and 2,4-dichlorophenoxyacetic acid. They also found that the method using EDLs irradiated by MW was superior to the ordinary mercury lamp outside MW oven.

The objective of this study is to evaluate the efficacy of photocatalytic degradation of methylene blue (MB) using MW powered EDLs (PCD/EDLs), and to investigate the factors affecting the decomposition efficiency in the PCD/EDLs process.

2. Materials and methods

2.1. Chemicals

MB and absolute ethanol are of analytical reagent grade. Tetrabutyl titanate and diethanolamine are of chemical purity. All reagents were purchased from Shanghai Chemical Reagent Company.

2.2. Preparation and characterization of TiO$_2$ catalyst

The precursor solutions for TiO$_2$ were prepared by the following method [11]. Eighty-five milliliters tetrabutyl

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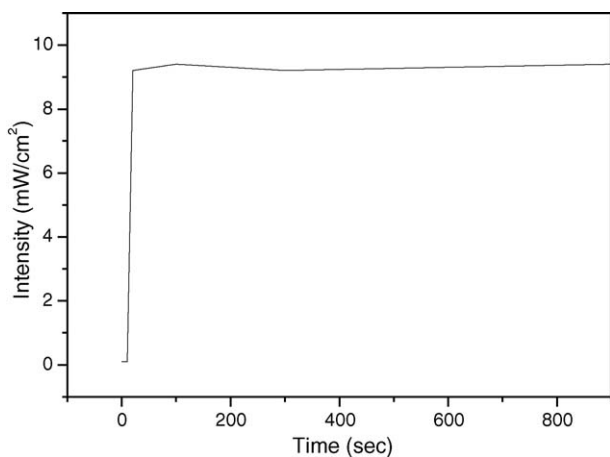*E-mail address:* envidean@nju.edu.cn (C. Sun).

Fig. 1. The light intensity in the wavelength range 250–300 nm in the flask as a function of time. MW energy = 900 W; solution volume = 50 ml; EDLs-4 (four 10 mm × 50 mm EDLs).
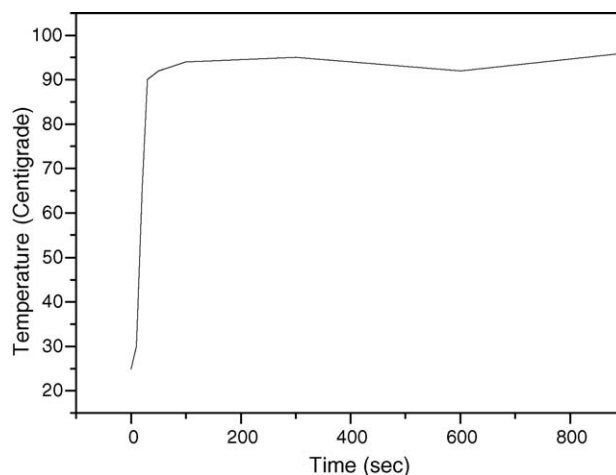

Fig. 2. The temperature in the flask as a function of time. MW energy = 900 W; solution volume = 50 ml; EDLs-4 (four 10 mm × 50 mm EDLs).

titanate solution was mixed with 336 ml absolute ethanol and 24 ml diethanolamine, and further mixed with a solution of water/ethanol (4.5 ml water in 50 ml ethanol). The whole solution stirred for 4 h at room temperature. After the formation of semi-transparency gels, the solution was dehydrated at 80 °C, and then calcined at 550 °C for 1 h to obtain TiO_2 particles.

TiO_2 powders had been characterized by X-ray diffraction (X'TRA, ARL) with Cu Kα irradiation ($\lambda = 0.15406$ nm). The accelerating voltage and emission current were 45 kV and 40 mA, respectively, and scanning speed of $0.02° s^{-1}$ was used. Specific surface areas of the semiconductor were measured by BET method with a Micromeritics ASAP2020.

2.3. Apparatus

In the MW oven (330 mm × 330 mm × 200 mm, 900 W maximal MW output, made in Midea Company), there is a flat-bottom flask (250 ml), with which a 600 mm long water reflux condenser is connected through a communication pipe. An aperture is made at the top of the oven for the communication pipe to get through. Note that an aluminum tube fixed in the aperture is used to eliminate MW leaking. The limit on the safe stray leakage of MW power density is kept below 0.5 mW/cm^2 at 2450 MHz measured at 200 mm distance from the aperture.

EDLs (10 mm × 50 mm, made by Nanhai Company in China) were manufactured according to reference [12]. EDLs generate UV–vis light in the MW oven. Light intensity in the flask was measured using UV and Lux Meter (ZDZ-1, made in Shanghai). Fig. 1 shows the light intensity (in the wavelength range 250–300 nm) as a function of time. Temperature in the flask was measured by quickly stopping the MW oven and was found to be less than 100 °C. The temperature as a function of time is illustrated in Fig. 2.

2.4. Experimental procedures

For the process of PCD/EDLs, 50 ml of MB solution was put into the vessel with pre-weighed amounts TiO_2. Then EDLs

were carefully put into the flask. MW oven was timing when reaction began. Samples were drawn at regular time and immediately centrifuged (Biofuge stratos, Kendro Laboratory Products) at 20 °C, 15,000 rpm to remove catalyst particles for analysis. For the process of MW, both TiO_2 and EDLs were not put into the flask while other procedures were identical with the above. For the process of MW/TiO_2, no EDLs was added, and for the process of direct photolysis using MW powered EDLs (DP/EDLs), no TiO_2 was added, while other procedures were the same as that of the PCD/EDLs process.

2.5. Analysis

Temporal absorption spectral changes at the wavelength of 665 nm during the decomposition of MB were monitored on a Shimadzu UV-2100 spectrophotometer. The absorption was converted to the MB concentration referring to a standard curve showing a linear behavior between the concentration and the absorption at this wavelength. Total organic carbon (TOC) was determined with Shimadzu TOC-5000 analyzer.

3. Results and discussion

3.1. Characterization of TiO_2 powders

TiO_2 powders are composed of anatase and rutile crystals through XRD analysis. The phase contents of TiO_2 are 85% anatase and 15% rutile calculated from the integrated intensity of anatase (1 0 1) and rutile (1 1 0) peak. Mean crystallite size of the catalyst is 21 nm calculated by Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where $k = 0.89$ (constant), $\lambda = 0.1540$ nm (the wavelength of emission of the device), β the integral width and θ is the position in the radian.

The particle surface areas of TiO_2 catalyst are 36 m^2/g determined by nitrogen adsorption using BET surface area analysis.
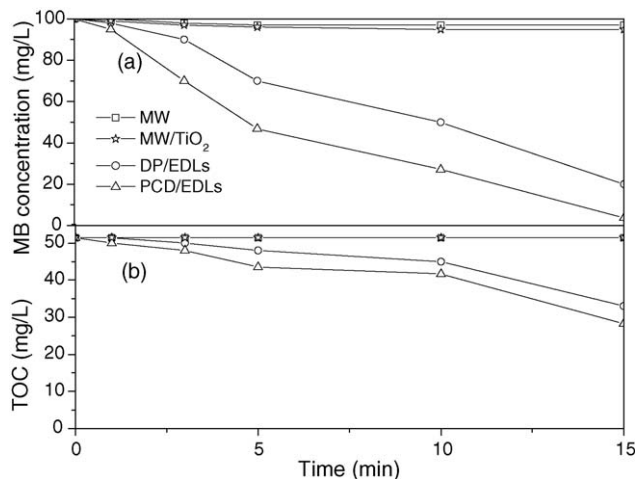
Fig. 3. Comparison of MW, MW/TiO$_2$, MADP and MAPC processes on MB decomposition (a) and mineralization (b). C_{0MB} = 100 mg/l; MW energy = 900 W; EDLs-4; C_{TiO_2} = 2 mg/l; solution volume = 50 ml; initial pH 7.

3.2. Comparison of MW, MW/TiO$_2$, DP/EDLs and PCD/EDLs

Domestic MW ovens generally operate at a frequency of 2.45 GHz. Dipolar substance, such as water, can be thoroughly heated by dielectric heating of MW irradiation [13]. Because the experiment was conducted under high temperature and atmospheric pressure, leaking of MB was checked first. It was found that cooling effect of the water reflux condenser was well, and MB on the glass wall was less than 1%. The light intensity in the flask was measured to be 9.4 mW/cm^2 in the wavelength range 250–300 nm and 440 cd/m^2 in the wavelength range 400–760 nm under the condition of MW energy = 900 W, EDLs-4 (four 10 mm × 50 mm EDLs), solution volume = 50 ml.

In order to evaluate the efficacy of this designed setup on MB decomposition and mineralization, four processes were investigated as: (1) MW, (2) MW/TiO$_2$, (3) DP/EDLs without addition of TiO$_2$ catalyst and (4) PCD/EDLs. Results are summarized in Fig. 3.

For the process of only MW, decrease of MB concentration was 3% with no obvious loss of TOC in 15 min irradiation. While for the MW/TiO$_2$ process, removal of MB was slightly higher (about 5%), indicating that small quantity of MB was adsorbed on the surfaces of TiO$_2$ particles.

For the DP/EDLs process without TiO$_2$ catalyst, removal of MB was 80%, corresponding mineralization efficiency was 36% after 15 min reaction. The mechanism of the direct photolysis of MB can be concluded as the following. MB has a maximum absorbance at 665 nm. And for the light generated by EDLs, its spectrum is in the range of 250–760 nm and the intensity of the part of visible light is comparatively high (440 cd/m^2 in the wavelength range 400–760 nm). So dye of MB can absorb the light energy and go to an excited singlet state with all electron spins paired and some electrons in energy orbital higher than ground state energy. Then the dye immediately goes to a triplet state resulting in some electron spins unpaired and with higher than ground state energy. Finally, the excited or activated

molecule dissipates this energy as heat, light or chemical energy via dissociation or other pathways.

The best efficiency was observed when the process of PCD/EDLs was performed. MB of initial concentration 100 mg/l was mainly decomposed with TOC decreased 45% after 15 min irradiation. Decomposition rate of MB and TOC in the PCD/EDLs process was higher than that in the DP/EDLs process, suggesting that TiO$_2$ catalyst was effective on MB decomposition in the PCD/EDLs system. Relevant first-order kinetics of the decomposition of MB in the system DP/EDLs and PCD/EDLs were calculated to be $K_{DP/EDLs}$ = 0.10 min^{-1} and $K_{PCD/EDLs}$ = 0.21 min^{-1}, respectively. These data show that decomposition by the system PCD/EDLs is about two-fold faster than the system DP/EDLs. The possible mechanisms of MB decomposition in the PCD/EDLs process might include two aspects. (1) TiO$_2$ particles can absorb UV light at energies greater than their band gap energy 3.2 eV (i.e., at wavelengths below 387 nm) to generate electron–hole pairs. The valence band holes react with the surface bound HO$^-$ ions to form $^\bullet$OH radicals. Concomitantly, the conduction band electrons are scavenged by oxygen molecules to yield superoxide radical anions (O$_2^{\bullet-}$), which are combined with H$^+$ to form $^\bullet$OOH radicals. Thus, MB could be decomposed and mineralized by the active radicals ($^\bullet$OH or $^\bullet$OOH). (2) MB absorbs the visible light and converts to singlet and triplet excited states. When under UV–vis light irradiation, electron transfers from excited dye to semiconductor particles and yields conduction band, which then reacts with oxygen and H$^+$ to generate $^\bullet$OH or $^\bullet$OOH. MB is attacked by the active radicals and degraded at last [14–16].

The role of the MW is also important in the system PCD/EDLs. EDLs which generate UV–vis light are powered by MW. That means EDLs cannot generate any light without MW. More over, as reported earlier [17], integrating the photocatalytic method with MW irradiation can enhance the degradation of organic pollutants. The system PCD/EDLs likely generates additional defect sites on the TiO$_2$ particles that lead to a somewhat diminished electron/hole recombination and to a more efficient photocatalytic process.

3.3. Influence of factors on MB decomposition

The PCD/EDLs process was proved to be effective for MB decomposition and mineralization from the above study. Factors affecting the PCD/EDLs process were further investigated in the following study.

3.3.1. Effect of EDLs

The dependence of EDLs of different quantities on MB PCD/EDLs is depicted in Fig. 4. Removal rates increased as EDLs varied from EDLs-1 to EDLs-4. The rates were in the order of EDLs-4 (96%) > EDLs-3 (40%) > EDLs-2 (20%) > EDLs-1 (5%) after 15 min irradiation. Light intensities of EDLs in the wavelength range 250–300 nm were also measured and estimated to be in the sequence of EDLs-4 (9.4 mW/cm^2) > EDLs-3 (3.1 mW/cm^2) > EDLs-2 (2.2 mW/cm^2) > EDLs-1 (0 mW/cm^2). It was known that higher light intensity would result in higher
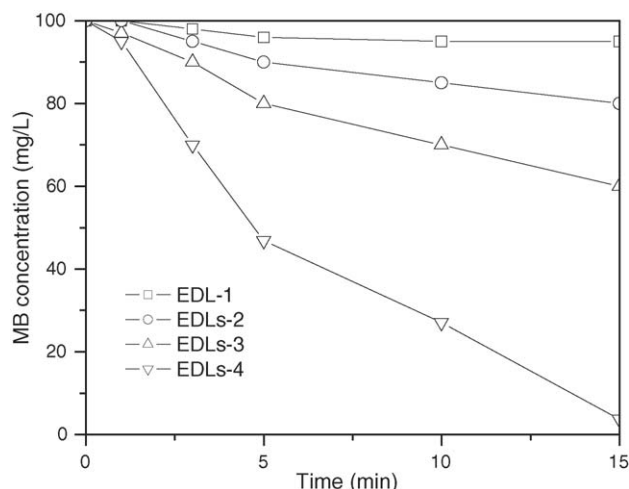
Fig. 4. Effect of EDLs on removal of MB in the MAPC process. $C_{0MB} = 100$ mg/l; MW energy = 900 W; $C_{TiO_2} = 2$ mg/l; solution volume = 50 ml; initial pH 7; EDLs-1 (a 10 mm × 50 mm EDL); EDLs-2 (two 10 mm × 50 mm EDLs); EDLs-3 (three 10 mm × 50 mm EDLs); EDLs-4 (four 10 mm × 50 mm EDLs).

photodegradation efficiency [18], which was in accordance with our results. Light intensity of EDLs-4 was the highest with the best decomposition efficiency, comparing with that of other EDLs. While the lowest decomposition efficiency was found for EDLs-1, for which no light was observed throughout experiments. It was suggested that small volume of total EDLs could not absorb enough energy to be irradiated as water (dielectric constant $\varepsilon = 80$) competed with EDLs in absorbing MW energy. Horikoshi et al. [19] also reported that light irradiance emitted by the electrodeless Hg lamp for the water-cooled system was constantly lower than that for the non-water-cooled system by 28–46% at 250 nm in the double-quartz cylindrical plasma photoreactor.

3.3.2. Effect of solution volume

Effect of solution volume varied from 50 to 100 ml on removal of MB was studied in the PCD/EDLs process. Experimental conditions were $C_{0MB} = 100$ mg/l, MW energy = 900 W, EDLs-4, $C_{TiO_2} = 2$ mg/l and initial pH 7. Decomposition rates of MB follow the ranking as 50 ml (96%) > 70 ml (45%) > 100 ml (5%). During the experiments, no illumination was observed for EDLs-4 in 100 ml solution in 15 min reaction, a non-continuous illumination (5.6 mW/cm^2) in 70 ml solution, while a continuous illumination in 50 ml solution (9.4 mW/cm^2). It was also found that the larger the solution volume it was, the lower the light intensity. The reason of larger solution volume with lower decomposition rate was ascribed to the decreasing illumination time and low light intensity of EDLs.

3.3.3. Effect of catalyst dosage

The effect of catalyst dosage on MB decomposition was also studied. Experimental conditions were initial MB concentration = 100 mg/l, MW output power = 900 W, EDLs-4, solution volume = 50 ml, pH 7. The catalyst dosage ranged from 1 to 10 g/l.

The best decomposition efficiencies were observed when TiO$_2$ dosages were in the range from 1 to 4 g/l. When the catalyst dosage increased to 10 g/l, the removal rate decreased to 85%. That might be the increasing amount of TiO$_2$ particles reducing the penetration depth of the incident light and leading to reduction in the percentage of dye decomposition. Note that removal rate of MB in the DP/EDLs process without TiO$_2$ catalyst reached almost 80%, which indicated that DP/EDLs played an important role in MB decomposition. However, the removal rate for 10 g/l TiO$_2$ was still higher than that without catalyst.

4. Conclusions

Degradation of MB in TiO$_2$ aqueous suspensions in the system PCD/EDLs was studied under atmospheric pressure. TiO$_2$ powders were characterized by XRD and BET method. Comparative experiments were studied and results show that decomposition and mineralization rates for the PCD/EDLs process was the highest compared to those for the MW, MW/TiO$_2$ and DP/EDLs processes. Optimal decomposition efficiency was observed in the PCD/EDLs process when under the condition of EDLs-4, solution volume of 50 ml and TiO$_2$ catalyst dosage ranged from 1 to 4 g/l. The PCD/EDLs method is effective in degrading MB and it might be applicable in MB polluted water in the future.

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