Kinetics of Photocatalytic Degradation of Methylene Blue in Aqueous Dispersions of TiO$_2$ Nanoparticles under UV-LED Irradiation

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Abstract We investigated the degradation of methylene blue (MB) as an organic dye pollutant upon photocatalytic oxidation of TiO$_2$ nanoparticles under UV-LED (395 nm) light irradiation. Effect of different parameters, including initial concentration of dye and catalyst dosage on the degradation rate of the dye were evaluated. We found that the photonic efficiency of the photocatalytic degradation rate of the dye was determined by the ratio between the initial concentration of the dye and the number of TiO$_2$ nanoparticles in the colloidal solution. The optimum photocatalytic degradation rate was achieved when the TiO$_2$ nanoparticles in the solution are well covered by dye molecules, providing an interpretation that MB–TiO$_2$ molecular interactions play the key role in the photoinduced oxidation and reduction, leading to the photocatalytic degradation. We also demonstrated that the energy activation of the photocatalytic degradation is related to diffusion-controlled reaction, indicating that the photocatalytic degradation of the dyes is diffusion-controlled reaction of free hydroxyl radicals.

Keywords: *photocatalysis, methylene blue, degradation, TiO$_2$ Nanoparticles, temperature effect*

1. Introduction

Environmental problems have been an increasing concern and worldwide issue, most of them related to the industrial wastes containing toxic and carcinogenic chemicals, such as heavy metal ions and dyes directly discharged into water streams or sewage systems [1]. Without removing the hazardous chemicals, when the polluted water streams go into rivers, the pollutants cause great risks to the aquatic ecosystem, water resources, and then the entire ecosystem inclusive of plants, animals, and humans. Among the hazard chemicals, those from textile dyeing effluents in wastewater have received great attention not only because of its toxicity but mainly due to its aesthetic effect, even at lower concentrations [2]. Therefore, adequate treatments, particularly, an effective removal of dyes from industrial wastes before discharging them into the sewage systems, water recycling systems, and water streams are indispensable.

There have been countless reports focused on the development of chemical, physical, and biological methods with high selectivity for the removal of dyes and other toxic substances from wastewater. The main approach is to utilize adsorption process by employing biosubstances or synthetic materials as adsorbents [3]. The most efficient and widely used adsorbent is activated carbon, but it is sometimes treated as a one-off adsorbent due to the high regeneration cost. On the other hand, biosubstances such as microorganisms and fruit skins have also been demonstrated to remove metal ions and dyes from water. This topic has been reviewed in detail, for instance, by Rafatullah et al. [4], Ngah et al. [5], and Crini [6].

Utilizing advanced oxidation processes, photocatalytic decomposition of the organic pollutants in water via their reactions with generated hydroxyl (OH$^•$) radicals at or near the surfaces of semiconductors, has also received much attention [7-12]. In general, metal oxide semiconductors have been intensively used for photocatalytic applications due mainly to its suitable band energy to the visible light energy to excite their electrons from valence to the conduction band [13,14,15]. This photocatalytic oxidation is of particular interest due to its ability to use the solar, UV, or visible light irradiation, and it can be conveniently used for the complete degradation of various hazardous

compounds, converting them into harmless mineral compounds. The pioneer research on this subject was the use of TiO_2 powder for the decomposition of highly polluting cyanide ions in water [16]. Following these studies, photocatalysis using TiO_2 for the degradation of wastewater pollutants has attracted a lot of attention due to its inherent photoactivity, chemical and biological stability, non-toxicity, low cost, and well known synthesis methods. It is known that large crystallites of TiO_2 show poor photocatalytic activities, but their activities are increased when their particle sizes is reduced down to nanometer-scales [17].

In this study, we focus on the degradation of methylene blue (MB) upon photocatalytic oxidation of TiO_2 nanoparticles under UV light irradiation. MB is mainly used as a biological stain due to its ability to color parts of cells and it is helpful in certain medical tests, but as an organic dye, MB is also one of the contaminants and pollutants in the environment which has many effects when it is in the body. Thus, we selected MB, as a model pollutant of cationic dyes. The photocatalytic performance of TiO_2 nanoparticles was assessed by the degradation rate of MB. As we anticipated, the degradation rate of MB depends on the ratio between MB molecules and the number of TiO_2 nanoparticles, providing an interpretation that MB–TiO_2 molecular interactions play the key role in the photoinduced oxidation and reduction.

2. Experimental Section

2.1. Materials

Commercially available rutile TiO_2 nanoparticles and MB dyes (molecular weight = 319.85 g) were purchased from Sigma Chemicals. They were used without further purification. The type of the TiO_2 nanoparticles is nanospheres with diameter and density being 100 nm and 4.23 g/cm^3, respectively. The crystalline phase of the TiO_2 nanoparticles was reconfirmed by infrared spectroscopy (Shimadzu, IRPrestise-21) with 2.0 cm^{-1} spectral resolution, and their morphology, type of nanoparticles, and size were evaluated by a scanning electron microscope imaging (JEOL, JSM-7610F). In order to characterize the electronic and optical properties of the nanoparticles in powder form, we have also measured their UV-vis diffuse reflectance using a single beam spectrophotometer (Hitachi, F-4500) and fluorescence spectra after excitation at 395 nm using a spectrofluorometer (Horiba Scientific). From the spectra, shown in Figure 1, we understand that rutile TiO_2 nanoparticles efficiently absorb photons in the UV region (less than 400 nm or 3.0 eV), as it has been discussed by Reyes-Coronado et al. [18], and the nanoparticles emit light in the visible region between 400 to 550 nm [19] which is strongly overlapped with the absorption spectrum of MB to facilitate efficient energy transfer.

2.2. Photoirradiation Setup

Photocatalytic reactions were carried out in a glass tubular reactor (2 cm diameter; 15 mL volume) transparent for UV light, as schematically shown in Figure 2. The tube consisting the reaction mixture of TiO_2 nanoparticles and MB dissolved in distilled water was irradiated with UV light from an LED (powered by a DC power supply of 2 mV), emitting at 395 nm. With this UV light irradiation, we can selectively excite TiO_2 nanoparticles, because MB has a very low extinction coefficient in the spectral range between 350 to 450 nm [2]. During the irradiation, the reaction mixture was also continuously stirred, while dispersion of UV light and disturbance from stray light were carefully blocked.

To evaluate the photocatalytic degradation rate, 10.0 mL MB solutions with concentrations of 15.0, 12.5, 10.0, 7.5, 5.0 ppm in distilled water were prepared. In each solution, 20 mg of TiO_2 powder were added. The mixtures were illuminated at different irradiation times of 0, 5, 10, 15, 30, 40, 50, 60, 80 and 100 minutes at room temperature (25°C). After the irradiation, the mixture was centrifuged at 3000 rpm for 15 min to separate the particulates. The supernatant was collected and subjected to absorption spectrum measurement using UV-visible spectrophotometer (Shimadzu UV-1601PC, Japan). The concentration of MB left in the solution was calculated from its absorption peak at 665 nm, at which it has an extinction coefficient of 7.4×10^4 cm^{-1} mol^{-1}, according to the Beer-Lambert Law. With such high extinction coefficient, concentration of MB in water as low as 1 mg/L or 1 ppm can be accurately detected by the spectroscopic technique [2].
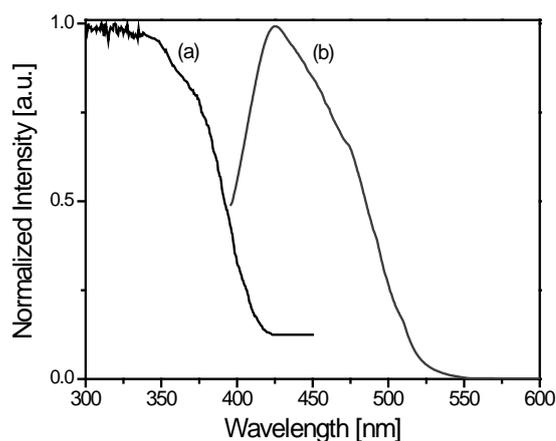

Figure 1. UV-visible reflectance (a) and fluorescence (b) spectra of TiO_2 nanoparticles
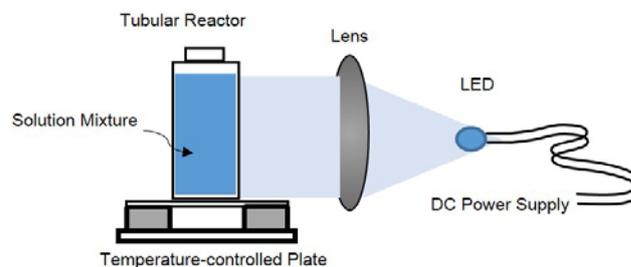

Figure 2. Schematic diagram of the experiment set-up for photocatalytic reactions

Effect of TiO_2 dosage was evaluated by varying the mass of TiO_2 in a fixed concentration of MB solutions at room temperature (25°C). In to each solution of 10.0 mL MB solutions (15 ppm), 0–35 mg of TiO_2 were added. The photocatalytic degradation rate was evaluated by the same procedure, namely the mixtures were irradiated at the same light power and irradiation times, followed by centrifugation

at the same speed after the irradiation, the supernatant was subjected to absorption spectrum measurement, and the concentration of MB left in the solution was determined from its absorption peak at 665 nm.

Kinetics of the photocatalytic degradation was investigated by evaluating the degradation of MB at different temperatures between 22 to 50 °C. In this case, the glass tubular reactor was placed on temperature-controlled hot plate. The concentration of MB and mass of TiO_2 were fixed at 15 ppm and 20 mg, respectively. The photocatalytic degradation rate was evaluated by the same procedure, as described above.

We note that variation in pH of the mixture would change the charges on the surface of the photocatalyst TiO_2 nanoparticles as well as on the organic compounds, leading to variation of photocatalytic degradation rate of the organic compounds. We found that pH of MB solution was 5.5, and it was not changed after mixing with TiO_2 nanoparticles or after irradiations. Thus, the pH of the colloidal mixture of MB and TiO_2 nanoparticles was kept as it is without any addition of acid or base.

2.3. Data Analysis

All the collected data were analyzed. The subsequent photodegradation of MB was evaluated by analyzing the absorption data which were fitted with single exponential functions, as described below.

3. Results and Discussion

3.1. Photodegradation of MB

Figure 3A representatively shows absorption spectra of MB before and after a series of illumination with UV light. It is clearly observed that the absorbance decreases, demonstrating the degradation of MB, with irradiation time due to the photocatalytic reaction. The photocatalytic reaction pathway is believed to involve the reaction of MB with the generated OH• radicals, resulting in N-demethylation of its auxochromic dimethylamine groups. Such demethylization depredates MB into a compound with a short absorption wavelength, in addition to H_2O and CO_2 [20]. It is noted that the degradation rate of MB is reduced with increasing initial MB concentration, indicating that the photonic efficiency decreases rapidly with increasing initial concentration of MB. This behavior has been reported earlier by Jang et al. [21].

The photocatalytic degradation rate was deduced from the plot of the concentration of MB as a function of irradiation time up to 100 min irradiations, as shown in Figure 3B. For all initial concentrations of MB, the degradation follows the first order reaction, as normally observed in photocatalytic reactions of organic compounds. Therefore, the time-dependent plot was fitted with either a single exponential function, $[MB]_t = [MB]_0 e^{-kt}$, or a logarithmic function, $\ln[MB]_t = -kt + \ln [MB]_0$. Here $[MB]_0$ and $[MB]_t$ is the initial concentration of MB and the concentration of MB after t irradiation time, respectively, and k is the rate constant of the photocatalytic degradation.
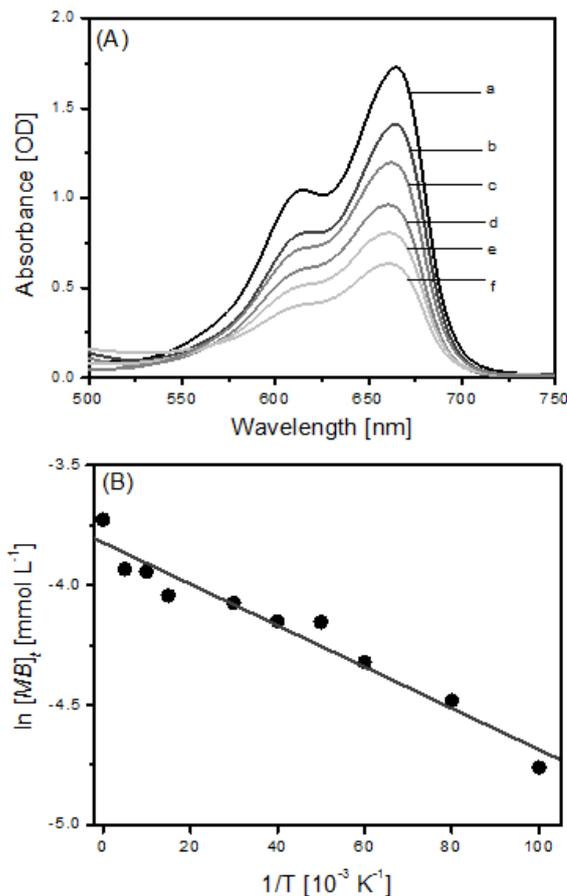

Figure 3. (A) A series of absorption spectra of MB after UV light illumination at (a) 0, (b) 5, (c) 30, (d) 60, (e) 80 and (f) 100 mins. (B) The concentration of MB as a function of irradiation time up to 100 min irradiations. The line is the best fit for a logarithmic function, $\ln[MB]_t = -kt + \ln [MB]_0$, from which k was deduced

As shown in Figure 4, k is smaller for higher $[MB]_0$, indicating that the photocatalytic degradation tends to be slower for higher $[MB]_0$. Similar trends of concentration-dependent photocatalytic degradation of MB has been reported by Dariani et al. for MB [17], Dai et al. [22], and Ling et al. [23]. It may not be surprising, in this case, for the same number of both TiO_2 nanoparticles and irradiated photons, the UV light penetrates into the colloidal solution and excites TiO_2 nanoparticles more easily in lower $[MB]_0$, resulting in more efficient photocatalytic degradation, although collision probability between MB molecules and excited TiO_2 nanoparticles is increased with the concentration of MB. In this sense, we may consider the formation of the by-products during the degradation of MB molecules. At high concentrations of MB, large amount of MB molecules are adsorbed on TiO_2 nanoparticles and absorb more photons of the UV irradiation, resulting in UV screening effect. At such high concentrations of MB, large amount of MB molecules do not have direct contact with TiO_2 nanoparticles neither with the generated OH• radicals, thus preventing them from the successful photocatalytic degradation reactions. Consequently, higher concentrations of MB give lower photonic efficiency. To exemplify further this issue, we have evaluated the photocatalytic degradation of MB at different dosage of TiO_2 as described in the following section.
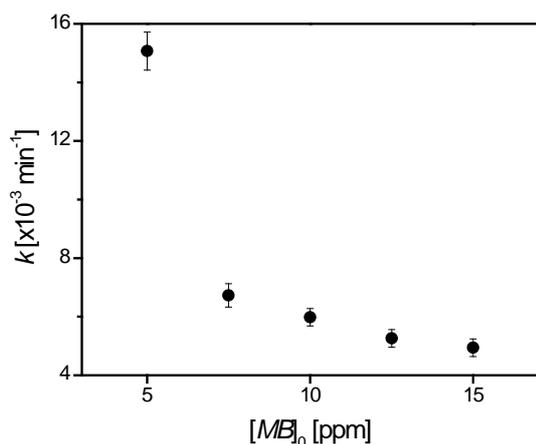
Figure 4. Plot of k as a function of $[MB]_0$. The TiO$_2$ dosage was 20 mg in 10 mL MB solutions

3.2. Effect of TiO$_2$ Dosage

Figure 5 shows the effect of TiO$_2$ mass (or the number of nanoparticles) on photocatalytic degradation rate of 15.0 ppm MB within 100-min UV light irradiations. It is clearly observed that the photodegradation rate of MB increases with the mass or number of TiO$_2$ nanoparticles, however it reaches a maximum, and after which the photodegradation rate tends to decrease with high number of TiO$_2$ nanoparticles.
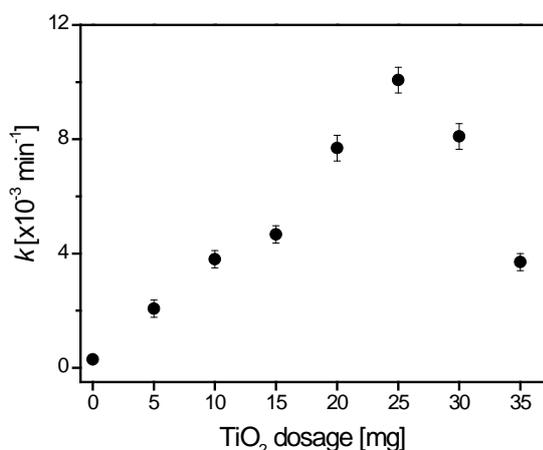

Figure 5. Plot of k as a function TiO$_2$ dosage in 10 mL MB solutions at $[MB]_0$ 15 ppm

This finding suggests that TiO$_2$ has a good photocatalytic performance [22,24], thus at higher dosage of TiO$_2$ there will be a higher probability for the photocatalyst to absorb photons required to generate electrons in the conduction band, leading to the higher concentration of generated OH$^\bullet$ radicals which is responsible to degrade the organic compounds [24]. However, it should also be mentioned that the colloidal mixture becomes more turbid at higher density of TiO$_2$ nanoparticles. Thus, the UV light is readily absorbed at the tubular reactor, and it requires higher light power or larger number of photons to excite the larger number of TiO$_2$ nanoparticles in the mixture. For the constant power of the UV light, at one state of large quantity of TiO$_2$ nanoparticles, the photonic efficiency will be saturated and decreased at larger quantity of TiO$_2$ [25]. Thus, basically, the degradation of MB in the photocatalysis

process increases, reaches a maximum, and decreases with increasing TiO$_2$ dosage.

We note that, under our experimental conditions, the optimum photocatalytic degradation rate of MB was achieved when $[MB]_0$ was 15.0 ppm and mass of TiO$_2$ nanoparticles was 25.0 mg. As the excitation wavelength is much smaller than the size of TiO$_2$ nanoparticles, we may exclude the effect of light absorption cross section in the colloidal mixtures with different number of the TiO$_2$ nanoparticles. Thus, to understand the optimum condition of the photocatalysis, we consider the coverage of MB on the TiO$_2$ nanoparticles. Based on molecular weight of MB, density, and size of TiO$_2$ nanoparticles, we can estimate that the optimum photocatalytic degradation rate is when the ratio between MB molecules and the number TiO$_2$ nanoparticles is $2.8 \times 10^{17} : 1.1 \times 10^{13}$ or it is roughly 2.5×10^4 MB molecules per individual TiO$_2$ nanoparticles. Though the molecular size of MB$^+$ based on van der Waals radii is 112 Å^2 [26], an effective molecular diameter of such a three membered rings is approximately 1–1.5 nm [27]. Thus, for monolayer coverage of MB on the TiO$_2$ nanoparticles with diameter of 100 nm, we can estimate that there are also about ~2.5×10^4 MB molecules adsorbed on the surface of individual nanoparticles. This means the optimum photocatalytic degradation rate was achieved when the TiO$_2$ nanoparticles in the colloidal solution are well covered by MB molecules. Thus, we can anticipate that the degradation rate becomes slower when the MB molecules and the number of TiO$_2$ nanoparticles in the colloidal mixtures are not at the optimum ratio. This further provide an interpretation that MB–TiO$_2$ molecular interactions play the key role in the photoinduced oxidation and reduction, leading to the photocatalytic degradation.

3.3. Temperature Dependence of k

The photocatalytic degradation rate of MB increases with increasing temperature, as shown in Figure 6 for the plot of temperature dependence of the degradation rate. The data points were fitted with Arrhenius equation, $k = Ae^{-E_a/RT}$, (where A is the pre-exponential factor related to the frequency of successful degradation reaction, E_a is the activation energy, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), and T is the absolute temperature), giving E_a of the first-order photocatalytic degradation reaction to be 14.03 kJ mol^{-1}. Comparable values (13.09 and 14.45 kJ mol^{-1}) for the decolorization of MB by photocatalysis of TiO$_2$ nanoparticles can be found in the literature for different temperature ranges and experimental conditions [28,29].

We may note that the E_a value is much lower than that normally observed for a chemical reaction [30]. To understand this issue, we should consider that the photocatalytic oxidation and reduction process is initiated by photonic activation, rather than by heating [31]. Thus, E_a might be ascribed to the potential barrier of the photocatalytic degradation which is related to diffusion-controlled reaction, where the activated state is a well solvated structure formed between the MB dyes and generated OH$^\bullet$ radicals. Thus, we consider that E_a of the photocatalytic degradation should be very close to those of a reaction of OH$^\bullet$ radicals. In other words, the

photocatalytic degradation of the dyes is controlled by the diffusion and reaction of OH$^\bullet$ radicals.
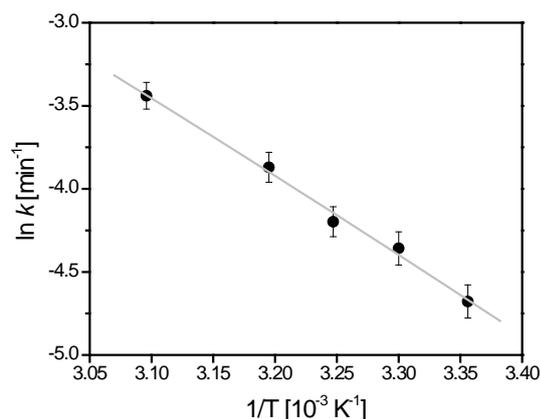

Figure 6. Arrhenius plot of k against inverse temperature, $1/T$, of the photocatalytic degradation of MB. The temperature range was 25 to 50 °C, $[MB]_0$ was 15 ppm, and TiO$_2$ dosage was 20 mg in 10 mL. The solid line is the best fit, from which the energy of activation for photocatalytic degradation, E_a, was deduced

4. Conclusions

Degradation of MB in aqueous solutions upon photocatalytic oxidation of the rutile TiO$_2$ nanoparticles under UV light irradiation, a system which is a suitable model for wastewater photodegradation under sunlight, has been investigated. As anticipated, the TiO$_2$ nanoparticles show good photocatalytic activity in decomposing MB. We demonstrated that the photonic efficiency of the photocatalytic degradation of MB is actually determined by the ratio between the initial concentration of MB and the number of TiO$_2$ nanoparticles in the solution. The optimum photocatalytic degradation rate was achieved when the TiO$_2$ nanoparticles in the colloidal solution were well covered by MB molecules. This further provide an interpretation that MB–TiO$_2$ molecular interactions play the key role in the photoinduced oxidation and reduction, leading to the photocatalytic degradation. We found that the first-order photocatalytic degradation reaction of MB is 14.03 kJ mol^{-1}, which should be very close to those of a reaction of OH$^\bullet$ radicals, indicating that the photocatalytic degradation of the dyes is diffusion-controlled reaction of OH$^\bullet$ radicals.

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Statement of Competing Interests

The authors have no competing interest.

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