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Enhanced photocatalytic degradation of methylene blue under vacuum ultraviolet irradiation

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ABSTRACT

A vacuum ultraviolet (VUV) lamp was used as the irradiation of photocatalysis to enhance the degradation of methylene blue (MB), a model dye compound. In contrast to photocatalysis under 254 nm UV irradiation (UV/TiO₂), photocatalysis under VUV irradiation (VUV/TiO₂) exhibited much higher efficiency in MB degradation and mineralization and needed less TiO₂ dosage. The rate constant of MB degradation in VUV/TiO₂ (0.0793 min⁻¹) is about 4 times of that of UV/TiO₂ (0.0205 min⁻¹). The MB mineralization rate is also greatly increased from 12.5% in UV/TiO₂ to 47.7% in VUV/TiO₂ after 60 min of irradiation. Multiple advanced oxidation processes including photocatalytic oxidation and VUV photo-oxidation coexist in VUV/TiO₂ to substantially produce highly reactive species (such as •OH and energetic photons), which is responsible for efficient degradation and mineralization of MB.

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1. Introduction

A large amount of wastewater containing dyestuffs with intensive color and toxicity can be introduced into aquatic systems from textile industry. It causes a great deal of environmental problems around the world [1-3] and has become one of the key concerns of sewage treatment [4]. Many technological approaches, including physical methods (such as coagulation and adsorption) [4], biological methods [5] and chemical methods (such as NaClO and ozonation) [6] have been developed for reducing dye pollution. However, conventional treatment methods are difficult to meet the stringent environmental quality standards required these days. For example, biological methods are not ineffective in decolorizing textile effluents since many dye compounds are recalcitrant organic molecules or non-biodegradable [7]. Coagulation flocculation is not efficient for the removal of soluble reactive dyestuff. In addition, substantial sludge will be generated in these two processes and the sludge require further treatment [1], which may greatly increase the cost of wastewater treatment.

Photocatalytic oxidation (PCO) is regarded as a promising technology for dye wastewater treatment due to its strong capacity of oxidization and environmentally friendliness [8,9], whereas, its

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application is greatly limited by inefficient oxidant generation and low degradation capacity [8,9]. In order to improve the efficiency of PCO, many modification methods have been adopted, including assistance of hydrogen peroxide [10], microwave [11,12] and ozone [13]. Nevertheless, all these processes need additional oxidants or equipment to generate •OH, making it cost prohibitive for full-scale operation [14]. More recently, vacuum ultraviolet (VUV) photo-oxidation of wastewater has attracted much attention since it exhibits an advantage of being an additive-free process, and thereby may make commercially viable [15]. It has been shown to be effective for the treatment of certain types of wastewater such as perfluorodecanoic acid, SDBS surfactants, geosmin and 2methylisoborneol [15–19]. Nevertheless, unfavorable by-products and intermediates radicals can be formed depending on the complexity of the organics degraded in this process [16-18]. In addition, VUV photo-oxidation has a limited capacity of •OH formation, resulting in restricted oxidation and mineralization rate [17].

Methylene blue (MB) is an intensely colored compound which is used in dyeing and printing textiles and is a common water pollutant [20]. In this study, a VUV lamp was used as the irradiation of photocatalysis to enhance the degradation of MB. Its performance was compared with photocatalysis under 254 nm UV irradiation (UV/TiO₂). The mechanism leading to excellent performance of VUV/TiO₂ was discussed. This is the first attempt to remove dye pollutants using VUV/TiO₂. This efficient process presents a promising technology for dye treatment.



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Fig. 1. The schematic diagram of the PCO reactor.

2. Experimental and methods

2.1. Reagents and materials

MB (Tianjing Chemical Co., Ltd., China) was analytical grade and used as received. Commercial TiO_2 powder, Degussa P25 with BET surface area of $50.8 \text{ m}^2/\text{g}$ and average particle size of 22.1 nm, was utilized as the photocatalyst.

2.2. Measurement scheme

The MB solution was analyzed by a UV-Vis spectrometer (Jenway 6105, Keison) at the wavelength of 664 nm. The MB concentration in water was calculated using calibration curves. The total organic carbon (TOC) in the solution was measured with a Shimadzu VCPH TOC analyzer. The inorganic ion products from MB degradation were determined using ionic chromatography (IC, Metrohm 882) with a Metrosep A Supp 5 guard column (250 mm/4 mm). A gradient elution of a 3.2 mM Na₂CO₃ and 1 mM NaHCO₃ solution was used. The intermediates of MB degradation were identified by a liquid chromatography-mass spectrometry (LC-MS) system (LCQ DECA XP, Thermo Finnigan) using an Agilent Zorbax SB-C18 column (150 mm \times 4.6 mm) packed with 5 μ m particle size. The mobile phase consisted of two solutions namely A and B. Solution A was made from 0.1 M ammonium acetate and acetic acid (pH 5.3), whereas solution B was acetonitrile [21]. The gradient elution was from 5% to 95% in 30 min, the flow rate was 0.8 mL/min and the injection volume was 100 µL. The mass spectrometer was equipped with an electrospray ionization source and operated in positive polarity. The mass range was from 50 to 300 m/z.

The schematic diagram of the PCO reactor is presented in Fig. 1. One 500 mL glass beaker with a diameter of 10 cm was used as the reaction vessel and placed on a magnetic stirrer. In a typical experiment, 400 mL of 20 mg/L dye solution was poured into the beaker. TiO₂ powder was added into the solution and well spread by a magnetic stirrer with a mixing rate of 800 r/min. Two types of low-pressure mercury lamps (7 W) were used to provide UV illumination: a UV lamp emitting at 254 nm (ZW7D12W-H115, Cnlight) and a VUV lamp emitting about 10% 185 nm UV radiation and about 90% 254 nm UV radiation (ZW7D12Y-H115, Cnlight). Both UV lamps are H-type with a length of 11.5 cm. The effective length of lamp in MB solution is 10 cm. Prior to irradiation, the solution and TiO₂ powder were allowed to be fully mixed under stirring and equilibrate in the dark for 30 min. Samples were collected at regular intervals, and centrifuged to remove the catalyst particles prior to analysis by UV-Vis spectrometer and TOC analyzer. For oxygen rich conditions, oxygen from cylinder was bubbled at a flow of 0.2 L/min. This ensured the reaction solution was kept saturated by the continuous supply of oxygen at a constant rate when required.

Degradation efficiency and mineralization rate were calculated using the following equations:

Degradation efficiency (%) =
$$\frac{C_0 - C_t}{C_0} \times 100$$
 (1)

Mineralization rate (%) =
$$\frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0}$$
 (2)

where C_0 and C_t represents the initial concentration of MB and those at time t, and TOC₀ and TOC_t represents the initial concentration of TOC and those at time t, respectively. The degradation efficiency and mineralization rate may not be identical since organic intermediates can be generated during the degradation of pollutants. Compared with degradation efficiency, mineralization rate provide a better understanding of the capability of transferring pollutants into harmless inorganic products.

3. Results and discussion

3.1. MB degradation

Fig. 2a compares the MB concentration as a function of irradiation time in different processes. The MB concentration slightly dropped from 20 mg/L to 19.2 mg/L in the presence of TiO₂ after reaching adsorption equilibrium, revealing that the adsorption from TiO₂ is not significant. Almost no reaction was observed for 254 nm UV irradiation alone, indicating that the direct photodegradation by 254 nm UV irradiation can be neglected. The concentration of MB tended to decrease exponentially with irradiation time in the other processes. VUV/TiO₂ obtained a much faster degradation of MB than UV/TiO₂. The MB concentration in UV/TiO₂ dropped 6.2 mg/L after 20 min of irradiation; however, it



Fig. 2. Time course of MB concentration (a) and rate constant of MB degradation (b) (TiO₂ dosage = 0.5 g/L, C₀ = 20 mg/L).

was decreased to only $1.1 \text{ mg/L in VUV/TiO}_2$. In contrast to UV/TiO₂, VUV/TiO₂ can provide more processes such as photo-oxidation for MB degradation. It can be seen from that the MB concentration in VUV dropped to 4.2 mg/L, indicating that VUV photo-oxidation can directly degrade MB in the absence of TiO₂.

To analyze degradation kinetics, simplified apparent pseudofirst-order of kinetics rates were obtained for MB degradation using Eq. (3):

$$\ln \frac{C_0}{C_t} = k_t t \tag{3}$$

where k_t was the apparent pseudo-first-order rate constant of initial degradation (expressed in units of min⁻¹), C_t and C_0 represents the transient and initial concentrations of MB, respectively. The rate constant k_t was calculated from the slope of the $\ln(C_0/C_t)$ versus t, as shown in Fig. 2b. It can be found that the degradation of MB shows apparent pseudo-first-order of kinetics. The rate constant of MB degradation was 0.0205 and 0.0468 min⁻¹ in the UV/TiO₂ and VUV process, respectively. However, it was greatly increased to 0.0793 min⁻¹ for the VUV/TiO₂ process, which was about 4 and 2 times of that in the UV/TiO₂ and VUV process. The rate constant of VUV/TiO₂ process was even higher than the sum of that of UV/TiO₂ and VUV process, indicating that synergetic effect occurred during the MB degradation in the VUV/TiO₂ process. The VUV photo-oxidation and UV/TiO₂ process coexisted and synergistically degraded pollutants in the VUV/TiO₂ system.

3.2. Effect of TiO₂ dosage

The dosage of photocatalyst is an important factor of PCO for the sake of the operating cost and its effect on the removal efficiency. Various dosage of TiO₂ was used in the PCO processes and its effect on MB degradation is presented in Fig. 3. The removal efficiency of MB after 60 min of irradiation is only 79.6% with 0.5 g/L TiO₂ dosage while it greatly increased to 98.5% with 1 g/L TiO₂ dosage in the UV/TiO₂ process (Fig. 3a). The increase of TiO₂ dosage can improve the molar ratio of TiO₂/MB and provide more active centers for photocatalytic oxidation, which favors MB degradation. The maximum removal efficiency was obtained with 1.5 g/L TiO₂ dosage while further increase of TiO₂ dosage contrarily only caused a slight decrease of removal efficiency. In aqueous photoreaction systems, the existence of gradient light intensity throughout the reaction solution is one of important restrictions to the efficiency of overall photoreaction. It highly relies on the optical properties of the catalyst such as light absorption and scattering effects, the particle size of the catalyst and the degree of agglomeration in its slurry [22]. Beyond such an optimum dosage, the light intensity inside the photoreactor declined sharply along with an increased distance from the UV lamp due to serious light scattering and agglomeration resulting from a high number of catalyst particles in aqueous suspension [14,22]. Considering both the favorable and the unfavorable effect of the increased TiO₂ dosage, the overall degradation efficiency of MB did not change too much as it is over 1 g/L. Similarly, an optimum TiO₂ dosage of 1 g/L was also observed for the VUV/TiO₂ process (Fig. 3b). However, the removal efficiency of MB was kept at very high level of 98.2% even with 0.5 g/L TiO₂ dosage. The TiO₂ dosage had less influence in the VUV/TiO₂ process than the UV/TiO₂ process. As shown in Fig. 2, VUV photo-oxidation, which happened in the absence of TiO₂, was also much involved in MB degradation besides PCO in the VUV/TiO₂ process. One of the disadvantages of conventional photocatalysis is the requirement of large amounts of TiO₂ photocatalyst. Compared with UV/TiO₂ process, the use of photocatalyst can be substantially reduced due to the presence of multiple oxidation processes in the VUV/TiO₂ system, which can greatly cut down the cost and makes it more capable for industrial application.

3.3. Mineralization rate

Both UV/TiO₂ and VUV/TiO₂ obtained high MB removal efficiency with TiO₂ dosage of 1 g/L, as previously described. Their degradation and mineralization rate of MB under this condition is compared and the results are presented in Fig. 4. With TiO₂ dosage of 1 g/L, UV/TiO₂ achieved higher degradation efficiency than VUV, which is different from the result with TiO₂ dosage of 0.5 g/L (Fig. 2a). Both the degradation and the mineralization rate, especially the latter, were significantly raised in VUV/TiO₂ when compared with the UV/TiO₂. The mineralization rates were only 24.2% and 3.5% after 30 min of irradiation in the UV/TiO₂ and VUV process, respectively. However, it is greatly increased to 35.5% in VUV/TiO₂. Comparing Fig. 4a and b, it can be observed that the MB mineralization rate is much smaller than the degradation efficiency. For example, nearly 100% degradation efficiency of MB can be obtained on all the processes after 60 min of irradiation (Fig. 4a) while the corresponding mineralization rate is only 47.7%, 35.8% and 12.5% for the VUV/TiO₂, UV/TiO₂ and VUV process (Fig. 4b), respectively. The results suggest that MB is quickly converted to intermediate products while it takes a relatively long time to mineralize intermediate products. This observation agrees with SDBS oxidation in the previous studies, in which intermediates such as ketones, alcohols, and carboxylic acids have been observed [17,23]. Compared with VUV alone, photocatalysis under irradiation of either UV or VUV light both obtained much higher mineralization rate, indicating that the presence of TiO₂ can promote the



Fig. 3. Effect of TiO₂ dosage on degradation efficiency of MB ($C_0 = 20 \text{ mg/L}$).



Fig. 4. Time course of degradation and mineralization rate (TiO₂ dosage = 1 g/L, $C_0 = 20 \text{ mg/L}$).

mineralization of pollutants. Similar phenomena were also observed in the degradation of *p*-chlorobenzoic acid in these processes [24]. This is probably due to intermediate degradation on the surface of photocatalyst [24] and the strong oxidation capability of •OH in the PCO process.

3.4. Degradation mechanism of VUV/TiO₂ process

The detailed mechanism of the photocatalysis has been intensively discussed in the literature [25–29]. Electron–hole pairs and •OH are considered as the major oxidative species in PCO [26,28,29]. As for VUV, it is usually regarded that •OH, generated from the photo-oxidation of water, is mainly responsible for the degradation of pollutants [16,18]. The •OH is produced mainly via a series of reactions ((R1)–(R4)) [16,18,24], among which (R1) is the principal reaction.

$$H_2O + hv(185 \,\mathrm{nm}) \to {}^{\bullet}OH + {}^{\bullet}H \tag{R1}$$

$$O_2 + {}^{\bullet}H \rightarrow HO_2 {}^{\bullet}$$
 (R2)

$$\mathrm{HO}_{2}^{\bullet} + {}^{\bullet}\mathrm{H} \to \mathrm{H}_{2}\mathrm{O}_{2} \tag{R3}$$

$$H_2O_2 + h\nu(254\,\mathrm{nm}) \to 2^{\bullet}OH \tag{R4}$$

However, the contribution of direct VUV photolysis, i.e. energetic photons, is generally ignored during degradation of pollutants in previous studies [16,18]. It should not be excluded during the degradation of pollutants. It is known that 185 nm wavelength corresponds to photon energy of 6.7 eV, which is higher than the bond dissociation energy (BDE) of water molecular [30] and can dissociate water to form •OH [14,17]. In addition, it can directly dissociate organic pollutants with BDE lower than 6.7 eV. The BDE data of MB molecules and water are shown in Table 1. It can be seen that the BDE of MB molecular is much smaller than photon energy of 185 nm radiation as well as water molecular. According to the BDE theory, the lower the BDE is, the more active the chemical bond is and the

BDE in a MB and water molecule [30,31].

Molecule bonds	Bond energy (kcal/mol)	Bond energy (eV)
CH ₃ —N(CH ₃)C ₆ H ₅	70.8	3.07
$N(CH_3)_2 - C_6H_5$	93.2	4.04
C ₆ H ₅ —NH—C ₆ H ₅	87.4	3.79
$C_6H_5 - S - C_6H_5$	76.0	3.30
C_6H_5 — NH_2	102.6	4.45
Н—ОН	120.2	5.21

The chemical bonds corresponding to the given BDE are shown as "--".

easier it is for old bonds to break and new bonds to form [31]. Compared with water molecular, MB molecular can more easily to be destructed by energetic photons.

Fig. 4 gives another evidence of the contribution of direct photolysis in degradation of MB. UV/TiO₂ and VUV obtained similar MB degradation efficiency after 60 min of irradiation. Nevertheless, the mineralization rate in the former is 36%, which is about 3 times of the mineralization rate of 12.5% in VUV. The results indicate that the reactive species responsible for MB degradation are possibly different in the two processes. There should be additional reactive species involved in MB degradation besides •OH in the VUV process. In the VUV process, the degradation efficiency (95.8%) is much larger than the mineralization rate (12.5%) after 60 min of irradiation, indicating that many organic intermediates are generated from MB dissociation by energetic photons. This was confirmed by LC-MS results. Azure B and thionin were identified in the MB solution after degradation using LC-MS. However, •OH is the main oxidant in the UV/TiO₂ process [26,28,29]. It is well known that •OH is highly reactive, non-selective, and capable of complete oxidation of organic pollutants [16]. The different potential of complete oxidation of pollutants between energetic photons and •OH may be responsible for their discrepancy in mineralization rate.

The anion products were further identified using IC method. It can be observed that Cl⁻, NO_3^- and SO_4^{2-} were formed during MB degradation. Fig. 5 is a representative IC spectrum of MB solution after reaction of 120 min in the VUV/TiO₂ process. The anion concentrations at different reaction times were measured and the results are shown in Fig. 6. It is interesting to find that Cl⁻, NO₃⁻ and SO_4^{2-} show different generation rates. Cl^- concentration quickly reached the calculated Cl⁻ concentration (2.2 mg/L) of complete MB degradation after a reaction of 10 min, indicating that Cl⁻ is easily detached from MB molecules. Although NO₃⁻ concentration can reach a stable value after a reaction of 10 min, it is only about of 1/3 of the calculated NO₃⁻ concentration (11.6 mg/L) of complete MB degradation, indicating that only partial N-C of MB was oxidized into NO₃⁻. Unlike Cl⁻ and NO₃⁻, the SO₄²⁻ concentration gradually increased with reaction time and reached the maximum value, which is close to the calculated SO_4^{2-} concentration (5 mg/L) of complete MB degradation, after a reaction of 120 min. This result shows that the S–C bond of MB is more difficult to be broken down than its N–C bond.

Based on BDE analysis of MB, and the inorganic ions and intermediates from MB degradation indentified in this and previous work [21,31], the possible pathways of MB degradation by the VUV/TiO₂ process are proposed in Fig. 7. Different from the pathways of MB PCO in which •OH is mainly involved in the opening of



Fig. 5. Determination of Cl⁻, NO_3^- and SO_4^{2-} anions of MB degradation by VUV/TiO₂ after reaction of 120 min by ion chromatography (TiO₂ dosage = 1 g/L, C_0 = 20 mg/L).

aromatic ring and oxidation [21,31], energetic photons also play an important role in VUV. During the dissolution of MB, Cl⁻ is first ionized and exists in the detached state. The methyl (CH₃) connected to ⁷C and ¹²C has the lowest BDE value in the MB molecular structure and is first broken down by radicals and oxidized into HCHO, Azure B and thionin. Azure B and thionin were identified by LC–MS, as previously described. N–C and S–C are the most active bonds of thionin molecule and are further broken down[31]. N in the N–C bond is oxidized into NO₃⁻ and S in the S–C bond is oxidized into –HSO₃, which is still connected to ⁹C. The intermediates of thionin oxidation were further oxidized into a single ring structure, which finally oxidized into harmless substances (H₂O and CO₂) or ions (such as SO₄^{2–} and NH₄⁺).

VUV/TiO₂ is a more complex system than VUV alone. Numerous sub-processes and reactions are involved in formation of oxidants and the degradation of pollutants in VUV/TiO₂. Multiple AOPs (such as VUV photolysis and PCO) coexist to substantially produce highly reactive species (such as •OH and energetic photons). In addition, TiO₂ can absorb both MB and VUV irradiation and provide active sites for MB degradation by VUV photolysis. The VUV/TiO₂ process can overcome the limitations of individual conventional PCO or VUV photo-oxidation.



Fig. 6. Time course of concentration Cl⁻, NO₃⁻ and SO₄²⁻ anions during MB degradation by VUV/TiO₂ (TiO₂ dosage = 0.5 g/L, C₀ = 20 mg/L).



Fig. 7. Proposed pathway of MB degradation by VUV/TiO₂ process.



Fig. 8. Effect of oxygen bubbling on reaction constant rate of MB degradation (TiO₂ dosage = 0.5 g/L, $C_0 = 20 \text{ mg/L}$).

3.5. Effect of oxygen bubbling

Oxygen can be dissociated by 185 nm UV irradiation to generate ozone in air [32]. It is well known that ozone is a very strong oxidant and may affect MB degradation. Fig. 8 shows the effect of oxygen bubbling on reaction constant rate of MB degradation. It can be found that oxygen did not significantly increase reaction constant rate in all processes, which well agrees with the observation in the previous studies [17,24]. This is attributed to weak absorption coefficient of oxygen at 185 nm and low oxygen concentration in water [24]. Oxygen itself hardly directly absorbed 185 nm light to form •OH or ozone in water [24]. Nevertheless, highly reactive •OH can be abundantly produced by different ways either in the presence or in the absence of dissolved oxygen in aqueous solution [17].

4. Conclusions

VUV/TiO₂ obtained much higher degradation efficiency and mineralization rate than conventional UV/TiO₂. The MB concentration was dropped from 6.2 mg/L in UV/TiO₂ to only 1.1 mg/L in VUV/TiO₂ after 20 min of irradiation. The rate constant of MB degradation in VUV/TiO₂ (0.0793 min⁻¹) is about 4 times of that of the former (0.0205 min⁻¹). The MB mineralization rate is also greatly increased from 12.5% in UV/TiO₂ to 47.7% in VUV/TiO₂ after 60 min of irradiation. Multiple advanced oxidation processes including PCO and VUV photo-oxidation coexist in VUV/TiO₂ to substantially produce highly reactive species (such as •OH and energetic photons), which is responsible for higher MB degradation and mineralization efficiency. In addition, VUV/TiO₂ has advantages such as lower cost and less TiO₂ dosage over conventional UV/TiO₂, which makes VUV/TiO₂ more capable for industrial application.

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