



VIS-light-induced photocatalytic degradation of methylene blue (MB) dye using PoPD/TiO₂ composite photocatalysts

Hui-Long Wang, De-Ying Zhao, Wen-Feng Jiang*

*Department of Chemistry, Dalian University of Technology, Dalian 116023, China
Tel. +86 411 84708941; Fax: +86 411 84708590; email: hlwang@dlut.edu.cn*

Received 11 May 2012; Accepted 30 July 2012

ABSTRACT

In this study, the photocatalytic degradation of methylene blue (MB) was studied experimentally over poly-*o*-phenylenediamine/TiO₂ composite (PoPD/TiO₂) photocatalysts irradiated with a light source simulating solar light. The effect of operational parameters, i.e. pH of the solution, photocatalyst content, irradiation time, initial MB concentration, and temperature, on the photocatalytic degradation efficiency was explored and the results obtained were fitted with Langmuir-Hinshelwood model to investigate the degradation kinetics and discussed in detail. Results show that the PoPD/TiO₂ composites exhibit significantly higher photocatalytic activity than that of pure TiO₂ on the degradation of MB aqueous solution under visible light irradiation. The enhanced photocatalytic activity of PoPD-sensitized TiO₂ composite catalysts can be attributed to the charge transfer from PoPD to TiO₂ and efficient separation of e⁻-h⁺ pairs on the interface of PoPD and TiO₂. The repeatability of photocatalytic activity was also tested. A plausible mechanism was proposed and discussed on the basis of experimental results.

Keywords: Photocatalysis; Poly-*o*-phenylenediamine; Titanium dioxide; Methylene blue; Wastewater treatment

1. Introduction

Organic synthetic dyes represent a class of colored chemicals which are widely used in textile, paper, color photography, pharmaceutical, cosmetic, and other industries [1]. The runoffs from these manufacturing and industries require proper treatment before they are discharged to the environment because the color and toxicity caused by dyestuffs may pose objectionable impact on ecosystem [2]. Due to the stability and resistance to biodegradability of synthetic dyes, conventional biological treatment methods are ineffective for discoloration and degradation. The main disadvantage

of traditional methods for the removal of colored synthetic dyes, such as adsorption [3,4], nanofiltration [5], solvent extraction [6], coagulation–flocculation [7], is associated the fact that they are non destructive and their action is limited to transfer pollutants from water to another phase [8]. Thus, finding the new treatment methods which would conduct complete decomposition of synthetic dyes is highly desired.

In this context, advanced oxidation processes (AOPs) have been employed as alternative pollution remediation technologies for decolorizing and reducing biorecalcitrance of industrial effluents with synthetic dyes [9]. The AOPs involve, primarily, the formation of powerful and non-selective oxidizing agent, the hydroxyl radical (HO[•]), to destroy hazard-

*Corresponding author.

ous pollutants dissolved in wastewater. Of the various AOPs employed in water treatment, heterogeneous photocatalysis with TiO_2 is often used for decomposition of numerous of organic synthetic dyes [10]. The reason for the increased interest in this method is that the process can be carried out under ambient conditions and the usually used photocatalyst TiO_2 has the advantages of high chemical stability, high photocatalytic activity, nontoxicity, and relative low price [11]. In addition, TiO_2 is capable of mineralization of a wide range of organic compounds to harmless CO_2 and H_2O . However, owing to its wide band gap of 3.2 eV, normal anatase TiO_2 can be only triggered by near UltraViolet (UV) radiation (<387 nm) that encompass only about 3–5% of natural solar radiation, which limits the uses of TiO_2 in applications such as waste-water treatment [12,13]. Strategies that have been investigated to address this obstacle include doping TiO_2 with transition metals [14–16], nonmetal atoms [17–19], or dye photosensitization [20].

At present, much attention is paid to conducting polymers, which are used as photo-sensitizer to modify wide band gap semiconductors such as TiO_2 [21], CdS [22] and CdSe [23] due to their high absorption coefficients in the visible part of the spectrum, high mobility of charge carriers, and good stability [24,25]. As a typical conducting polymer, poly-*o*-phenylenediamine (PoPD) has attracted considerable attention since its discovery. Recently, we have demonstrated the synthesis of nanometer PoPD/ TiO_2 composite photocatalysts by UV light photoinitiating method [26]. The introduction of PoPD to TiO_2 can enhance the photocatalytic efficiency of TiO_2 under visible light irradiation effectively and the PoPD/ TiO_2 composite photocatalysts exhibited easy separation and less deactivation after several runs.

In the present study, we build on our previous body of work by investigating the photocatalytic degradation of a model organic dye, methylene blue (MB), over PoPD/ TiO_2 composites irradiated with a source simulating the solar spectrum (Xe-arc lamp). The degradation products of MB using TiO_2 have been studied extensively and many of the intermediates during the MB degradation process have been already identified [27]. Therefore, the goal of this study is to focus on the photocatalytic degradation of MB by the PoPD/ TiO_2 composites, and examining the influence of various parameters on the photocatalytic degradation. The effects of operational parameters, such as dye concentration, pH of the solution, catalyst concentration, irradiation time, and temperature, on the degradation effi-

ciency were investigated thoroughly. The results reported here are critical and necessary inputs in the development of processes that can use the PoPD/ TiO_2 composites in the disposal of organic pollutants in water.

2. Experimental

2.1. Materials and chemicals

Unless otherwise noted, MB, *o*-phenylenediamine (oPD), absolute ethanol, ethyl ether, hydrochloric acid, and sodium hydroxide were of reagent grade purchased from Sinopharm Chemical Reagent Co. Ltd., China and used without further purification. Ultra-pure water was generated from a Milli-Q-Academic water purification system (Millipore). The working solutions were prepared freshly before all experiments. Solution pH was adjusted by using diluted solutions (1 mol L^{-1}) of HCl or NaOH. Nanocrystalline anatase TiO_2 with an average particle size of *ca.* 18 nm and BET-specific surface area of *ca.* $80 \text{ m}^2 \text{ g}^{-1}$ was prepared by sol-gel hydrolysis and condensation of ethanol solutions of titanium (IV) butoxide in our laboratory. The details of the preparation procedures were similar to that described in our previous work [28,29].

The synthesis of the PoPD/ TiO_2 composites has been reported in detail in our recent work [26]. Briefly, PoPD/ TiO_2 composites were formed by the 'in situ' polymerization of oPD ($100 \text{ mL } 55.5 \text{ mmol L}^{-1}$) on the surface of TiO_2 (0.5 g) with UV light photoinitiating method. The pH of the reaction mixture was adjusted to 4.0, and then, the mixture was exposed to illumination of high-pressure mercury lamp (500 W) for 10 min to initiate the polymerization reaction. Afterward, the high-pressure mercury lamp was turned off and the polymerization reaction was allowed to proceed for 24 h at 20°C . The obtained solids were washed with absolute ethanol, ethyl ether, and distilled water, respectively. Finally, the resulting products, PoPD/ TiO_2 composites, were dried in vacuum for 24 h. The resulting PoPD/ TiO_2 composite photocatalysts were characterized by XRD, TEM, FTIR, and UV-vis spectra. It can be found from the characterizations that there are PoPD and TiO_2 in the composites. PoPD deposited on the surface of TiO_2 particles has no influence on the crystalline structure of TiO_2 . Comparing to pure TiO_2 , the PoPD/ TiO_2 composites showed obvious absorption at wavelengths above 400 nm with a red shift in the band gap transition. Complete details of the characterizations of PoPD/ TiO_2 composites are available elsewhere [26].

2.2. Experimental procedures and techniques

The photocatalytic experiments were conducted in an XPA-7 photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China). The photocatalytic reactor consisted of quartz reactors and an illumination source. A 500 W xenon lamp (Institute of Electric Light Source, Beijing) with a 420 nm cutoff filter was used as light source to mimic solar irradiation. The quartz reactors were vertically placed at a fixed distance from the lamp. The distance from the lamp to quartz reactor was about 3.5 cm. The light intensity at the position of quartz tubes was measured using an illumination meter (ST-80C, Beijing Normal University, China) and the average light intensity over the duration of each experiment was calculated to be 2.652×10^4 lx. The reaction system was cooled by

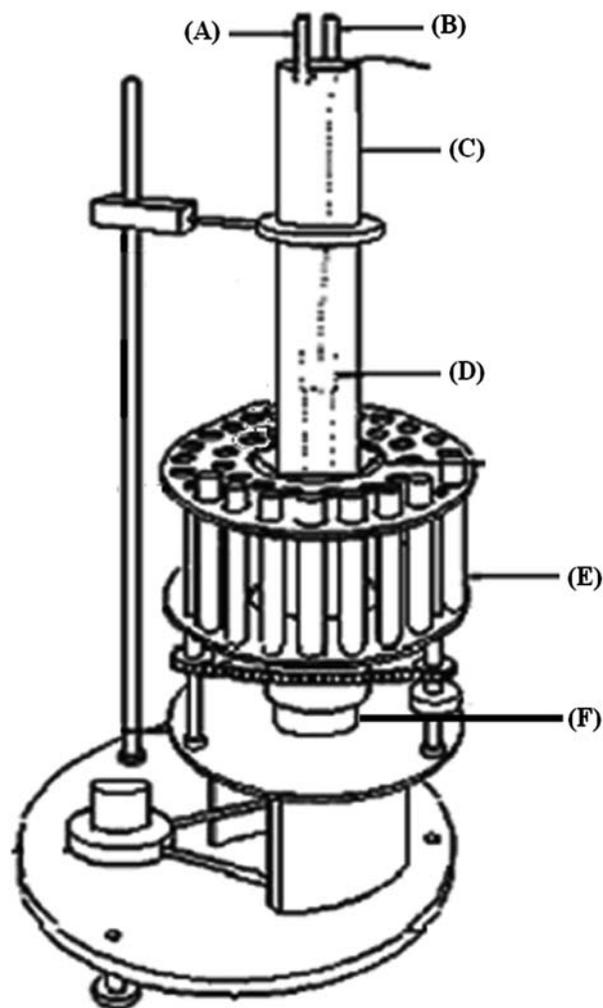


Fig. 1. Schematic diagram of photochemical reactor: (A) cooling inlet; (B) cooling outlet; (C) water-cooled quartz jacket; (D) Xe-arc lamp; (E) quartz reactor; and (F) rotation axis.

circulating water and maintained at certain temperature. The schematic diagram of photochemical reactor is depicted in Fig. 1.

The photocatalytic reaction was carried out in a quartz reactor. The reaction volume was 40 mL with desired concentrations of PoPD/TiO₂ composite sample and MB. After stirring continuously in the dark for 60 min to ensure establishment of adsorption/desorption equilibrium between the dye and as prepared photocatalyst samples, the suspension was irradiated with a 500 W xenon lamp and it was treated as the starting point ($t=0$) of the photocatalytic reaction, where the concentration of MB was designated as C_0 . The suspension was magnetically stirred during the illumination. During the experiment aliquots of the reaction, solution was taken from the suspension for analysis at appropriate time intervals. The photocatalyst was immediately removed from the samples after centrifugation and filtration with a syringe filter (0.22 μ m). The progress of photocatalytic degradation was monitored through measuring the characteristic absorbance of the solution samples by a UV-760CRT UV-Vis spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd.) at $\lambda_{\max}=664$ nm. The photocatalytic degradation efficiency ($\eta\%$) under various conditions was calculated as follows:

$$\eta\% = (C_0 - C)C_0 \times 100 \quad (1)$$

Where C_0 and C represent the initial and residual concentrations of MB in the photocatalytic reaction solution. All the experiments were performed in triplicate and the mean values were reported.

The pH of the point of zero charge (pH_{pzc}) was measured by pH drift method [30]. A 50 mL of 0.05 mol L^{-1} NaCl solutions were placed in a series of conical borosilicate flasks, thermostatted at 25°C , and N_2 was bubbled through the NaCl solutions to remove dissolved CO_2 until the initial pH stabilized. The pH of the solutions was then adjusted to successive initial values between 2.0 and 12.0, by adding either HCl or NaOH and 0.15 g of catalyst was added to each of the flasks. The final pH, reached stable after 24 h, was measured and plotted against the initial pH. The pH_{zpc} was noted at the pH in which the initial pH equals the final pH. The pH of the solution was measured by using a Mettler-Toledo (model Delta 320-S) digital pH meter.

3. Results and discussion

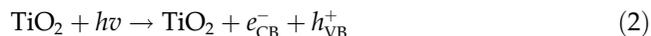
The effect of operational parameters, including pH of the solution, MB concentration, photocatalyst content, irradiation time, and temperature, was examined

using the apparatus and following the procedures described above. The results are delineated below.

3.1. Effect of initial pH

The pH of a solution is an important parameter in photocatalytic reactions, since it influences catalyst surface charge, adsorption and dissociation of substrate, oxidation potential of the valence band, and other physicochemical properties of the system [31]. The effect of initial pH on the degradation of MB was investigated by keeping all other experimental conditions constant and varying the initial pH of the MB solution from 1 to 12 (Fig. 2). The experimental results reveal that the photodegradation efficiency increases with pH up to 7.22 and decreases beyond 10.31. The photocatalytic degradation efficiency stays at a high level in the pH range 7–10 and an optimum pH of approximately 7.23 for best performance. It is obvious that photodegradation of MB is strongly favored at pH values near neutrality or weak basicity.

The observed effect of the pH on the degradation efficiency is due to different photoreaction mechanisms operable at various pH and pH-dependence of the chemisorptive properties of TiO_2 . The possible reaction mechanisms that contribute to MB degradation can involve the direct reaction by the photogenerated positive holes or oxidation through successive attacks by hydroxyl radicals or superoxide species [32]. The hydroxyl radical, in particular, is an extremely strong non selective oxidant and responsible for the oxidation of organic pollutants [33]. The pH of the solution affects the formation of hydroxyl radicals as it can be inferred from the following equations [34]:



The formation of hydroxyl radicals could be thermodynamically unfavorable and thus, suppressed because of the high redox potentials of Eqs. (3)–(4) in acidic condition. At neutral or basic conditions, the presence of large quantities of OH^- ions favors the formation of the oxidizing HO^\bullet radicals, thereby resulting in an increased photocatalytic degradation efficiency of MB. Besides, the pH of the solution significantly affects the charge on the TiO_2 particles and the positions of the conductance and valence bands [35]. This pH-dependence of surface charge is consistent with the pzc of the photocatalyst used. The pH_{pzc} value was determined to be approximately 6.21 and 5.69 for pure TiO_2 and PoPD/ TiO_2 composite, respectively, as shown in Fig. 3. The pH_{pzc} of PoPD/ TiO_2 composite shifted to a lower value compared with that of TiO_2 , which indicates that more negative sites are available on the catalyst surface near neutral and weak basic pH solutions, resulting a strong adsorption of MB on the PoPD/ TiO_2 composite particles because of the electrostatic attraction between the negatively charged PoPD/ TiO_2 composite catalyst and cationic MB. As a result, the very low and high pH values are not favorable to the photocatalytic degradation of MB.

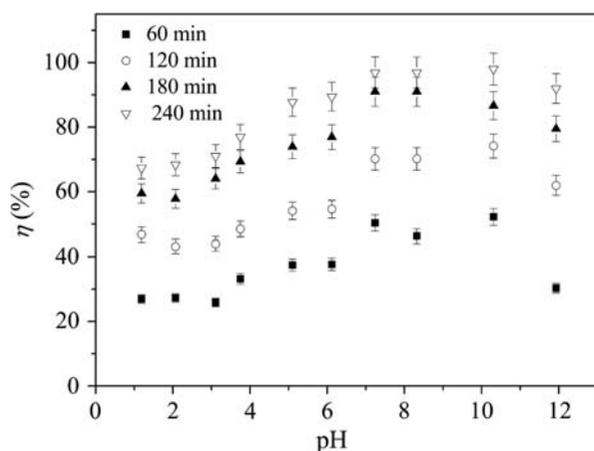


Fig. 2. Effect of the pH on the photocatalytic degradation of aqueous solution of MB. Conditions: $[\text{MB}]_0 = 15.63 \text{ mg L}^{-1}$, $[\text{catalyst}] = 6.0 \text{ g L}^{-1}$, $T = 30^\circ\text{C}$.

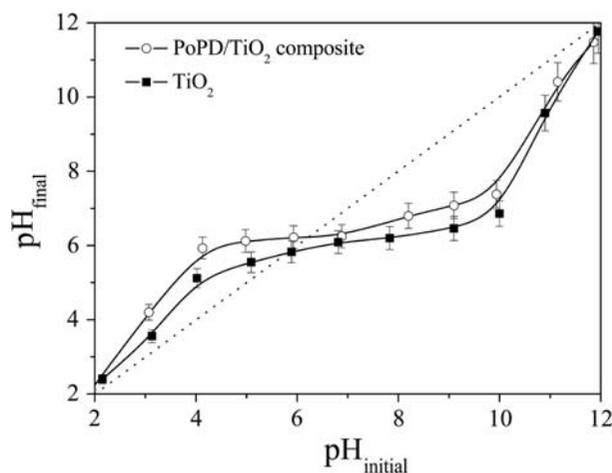


Fig. 3. Plots for the determination of pH_{pzc} of TiO_2 and PoPD/ TiO_2 composite.

3.2. Effect of catalyst concentration

To understand the optimum catalyst amount required for the effective photocatalytic degradation of MB, experiments were performed to study the variations in the photocatalytic degradation efficiency at different catalyst concentration ranging from 2.0 to 12.0 g L⁻¹. The results are illustrated in Fig. 4. As observed in Fig. 4, the degradation efficiency increases with increasing the photocatalyst concentration up to 6.0 g L⁻¹. However, for catalyst contents above 6.0 g L⁻¹, there are not significant changes and the degradation efficiency decreases slightly. Within the range of catalyst content from 2.0 to 6.0 g L⁻¹, the observed enhancement in degradation may be due to an increased number of available absorption and catalytic sites on the surface of PoPD/TiO₂ catalyst. Increase of the catalyst concentration more than 6.0 g L⁻¹ results in the decrease of degradation efficiency. This phenomenon is due to the so-called ‘shielding effect’ caused by the suspended catalyst layers located closer to the radiation source and agglomeration of catalyst particles at a higher level of catalyst amount. As a result of these, the penetration of light into the solution and the number of available active sites are decreased which in turn reduce the formation of •OH radicals and photocatalytic degradation efficiency. The result indicates that an optimized catalyst concentration (6.0 g L⁻¹) is necessary for enhancing the degradation efficiency.

3.3. Effect of irradiation time

The effect of irradiation time on the photocatalytic degradation of MB from its aqueous solution was

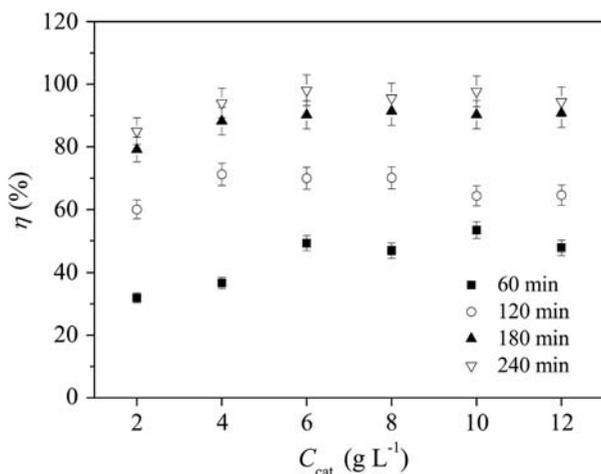


Fig. 4. Effect of the PoPD/TiO₂ composite catalyst concentration on the photocatalytic degradation of aqueous solution of MB. Conditions: [MB]₀ = 15.63 mg L⁻¹, pH 7.23, T = 30 °C.

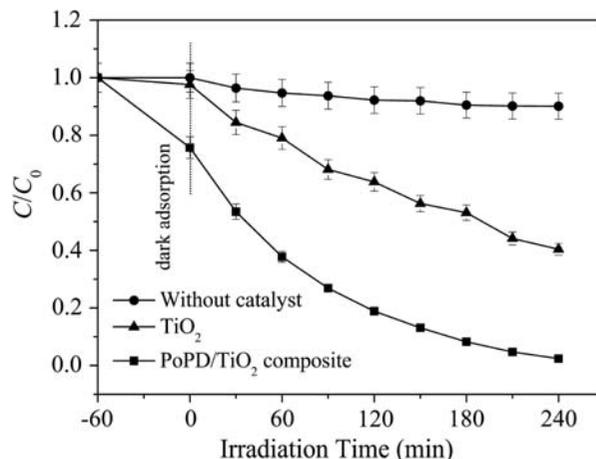


Fig. 5. Degradation of MB as a function of time of illumination. Conditions: [MB]₀ = 15.63 mg L⁻¹, [catalyst] = 6.0 g L⁻¹, pH 7.23, T = 30 °C.

investigated under the optimized experimental conditions. The results are illustrated in Fig. 5. It is obvious that the degree of photocatalytic degradation of MB is less than 10% in the absence of photocatalyst under visible light irradiation for 240 min. The photolysis of MB is negligibly small as compared with the results obtained in the presence of TiO₂ or PoPD/TiO₂ composite photocatalyst. The PoPD/TiO₂ composite can achieve almost 100% MB removal for 240 min while pure TiO₂ achieved only 60% MB removal for the same irradiation time. The photocatalytic activity of PoPD/TiO₂ composite is remarkably superior to that of TiO₂. The observed enhancement in degradation is due to the synergetic effect between TiO₂ and PoPD. The role played by PoPD can be illustrated by injecting electrons into TiO₂ conducting band under light irradiation and triggering the formation of very reactive radicals super-oxide radical ion (O₂⁻) and hydroxyl radical (HO•), which are responsible for the photodegradation of MB. For pure TiO₂ or PoPD/TiO₂ composite, the degree of photocatalytic degradation of MB increases with time, up to 240 min, and thereafter, it levels off. This indicates that degradation of 15.63 mg L⁻¹ of MB at pH 7.23 with catalyst concentration of 6.0 g L⁻¹ for 240 min is the optimum irradiation time.

The degree of photodegradation as a function of time was investigated by UV–visible absorption spectra. The MB exhibits a major characteristic absorption peak at 664 nm, which progressively disappeared upon visible light irradiation indicating that the decomposition of MB was taking place. The rate of change of absorbance of MB caused by photodegradation with PoPD/TiO₂ composite particles is well described by a mono-exponential curve suggesting

that the photocatalytic degradation reaction appears to follow pseudo-first-order kinetics.

It is noticeable that the initial concentration of MB decreases in the bulk solution even before photocatalysis reaction occurs, because of adsorption of MB onto the catalyst surface. In order to take this effect in account, the studies of adsorption of TiO₂ and PoPD/TiO₂ composite particles to MB in the dark condition were conducted under the same experimental conditions. The results showed that only 2.4% of MB absorbed on pure TiO₂ in the dark after 60 min in solution, while the amount of MB removed by the PoPD/TiO₂ composite was 24.3%. By comparison of the values MB removed with and without visible light irradiation, it can be affirmed that the removal of MB is mainly due to photocatalytic degradation instead of only to adsorption on the catalyst.

3.4. Effect of initial MB concentration and kinetics of photocatalytic degradation

The effect of initial MB concentrations on photocatalytic degradation in the presence of PoPD/TiO₂ composite photocatalyst was investigated from 2.12 to 19.93 mg L⁻¹. The results show that the photocatalytic degradation efficiency of MB decreases with an increase in the initial concentration of MB. This can be as a result of blocking of the photocatalytically active sites on the catalyst and reducing the interaction of photons with these sites. Besides, a fraction of light may be absorbed by the MB molecules in aqueous solution rather than the catalyst particles for high MB concentration, which can also reduce the efficiency of the photocatalytic reaction to a certain extent. Using a modified Langmuir–Hinshelwood model, the rate of degradation can be expressed as:

$$r = -\frac{dC}{dt} = \frac{k_r KC}{1 + KC} \quad (6)$$

The integral form of the Eq. (6) is:

$$t = \left(\frac{1}{k_r K}\right) \ln\left(\frac{C_0}{C}\right) + \frac{C_0 - C}{k_r} \quad (7)$$

Where t refers to the irradiation time, C_0 is initial concentration of MB and C is the concentration of MB at time t , r represents the rate of degradation, K is the equilibrium constant for the adsorption of MB on the catalyst, and k_r reflects the limiting rate of the reaction at the maximum coverage at the experimental conditions.

At low initial concentration of MB, the second term in the Eq. (7) becomes insignificant and hence, it can be neglected [36]:

$$\ln\left(\frac{C_0}{C}\right) = k_r K t = k_{app} t \quad (8)$$

Where k_{app} is the apparent rate constant of the photocatalytic degradation reaction.

The applicability of Langmuir–Hinshelwood equation for the photocatalytic degradation of MB has been confirmed by the good linearity between $\ln(C_0/C)$ vs. t plot for each MB concentration values studied (Fig. 6). The apparent rate constant, k_{app} (min⁻¹), calculated from the slopes of the lines decreases as the initial MB concentration increase in the solution.

3.5. Effect of temperature

The influence of temperature on the photocatalytic degradation of MB was investigated under the optimized experimental conditions by varying the temperature range from 20 to 70°C (Fig. 7). The efficiency of the degradation process is found to increase with increasing temperature. A significant increase is noticed in the apparent reaction rate constant k_{app} from 6.981×10^{-3} to 1.928×10^{-2} min⁻¹ when the reaction temperature is increased from 20 to 70°C. It is suggested that at a higher temperature, the diffusion rate of MB in solution is reasonable resulting in the improvement of the degradation efficiency. Besides, more available active surface centers are probable situations at a higher temperature, which means, PoPD/TiO₂ composite exhibits better photocatalytic performance for MB degradation at high temperature than that at low temperature. The photocatalytic degradation reaction can be regarded as an Arrhenius-type process and the calculated value of the apparent activation energy E_a is 15.69 kJ mol⁻¹. Although higher

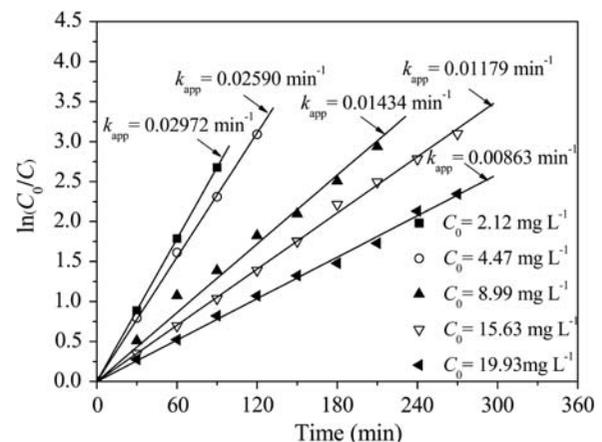


Fig. 6. Kinetics of MB degradation for various initial concentrations in the presence of PoPD/TiO₂ composite photocatalyst.

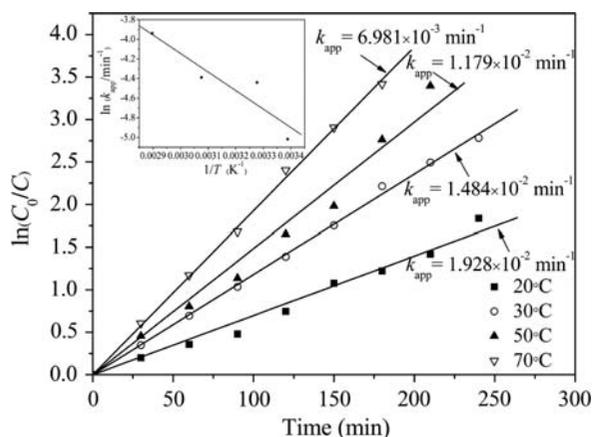


Fig. 7. Kinetics of MB degradation at different temperatures in the presence of PoPD/TiO₂ composite photocatalyst. Inset: Arrhenius plot of the temperature dependence of apparent rate constants of the photocatalytic degradation reaction.

temperature favors the degradation of MB in solution, an increase in operation cost is inevitable due to more energy consumed in the process. The degradation efficiency reached over 90% in 240 min at all temperatures studied and photocatalytic degradation of organic contaminants at room temperature could be highly economical compared with the processes at high temperature, so room temperature (30°C) was selected for further experiments.

3.6. The repeatability of photocatalyst activity

The repetitive use is very important for the practical application of photocatalyst. So, recycling experiments were carried out to examine the stability of

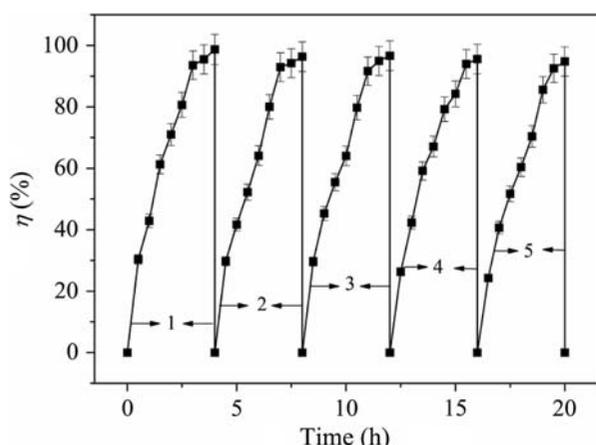


Fig. 8. Results of recycling studies. Conditions: $[\text{MB}]_0 = 15.63 \text{ mg L}^{-1}$, $[\text{catalyst}] = 6.0 \text{ g L}^{-1}$, pH 7.23, irradiation time 240 min, $T = 30^\circ\text{C}$.

PoPD/TiO₂ composite photocatalyst (Fig. 8). After the completion of the degradation, the catalyst at the end of I cycle was collected and utilized for the next cycle by keeping other reaction conditions constant. Noticeably, the catalysis efficiency of the composite photocatalyst was still higher than 90% after be used for five cycles. This indicates that the photocatalytic activity of the PoPD/TiO₂ composite has good repeatability. The reduction in the photocatalytic degradation efficiency among the cycles may be due to the formation of by-products and their accumulation in the cavities and on the active surface sites of the catalyst.

3.7. Postulated mechanism

Based on the experimental results above, it could be concluded that the PoPD-sensitized nanocrystalline TiO₂ composite photocatalysts (PoPD/TiO₂) exhibit better photocatalytic activity than pure TiO₂ in the degradation of MB under visible light irradiation. This can be attributed to the charge transfer from photoexcited PoPD to TiO₂ and efficient separation of h^+e^- pairs (Fig. 9). As a typical conductive polymer, the conductive PoPD layer on the surface of TiO₂ can absorb the visible light irradiation and transfer the photogenerated electron (e^-) into the conduction band of the TiO₂ particles efficiently. At the same time, a positive charged hole (h^+) might be created by electron migrating from TiO₂ valence band to PoPD. This charge separation suppresses the recombination of h^+ and e^- . The h^+ can react with water to generate hydroxyl radicals, while e^- can react with absorbed molecular oxygen reducing it to superoxide radical anion. The

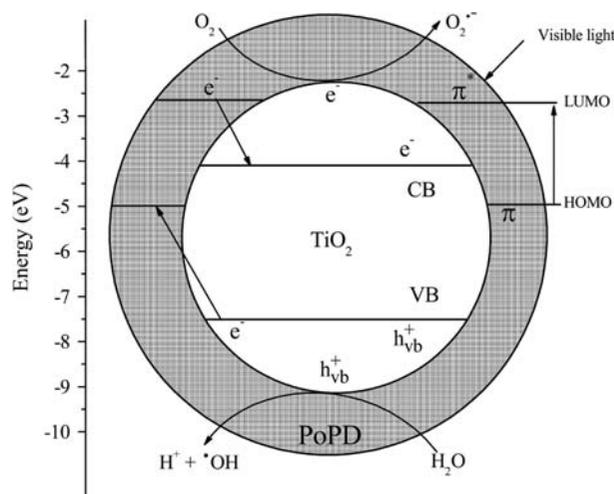
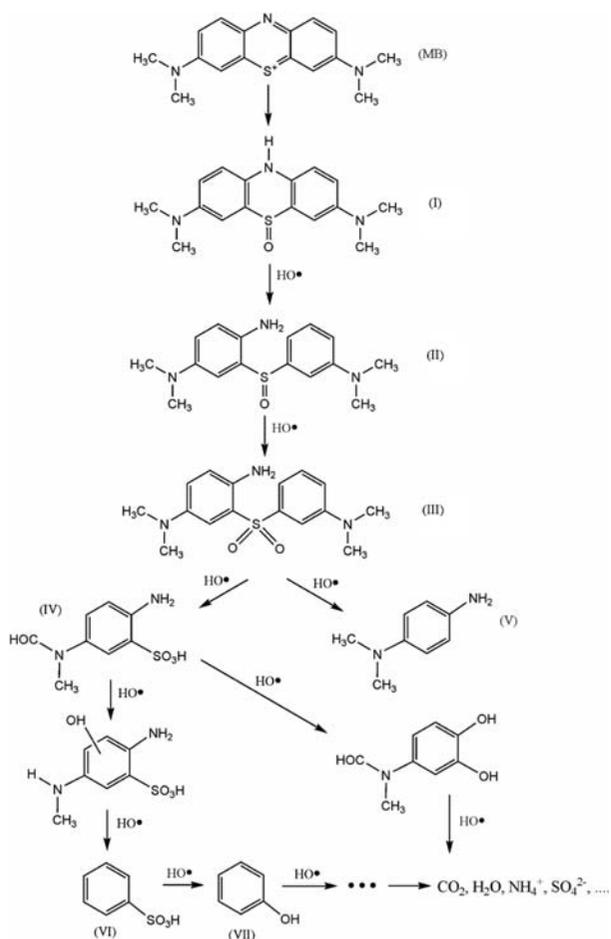
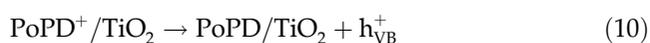
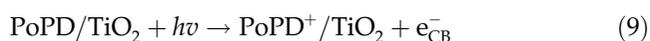


Fig. 9. The schematic diagram illustrating the principle of charge separation and photocatalytic activity for the PoPD/TiO₂ composite.

generated reactive hydroxyl radical $\cdot\text{OH}$ and superoxide O_2^- are responsible for the photocatalytic degradation of organic pollutants. Similar electron transfer between inorganic or organic conductive materials and TiO_2 and the enhanced photocatalytic activity of the corresponding composites was also observed in systems such as multi-walled carbon nanotubes (MWCNTs)/ TiO_2 [29] and polyaniline (PAN)/ TiO_2 [21,37].

The role played by PoPD can be presented as follows:



Scheme 1. Postulated photocatalytic degradation pathway of MB.

In the TiO_2 photocatalytic degradation process, oxidative degradation of MB occurred generally by the attack of $\cdot\text{OH}$ radicals, known as highly reactive electrophilic oxidants. Generally, the sites near the $\text{C}-\text{S}^+=\text{C}$ functional group and the central imino-group are the attack area in photocatalytic degradation process. The main identified intermediates resulting from MB degradation are sulfoxide, sulfone, sulfonic acid, and substituted aniline [27]. Based on these, though intermediates forming in the photocatalytic degradation process of MB were not identified, the mechanism suggested by Houas et al. [38] was also postulated in our system (Scheme 1). The first step in MB photocatalytic degradation is the attack of hydroxyl radicals to the $\text{C}-\text{S}^+=\text{C}$ functional group of MB (I), which is in direct coulombic interaction with anionic TiO_2 surface as evidenced by the influence of the pH of the solution. The resulting sulfoxide also undergoes a ring-opening reaction at the N heteroatom, yielding a substituted aniline (II). The reaction proceeds with subsequent attacks of hydroxyl radicals, producing the sulfone (III) and causing the definitive dissociation of the two benzenic rings (IV and V). Further, hydroxyl radical attacks result in the formation of molecules of sulfonic acid (VI) and phenolic compound (VII). Finally, MB and most of the degradation intermediates originated from the initial opening of the central aromatic and their subsequent metabolites are slowly oxidized to small molecules, such as H_2O , CO_2 , and inorganic cations and anions such as SO_4^{2-} and NH_4^+ .

4. Conclusions

In conclusion, photocatalytic processes with the use of poly-*o*-phenylenediamine/ TiO_2 composite (PoPD/ TiO_2) photocatalysts can be efficiently applied for the degradation of methylene (MB) aqueous solution under visible light irradiation. As a photosensitizer to TiO_2 , PoPD can improve the photocatalytic activity of TiO_2 efficiently. The PoPD/ TiO_2 composite catalysts exhibited higher activity for photocatalytic degradation of MB than TiO_2 -only material. The satisfactory photocatalytic degradation efficiency can be achieved with the use of optimal operational parameters. The optimal conditions were a MB concentration of 15.63 mg L^{-1} at pH 7.23 with catalyst concentration of 6.0 g L^{-1} under visible light irradiation for 240 min. Further kinetic studies reveal that the photocatalytic degradation followed pseudo-first-order kinetics with respect to MB concentration. In addition, the degree of photocatalytic degradation increased with an increase in temperature. The photocatalyst was used for five cycles with degradation efficiency still higher than 90%. The results of the study showed the feasible and

potential use of PoPD/TiO₂ composites in photocatalytic degradation of colored dye wastewaters.

Acknowledgements

We gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (Grant No. 20977013). Partial support by the Fundamental Research Funds for the Central Universities (DUT10LK26) is also acknowledged.

References

- [1] Z. Zheng, R.E. Levin, J.L. Pinkham, K. Shetty, Decolorization of polymeric dyes by a novel penicillium isolate, *Proc. Biochem.* 34 (1999) 31–37.
- [2] K.T. Fletcher, Design the environment and textiles: developing strategies for environmental impact reduction, *J. Text. Inst.* 89 (1998) 72–80.
- [3] H. Deng, J.J. Lu, G. Li, G.L. Zhang, X.G. Wang, Adsorption of methylene blue on adsorbent materials produced from cotton stalk, *Chem. Eng. J.* 172 (2011) 326–334.
- [4] M.S.M. Eldin, S.A. El-Sakka, M.M. El-Masry, I.I. Abdel-Gawad, S.S. Garybe, Removal of methylene blue dye from aqueous medium by nano poly acrylonitrile particles, *Desalin. Water Treat.* 44 (2012) 151–160.
- [5] S.A. Avlonitis, I. Poullos, D. Sotiriou, M. Pappas, K. Moutesis, Simulated cotton dye effluents treatment and reuse by nanofiltration, *Desalination* 221 (2008) 259–267.
- [6] P. Pandit, S. Basu, Removal of ionic dyes from water by solvent extraction using reversed micelles, *Environ. Sci. Technol.* 38 (2004) 2435–2442.
- [7] L.W. Man, P. Kumar, T.T. Teng, K.L. Wasewar, Design of experiments for Malachite Green dye removal from wastewater using thermolysis–coagulation–flocculation, *Desalin. Water Treat.* 40 (2012) 260–271.
- [8] N. Serpone, Brief introductory remarks on heterogeneous photocatalysis, *Sol. Energy Mater. Sol. Cells* 38 (1995) 369–379.
- [9] I.K. Konstantinou, T.A. Albanis, TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review, *Appl. Catal. B: Environ.* 49 (2004) 1–14.
- [10] A.D. Paola, E. García-López, G. Marci, L. Palmisano, A survey of photocatalytic materials for environmental remediation, *J. Hazard. Mater.* 211–212 (2012) 3–29.
- [11] S.K. Sharma, H. Bhunia, P. Kumar, Photocatalytic decolorization kinetics and adsorption isotherms of a mixture of two anionic azo dyes: reactive Red 120 and Reactive Black 5, *Desalin. Water Treat.* 44 (2012) 261–268.
- [12] A. Heller, Chemistry and applications of photocatalytic oxidation of thin organic films, *Adv. Chem. Res.* 28 (1995) 503–508.
- [13] A.L. Linesbigler, G. Lu, J.T. Yates, Photocatalysis on TiO₂ surfaces: principles, mechanisms and selected results, *Chem. Rev.* 95 (1995) 735–758.
- [14] X.Z. Li, F.B. Li, C.L. Yang, W.K. Ge, Photocatalytic activity of WO_x-TiO₂ under visible light irradiation, *J. Photochem. Photobiol. A: Chem.* 141 (2001) 209–217.
- [15] H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, B. Neppolian, M. Anpo, Photocatalytic degradation of organic compounds diluted in water using visiblelight-responsive metal ion-implanted TiO₂ catalysts: Fe ion-implanted TiO₂, *Catal. Today* 84 (2003) 191–196.
- [16] M.H. Habibi, R. Kamrani, Photocatalytic mineralization of methylene blue from water by a heterogeneous copper-titania nanocomposite film, *Desalin. Water Treat.* 46 (2012) 278–284.
- [17] S. Liu, X. Chen, A visible light response TiO₂ photocatalyst realized by cationic S-doping and its application for phenol degradation, *J. Hazard. Mater.* 152 (2008) 48–55.
- [18] B. Wawrzyniak, A.W. Morawski, Solar-light-induced photocatalytic decomposition of two azo dyes on new TiO₂ photocatalyst containing nitrogen, *Appl. Catal., B: Environ.* 62 (2006) 150–158.
- [19] S. Sakthivel, H. Kisch, Daylight photocatalysis by carbon-modified titanium dioxide, *Angew. Chem., Int. Ed.* 42 (2003) 4908–4911.
- [20] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye sensitized colloidal TiO₂ films, *Nature* 353 (1991) 737–740.
- [21] X. Li, D. Wang, G. Cheng, Q. Luo, J. An, Y. Wang, Preparation of polyaniline-modified TiO₂ nanoparticles and their photocatalytic activity under visible light illumination, *Appl. Catal. B: Environ.* 81 (2008) 267–273.
- [22] P.K. Khanna, M.V. Kulkarni, N. Singh, S.P. Lonkar, V.V.V.S. Subbarao, A.K. Viswanath, Synthesis of HCl doped polyaniline–CdS nanocomposite by use of organometallic cadmium precursor, *Mater. Chem. Phys.* 95 (2006) 24–28.
- [23] Y. Haldorai, V.H. Nguyen, J.J. Shim, Synthesis of polyaniline/Q-CdSe composite via ultrasonically assisted dynamic inverse emulsion polymerization, *Colloid. Polym. Sci.* 289 (2011) 849–854.
- [24] A. Pron, P. Rannou, Processible conjugated polymers: from organic semiconductors to organic metals and superconductors, *Prog. Polym. Sci.* 27 (2002) 135–190.
- [25] B.A. Rozenberg, R. Tenne, Polymer-assisted fabrication of nanoparticles and nanocomposites, *Prog. Polym. Sci.* 33 (2008) 40–112.
- [26] H.L. Wang, D.Y. Zhao, W.F. Jiang, Synthesis and photocatalytic activity of poly-o-phenylenediamine (PoPD)/TiO₂ composite under VIS-light irradiation, *Synth. Met.* 162 (2012) 296–302.
- [27] H. Gnaser, M.R. Savina, W.F. Calaway, C.E. Tripa, I.V. Veryovkin, M.J. Pellin, Photocatalytic degradation of methylene blue on nanocrystalline TiO₂: surface mass spectrometry of reaction intermediates, *Int. J. Mass Spectrom.* 245 (2005) 61–67.
- [28] H. Wang, H.L. Wang, W.F. Jiang, Z.Q. Li, Photocatalytic degradation of 2,4-dinitrophenol (DNP) by multi-walled carbon nanotubes (MWCNTs)/TiO₂ composite in aqueous solution under solar irradiation, *Water Res.* 43 (2009) 204–210.
- [29] H. Wang, H.L. Wang, W.F. Jiang, Solar photocatalytic degradation of 2,6-dinitro-p-cresol (DNPC) using multi-walled carbon nanotubes (MWCNTs)-TiO₂ composite photocatalysts, *Chemosphere* 75 (2009) 1105–1111.
- [30] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marín, On the characterization of acidic and basic surface sites on carbons by various techniques, *Carbon* 37 (1999) 1215–1221.
- [31] M.V. Shankar, S. Anandan, N. Venkatachalam, B. Arabindoo, V. Murugesan, Novel thin-film reactor for photocatalytic degradation of pesticides in aqueous solutions, *J. Chem. Technol. Biotechnol.* 79 (2004) 1279–1285.
- [32] D. Yang, X. Ni, W. Chen, Z. Weng, The observation of photo-Kolbe reaction as a novel pathway to initiate photocatalytic polymerization over oxide semiconductor nanoparticles, *J. Photochem. Photobiol., A: Chem.* 195 (2008) 323–329.
- [33] S.R. Sarathy, M. Mohseni, The impact of UV/H₂O₂ advanced oxidation on molecular size distribution of chromophoric natural organic matter, *Environ. Sci. Technol.* 41 (2007) 8315–8320.
- [34] K.M. Parida, N. Sahu, N.R. Biswal, B. Naik, A.C. Pradhan, Preparation, characterization, and photocatalytic activity of sulfate-modified titania for degradation of methyl orange under visible light, *J. Colloid. Interface Sci.* 318 (2008) 231–237.

- [35] M.R. Sohrabi, M. Ghavami, Photocatalytic degradation of Direct Red 23 dye using UV/TiO₂: effect of operational parameters, *J. Hazard. Mater.* 153 (2008) 1235–1239.
- [36] K.H. Wang, Y.H. Hsieh, M.Y. Chou, C.Y. Chang, Photocatalytic degradation of 2-chloro and 2-nitrophenol by titanium dioxide suspensions in aqueous solution, *Appl. Catal., B: Environ.* 21 (1999) 1–8.
- [37] S. Min, F. Wang, Y. Han, An investigation on synthesis and photocatalytic activity of polyaniline sensitized nanocrystalline TiO₂ composites, *J. Mater. Sci.* 42 (2007) 9966–9972.
- [38] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, Photocatalytic degradation pathway of methylene blue in water, *Appl. Catal., B: Environ.* 31 (2001) 145–157.