Original Article

Photocatalytic decolorization of basic dye by TiO$_2$ nanoparticle in photoreactor

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Abstract

Photocatalytic decolorization of rhodamine B (RB) and malachite green (MG) basic dyes in aqueous solution was evaluated using TiO$_2$ powder as a semiconductor photocatalyst under UV black light irradiation. A 0.5 L batch photoreactor containing dyeing solution was installed in a stainless steel chamber with air cooling under irradiation. The TiO$_2$ powder was characterized by XRD observation and it was shown that the nanoparticles could be identified as 73 nm anatase crystals. The effects of operational parameters such as light intensity (0-114 W/m^2), initial dye concentration (10-30 mg/L), and TiO$_2$ powder loading (0.5-1.5 g/L) on the decolorization of dye samples were examined. The photocatalytic decolorization rate depended on the pollutant's structure, such that the MG dye could be removed faster than the RB dye. Decolorization efficiency (%) of the photocatalytic system increased with increasing TiO$_2$ loading and light intensity; however, it decreased with increasing initial dye concentration. A loading of 1.5 g TiO$_2$/L, initial dye concentration of 20 mg/L, and light intensity of 114 W/m^2 were found to yield the highest removal efficiency of dye solution based on time requirement. The kinetics are of first order and depend on the TiO$_2$ powder loading and dye structure. The research had a perfect application foreground.

Keywords: photocatalytic, titanium dioxide, decolorization, uv light irradiation, photoreactor

1. Introduction

Presently, the textile industry is expanding worldwide, especially in developing countries. Dyes and pigments have been utilized for industrial coloring of cloth, cotton, paper, leather, wool, silk and nylon. Basic dyes normally used are in a group of complex organic materials based fundamentally on the chromophore structure. Color in the dyes is invariably explained as the presence of chromophore in atomic configurations and complex chain structures that are sustainable and stable in nature. In addition, dyes are either toxic or mutagenic and carcinogenic due to the presence of metals and other chemicals in their structure (Aksu and Cagatay, 2006). Therefore, wastewater containing the dyes is usually toxic, resistant to biodegradation, persistent in the environment, and difficult to be treated by general methods. As a consequence, there is a continuous increase in environmental contamination and global concerns of discharge of dyestuff effluents into the aquatic system (Ao *et al.*, 2007). The dyeing wastewater discharge not only affects the environment but also reduces light penetration through the water surface needed for photosynthesis activity of aquatic organisms.

Rhodamine B (RB) and malachite green (MG) are basic dyes that have become more important in the textile industry due to their more rigid structures than other organic dyes. Their cationic structure is best applied to anionic fabrics which contain negative charges (Suwannawong, 2010). The dyes are brilliant and most fluorescent among other synthetic dyes. In addition, the chromophore in their structures is

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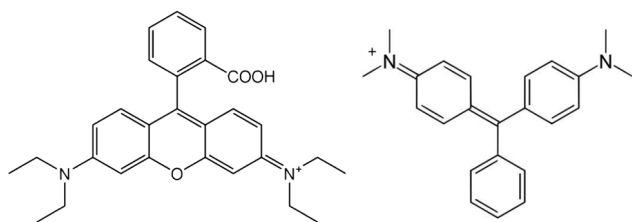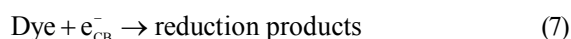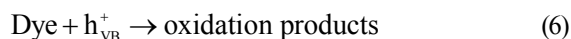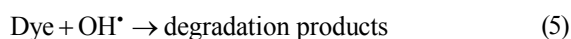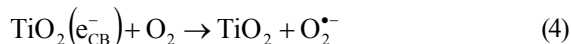* Corresponding author.
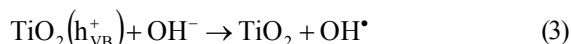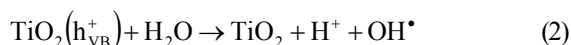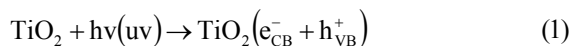 Email address: juntima.c@psu.ac.th

Figure 1. Molecular structure of rhodamine B and malachite green.

known to be carcinogenic. RB and MG have been extensive-+ly used around the world in silk, wool, and cotton dyeing industries (Maalej-Kammoun *et al.*, 2009). The molecular structures of the RB and MG compounds are shown in Figure 1. Recently, increasing use of these dyes has been linked to increase risks of cancer (Soylak *et al.*, 2011). A number of methods have been developed in recent years for their degradation and treatment.

Commonly, the use of conventional methods for the treatment of dye effluents, such as chemical coagulation/flocculation, precipitation, and ozonation, may exhibit high operational costs and cause secondary pollution. The use of advance oxidation by Fenton reagent in wastewater treatment leads to sludge generation in the water system. (Pignatello *et al.*, 2007). In the past few years, extensive research has been undertaken to develop alternative and economical technologies by heterogeneous photocatalytic degradation for dye decolorization and treatment of textile effluents. Photocatalytic oxidation processes have been prevalently applied as techniques for destruction of organic contaminant in wastewater. Due to the non-toxic, insoluble, inexpensive, and highly reactive nature, titanium dioxide (TiO_2) semiconductor under UV irradiation has been generally used as a photocatalyst to oxidize dye wastewater (Daneshvar *et al.*, 2004 and Sikong *et al.*, 2010). By using the UV light irradiation with photon of energy equal to or higher than a band gap energy (3.2 eV Eg.), the TiO_2 photocatalyst generates electron/hole pairs with free electrons in the empty conduction band.

The electron/hole pairs are created and go across the band gap to the conduction band, while holes (h^+) stay in the valence band as formulated in Eq. (1). In aqueous solution, the h^+ is scavenged by surface hydroxyl groups or H_2O molecules to produce highly reactive and non selective hydroxyl radicals ($OH^•$), as shown in Eqs. (2) and (3). In addition, the photo-generated electrons in the conduction band could react with O_2 acceptors to produce superoxide radical anion ($O_2^{•-}$) of oxygen in Eq. (4) (Konstantinou and Albanis, 2004). The $OH^•$ are considered to be the dominant oxidizing agent contributing to the destruction of organic pollutants (Bekbolet *et al.*, 2001). Degradation mechanisms of the dye molecule under the contact with visible light irradiation and photocatalyst are summarized in Eqs. (5) - (7). According to these mechanisms, the relevant reactions at the semiconductor surface causing the degradation of dyes can be expressed as follows:

$$TiO_2 + hv(uv) \rightarrow TiO_2\left(e_{CB}^- + h_{VB}^+\right) \tag{1}$$

$$TiO_2\left(h_{VB}^+\right) + H_2O \rightarrow TiO_2 + H^+ + OH^• \tag{2}$$

$$TiO_2\left(h_{VB}^+\right) + OH^- \rightarrow TiO_2 + OH^• \tag{3}$$

$$TiO_2\left(e_{CB}^-\right) + O_2 \rightarrow TiO_2 + O_2^{•-} \tag{4}$$

$$Dye + OH^• \rightarrow degradation\ products \tag{5}$$

$$Dye + h_{VB}^+ \rightarrow oxidation\ products \tag{6}$$

$$Dye + e_{CB}^- \rightarrow reduction\ products \tag{7}$$

In the present study, photocatalytic decolorization of the rhodamine B (RB) and malachite green (MG) synthetic dye solutions was investigated under batch photoreactor. The photocatalytic system consisted of a photoreactor filled with the dye solution, and TiO_2 powder photocatalyst under a UV black light source. The average size of TiO_2 powder photocatalyst was characterized by XRD. In this work, effects of operating parameters, such as TiO_2 powder photocatalyst loading (0.5-1.5 g/L), type of synthetic dye (RB and MG), dye concentration (10-30 mg/L), and light intensity (0-114 W/m²) were examined. Furthermore, the kinetics of the decolorization reaction was then investigated to optimize the process under varying conditions of initial dye concentration and TiO_2 powder loading.

2. Materials and Methods

2.1 Material

Rhodamine B (RB) and malachite green (MG) (basic dyes) were used as sample compounds. The main photocatalytic chemical, titanium dioxide (TiO_2) nanocrystalline white color powder (AR grade, Carlo Erba, Milano, Italy), was characterized as anatase phase and tetragonal structure. BET surface area and pore volume were 8.37 m²/g and 0.0786 cm³/g, respectively. XRD of the TiO_2 powder was determined by X-ray diffractometer (PHILIPS X'Pert MPD, the Netherlands). The dye powders and deionized water were used to prepare all synthesized dye solutions. UV fluorescence black light lamps (8W, F20T12-BLB, USA) with a wavelength of 345-400 nm acted as the light source for photocatalytic process in this work.

2.2 Experimental

Decolorization of the synthesized dye solution experiments was conducted in a batch-scale photocatalytic reactor under the UV light source. The experiments were performed in a closed stainless chamber ($\pi \times 20^2 \times 50$ cm³) to avoid interference from ambient lights. The 5 UV lamps were vertically installed inside the UV chamber with air flow through for cooling purpose. In the photocatalysis studies, irradiation experiments were carried out in 0.5 L Pyrex beaker reactor ($\pi \times 5^2 \times 12$ cm³) containing 0.4 L of synthetic dye solution. The reactor was placed at the center of the chamber. The photo-
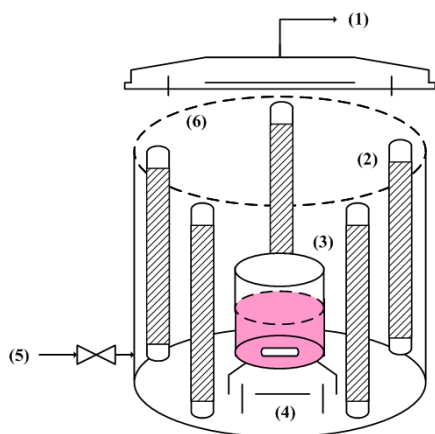
Figure 2. Illustration of experimental apparatus: (1) air outlet; (2) UV lamp; (3) reactor; (4) stirrer; (5) air inlet; (6) chamber.

reactor in this study is illustrated in Figure 2.

The synthetic dye solutions were prepared as follows: RB at concentration range of 10-30 mg/L and natural pH of 6.50-4.35; MG at same concentration range but with natural pH of 4.84-4.26. These were subjected to decolorization process in the photoreactor. The TiO_2 powder was introduced in the dye solutions at concentrations of 0.5, 1.0, and 1.5 g/L dye solution. In all conditions, the aqueous dye solutions were magnetically stirred well at 250 rpm under UV irradiation.

XRD technique was used to study crystalline phase identification and to estimate the crystalline size of each phase at room temperature. The powder XRD pattern of TiO_2 powder was recorded and operated at 40 eV and 30 mA using CuK_a radiation and graphite monochromator.

2.3 Decolorization analysis

The change of dye concentration in the photoreactor was determined quantitatively by measuring absorbance using UV-vis spectrophotometer (Specord S100, Analytik Jena GmbH, Germany). Calibration curves (linear, $R^2 = 0.999$) of the dye solution were constructed from standard synthetic dye solution at various concentrations. During UV irradiation, the sample solutions were taken from the photoreactor every 30 minutes until clear solutions were obtained. The samples were centrifuged to separate the TiO_2 catalyst for measuring the absorbance of the solutions. Efficiency of the decolorization system at irradiation time was calculated by Eq. (8)

$$\text{Decolorization Eff.}(\%) = \left(\frac{C_0 - C}{C_0} \right) \times 100 \qquad (8)$$

where C_0 (mg/L) and C (mg/L) represent the concentration of either dye solution for the initial (not yet irradiated) and at time t, respectively, of the test sample. From the equation, the decolorization efficiency (%) indicates the percentage of the net concentration change. In each case, the plot of C / C_0 (where C and C_0 are concentrations of the photolyzed solu-

tion at time t and initially) describes the decolorization degree of the dye solution.

3. Results and Discussion

3.1 XRD analysis

The average size (D) of the TiO_2 anatase crystalline powder was calculated from the width of the main diffraction peak (101) (shown in Figure 3) according to Scherrer's equation: $D = (k\lambda)/(\beta \cos \theta)$ (where k is the Scherrer constant (0.89)), λ is the wavelength of the X-ray irradiation and is equal to 0.15406 nm, β is the full width at half maximum (FWHM) and θ is the X-ray diffraction peak. Identification of the crystalline phase of the TiO_2 as anatase was at $2\theta = 25.35$ (101). The calculated result indicated that the average size was about 73 nm.

3.2 Decolorization of RB and MG dye solution

The UV irradiation result on decolorization of RB and MG dye solutions in the presence of the TiO_2 powder photocatalyst (1.0 g TiO_2/L) as a function of irradiation time is presented in Figure 4. The results showed that the dyes decomposed under the TiO_2/irradiation and the decolorization efficiency of both the RB and MG solutions gradually increased along with irradiation time. However, decolorization of the MG dye exhibited higher efficiency than that of the RB dye at any irradiation moment. The effectiveness of the basic dye destruction was due to different characteristics and pollutant eradication was possible by photocatalysis under light irradiation. Decolorization of the MG dye in the presence of TiO_2 powder reached 76.3% within 60 min. light irradiation, while that of the RG dye was 72.1% in the same time period.

Figure 5(a) and 5(b) show the absorption spectra changes of RB and MG dye solutions during the photocatalytic process by the TiO_2 catalyst. The characteristic peaks of
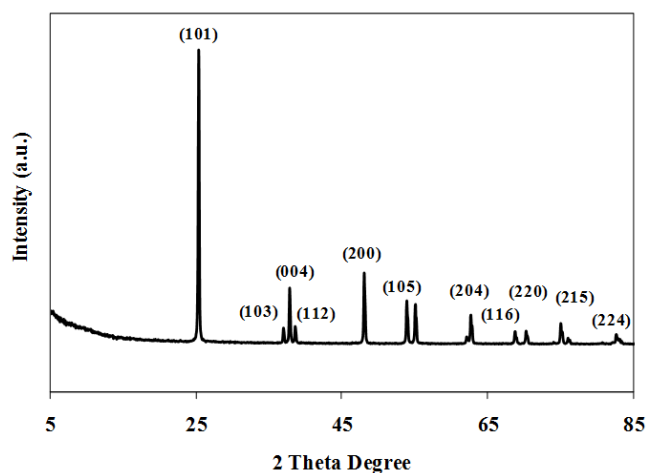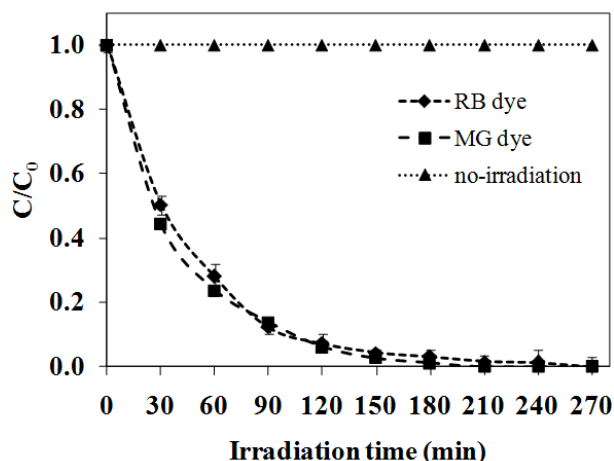

Figure 3. XRD pattern of the TiO_2 powder.

Figure 4. Decolorization results of RB and MG dye solutions in the presence of TiO_2 photocatalyst as a function of irradiation time at 20 mg dye/L and 1.0 g TiO_2/L.

the RB and MG dyes showed absorption at 548 and 618 nm, respectively. The decrease of absorption peak means that the double bond of the chromophore in the dye structure had been destroyed after irradiation with the TiO_2 photocatalyst. The peak became gradually smoother with increasing irradiation time, which means that sufficient photocatalystic reaction had been gained to destroy the chromophore of the dyes, which is confirmed by Figure 5(c) and 5(d).

## 3.3 The effects of UV light intensity on decolorization

The intensity of the UV light irradiation source is an important parameter for degradation of dye in aqueous solution using TiO_2 catalyst powder in photocatalytic reactor (Konstantinou and Albanis, 2004). The effects of irradiation intensity in the range of 0-114 W/m^2 by variation of black light lamp irradiation on decolorization of the RB dye were studied. The curve of the synthesized RB dye in solution by photo-decolorization with irradiation time was investigated (Figure 6).

The results indicated that an increase in the irradiation intensity of black light lamps enhanced the RB dye decolorization by photoreactor. This is likely because at high intensity of light involving more radiation in the UV intensity, more radicals fall on the catalyst, hence more $OH^\bullet$ are produced, which leads to an increase of the decolorization. There are more photons per unit time and unit area at higher light intensity (Ollis *et al.*, 1991). Thus the chances of photon activation on the photocatalyst surface increase also. The light intensity at 114 W/m^2 was the strongest comparing to other light intensities in this set.
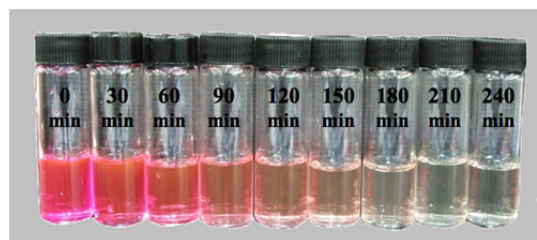
After 90 min of exposure, the percentage of decolorization efficiency was 42.1 and 87.8 when using black light lamp intensities of 23 W/m^2 and 114 W/m^2, respectively. It was found that the 114 W/m^2 intensity yielded the best
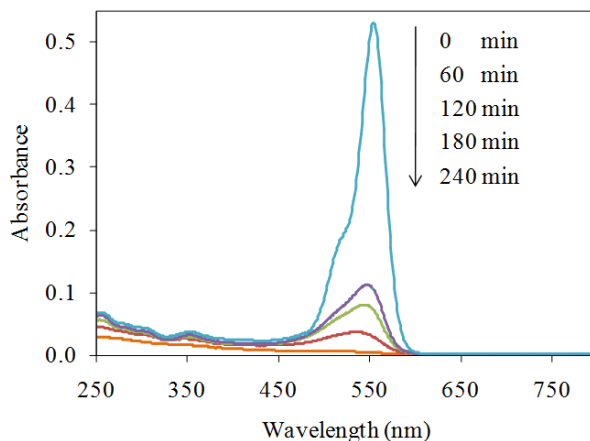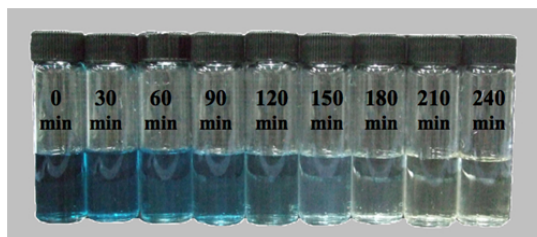

(a)
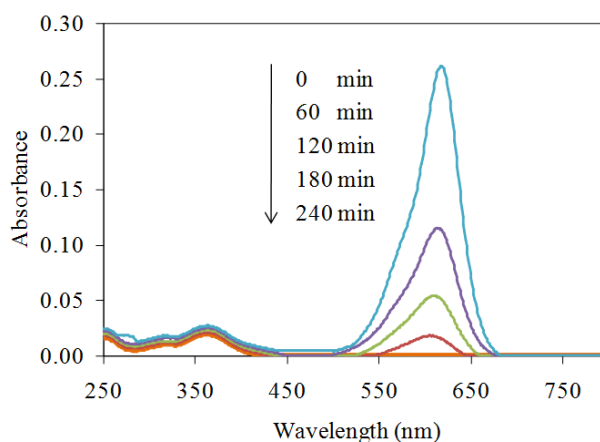
(b)

(c)

(d)

Figure 5. The UV-vis absorption spectral changes of RB (a) and MG (b) (20 mg dye/L) during the photocatalytic process under irradiation (114 W/m^2) using 1.0 g TiO_2/L loading; and the photographs of the photo-decolorization samples of RB (c) and MG (d) measuring every 30 min.
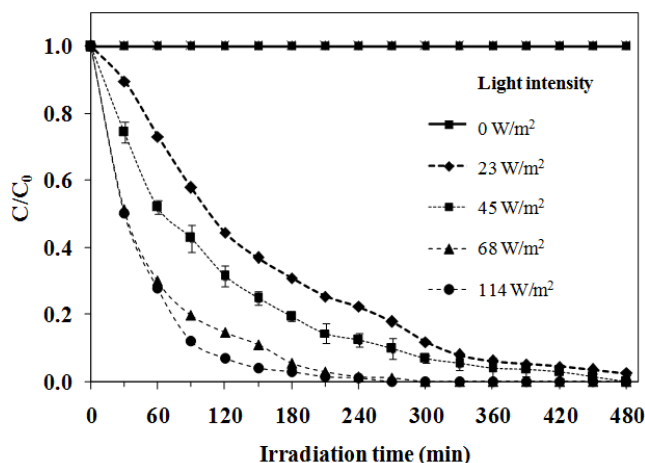
Figure 6. Decolorization of RB dye solution over various light intensity as a function of irradiation time under black light irradiation using 1.0 g TiO$_2$/L and 20 mg RB dye/L.

Figure 7. Effect of TiO$_2$ powder photocatalyst loading on decolorization Eff. (%) of RB and MG dyes (20 mg dye/L) at irradiation time of 60 min.

activity in dye decolorization of the RB dye and almost complete decolorization (approaching 90%) of the dye was achieved within 120 min. However, the decolorization efficiency was not significantly different between the light intensity of 68 and 114 W/m^2. The presence of TiO$_2$ (0.5-1.5 g/L) without irradiation could not achieve decolorization of the dye solution.

3.4 The effects of TiO$_2$ loading on photocatalytic decolorization

The concentration of TiO$_2$ powder photocatalyst loading is an important factor for dye removal from solution. Photocatalyst loading affected the number of active sites on the photocatalyst surface and led to OH$^•$ generation (Nishio *et al.*, 2006). Figure 7 shows the photocatalytic decolorization of RB and MG dyes in aqueous solutions at 60 min irradiation time as a function of different TiO$_2$ loading (0.5-1.5 g TiO$_2$/L dye solution). The decolorization efficiency (%) at the loading of 0.5 g TiO$_2$/L was lower than that of the TiO$_2$ powder loading at 1.5 g TiO$_2$/L. The increasing TiO$_2$ loading amount had resulted in the decrease in the time required for decolorization. This was because of the increase in the number of active sites on the photocatalyst surface that led to the increase in the number of OH$^•$. Moreover, the MG dye in aqueous solution decomposed more when compared to the RB dye solution. This could be explained on the basis that the RB dye solution has a higher complex structure than the MG dye solution.

The decolorization results for the RB and MG dye solutions (20 mg/L) in the presence of TiO$_2$ photocatalyst are shown, respectively, in Figures 8(a) and 8(b). It could be seen that the efficiency of RB decolorization in the dye solution, in the presence of 1.0 g TiO$_2$/L solution, approached 100% in 270 min, whereas the time required for the MG dye to attain the same efficiency was only 210 min. However, further
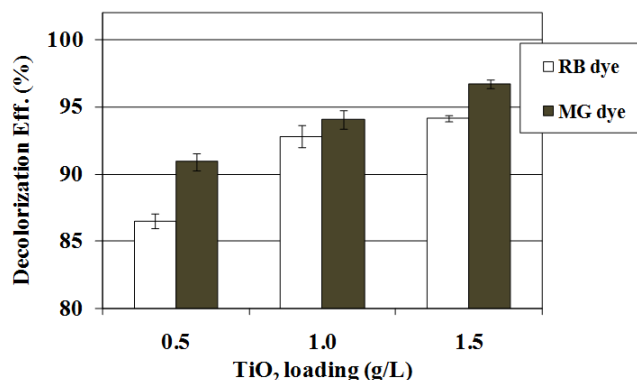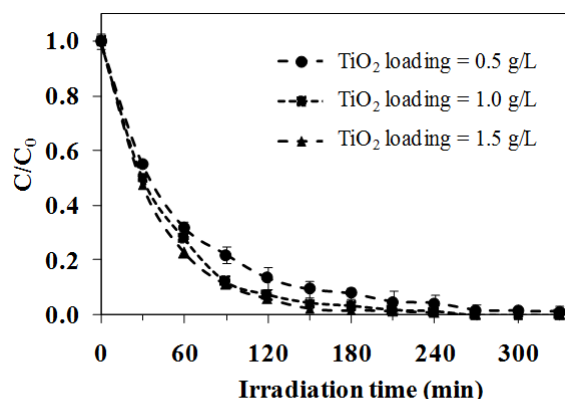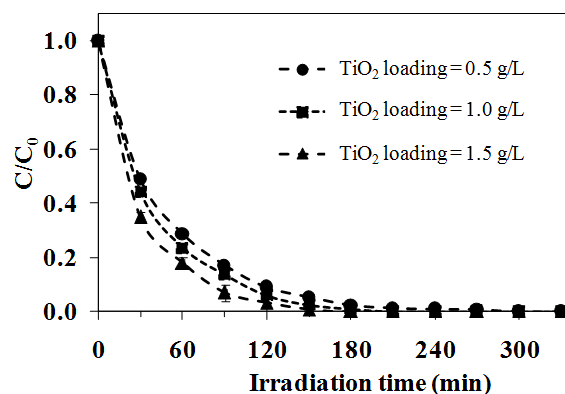

(a)

(b)

Figure 8. Decolorization of 20 mg/L RB (a) and MG (b) dye solutions under black light irradiation at various loading of TiO$_2$ powder photocatalyst and light intensity of 114 W/m^2.

increases in the photocatalyst loading (> 1.0 g TiO$_2$/L) did not lead to significant higher decolorization efficiency. This may be due to the fact that at high TiO$_2$ loadings the TiO$_2$ particles tend to aggregate, which reduces the catalytic activities by

reducing the specific surface area of the TiO_2 powder catalyst (Singh *et al.*, 2008). Therefore, a TiO_2 loading of 1.0 g/L was selected as the optimal value for the photocatalyst experiments based on the time required, 270 min and 210 min respectively, for the RB and MG decolorization. Decolorization of RB and MG dye solutions at 20 mg/L dye solution concentration, by any light irradiation intensities, in the absence of TiO_2 powder is impossible. During UV irradiation of the RB dye solution without TiO_2 photolysis, results showed that the dye concentration of the dye - and hence decolorization - remained unchanged regardless of UV black light irradiation intensities. This indicates no photo-decolorization by direct photolysis.

3.5 The effects of initial dye concentration on decolorization

Figure 9(a) shows the plot of decolorization efficiency (%) as a function of irradiation time with respect to different initial concentrations of the RB dye solution. It presents a high efficiency at low initial concentration of the dye (10 mg/L). As the initial concentration of the dye increased, the decolorization efficiency was reduced. The possible reason is that, as the initial concentration of the dye was increased, the molecules of the dye inhibited light penetration (Nam *et al.*, 2002). The dye molecules were not degraded immediately because the intensity of light and the catalyst amount was constant and also the light penetration was less. As the dye concentration increased, the solution color became more intense and the path length of the photons entering the solution was decreased, thereby fewer photons could reach the photocatalyst surface. Moreover, the production process of $OH^{\bullet}$ and $O_2^{\bullet-}$ was reduced. Therefore, the decolorization efficiency was reduced.

The time required for decolorization (under various dye concentrations at 10 mg/L to 30 mg/L, and 1.0 g TiO_2/L) increased with increasing irradiation time. Decolorization efficiencies (%) of the RB dye at solution concentrations of 10,
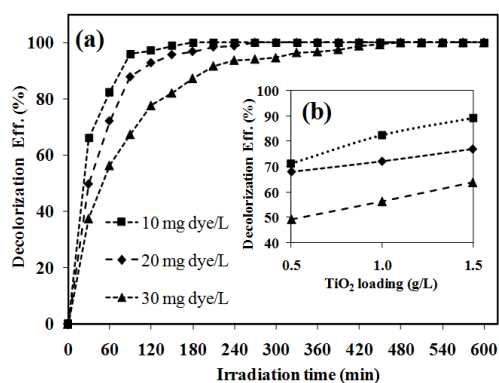
20, and 30 mg/L in 1.0 g TiO_2 powder photocatalyst under 114 W/m^2 light irradiation were, respectively, 82.4, 72.2, and 56.4 (Figure 9(b)). Decolorization of the dye solution at 30 mg/L, however, was found to yield an unacceptably low efficiency, even under the highest loading of 1.5 mg/L, that was not enough for the required level of degradation to destroy the complex structure of the dye solution under the UV light irradiation.

3.6 Kinetics

The Langmuir-Hinshelwood model has been used to describe the mineralization process kinetics that assumes automatically that reactions take place at the surface of the catalyst particles (Laoufi *et al.*, 2008). The decolorization rate of the photocatalytic process can also be effectively described by the model (Eq. (9)) (Konstantinou and Albanis, 2004). Catalyst loading induces catalytic activities that are influenced by the specific surface area of TiO_2 powder catalyst that lead to an increase in reaction rate for decolorization (Mehrotra *et al.*, 2003). The reaction rate as a function of catalyst loading in the photocatalytic oxidation process has been investigated by several authors (San *et al.*, 2001; Saquib and Muneer, 2002).

$$r = -\frac{dC}{dt} = \frac{kKC}{1+KC} \tag{9}$$

where r is the oxidation rate of the reactant (mg/L.min), C is the concentration of the reactant (mg/L), t is the irradiation time (min), k is the reaction rate constant (mg/min) relating to the reaction properties of solute which depend on reaction conditions, K is the adsorption coefficient of dye solution (L/mg).

Integrating Eq. (9) from time = 0 to t, and concentration from C_0 to C, yields:

$$t = \frac{1}{Kk}\ln\left(\frac{C_0}{C}\right) + \frac{1}{k}\left(C_0 - C\right) \tag{10}$$

where C_0 is the initial concentration of reactant (mg/L) and C is the concentration of the reactant at time t (mg/L)

At low substrate concentrations, the second term on the right-hand side of Eq. (10) can be neglected and the equation can be simplified to be a first-order equation (Eq. (11)):

$$\ln\left(\frac{C_0}{C}\right) \cong kKt = k't \tag{11}$$

where k' is the apparent rate constant (min^{-1}) which can be determined from the slope of the curve obtained.

To determine the effect of TiO_2 catalyst loading on the reaction rate of RB and MG dye decolorization, several experiments were conducted at TiO_2 loading of 0.5-1.5 g/L and dye concentration of 20 mg/L. Data were plotted of the linear transform, $-\ln\left(C/C_0\right)$, versus the irradiation time to derive the slope k' according to equation (11), and are shown in Figure 10. Under our experiment conditions, the data of the various TiO_2 loadings are in good agreement with a first

Figure 9. Decolorization Eff. (%) of RB dye concentration as a function of irradiation time at TiO_2 loading of 1.0 g/L (a) and as a function of TiO_2 powder loading (0.5 -1.5 g/L) at irradiation time of 60 min (b), under light intensity of 114 W/m^2.

order reaction and are straight lines. The first order kinetics expression can be successfully applied to analyze the heterogeneous photocatalytic reaction of the dye solution. The correlation coefficient, R^2, obtained are in the range of 0.973-0.996 which indicate good fitting of the data, and also are in good accordance with the results of Akpan and Hameed, (2011).

     In general, photocatalytic activity increases with increasing value of (Mozia *et al.*, 2009). The results plotted in Figure 10 confirm the positive influence of the increasing number of TiO_2 active sites on the process kinetics. The data clearly indicate that an increase in amount of catalyst loading increased the rate of decolorization up to a certain catalyst amount. The increase in the decolorization rate may be explained by the fragmentation of the catalyst which produces higher surface area (Dixit *et al.*, 2010).

     The highest of the apparent rate constants k' of RB and MG dye solutions were 0.022 and 0.030 min^{-1} at 1.5 g TiO_2/L, respectively. These results lead to the highest effi-

ciency under these conditions. In contrast, the rate of decolorization was lowest when the catalyst loading was 0.5 g TiO_2/L for both dyes. These observations can be explained by the photocatalyst optical properties being the main cause for the differences. The total active surface area increases with increasing catalyst loading because of the increases in the number of $OH^\bullet$ and $O_2^{\bullet-}$ (Laoufi *et al.*, 2008). When the rate constant k' between the RB and MG dye solutions are compared, it can be seen that photocatalysis conducted in the MG dye yielded higher rate constant k' than the RB dye, under the same conditions.
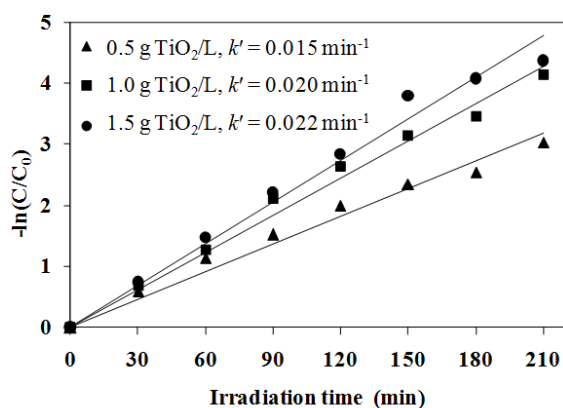
4. Conclusion

     Photocatalytic decolorization of synthetic RB and MG basic dye solutions were performed in a photo-batch reactor using TiO_2 powder as photocatalyst and under UV black light irradiation. The effects on decolorization of initial concentration, light intensity, and TiO_2 powder loading with respect to system efficiency and kinetics. The photocatalyst was characterized by XRD observation and it was shown that the fine TiO_2 powder could be identified as anatase crystals of 73 nm in size. The MG dye in aqueous solution showed higher decomposability by photocatalytic decolorization, requiring less time than the RB dye solution treatment. The two dye structures belong to different chemical groups. From the experiments, decolorization efficiency (%) increased with increasing TiO_2 loading and UV black light intensity. On the other hand, its efficiency decreased with increasing initial dye concentration. We have found that the most suitable condition for removal of dyes at initial 20 mg/L dye concentration is a TiO_2 loading of 1.0 g/L, together with light intensity of 114 W/m^2 based on time constraints, 270 min for the RB dye and 210 min for the MG dye. The Langmuir equation was found to fit well, yielding good linear correlations and good fits for the decolorization experiments. Its kinetics largely follow a first order equation and depend on the TiO_2 powder loading as well as the dye structure.
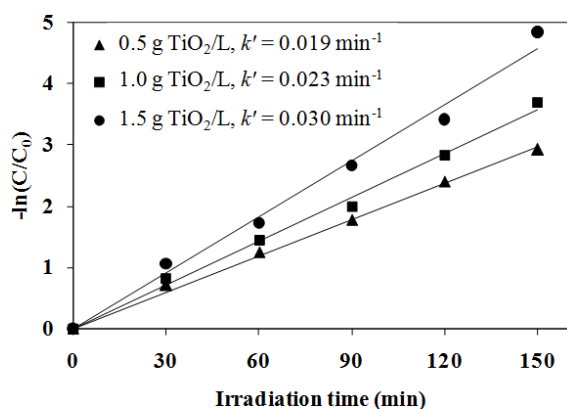
(a)

(b)

Figure 10. Langmuir fitting for RB (a) and MG (b) dye solution decolorization in the presence of TiO_2 powder photocatalyst with irradiation time at dye concentration of 20 mg/L and light intensity of 114 W/m^2.

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