

Original Article

Decolorization of dyeing wastewater in continuous photoreactors using TiO_2 coated glass tube media

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Abstract

The present study deals with a decolorization development of malachite green (MG) dyeing wastewater using TiO_2 thin films coated glass tube media in photoreactor. The TiO_2 photocatalyst was synthesized by three methods: TTIP sol-gel, TiO_2 powder-modified sol, and TiO_2 powder suspension coating on raschig ring glass tube media and was investigated crystallinity phase by SEM, XRD, and AFM. Degradation kinetics of the dyeing wastewater by photocatalytic was carried out under UV light irradiation. The Langmuir first-order model provided the best fit to the experimental data. The catalyst prepared by powder suspension technique and coated on glass tube had given the highest of decolorization kinetics and efficiency. Continuous photoreactor packed with the TiO_2 coating media was designed and proven to be the high effectiveness for MG dyeing degradation and stable throughout the recyclability test. The light intensity, dye solution flow rate, and TiO_2 loading were the most important parameters that response to decolorization efficiency. The optimum condition of photo decolorization of MG dye solution can be obtained from RSM model. Effectiveness of the synthesized TiO_2 thin films using suspension technique and the continuous photoreactor design were obtained with a great potential to be proven for wastewater treatment at industrial scale.

Keywords: powder suspension, photocatalytic system, TiO_2 thin films; packed-bed column, continuous photoreactor

1. Introduction

The growing use of textile dyes as well as the wide variety of synthetic dyes used today increasingly contaminate the wastewaters with dyestuff and by this becoming a significant source of pollution worldwide (Pignatello *et al.*, 2007). The release of those effluents introduces high loads of dyes into water reservoirs (Bisschops and Spanjers, 2003). Being discharged into the environment, these dyes not only impart to colors of water sources but also damage living organisms by stopping the reoxygenation capacity of water, blocking sunlight, and therefore disturbing the natural

growth activity of aquatic life (Wang, 2008; Song and Bo Bai, 2010). Malachite green dye (MG), a tri-phenyl methane cationic dye, has been widely used for the dyeing of cotton, textile, tannery, food, paper, pulp, printing, cosmetics, plastic, pharmaceuticals, and dye houses (Ahmad and Kumar, 2010; Ai *et al.*, 2010; Ding *et al.*, 2012). However, MG is very dangerous and highly cytotoxic to mammalian cells, and also acts as a liver tumor-enhancing agent. The dye, released into aquatic environments without any treatment, inhibits the development of aquatic animals and plants by blocking out sunlight penetration and it is also toxic to major microorganisms (Bekci *et al.*, 2009). Thus, the dye removal from wastewater effluent is a major environmental concern (Khehra *et al.*, 2005). Most common treatment methods, including adsorption, chlorination, or ozonation, are not efficient enough and it is quite expensive to remove these compounds,

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which also can cause secondary pollution. Biological treatment is a proven method and cost effective. However, it has been reported that the majority of dyes are adsorbed on the sludge and that they have very long degradation time, due to the biorecalcitrant nature of the dyes molecules. This leads to a search for highly effective method to degrade the dye into environmentally compatible products (Toor *et al.*, 2006). Advanced oxidation processes applying, titanium dioxide (TiO_2) photocatalysis have been successfully used to degrade pollutants from the textile industry (Mozia *et al.*, 2009). TiO_2 semiconductor is broadly used as a photocatalyst because of its non-toxicity, photochemical stability, and low production cost (Hoffman *et al.*, 1995). The TiO_2 photocatalysis degradation involves the generation of free radicals. These radicals can oxidize pollutants in the photocatalytic oxidation processes and the degradation of the dye (Hoffman *et al.*, 1995). However, the use of conventional TiO_2 powder catalyst on wastewater decolorization has disadvantages regarding the separation and reuse after reaction (Chen *et al.*, 2006). In applications dealing with wastewater, photoreactors utilizing the TiO_2 catalyst as coated films on an appropriate supporter have a unique advantage. This is because the filtration step to separate and reuse the catalyst is not required for the treated effluent. Therefore, more studies are devoted to the design and development of highly active coating-type TiO_2 photocatalytic films (Malato *et al.*, 2002). The sol-gel method is considered as an effective approach for the preparation of immobilized TiO_2 films on various substrates (Shang *et al.*, 2003). Coating of TiO_2 powder on supporting media by powders-modified sol technique is possibly used because this technique is easy and does not require any complicated equipment (Shang *et al.*, 2003).

In the present research work, the objective was to perform photocatalytic decolorization of the malachite green (MG) synthetic dye. TiO_2 thin films coating on raschig ring glass tube substrate materials was synthesized by TTIP sol-gel, TiO_2 powder-modified sol and TiO_2 powder suspension technique characterized, and used under UV black light source. Kinetics of the decolorization reaction was then studied to optimize the process under varying conditions by batch photoreactor. The effect of TiO_2 loading in catalytic preparation on the dye decolorization process was also considered. The continuous model photocatalytic reactor carried out in packed-bed glass column reactor with TiO_2 coating on glass tube substrate. Furthermore, response surface methodology (RSM) was applied to optimize three independent parameters, including UV black light intensity, dye solution flow rate, and TiO_2 loading.

2. Materials and Methods

2.1 Chemicals

Titanium (IV) isopropoxide (TTIP, 99.95% Fluka Sigma-Aldrich) and the commercial titanium dioxide powder

(TiO_2) (Degussa P-25, ca. 80% anatase, 20% rutile) were used as starting materials having a BET surface area of $50 \text{ m}^2/\text{g}$. Ethanol (99.9%; Merck, Germany) was used as a solvent. Nitric acid (HNO_3) (J.T. Baker, Thailand) was used for pH adjustments. Polyethylene glycol (PEG, 99.9% Mw 4000 Fluka Sigma-Aldrich) was used as binder. The dye, malachite green powder (MG) (reagent grade) from Direct Dyestuff Ltd, Thailand without further purification was used as a test pollutant (Asia Dyestuff Company). A dye solution for decolorization testing was prepared by deionized water at designed concentration and used as the stock solution for all studies. UV fluorescence black light lamps (8W, F20T12-BLB, U.S.A.) with a wavelength of 345-400 nm were the light sources for the photocatalytic performance in this work.

2.2 Experimental details

2.2.1 Preparation of TiO_2 thin films

TiO_2 thin films on glass tube substrate were prepared by TTIP sol-gel, powder-modified sol, and powder suspension method in order to investigate the decolorization of dye solution in the present of ultraviolet light. The preparation details are as following:

1. The TTIP sol-gel method was performed by dissolving TTIP 10 mL in 150 mL ethanol together with 1.5 g PEG; stirred at room temperature and adjusted to pH 3. The solutions were kept in a refrigerator for approximately 24 hrs until the sol turned into a low viscosity clear gel.

2. The powder-modified sol method was used for improving the photocatalytic process. TiO_2 powder (Degussa P-25) was added in TTIP sol-gel to get modified sol. In this research, commercial TiO_2 powder (Degussa P-25) of 0.2-0.4 g. TTIP sol-gel and TiO_2 powder (Degussa P-25) were mixed under vigorously stirring at room temperature and kept in a refrigerator for approximately 24 hrs until the sol turned into a low viscosity clear gel.

3. For the powder suspension method, TiO_2 powder (Degussa P-25) as small catalyst particles were suspended in liquid phase using ethanol as a solvent. The TiO_2 powder (Degussa P-25) of 4.0-7.0 g was mixed in 150 mL ethanol and 1.5 g of PEG was added into the mixed precursor solution under vigorously stirring at room temperature for 1 hr to minimize the formation of large agglomerates.

The raschig ring glass tube substrate (0.8 cm of diameter and 2 cm of length) was cleaned with diluted HNO_3 solution and dried at 100°C for 24 hrs. The glass tube substrate was coated by the prepared solutions to form TiO_2 thin films using the dip coating method. The coated substrate was dried at the temperature of 100°C for 24 hrs then calcinated at 600°C for 1 hr.

2.2.2 Characterization of TiO_2 films

The phase crystallite of TiO_2 thin film coating on glass tube substrate was characterized using X-ray diffraction

analysis using X-ray diffractometer (PHILIP X'Pert MPD) with CuK_α radiation. The morphology of samples and specific surface areas were characterized by scanning electron microscope (SEM). The morphology and the films roughness of TiO_2 films were observed using atomic force microscopy (AFM). The UV-vis spectra of the dye were recorded from 200-800 nm using a UV-vis spectrophotometer (UV-2401). The maximum absorbance wavelength (λ_{max}) of MG dye was 618 nm from the spectra.

2.2.3 Experimental set-up for kinetics measurements

The apparatus of photoreactor (Figure 1) was designed in order to be used for kinetics measurements. The setup consisted of a UV chamber made up of closed stainless ($\pi \times 20^2 \times 50 \text{ cm}^3$) consisting of 5×8 W UV black light lamps, installed inside of the chamber. Air cooling was introduced through the UV chamber that helped to maintain a constant room temperature ($30 \pm 2^\circ\text{C}$). The synthetic MG dye solution was prepared at a fixed concentration of 5 mg/L to perform decolorization in 250 mL Pyrex beaker reactor ($\pi \times 2^2 \times 6 \text{ cm}^3$) under UV light irradiation. A 100 mL MG solution with a concentration of 5 mg/L was mixed with 15 pieces of photocatalyst (TTIP sol-gel, TiO_2 powder-modified sol and TiO_2 powder suspension). The reactor with dye solution and photocatalyst was placed at the center of the UV chamber and magnetically stirred at 250 rpm. During UV irradiation, the sample solutions were taken from the photoreactor every 15 min until getting a clear solution. After photo-treatment for a certain time, the concentration of the treated solution was measured by UV-vis spectrophotometer. Decolorization efficiency of the MG dye in solution was defined by Equation 1 as follow:

$$\text{Efficiency}(\%) = \left(\frac{C_0 - C}{C_0} \right) \times 100 \quad (1)$$

where C_0 (mg/L) and C (mg/L) are the concentration of dye at λ_{max} for the initial (not yet irradiated) and at reaction time t , respectively, of the test sample. From the equation, efficiency (%) is the decolorization efficiency (%) indicates the

percentage of the net concentration change. In a case of C/C_0 plot can describe for decolorization of dye solution.

2.2.4 Continuous flow photocatalytic reactor set-up

The decolorization of MG dyeing wastewater was performed using TiO_2 coating on glass tube substrate raschig ring type as photocatalyst media under UV irradiations in continuous packed-bed reactor laboratory scale. Continuous down-flow packed-bed glass column (internal diameter of 5 cm and column height of 30 cm) were packed by the TiO_2 -coated raschig ring glass packing media. The glass columns were vertically installed in a cylindrical stainless steel chamber ($\pi \times 20^2 \times 50 \text{ cm}^3$) with vertically fixed UV lights at the chamber wall. UV lights ($23-114 \text{ W/m}^2$) at 345-400 nm wavelengths (power consumption of 8 W per lamp) were used as the light source of photocatalytic reaction. Air blowing was introduced through the chamber to maintain the system at constant room temperature. The MG dye solution (10 mg/L) was continuously flown by a peristaltic pump to the glass columns for decolorization testing. The specific design of continuous flow photocatalytic reactor system for decolorization of the dyeing wastewater and the laboratory scale set up of photocatalytic packed column with TiO_2 -coated raschig ring glass packing media in continuous operating mode for decolorization of the dye pollutant are shown in Figure 2.

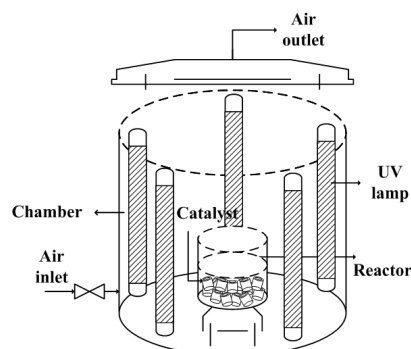


Figure 1. Illustration of kinetics experimental apparatus.

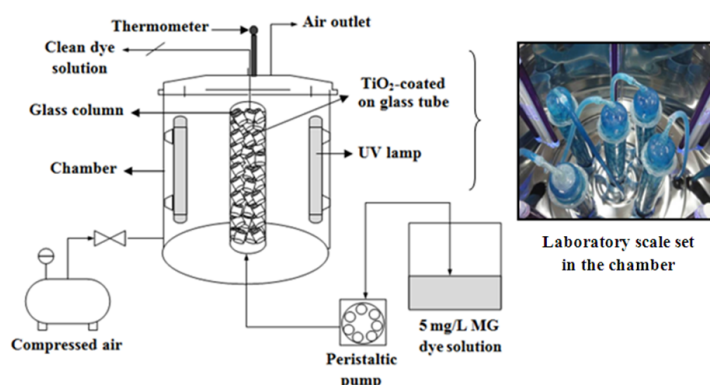


Figure 2. Illustration of experimental set up for continuous photocatalytic reactor and laboratory scale set up in chamber.

2.2.5 Experimental design and data analysis

Response surface methodology was adopted to study the simultaneous effect of process variables on the response of decolorization efficiency (%) in continuous flow photocatalytic reactor. The experiments were based on a three-factor central composite design (CCD). Analysis of the experimental data was supported by the statistical graphics Design expert (version 8.0.7.1) software for regression and graphical analyses of the obtained data and optimization were performed on the relevant conditions of variables in order to predict the best value of the responses. CCD and RSM were established with the help of the Design Expert software program.

The three significant independent process variables considered in this study were light intensity of 45-114 W/m² (X_1), dye solution flow rate of 10-80 mL/min (X_2), and TiO₂ loading of 1.0-5.0 g (1-5 column) (X_3). The responses can be simply related to the independent factors by a quadratic model consisting of linear, two factorial, and quadratic terms as given in Equation 2. Applying the values of the codes was calculated as shown in Table 1.

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \left(\sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} x_i x_j \right)_{i < j} \quad (2)$$

where y is the predicted response evaluated, x_i and x_j are the independent variables, β_0 is the constant coefficient, β_i , β_{ij} , and β_{ii} are the interaction coefficients of linear, quadratic and second-order terms, respectively, and k is the number of studied factors. The variables were coded according to Equation 3:

$$x_i = \frac{(X_i - X_0)}{\Delta X_i}, i = 1, 2, 3 \quad (3)$$

where x_i is the independent variable coded value, X_i is the independent variable real value, X_0 is the independent variable real value on the centre point and ΔX_i is the step changing value.

Analysis of variance (ANOVA) was used for graphical analyses of the data. The quality of the fit was expressed by the value of correlation coefficient (R^2), and its statistical significance was checked by F-value (Fisher variation ratio). Model terms were evaluated by the P-value (probability) with 95% confidence level (Amari *et al.*, 2008). Three-dimensional plots were obtained for dye decolorization efficiency (%) based on the effects of the three variables at five levels.

3. Results and Discussion

3.1 The morphology of TiO₂ thin film

Figure 3 shows the surface morphology of TTIP sol-gel, 0.4 g TiO₂ powder-modified sol, and 6.0 g TiO₂ powder suspension coating on glass tube substrate that was examined using SEM analysis. It can be observed from Figure 3(a) that the morphology of TiO₂ films prepared by TTIP sol-gel was smooth without the presence of any visible agglomerates and flat surface. On the other hand, small particle of P-25 powder was found dispersing on surface of the thin films prepared by the powder-modified sol method, Figure 3(b). In Figure 3(c) the surface of the coated sample with TiO₂ films prepared by powder suspension of 6.0 g (P-25 powder) shows visible agglomerates, a rough surface and well distributed nanosized particles on the surface.

3.2 XRD analysis

The X-ray diffraction patterns of TiO₂ thin films prepared by TTIP sol-gel, 0.4 g TiO₂ powder-modified sol,

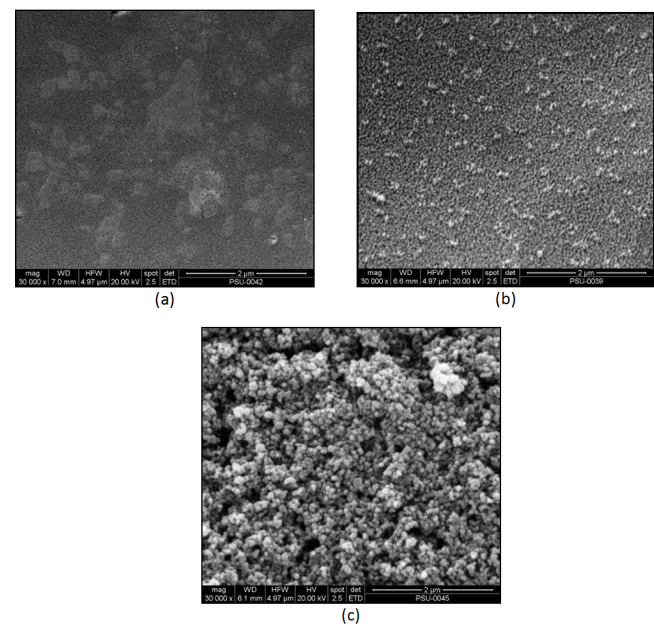


Figure 3. SEM images of TiO₂ thin films on glass tube substrate prepared by TTIP sol-gel (a), 0.4 g TiO₂ powder-modified sol (b), and 6.0 g TiO₂ powder suspension (c).

Table 1. Independent variables and their levels for CCD experimental design.

Independent Variables	Symbol	Coded variable levels				
		$-\alpha$	-1	0	+1	$+\alpha$
UV light intensity (w/m ²)	X_1	45	59	80	100	114
Dye solution flow rate (mL/min)	X_2	10	24	45	66	80
TiO ₂ coated media loading (g)	X_3	1	2	3	4	5

and 6.0 g TiO_2 powder suspension coating on glass tube substrate are illustrated in Figure 4. The anatase and rutile titanium dioxide phases are marked with 'A' and 'R', respectively, anatase phase (1 0 1) with the peak at two-theta of 25.36° was observed for TiO_2 thin films prepared by the three techniques. The XRD patterns of samples in Figure 4(a) and (b) indicate that they are the pure anatase phases which were prepared by TTIP sol-gel and powder-modified sol. The height of the anatase peak indicates the low crystallinity of the thin film structure. However, the thin film coated TiO_2 prepared by powder suspension clearly showed both anatase and rutile phase as shown in Figure 4(c). The high rutile phase was found in a significant amount in the film prepared by powder suspension technique, corresponding to (1 1 0) crystal facets of TiO_2 , which indicates that the thin film had a high crystallinity structure. The rutile phase was produced from the Degussa P-25 TiO_2 powder catalysts.

3.3 Effect of TiO_2 preparation technique on decolorization of MG

The decolorization of MG dye solutions by photocatalytic as a function of TiO_2 preparation technique with irradiation time is presented in Figure 5(a). In the presence of TiO_2 catalyst and UV light irradiation, the decolorization efficiency increased significantly due to the photocatalytic reaction time. The efficiency of TTIP sol-gel and the TiO_2 films prepared from 0.4 g powder-modified sol showed significantly lower efficiency because films contain a small amount of P-25 TiO_2 powder and a small active site area indicated low photoactivity. The effects of P-25 TiO_2 loading in the powder suspension method can be seen in the Figure 5(b). Films which contain a larger amount of P-25 TiO_2 powder and have larger active site areas (more crystallinity structure) would be expected to give more photoactivity since TiO_2 coated material is the most photoactive form for degradation of dye substance. The increase in number of active sites on the photocatalyst surface led to an increase of the number of OH^\bullet (Dixit *et al.*, 2010). It could be seen that the efficiency of MG decolorized in dye solution was up to 100% within the irradiation time of 90 min by the of 7.0 g TiO_2 powder suspension coating on glass tube substrate. The result showed that the total active surface area increases with crystallinity structure because of the increases in the number of OH^\bullet and O_2^\bullet (Laoufi *et al.*, 2008).

3.4 AFM analysis

The surface morphologies of the TiO_2 films deposited on glass tube substrate for fresh and after decolorization performing in photoreactor were examined by AFM as shown in Figure 6. The surface roughness seems to correlate to the crystallite or grain size and the closed size distribution of TiO_2 thin films. The TiO_2 thin films from powder suspension technique have a high surface morphology and surface roughness. Grooves on the thin film surface give the advantages

on the embedded of dyeing molecules. Deeper embeddings from the surface will have stronger-electrostatic forces to interact with the dye molecules. Therefore, the higher surface morphology and surface roughness can help to bind more dye molecules onto the surface and therefore a higher number of photocatalytic reactions can take place. It also was found that the surface morphology of TiO_2 thin films is smooth with roughness values of 276 and 102 nm for the fresh, Figure 6(a), and used catalyst, Figure 6(b), respectively.

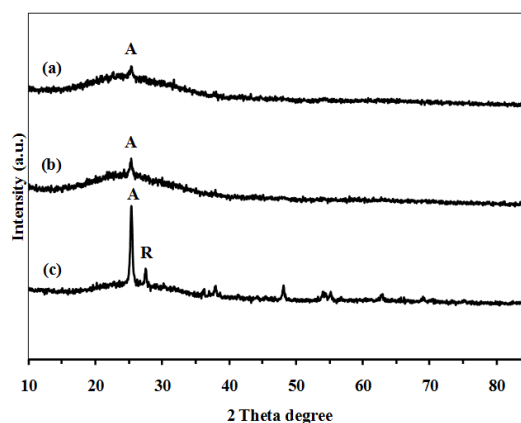


Figure 4. XRD patterns of TiO_2 thin films prepared by TTIP sol-gel (a), 0.4 g TiO_2 powder-modified sol (b), and 6.0 g TiO_2 powder suspension (c).

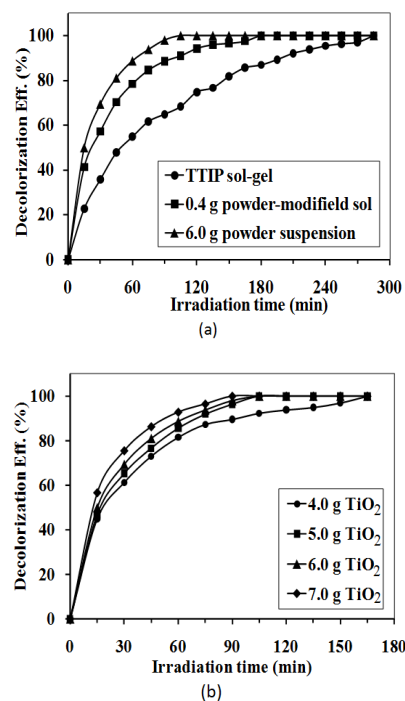


Figure 5. Decolorization of 5 mg/L MG dye solution in photocatalytic reactor by TiO_2 coated on glass tube; using TTIP sol-gel, 0.4 g powder-modified sol, and 6.0 g powder suspension (a); 4.0-7.0 g TiO_2 loading in powder suspension technique (b).

The surface roughness of TiO₂ thin films decreased after using because of the lost of TiO₂ particle by scraping between dyeing solution and surface thin film.

3.5 Kinetics

The Langmuir-Hinshelwood model has been used to describe the mineralization process kinetics and to assume automatically that reactions take place at the surface of the catalyst particle. The decolorization rate of photocatalytic process can be effectively described by the model as shown in Equation 4. (Laoufi *et al.*, 2008):

$$r = -\frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (4)$$

The integration of Equation 4 is:

$$t = \frac{1}{Kk} \ln\left(\frac{C_0}{C}\right) + \frac{1}{k}(C_0 - C) \quad (5)$$

At low substrate concentrations, the second term on the right-hand side of Equation 5 can be simplified to a first-order equation (Equation 6)

$$\ln\left(\frac{C_0}{C}\right) \cong kKt = k't \quad (6)$$

where r is the oxidation rate of the reactant (mg/L min), C_0 is the initial concentration of reactant (mg/L), C is the concentration of the reactant at time t (mg/L), t is the irradiation time, k is the reaction rate constant (mg/min) related to the reaction properties of solute which depends on the reaction conditions, K is the adsorption coefficient of dye solution (L/mg), and k' is the apparent rate constant (min⁻¹) which can be determined from slope of the curve obtained.

To determine the effect of catalyst preparation method and TiO₂ loading on the reaction rate of MG dye decolorization, several experiments were conducted. TTIP sol-gel, 0.4 g TiO₂ powder-modified sol, and 4.0-7.0 g TiO₂ powder suspension were prepared for coating on glass tube substrate and used in the experiments. The data was plotted between linear transforms $-\ln(C/C_0)$ versus irradiation time to get slope equal to k' according to Equation 6 as shown in Figure 7. For our experimental conditions, the data of various TiO₂ were in good agreement with a first order reaction and giving a straight line. The first order kinetics expression can be successfully applied to analyze the heterogeneous photocatalytic reaction of the dye solution. The correlation coefficient, R^2 was in the range of 0.964-0.993, which indicated a very good fitting.

The highest of apparent rate constants of MG dye decolorization were 0.041 (min⁻¹) at the condition of 7.0 g powder suspension which lead to the highest decolorization efficiency and was chosen for testing in the continuous process. On the other hand, this lowers down of the decolorization rate by powder-modified sol and sol-gel method, respectively. Therefore, an increase in the number of TiO₂ active sites by powder suspension technique for coating on

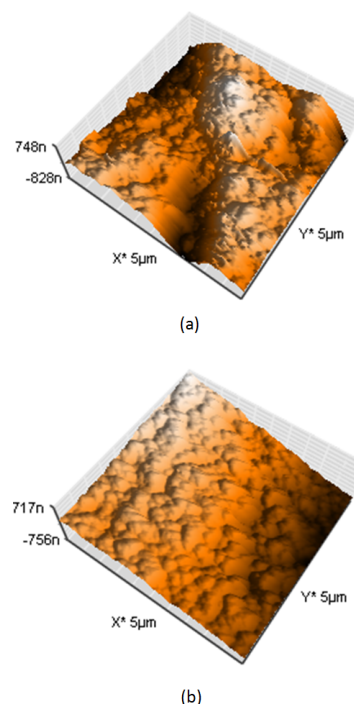


Figure 6. AFM illustration of TiO₂ thin films on glass tube substrate at 6.0 g TiO₂ loading by powder suspension method; fresh (a) and after used (b) for decolorization of MG dye.

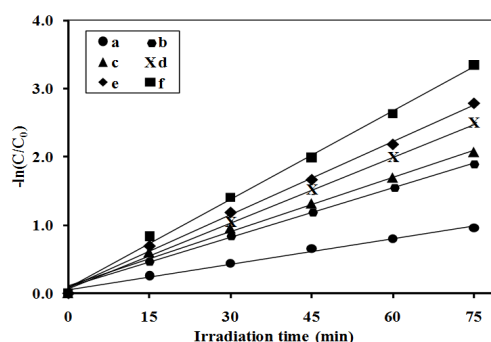


Figure 7. Langmuir fit of photocatalytic decolorization by TiO₂ catalyst prepared by TTIP sol-gel (a), 0.4 powder-modified sol (b), 4.0 g (c), 5.0 g (d), 6.0 g (e) and 7.0 g (f) powder suspension with coating on glass tube substrate.

the glass tube substrate has a positive influence on the process kinetics.

3.6 Decolorization of MG in continuous photocatalytic reactor

Photocatalytic activity of TiO₂ thin films catalyst coating on raschig ring glass tube substrate was tested for decolorization in packed-bed glass column of continuous photo-reactor under UV light irradiation. The continuous photocatalyst system was steady-state controlled by the dye solution flow up rate at 20 mL/min, the catalyst media loading

of 5.0 g (g of TiO₂ coated on media) (five columns), and the light intensity of 114 W/m² (10 mg/L dye solution). Under continuous flow conditions at constant residence time and photocatalytic parameters, decolorization efficiency was recorded for the main effect of working time. It was found that the experiment achieved 81% decolorization efficiency along the experimental period. The key mechanism of dye removal was undoubtedly photo activity, the presence of UV light irradiation and TiO₂ thin film coated on the media, shows that dye removal by photocatalytic could result in fact from several complex mechanisms.

The dye solution flow rate of 10-20 mL/min was varied to study for the effect of flow rate on dye decolorization efficiency. The efficiency (%) was found to be 95% throughout the experiment when the flow rate was controlled at 10 mL/min, whereas efficiency (%) was 82% for 20 mL/min dye solution flow rate. In the case of higher flow rates, the contact time between catalyst and dye solution decreased and it was not sufficient to get high decolorization efficiency. These results indicated that the dye solution flow rate was an important parameter for decolorization of dye solution in photocatalytic continuous system.

3.7 Model fitting and statistical analysis

The central composite design has been used for fitting a second-order model from experimental runs for designing chemical processes and analyzing the process results (Amari *et al.*, 2008). Response surface methodology was employed for mathematical model formation and optimization perform-

ing for decolorization of dyeing solution in photocatalytic continuous reactor. UV light intensity, dyeing solution flow rate, and the amount of TiO₂ catalyst media loading were considered as the independent variable, while percentage of decolorization efficiency (%) was considered as the dependent variable (response). The complete experimental design matrix and associated responses based on experimental runs were proposed in Table 2.

An empirical second-order polynomial expressing the efficiency (%). response from experimental data was fitted as a function of the independent variables and proposed by the following quadratic Equation 7.

$$Y = 36.60 + 2.95X_1 - 16.69X_2 + 5.33X_3 + 1.34X_1X_2 - 2.59X_1X_3 - 1.23X_1^2 + 6.45X_2^2 \quad (7)$$

where y is the decolorization efficiency and X_1 , X_2 , and X_3 , the independent variables as described in Table 1.

The response surface model developed in this study for predicting efficiency (%) was adequate as indicated model explains perfectly experimental range studied (R^2 adjusted = 0.9954). The model F-value of 497.02 implies the significance of the model. The degree of significance of each factor was represented in this table by its p-value; when a factor has a p-value smaller than 0.05, it influences the decolorization response at a confidence level of 0.95 ($p < 0.05$). The linear effect of all three variables, i.e., light intensity, dyeing solution flow rate, and amount of TiO₂ catalyst media ($p < 0.0001$) was highly significant for decolorization responses. The two quadratic effects and two interaction effects appeared as

Table 2. Central composite design consisting of experiments for the study of experimental factors in coded and actual values with responses from experimental results.

Standard run no.	Run	Coded values			Actual values			Response values
		X_1	X_2	X_3	X_1 (W/m ²)	X_2 (mL/min)	X_3 (g)	% Eff.
1	16	0	0	0	80	45	3	35.32
2	5	-1	-1	+1	59	24	4	60.23
3	2	+1	-1	-1	100	24	2	53.12
4	6	+1	-1	+1	100	24	4	68.89
5	15	0	0	0	80	45	3	36.25
6	11	0	-a	0	80	10	3	80.96
7	13	0	0	-a	80	45	1	27.57
8	17	0	0	0	80	45	3	37.53
9	9	-a	0	0	45	45	3	27.76
10	12	0	+a	0	80	80	3	28.06
11	1	0	-a	0	59	24	2	55.45
12	8	-1	-1	-1	100	66	4	36.74
13	3	-1	+1	-1	59	66	2	17.46
14	4	+1	+1	-1	100	66	2	21.11
15	7	-1	+1	+1	59	66	4	23.37
16	14	0	0	+a	80	45	5	45.79
17	10	+a	0	0	114	45	3	37.85

significant in the model. The stepwise elimination procedure was selected to automatically reduce the insignificant terms and the resulting ANOVA data for the reduced quadratic model of total flux. By applying multiple regression analysis on the experimental data, the reduced quadratic equation in terms of coded factors was obtained as Equation 7.

3.8 Analysis of response surfaces

We used statistical software to construct the three-dimensional response surface from model prediction. Figure 8(a) and (b) show the relative effects of two variables on percentage of decolorization efficiency, keeping the third variable at a constant level. All 3D plots can be used to explain and identify the effect of each variables and major interactions between the variables.

3.8.1 Effect of light intensity and dyeing solution flow rate

The 3D plot in Figure 8(a) indicates significant interaction between light intensity (X_1) and dye solution flow rate (X_2) on the decolorization efficiency (%) of continuous photocatalytic system. It is observed that the treatment efficiency significantly increases with decreasing dyeing solution flow rate. However, the light intensity has no significant effect on the decolorization efficiency at MG dye concentration of 10 mg/L. The highest efficiency (%) of the decolorization was reached at a dye solution flow rate of 10 mL/min and light intensity of 114 W/m². However, the interaction of light intensity at the lowest value of 45 W/m² and the highest dye solution flow rate of 80 mL/min presented the lowest efficiency (%). The dyeing solution flow rate is an important parameter for the decolorization using TiO₂ catalyst in continuous photocatalytic reactor. Longer contacting time between dyeing and thin film surface is reached in the photocatalytic continuous reactor according to lower liquid flow rate. The results indicated that an increase in the irradiation intensity of black light lamps enhanced the MG dye decolorization by continuous photoreactor. This is likely because at high light intensity more radiation in the UV intensity occurs, and therefore more radicals fall on the catalyst, hence more OH[•] are produced which leads to an increase in the decolorization performing. There are more photons per unit time and unit area at higher light intensity (Ollis *et al.*, 1991).

3.8.2 Effect of light intensity and TiO₂ catalyst media loading

The response surface plot in Figure 8(b) showed the effect of light intensity and TiO₂ catalyst media loading at 5 mg/L of MG dye solution as an estimate of efficiency (%). The highest percentage of decolorization efficiency of MG dye solution occurred when both of the independent factors, light intensity and TiO₂ loading, were kept at their maximum. The interaction (X_1X_3) exemplifies the real importance of TiO₂ media loading on the decolorization of dye solution. The

increase in TiO₂ loading led to the increasing in number of active sites on the photocatalyst surface that led to the increase in the number of OH[•]. The increase in the amount of active sites in accordance with the increase in TiO₂ photocatalyst loading consequently lead to an enhancement of the production of OH[•] radicals (Alabdulkarema *et al.*, 2011). It is found that increasing the light intensity the decolorization efficiencies of dye increases which is similar to the photo-decolorization of dyes catalyzed by TiO₂ powder (Chanathaworn *et al.*, 2012).

4. Conclusion

TiO₂ thin films coating on raschig ring glass tube substrate was effectively synthesized by P-25 TiO₂ powder suspension technique. The TiO₂ on glass tube media can increase the contacting area between TiO₂ thin films and dyeing wastewater which improve light penetration for the photocatalytic continuous system. The kinetics have largely followed a first-order by the Langmuir-Hinshelwood model and depended on TiO₂ loading and catalyst preparation. Packed-bed glass column continuous photoreactor with TiO₂ coated media assisted decolorization of dyeing wastewater under UV-irradiation. The system revealed that dye solution can be continuously removed with high decolorization

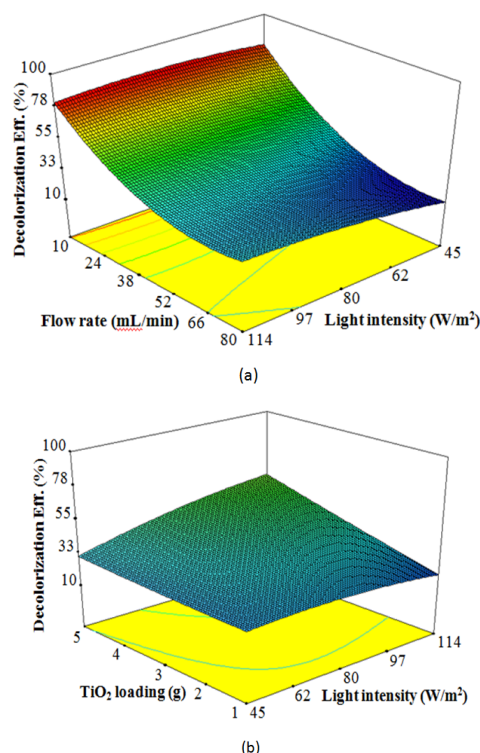


Figure 8. 3D surface plot on the effect of light intensity (X_1) and dyeing solution flow rate (X_2) on decolorization efficiency (%) (a), 3D surface plot on the effect of light intensity (X_1) and TiO₂ catalyst media loading (X_3) on decolorization efficiency (b), at 5 mg/L MG dye concentration.

efficiency (%) and remained stable throughout the recyclability test. The parameters, light intensity, dye solution flow rate, and TiO_2 loading were the most important ones for the decolorization efficiency. The optimization using a response surface methodology based on the CCD could save the time and efforts by the estimate of the optimum conditions of maximum decolorization of dyeing wastewater.

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