

Research Article

Factors Determining the Removal Efficiency of Procion MX in Waters Using Titanate Nanotubes Catalyzed by UV Irradiation

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The treatment of wastewater from the textile industry containing organic dyes faces many challenges since these compounds resist the biodegradation process in conventional treatment units. Among the physicochemical processes, photocatalysis is considered a facile, cheap, and environmental-friendly technology for treating persistent organic pollutants in waters at low concentrations. This study investigated several physicochemical factors determining the photocatalytic activity of titanate nanotubes (TNTs) to remove Procion MX 032 (PMX), an azo dye, in waters. Degradation of PMX by photocatalytic oxidation process at room temperature (30°C) was set up with the UV irradiation in the presence of different types of photocatalyst such as ST-01 (100% anatase), industrial TiO₂, TNTs calcined at 120°C and 500°C. Effect of reaction time, catalyst amount, pH, light wavelength and intensity, and oxidants was investigated. Consequently, TNTs calcined at 500°C provided the highest removal efficiency. The photocatalytic oxidation of PMX by TNT calcined at 500°C was affected by pH variation, getting the highest removal at pH of 8, and inhibited with the presence of H₂O₂ and O₂. Particularly, the PMX degradation using titanate nanotubes was optimized under the UV-A intensity of 100 W/m². The dye was degraded by more than 95% at the TNTs concentration of 75 mg/L and pH 8.0 after 90 min. The results suggest that photocatalysis using TNTs can be a simple but efficient treatment method to remove PMX and potentially be applied for the treatment of wastewaters containing dyes.

1. Introduction

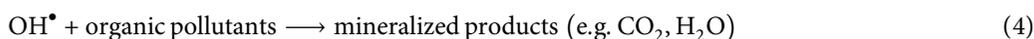
Textile industries produce a large amount of wastewater which contains a high concentration of inorganic salts and different types of reactive dyes for coloring clothes [1, 2]. These reactive dyes cause aesthetic problems, an increase of chemical oxygen demand of the wastewater [3]. They may result in inhibition, eutrophication, and perturbation of the ecosystem because of their toxic and mutagenic effect [4], even at low concentrations [5], that should be removed from wastewater before discharging into the water environment. Among different types of dye, Procion MX is a commonly

used fabric reactive dye belonging to the dichlorotriazine class [6]. Several types of Procion MX were selected as the color target in wastewater treatment, such as Procion Red MX-5B [3], Procion Red MX 3B [7], Procion Blue MX-R [8], and Procion Brown MX-5BR [9], but the treatment wastewater containing Procion MX 032 (color name of Carmine Red) (hereinafter referred to as PMX) has been rarely found except one report from Nguyen et al. [10].

The requirement for wastewater treatment becomes more and more strict in Vietnam in order to prevent the serious pollution of the water environment. Although contributing a small portion of the wastewater treatment field, research on the

treatment of textile and printing wastewaters has been attracted much attention due to their visible color of dyes and pigments and their refractory properties for treatment by traditional biological processes [11]. The available techniques for textile wastewater treatment are traditional methods (e.g., anaerobic and aerobic biodegradation, chemical coagulation, ion exchange, and adsorption) and advanced oxidation processes (e.g., Fenton, electro-Fenton, photo-Fenton, and photocatalysis) [5]. Traditional physical and chemical methods have their limitation for low volume but a high concentration of dyes, which are not suitable for the treatment of wastewater with low dyes concentration after biological treatment [12]. Moreover, these processes, popularly chemical coagulation and adsorption, only transfer the pollution from one phase (e.g., liquid) to another phase (e.g., solid) without actual degradation of the pollutants. Regarding advanced oxidation processes,

Fenton and Fenton-like reactions are usually applied for high strength wastewater due to its high cost of chemicals (Fe(II), persulfate, and H₂O₂) or electricity. Therefore, photocatalysis, a destruction technique, is considered a promising technology to remove the low concentration of pollutants from aqueous phase systems for water purification and hazardous waste remediation [13], particularly for the advanced treatment of textile wastewater after biological processes. Moreover, accelerated physicochemical processes involved in photocatalysis reactions are either supplementary or complementary to some conventional approaches to transform hazardous chemical wastes such as organic and inorganic species into mineralized products. The major mechanism for photocatalytic degradation of organic pollutants in water using TiO₂ material under UV light is summarized in the following reactions [14]:



With important properties such as biological and chemical inert, long-term photo-stability, and most importantly, low-cost, TiO₂ is the most successful photocatalyst for the degradation of organic compounds [15]. TiO₂-based nanotubes (e.g., titanate nanotubes, TNTs) were firstly synthesized by Hoyer [16] applying the electrochemical method. TNTs provide larger specific surface areas and pore volumes, high ratios of length to tube diameter, and significant electron-transport capability [17, 18]. Studies widely used the hydrothermal synthesis method to quantitatively produce high-quality TNTs [17–19]. In previous works, TNTs calcined at different temperatures were applied for NO_x and Procion dyes removal, which showed high efficiencies and potential for environmental applications in air and wastewater treatment [10, 20]. However, the treatment condition for photocatalytic removals of PMX has not been systematically investigated.

Various factors such as type of catalyst, reaction time, amount of catalyst, solution pH, light, and oxidant have different effects on the performance of photocatalytic treatment of dyes and other pollutants in water and wastewater [21]. Studies showed that the types and properties of TiO₂ material, such as crystal phase, surface area, and particle size, could strongly affect photocatalytic processes [22–24]. Hydraulic retention time, catalyst dosage, solution pH, and light source are among other factors that usually determined the photocatalytic kinetics [25–40]. Solution pH has controlled the photocatalytic activity via regulating the surface charge of the photocatalyst, the speciation of pollutants, and the concentration of hydroxide ion in the solution [41–50]. Since the photocatalytic reaction is

initiated by light, its performance is influenced by the wavelength and intensity of the light source [51–55]. As electron receptors, the presence and effect of oxidants such as oxygen and hydrogen peroxide are usually investigated [48, 52, 56, 57]. Up to the present, there has not been any systematic investigation into how those factors regulate the efficiency and rate of photocatalytic removal of PMX using titanate nanotubes.

In this study, we synthesized TNTs and applied them for photocatalytic removal of PMX. The activity of synthesized TNTs was also compared with available and commercial TiO₂ materials. By investigating the effects of reaction time, catalyst amount, pH, wavelength, light intensity, and oxidants on PMX removal efficiency, appropriate conditions for the photocatalytic treatment of PMX using TNTs were suggested.

2. Materials and Methods

2.1. Chemicals and Photocatalyst Materials. ST-01 (100% anatase) was purchased from Ishihara Sangyo Kaisha (Japan). TiO₂ industrial (TiO₂·H₂O) was from China Steel Co. (Taiwan). Procion MX 032 (PMX) was from Jacquard (USA). Acid and base and other chemicals were purchased at analytical grade from Xilong (China).

2.2. Hydrothermal Preparation of TNTs. This TNTs synthesis procedure was modified from the works published in the literature [20, 58]. The aqueous mixture was first prepared with 180 mL of 10 M NaOH solution and 12 g of TiO₂ (P25,

Degussa, Merck) and ultrasonically treated for 60 min at room temperature (ca. 30°C) then hydrothermally treated in a Teflon autoclave at 135°C for 24 h. After that, the product was allowed to cool for 12 h, and the material was taken out, rinsed with 1000 mL deionized water, and followed by filtration. The collected material was treated into 1000 mL of deionized water at pH 1.6 (adjusted by HNO₃ solution) under ultrasonication for 30 min and filtered using a funnel filtration apparatus. The residue solid was subsequently gently washed with deionized water until neutral pH and dried at 120°C for 12 h to get the postprocessing product as TNT-100. TNT-500 was then prepared by heat-treatment of TNT-100 material at 500°C for 2 h. Characteristics of the TiO₂ materials used in this study are summarized in Table 1 and the transmission electron microscopy (TEM) images of the TNTs materials are presented in Figure 1. The X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), and TEM results were obtained by using XRD (X'Pert Pro MRD, PANalytical), BET (ASAP 2020, Micromeritics), and TEM (HT 7700, Hitachi) machines, respectively. The pH_{zpc} of the TNT-500 material was determined at pH 6.3 using a Zetasizer Nano ZS (Malvern Panalytical, UK).

2.3. Photocatalytic Experiments. These tests were to find out the optimum operational conditions for PMX treatment. Firstly, the experiment was conducted to compare the treatment efficiency among different TiO₂ catalysts, i.e., TNT-100, TNT-500, ST-01, and industrial TiO₂. TNT-100 and TNT-500 were synthesized using the alkali hydrothermal method as previously described. A stock solution of Procion MX 032 (PMX) (i.e., 0.1 g of PMX in 1 L of deionized water) was prepared for the photocatalytic experiments. For each test, 2 L of synthetic wastewater (i.e., 1 : 20 dilutions from the stock solution of PMX) at pH 6.3 with suspended TiO₂ catalysts (e.g., 0.1 g) was stirred for 90 min in the reactor. At 15 min irradiation time intervals, water samples were taken, centrifuged at 6000 rpm for 12 min, and analyzed for water color using a spectrophotometer (Hach DR5000, USA) at 455 nm.

Given the most effective catalyst from the first experiment, similar photocatalytic tests were conducted for maximum irradiation of 105 min to determine optimal irradiation time. Likewise, different concentrations of catalyst (0.025, 0.05, 0.1, 0.15, and 0.2 g), pH conditions (5.0, 6.0, 7.0, 8.0, and 9.0), irradiation wavelength (UV-A lamps (Panasonic) and UV-C lamps (Toshiba) of 8 W, Japan), and irradiation intensity (set up by adding 1 to 3 UV lamps) were also investigated. The maximum irradiance intensity of UV-A and UV-C lamps are achieved at wavelengths of 365 and 254 nm, respectively.

To assess the importance of oxidants (e.g., O₂ and H₂O₂) on the TiO₂ photocatalytic efficiency, two series of experiments were carried out with the optimal TiO₂ concentration at the optimal pH condition. Synthetic wastewater was firstly purged by N₂ gas for 30 min to minimize the amount of dissolved oxygen. Subsequently, the wastewater was continuously aerated with air at different flow rates (0.5, 1.0, 1.5, and 2.0 L/min) for a 90 min-catalytic process. The

experimental procedure for the H₂O₂-assisted batch was similar to the air-assisted batch and different amounts of H₂O₂ (1–100 mL) were added into the reactor.

The photocatalytic removal efficiency η (%) and removal capacity q (mg/g) of PMX can be calculated by the following equations:

$$\eta = \frac{C_0 - C}{C_0} \times 100\%, \quad (5)$$

$$q = \frac{C_0 - C}{m} \times V, \quad (6)$$

where C_0 and C (mg/L) are the initial and treated concentrations of PMX in the solution, respectively. V (L) is the solution volume and m (g) is the catalyst amount.

2.4. Photocatalytic Degradation Kinetics. Heterogeneous photocatalytic oxidation kinetics of many organic substrates have widely been analyzed for comparing the reaction rate between different photocatalytic systems. The initial concentration of PMX would affect the removal of PMX, following Langmuir–Hinshelwood rate equations [35, 36]. The pseudo-first-order kinetics is expressed in equations (7) and (8), where C is the concentration of PMX and k_{app} is the apparent first-order rate constant.

$$r = -\frac{dC}{dt} = k_{app}C, \quad (7)$$

$$\ln \frac{C_0}{C} = k_{app}t. \quad (8)$$

3. Results and Discussion

3.1. Effects of TiO₂ Catalysts. Results in Figure 2 showed that PMX removal efficiency using TNT-500 was the highest of 81.8% after 90 min of irradiation. Compared to other materials, PMX removal efficiency by TNT-500 was 2.45, 2.04, and 1.15 times higher than that of TNT-100, ST-01, and industrial TiO₂, respectively. This result is consistent with the previous study showing the effects of calcination temperature on the surface and structural distinction of the catalyst materials [20, 59, 60]. Accordingly, specific surface areas decreased in the order of TNT-100, ST-01, and TNT-500, which reflected the inverse trend of particle sizes. In a previous study, Jang et al. [22] concluded that the particle size and anatase crystal phase determined the catalytic activity in photodegradation of methylene blue. Even with the highest surface area and small particle/pore sizes, the amorphous phase of TNT-100 was photocatalytically inactive under UV light due to its low anatase crystallinity of TiO₂ structure. Amorphous TiO₂ owned much more structural disorders than anatase, thus increasing the electron-hole recombination and consequently suppressed the catalyst activity [23, 24]. Therefore, the TNT-100 material with nanotube morphology is not suitable for photocatalytic application. The photocatalytic activity of ST-01 was also low in this study, although it has a very high surface area and

TABLE 1: Properties of TiO₂ materials used in the photocatalysis experiments.

TiO ₂ materials	Morphology (by TEM)	Particle size/pore size (nm)	Crystalline phase (by XRD)	BET surface area (m ² /g)
ST-01	Nanoparticles*	7–8*	Anatase*	300.0
Industrial TiO ₂	Nanoparticles*	20–30*	Anatase*	120.0
TNT-100	Nanotubes	4.5 (pore size)	Amorphous	390.0
TNT-500	Nanorods	12.4 (pore size)	Anatase	106.3

Note: *information from the manufacture.

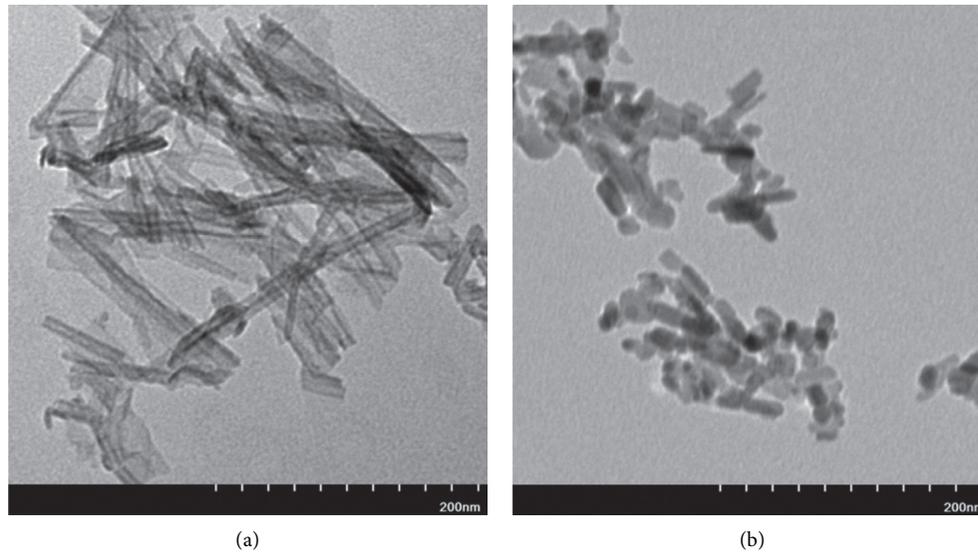


FIGURE 1: TEM images of (a) TNT-100 and (b) TNT-500.

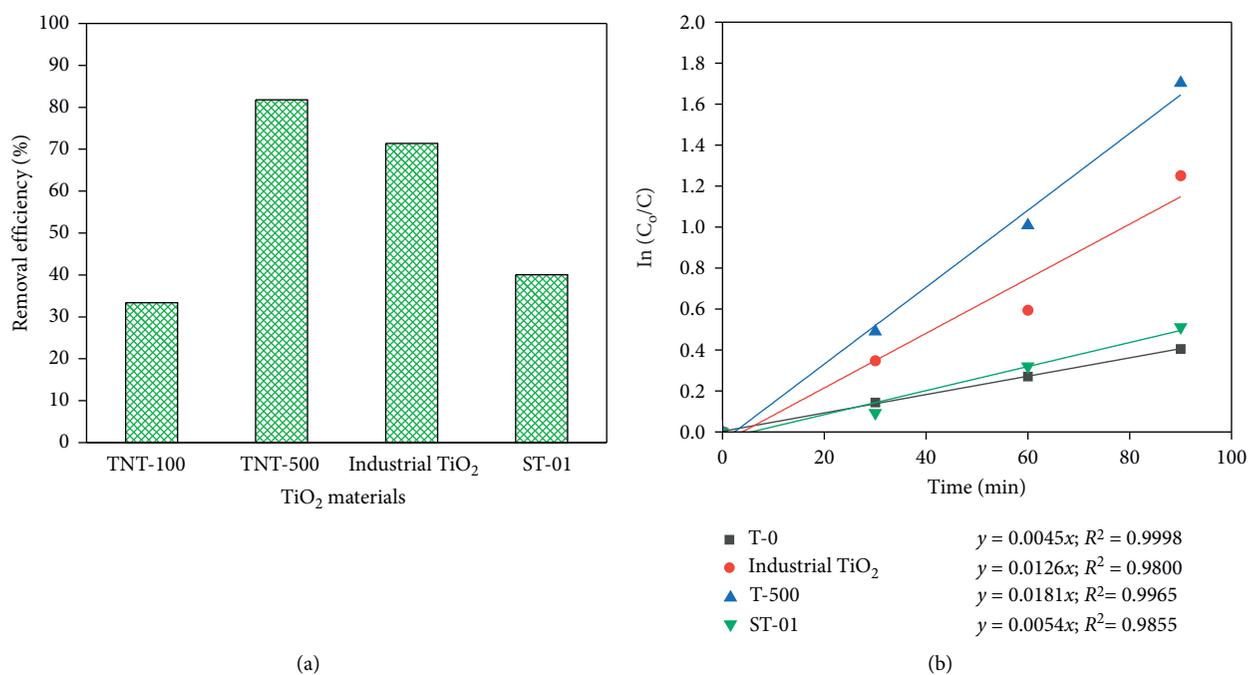


FIGURE 2: Procion MX removal efficiency (a) and pseudo-first-order kinetics fitting (b) of different TiO₂ materials (0.1 g of catalyst, pH 6.3, 1 UV-A light bulb, after 120 min).

anatase crystal phase, which could be due to the agglomeration of tiny particles and the high recombination of electron-hole in the photocatalyst with tiny particle size. Finally, the TNT-500 was slightly better than industrial TiO_2 for PMX removal, possibly due to its similar material properties (e.g., particle size, surface area, and anatase crystallinity). The slightly better activity of TNT-500 could be attributed to its 1D structure (i.e., nanorods), which is more efficient for charged carriers transfer, thus reducing the electron-hole recombination and enhances the photocatalytic activity.

Kinetics of PMX photodegradation using different TiO_2 catalysts are presented in Figure 2(b). The value of the rate constant (k_{app}) represented the amount of PMX in water transformed over time. Results showed that the rate constant of PMX photodegradation with TNT-500 was the highest (1.82×10^{-2}), which was 1.5, 3.7, and 3.8 times higher than those provided by industrial TiO_2 , ST-01, and TNT-100 catalysts, respectively. This result could confirm the effectiveness of the TNT-500 photocatalyst to remove PMX and this photocatalyst was applied for the next experiments.

3.2. Effects of the Reaction Time. Figure 3 presents the effect of reaction time on the PMX photodegradation using TNT-500. The color of water decreased significantly over time in all three experiments. The degradation efficiency increased from $28.2 \pm 6.9\%$ after 30 min to $75.5 \pm 2.3\%$ after 90 min of reactions. After 90 min, water color reduction was achieved in all experiments to satisfy the national technical regulation on industrial wastewater (QCVN 40:2011/BTNMT, Column A). Therefore, the reaction time of 90 min would be run in the next experiments. Further prolonged reaction time might not be preferred due to interference effects of surface sorption phenomena on the photocatalytic process [37, 38]. The increased irradiance times could favor the adsorption of the dyes and their intermediates on the catalyst surface and may reduce the removal efficiency of PMX. Moreover, a prolonging of the irradiation time could also accelerate the nanoparticle aggregation and results in the reduction of TiO_2 reactivity [39]. Consequently, the degradability of dye reduced because of the less availability of active sites on the catalyst surface for dye adsorption [40].

3.3. Effects of the Catalyst Concentration. For large-scale treatments, the amount of catalyst could be an economic issue affecting photodegradation rates. Experiments were conducted with different amounts of TNT-500, from 0.025, 0.05, 0.1, 0.15, 0.2, and 0.25 g in 2 L synthetic wastewater (i.e., at concentration of 12.5, 25, 50, 75, 100, and 125 mg/L, respectively) for 90 min (Figure 4). Results showed that the amount of catalysts was positively correlated with degradation efficiencies. The degradation efficiency was highest (95.3%) with 125 mg/L of TNT-500 and lowest (54.5%) with 12.5 mg/L of TNT-500. Particularly, in the range from 75 to 125 mg/L of TNT-500, reaction rates were slightly improved. By increasing the catalyst amount, the number of surface active sites available for PMX adsorption was expected to increase [26]. The overoptimum catalyst amount, however,

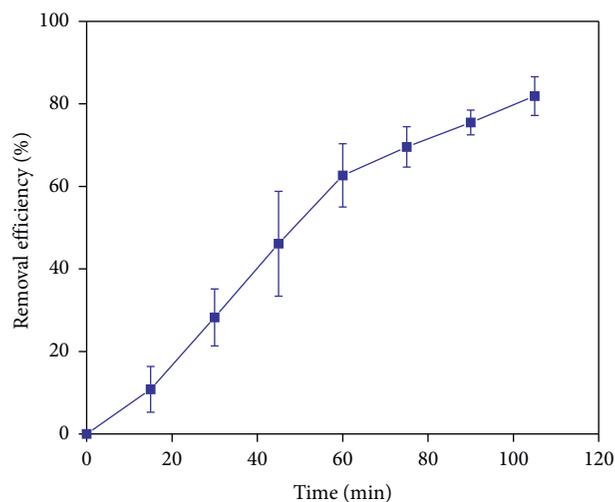


FIGURE 3: Removal efficiency of PMX using TNT-500 by time (0.1 g TNT-500, pH 6.3, 1 UV-A light bulb, $n = 3$).

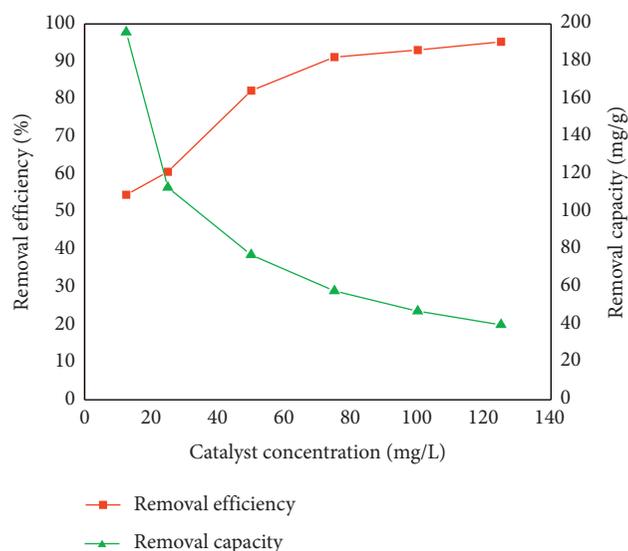


FIGURE 4: Effect of catalyst concentration (pH 6.3, 1 UV-A light bulb, 90 min of reaction time).

could result in counter effects. Firstly, the aggregation of nanoparticles and shielding effects might occur if the catalyst concentration was high [27, 28]. Secondly, a high concentration of nanoparticles induced the collision between ground-state and activated molecules and deactivating them [51, 61]. Thus, for the following experiments, the concentration of 75 mg/L TNT-500 was selected to optimize other operating conditions of the reactor. This concentration of photocatalysts was higher compared to that of Nguyen et al. [10], who applied a TNT concentration of 50 mg/L for PMX treatment with the initial color of 178–181 Pt-Co. However, this concentration was significantly lower than those of So et al. [52] with 500 mg/L of TiO_2 and 10 mM of H_2O_2 for the treatment of Procion Red MX-5B (at initial concentration C_0 of 40 mg/L), Sahel et al. [62] with 500 mg/L for Procion Red MX-5B (C_0 of 5–120 $\mu\text{mol/L}$), and Sari et al. [63] with

0.5–8 g/L of TiO₂ catalyst for Procion Red (C₀ of 150–300 mg/L). This lower optimum concentration of TNT found in this study would be due to the lower initial concentration of dye prepared (approximately 5 mg/L) since our target wastewater was with low dyes concentration after biological treatment.

Kinetic results showed that the amount of catalyst was also positively correlated with reaction rates. Degradation rates of PMX were highest at the highest catalyst concentration of 125 mg/L T-500 ($k_{app} = 3.0 \times 10^{-2} \text{ min}^{-1}$). This phenomenon was well known in heterogeneous catalysis reactions, where the reaction rates are exponentially increased with the increase of catalyst concentrations [29–31]. The irradiated photocatalyst could produce hydroxyl radicals, explaining the increase of reaction rates at higher catalyst concentrations [28]. However, a further increase in the amount of catalysts could reduce the degradation rate. The light scattering became more intensive and diminished the depth of photon infiltration [32, 33]. Beyond the optimum amount of catalysts, photodegradation activity was no longer positively correlated with the catalyst amount [34].

3.4. Effects of the Solution pH. It was reported that textile wastewater hardly met discharge criteria [64]. The pH of textile wastewaters usually varied in a broad range, representatively from 3.9 to 14 [65]. Hence, a set of experiments was conducted to evaluate the effect of pH variation, from 5.0 to 9.0, on PMX removal. As shown in Figure 5, the PMX photodegradation efficiency reduced from pH 5.0 to pH 7.0 and significantly increased to the highest value at pH 8.0, then again reduced at pH 9.0. It is stated that during photocatalytic reactions, varying pH of dye wastewaters essentially influenced either the adsorption and the breakdown of organic molecules [41, 42] or the active surface charge and the oxidation activity of catalysts [43]. The interaction between these factors affected differently on the dye removal, explaining the irregular effects of pH on the removal efficiency as observed in this study.

The ionization state of TiO₂ surfaces, of course, determined the adsorption of dye molecules, a crucial step before the photocatalytic oxidation occurred. Below the point of zero charges of the TNT-500 (i.e., $\text{pH}_{zpc} = 6.3$), TiO₂ surfaces are positively charged and possibly have a strong electrostatic attraction with negatively charged molecules [44]. Therefore, at pH 5.0, such as this experiment, the degradation efficiency was enhanced. The increased degradation rate of some azo dyes with pH decreases was observed elsewhere [45–47]. In addition, at low pH, the reduction by electrons in conduction bands may cause the cleavage of azo bonds [48]. At pH 7, the removal efficiency was lowest which could be due to this pH value being close to the pH of zero point charge of TiO₂ surface. Hence, electrostatic attraction between photocatalyst surface and negatively charged molecules (i.e., the Procion MX) was minimized. The lowest rate constant of the photodegradation reaction of a Procion red dye at pH 7 was also found in the work of Byrappa et al. [66] using Nd₂O₃ coated titania composite designer particulates as photocatalyst.

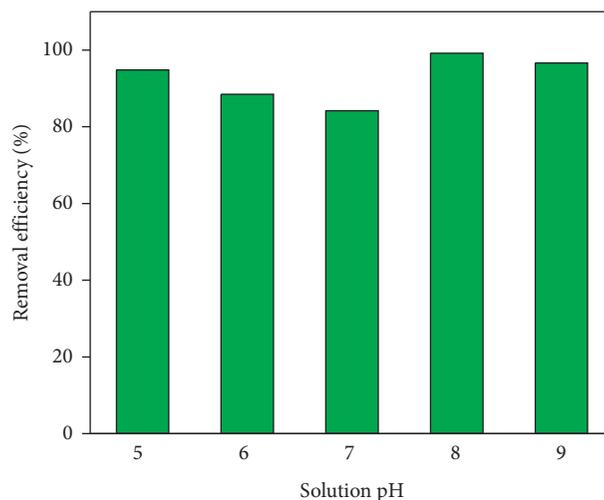


FIGURE 5: Effects of the pH solution (0.15 g TNT-500, 1 UV-A light bulb, 90 min of reaction time).

The contribution of pH on degradation kinetics of azo dyes was dynamic, following the attack of hydroxyl radical, the oxidation by the positive hole, and the reduction in conducting bands [48]. At higher pH, i.e., pH 8 and 9, hydroxide ions available on the TiO₂ surface were oxidized to produce hydroxyl radicals [49]. Consequently, hydroxyl radicals ($\bullet\text{OH}$) are predominant at alkaline conditions of this study, thus enhancing the process efficiency. The photocatalytic degradation of acidic and triazine-containing azo dyes presented consistent results [51, 52]. Nevertheless, at strong alkaline conditions (pH = 9–11), the degradation rate may be inhibited since hydroxyl radicals undergo very fast scavenging and they are incapable of reacting with dyes [50].

3.5. Effects of Light Wavelength and Intensity. Results of the experiment on PMX photodegradation with 1–3 UV-A lamps (8 W, Panasonic, Japan) and one UV-C lamp (8 W, Toshiba, Japan) are summarized in Figure 6. Compared to the reference condition without irradiation, the degradation efficiency of PMX with UV irradiation was higher after 90 min. Specifically, the degradation efficiency with UV-A irradiation (96.5–99.8%) was significantly higher than with UV-C irradiation (19.2%). Under UV-A irradiation, light intensities sourced from the experimental setup of one, two, and three UV-A lamps were 100, 200, and 300 W/m², respectively. The degradation efficiency was highest in the experiment with the strongest irradiance intensity. This is consistent with previous studies regarding the light intensity effect [51, 52]. Ollis et al. [53] stated that photocatalysis is a first-order reaction at low light intensities (0–200 W/m²) but a half order reaction at intermediate intensities (approximately 250 W/m²) or independent of the light intensities at high intensities. Particularly, the reactions predominantly involved electron-hole formation at low light intensities. However, as light intensities increased, electron-hole recombination is also engaged, resulting in the competence with electron-hole pair separation and lowering the reaction

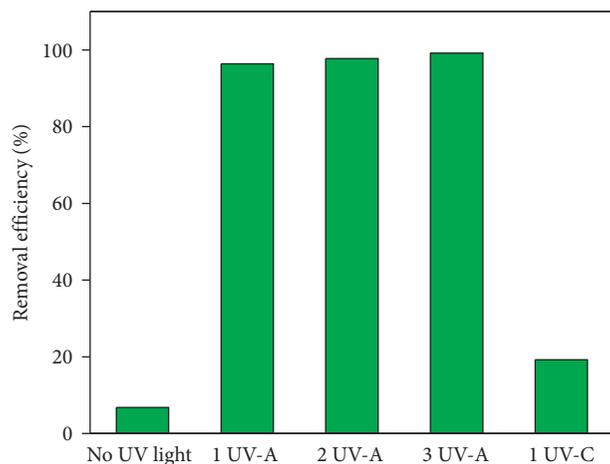


FIGURE 6: Effects of the irradiation wavelength and the irradiation intensity (pH 8, 0.15 g TNTs, 90 min of reaction time).

rate. Shen and Wang [54] reported that 90% of dye was removed at 82 W/m^2 and the removal efficiency insignificantly increased at 102 W/m^2 . Moreover, Chanathaworn et al. [55] reported a rhodamine B dye removal efficiency increased from 42.1 to 87.8% with light intensity from 23 to 114 W/m^2 after 90 min of irradiation, but the decolorization efficiency between 68 and 114 W/m^2 was not significantly different.

3.6. Effects of Additional Oxidants. The influence of oxygen on the PMX degradation during the UV/TiO₂ process was investigated. In a previous study, oxygen acted as an oxidizing agent to mineralize monochlorobenzene and reduced the reaction time needed for the complete decay [56]. Results showed that the degradation efficiency of PMX reduced with increased flows of aerated air (Figure 7). The highest degradation efficiency of PMX during the UV/TiO₂ process was 95.2% without any air supply, which decreased to 94.4% at the air supply rate of 0.5 L/min. The rate constant of the PMX degradation process was also reduced from $3.5 \times 10^{-2} \text{ min}^{-1}$ with 0.5 L/min of supplied air to $1.9 \times 10^{-2} \text{ min}^{-1}$ with 2.0 L/min of supplied air.

On the other hand, the addition of oxidants such as H₂O₂ was reported to enhance the photo-oxidation of azo dyes [52, 57]. H₂O₂ can produce hydroxyl radicals by reacting with photo-generated electrons. Because hydroxyl radical is either a strong oxidant or an electron scavenger, the electron-hole recombination at photocatalyst surfaces can be inhibited. Experiments with H₂O₂ showed that degradation efficiencies reduced with the addition of H₂O₂. The degradation efficiency decreased from 96.4% without H₂O₂ to 42.6% at the dosage of 1 mL of H₂O₂ (~5 mM) (Figure 8). The increase of H₂O₂ to 40 mL (~196 mM) continuously improved the degradation efficiency of up to 70.4%. The more adding of H₂O₂ up to 100 mL (~490 mM), however, gradually reduced the degradation efficiency to 49.6%. Kinetic data have confirmed the increased degradation rate with the addition of H₂O₂ in the range of 1–40 mL (~5–196 mM). The rate constant was highest with

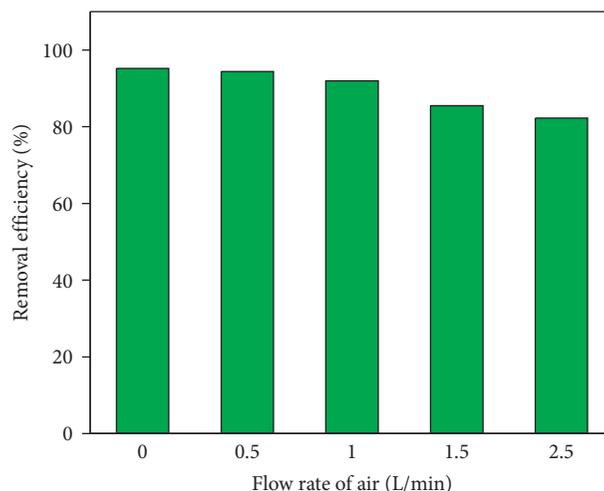


FIGURE 7: Effects of adding air at different flow rates (pH 8, 0.15 g TNTs, 1 UV-A light bulb, 90 min of reaction time).

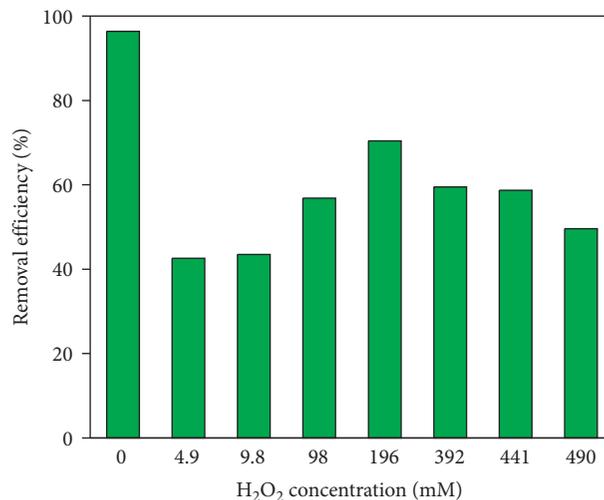


FIGURE 8: Effects of adding H₂O₂ (pH 8.0, 0.15 g TNTs, 1 UV-A light bulb, 90 min of reaction time).

the H₂O₂ amount of 40 mL (~196 mM), followed by a descending trend if the dosage of H₂O₂ continuously increased. Excessive amounts of H₂O₂ could impede the degradation due to H₂O₂ scavenging of valence band holes and •OH [48].

4. Conclusions

The photocatalytic oxidation of Procion MX 032 solutions using different synthesized forms of TiO₂ was characterized. Optimal operation conditions for the degradation of a 5 mg/L PMX solution at room temperature (30°C) were determined to be TiO₂ form of T-500, irradiation time of 90 min, TiO₂ concentration of 150 mg/L, initial pH solution of 8.0, light wavelength of UV-A > UV-C, and light intensity of 100 W/m^2 . Under these conditions, Procion MX was degraded in 90 min by more than 95% without the presence of additional oxidants such as H₂O₂ and O₂. These results

indicate that the photocatalytic oxidation with TiO₂ material can be used as a straightforward, competent, and economic treatment of textile wastewaters containing azo dyes. Further intensive study with characterizing TiO₂ after the photocatalytic reaction, adding radical scavengers, and identifying reaction intermediates is needed to propose the mechanism for the photocatalytic removal of PMX using TiO₂ material.

Data Availability

The experimental data used to support the findings of this study are included in the manuscript. The other data are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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