Photocatalytic Degradation of Textile Dyeing Wastewater Using Titanium Dioxide on a Fixed Substrate: Optimization of Process Parameters and Continuous Reactor Tests

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Abstract: Herein, a preparation of a mixed-phase titanium dioxide (TiO$_2$) thin layer on glass beads was developed using the modified spray method. This approach was determined to be affordable and easy to operate. Optimum conditions were investigated for the photodegradation of wastewater generated from textile dyeing by TiO$_2$-coated glass beads as a catalyst using the central composite design (CCD). An increase in the direct dye photodegradation rate was observed at lower direct dye concentrations when TiO$_2$ dosages were increased, and the initial pH value was decreased. The optimal conditions involving TiO$_2$ dosage, pH, UV intensity, and dye concentrations were 3 g/L, 5.0, 3000 µW/cm$^2$, and 50 mg/L, respectively, when administered at ambient temperatures. For the batch experiments, the direct dye removal efficiency at 93.7% was achieved within 24 h. The average direct dye removal efficiency was 67.8% and could be up to 80.2% when using a fixed-bed photocatalysis reactor during 30 d of continuous operation. The reused catalyst’s degradation efficiency was not significantly changed, indicating its capability for repeated reuse and the excellent stability of immobilized TiO$_2$ onto the glass beads. This study additionally found that high temperatures could increase the efficiency of color removal.

Keywords: fixed-bed reactor; fixed substrate; titanium dioxide; photocatalyst; textile dyeing wastewater; water pollution

1. Introduction

Traditional cultural practices that are at risk of extinction in many regions are preserved by artisan activity (such as the textile sector) which also creates jobs, particularly for women in developing countries [1,2]. However, the small-scale dyeing industry can generate a large amount of wastewater, which is frequently illegally released into the environment with inadequate or no treatment at all [3–5]. This highlights the need to develop and refine appropriate technology for textile dyeing wastewater treatment. An inexpensive and easy-to-operate treatment system is necessary for sustainable industrial wastewater management. With this technology, ancient cultural traditions can be preserved, while the sustainable preservation of the environment can also be achieved.

The conventional technologies employed for the textile dyeing wastewater treatment, such as chemical coagulation [6], the sonochemical treatment [7], and the utilization of...
aerobic and anaerobic ponds [4,8], are frequently associated with a significantly high investment cost and complicated operational techniques, rendering the owners of small dyeing facilities unable to afford such sophisticated treatment systems [9].

An alternate method of treating wastewater produced by the process of dyeing textiles is photocatalysis. Making use of light irradiation and a suitable photocatalyst such as titanium dioxide (TiO$_2$) [10], the majority of organic compounds are able to be oxidized to water, carbon dioxide, and other inorganic substances [11,12]. With this technique, the system can be illuminated by UV light produced by a UV lamp or sunlight [13,14]. Photocatalytic technology is a simple, low operating cost and is associated with a small reactor footprint [15]. Nowadays, it is common practice to immobilize a photocatalyst by coating a substrate with thin-film techniques because it is easier to separate the catalyst from the wastewater after the completion of the treatment [11]. Furthermore, treated effluent is able to be reused in the dyeing processes. As a result, zero water discharge is eventually achievable [15]. However, the conventional techniques for preparing TiO$_2$ thin film, i.e., the hydrothermal process [16] and the modified sol-gel method [17], are expensive and may not be appropriate for manufacturing on an industrial scale.

Accordingly, the modified spray method has been developed to prepare TiO$_2$ thin layers on glass beads [11]. This technology is inexpensive, simple, and capable of being upscaled for production. Specifically, it uses fewer chemicals and generates less hazardous waste [11,18] when compared to standard thin film preparation methods. It was also determined that the coating glass beads with TiO$_2$ retained stability at a high level even after the second application [11]. However, the optimum conditions for the photocatalysis of textile dyeing wastewater using the as-prepared catalyst have not yet been determined.

The objectives of this research were to determine the optimum conditions for the textile dyeing wastewater photocatalysis and to study the effects of initial pH, TiO$_2$ dosage, UV-A intensity, and dye concentrations on the organic dyes photodegradation rate under UV-A radiation using TiO$_2$-coated glass beads as a catalyst. A continuous column experiment was also conducted to study the possibility of using the as-prepared catalyst in full-scale applications. This will pave the way for future work that uses a lab-scale reactor, ultimately leading to the prototype of a low-cost system that could effectively be used in the small-scale dyeing industry.

2. Materials and methods
2.1. TiO$_2$ Coated Glass Beads Preparation

The spray media was a TTIP solution containing 1.04 M titanium (IV) isopropoxide. To prepare the solution, 20 mL of titanium (IV) isopropoxide (TTIP-97%; Sigma-Aldrich, Bangalore, India) was dissolved in 45 mL of isopropanol (C$_3$H$_7$O-99.8%; RCI Labscan Ltd., Bangkok, Thailand). Soda-lime glass beads with a diameter of 1 mm and a density of 2.1 g/cm$^3$ were used as substrates in this study. In order to eliminate any particles from the glass beads’ surface, they were cleaned by submerging them in 99.8% isopropanol for 30 min while being exposed to an ultrasonic wave.

The TTIP solution (65 mL) was sprayed onto 15.00 g of the glass beads using airbrush model HD-130 with a nozzle diameter of 0.3 mm, Taiwan. The entire spraying procedure required seven spraying cycles. Thereafter, based on visual inspection, the number of cycles was adjusted to confirm that the glass beads were completely coated with the TTIP solution (white color covered on glass beads). The glass beads were air-dried at ambient temperature for 10 min after each spraying session before the next cycle. After completing the entire process, the composite material was calcined at 700 °C for 3 h to form a mixed-phase of anatase and the rutile crystalline structure [11]. Glass beads were weighed before the spraying procedure and after completing the calcination process to quantify the amount of TiO$_2$ that coated on the composite materials. The average amount of TiO$_2$ in one gram of the composite material was 0.026 ± 0.001 g.
2.2. Synthesis of Textile Dyeing Wastewater

Direct Copper Blue 2B128 (C₃₄H₂₅N₅O₁₀Na₂S₂, molecular weight: 773.69 g/mol), which was supplied by a small-scale dyeing company located in Chiang Mai Province, Northern Thailand, was selected in this research study and named “Direct Blue”. Direct dyes are most broadly utilized in the industry due to their association with uncomplicated and straightforward dyeing procedures, short periods of dyeing cycles (around 3 h), low prices, and extensive market accessibility [19]. Direct Blue dye has been acknowledged as the preferred replacement for many natural dyes such as Hom (Strobilanthes cusia (Nees) Kuntze). This dye can also replicate the favorite blue color of traditional Northern Thai fabric referred to as Mo hom. This dye is also characterized as a small molecule anionic dye having single-component organic molecules [11].

Direct Blue was dissolved as the significant organic contaminant in the DI water to create synthetic textile dyeing wastewater at the desired concentrations (Tables 1 and 2). For example, 50.00 mg of Direct Blue was dissolved and adjusted to a final volume of 1.00 L in order to establish 50 mg/L of the synthetic direct dye wastewater. The synthetic dyeing wastewater used in this study only contained the direct dye to eliminate any other potential influence on the degree of color removal efficiency. The pH value of all involved synthetic wastewater was adjusted according to the desired values (Tables 1 and 2) using 1 M sodium hydroxide (NaOH-97.0% w/w; RCI Labscan Ltd., Bangkok, Thailand) or hydrochloric acid (HCl-37.0%; RCI Labscan Ltd., Bangkok, Thailand).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Uncoded Value</th>
</tr>
</thead>
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<tr>
<td>−α</td>
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<tr>
<td>TiO₂ dosage (g/L)</td>
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<tr>
<td>Initial pH</td>
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<tr>
<td>UV-A intensity (µW/cm²)</td>
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<tr>
<td>Dye concentration (mg/L)</td>
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Table 1. Range of process parameters tested in the batch experiments.

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<th>Parameters</th>
<th>Direct Dye Removal Efficiency (%)</th>
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<td>5.0</td>
</tr>
<tr>
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<td>5.0</td>
</tr>
<tr>
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<td>4</td>
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<td>5.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.75</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.25</td>
<td>9.0</td>
</tr>
<tr>
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<td>9.0</td>
</tr>
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<td></td>
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<td>2.25</td>
<td>9.0</td>
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<tr>
<td></td>
<td>9</td>
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<tr>
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</tr>
<tr>
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<td>12</td>
<td>2.25</td>
<td>5.0</td>
</tr>
<tr>
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<tr>
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<td>experiments</td>
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<td>3.00</td>
<td>7.0</td>
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</table>

Table 2. Experimental conditions tested in the batch experiments.
2.3. Photodegradation in Batch Experiments

All batch experiments were conducted in an opaque box (Figure 1) at ambient temperatures (27 ± 2 °C). In this study, central composite design (CCD) under response surface methodology (RSM) was applied to optimize the four significant variables, including TiO$_2$ dosage, initial pH, UV-A intensity, and dye concentration, respectively. The CCD consisted of $2^k$ factorial runs with $2^k$ axial runs and the number of center points, where $k$ is the number of factors or parameters [20]. The independent variables were coded to five levels for each experiment, including $-\alpha$, $-1$, 0, $+1$, and $+\alpha$, respectively (Table 1). The experiment used RSM to define the effects of TiO$_2$ dosage, initial pH, UV-A intensity, and dye concentration on the photodegradation rate of organic dyes. All experiments were conducted in duplicate.

![UV-A lamps diagram](image)

**Figure 1.** Diagram of batch-type experiments.

At this stage of the experiment, a plywood opaque box (width: 65, length: 85, and height: 65 cm) was employed. Eight 20-watt UV-A blacklight lamps (Philips TL-D) with a wavelength of approximately 365 nm were installed at the uppermost part inside the opaque box, as described in the study conducted by Chairungsri et al. [11]. The lab jack was adjusted to achieve the desired degree of UV-A intensity (Table 2), achieving maximum intensity of approximately 6000 W/cm$^2$. On the lab jack, a 1.5 L with a 17.5 cm diameter glass bowl was used as a batch reactor which was positioned in the middle inside the opaque box. The desirous amount of TiO$_2$-coated glass beads and 250 mL of textile dyeing wastewater, which varied initial pH and dye concentrations, were added to the batch.
reactor (Table 2). Thereafter, the reactor was exposed to UV-A radiation for 24 h. The samples were collected at 120, 240, 600, 1020, and 1440 min, respectively, to determine the pH and dye concentration.

The direct dye photodegradation rate was then determined through the pseudo-first-order reaction and was acknowledged as the response. Effects of the four variable factors on the photodegradation rate of direct dyes were analyzed using MINITAB 17.3.1 software at a 95% confidence level to develop the prediction equation and achieve optimum conditions. The model was validated by experimentally confirming the optimum condition over three replicates using the prediction equations.

A comparison of the effects of the different light sources, UV-A lamps and sunlight, was then made. In the sunlight case, the batch reactor was exposed to sunlight for around 6 h each day (10 a.m. to 4 p.m.) over a total period of 2 days (12 h) to achieve the peak amount of light intensity each day. It was found that the color removal rate efficiency improved when the reactor was exposed to sunlight rather than UV-A lamps. Thus, this study was committed to conducting even further investigations and found that temperature had a significant effect on the photodegradation rate. Therefore, a comparison of the experiments involving heated synthesis dyeing wastewater using UV-A lamps, non-heated synthesis dyeing wastewater using UV-A lamps, and non-heated synthesis dyeing wastewater using sunlight as a light source was made. The experiments required the use of a heater (IKA C-MAG HS 7, Staufen, Germany) attached to the batch reactor on the lab jack in order to maintain a temperature of 40 °C for the synthesis of dyeing wastewater.

2.4. Photodegradation Efficiency in Continuous Column Experiments

The doughnut-shaped fixed-bed photocatalysis reactor was made of polymethylmethacrylate and had a working volume of 3.2 L (height: 20, outer diameter: 15, and inner diameter: 10 cm). The reactor contained 50% by volume of TiO$_2$-coated glass beads (6 g of TiO$_2$). The bare glass beads (1050 g) were also added and mixed with the TiO$_2$-coated glass beads to maintain a similar level between the bed and wastewater. The fixed-bed photocatalysis reactor was positioned in the middle of the same opaque box used for the batch experiments. Three 40-watt UV-A blacklight lamps (WSFSWL Neoball-E) with a wavelength of approximately 365 nm were placed around the reactor inside the opaque box. The UV-A intensity (3000 µW/cm$^2$) was adjusted according to the distance between the UV-A lamp and the reactor. Synthetic textile dyeing wastewater was subsequently fed into the top of the reactor at a flow rate of 21 mL/h (HRT 24 h) using a peristaltic pump (Masterflex L/S, Cole-Farmer, Illinois, United States). The appropriate HRT (24 h) was calculated from the batch experiment at 100% direct dye photodegradation efficiency with a safety factor of two [21]. Three baffles were placed inside the reactor to prevent a short circuit. Details of the reactor and flow path are shown in Figure 2a,b. The effluent was then withdrawn from the top of the column from the inner chamber and analyzed for pH and dye concentration.
2.5. Analytical Methods

The X-ray diffraction (XRD) analysis was performed to analyze the composite materials with an X-ray diffractometer (D8 Advance, Bruker, Billerica, Massachusetts, United States) which employed a CuKα tube with $\lambda = 1.545 \text{ Å}$ as the X-ray source to assess the degrees of phase formation and phase transformation. Low vacuum scanning electron microscopy (LV-SEM, JEOL JSM 5910 LV, Tokyo, Japan) was used to analyze the elemental composition and morphology of composite materials through energy-dispersive X-ray spectroscopy (EDS). The pH was measured using an SG2 Mettler Toledo pH meter from the United States. The particle surface area was measured by the Brunauer–Emmett–Teller (BET) technique on Autosorb 1MP, Quantachrome, Austria. UV-A intensity was measured using a UVA/B Light Meter (Model 850009, Sper Scientific Ltd., Arizona, United States). Dye concentrations were employed to measure the absorbance at 564 nm using a Lambda
365 PerkinElmer UV/vis spectrophotometer, United States. The standard curve was used to interpret the concentration of the dye.

3. Results and Discussion

3.1. Characteristics of TiO$_2$-Coated Glass Beads

Calcining TiO$_2$-coated glass beads at 700 °C rendered optimum anatase (JCPDS 00-021-1272) and rutile (JCPDS 00-021-1276) ratio of 3.5:1 (Figure 3) along with a high degree of photocatalytic performance. According to the SEM results in Figure 4a, A high surface area of the TiO$_2$ particles that were coated on the glass beads’ surface was achieved (specific surface area: 16.73 m$^2$/g). The experiment also showed that the reused catalyst was still reserved the high surface area even after the second use (Figure 4b), indicating the reused catalyst was not changed in terms of degradation efficiency and the stability of the beads after exposed to the direct dye wastewater at pH 3–11. In addition, the study of Chairungsri et al. [11] found that there was no adsorption of Direct Blue dye on the TiO$_2$-coated glass beads under dark conditions.

![Figure 3. XRD patterns of immobilized TiO$_2$ particles coated on glass beads.](image)

![Figure 4. Characteristics of TiO$_2$-coated glass beads; (a) SEM images of virgin TiO$_2$-coated glass beads and (b) SEM images of used TiO$_2$-coated glass beads.](image)
3.2. Batch Experiment for Textile Dyeing Wastewater Treatment Optimization

3.2.1. Optimum Conditions for Photocatalysis of Textile Dyeing Wastewater

This study showed that the direct dye photodegradation rate was increased with the increase of the TiO$_2$ dosage and the decrease of the initial pH value (Figure 5). A lower degree of direct dye concentration yielded a higher direct dye photodegradation rate. A direct dye photodegradation efficiency of 93.7% was achieved from the experiment under optimum conditions, including TiO$_2$ dosage, initial pH, UV-A intensity, and dye concentrations of 3 g/L, 5.0, 3000 µW/cm$^2$, and 50 mg/L were used, respectively. With the dye concentration 50 mg/L, it was found that this is the average concentration detected in the real dyeing wastewater [22].

![Figure 5. Main effect plots showing the effects of the process parameters on the photodegradation rate of organic dyes.](image)

The results indicated that the TiO$_2$ dosage, initial pH, and dye concentrations were the significant factors ($p$-value < 0.05) (Figure 5 and Table 3). UV-A intensity within a range of 1000–4000 µW/cm$^2$ was found to have no significant effect on the direct dye photodegradation rate in the CCD experiments ($p$-value = 0.258). No significant two-way interaction effect was detected ($p$-value > 0.05) (Table 3). However, some parameters which existed in those two-way interactions are shown as significant factors in one-way interactions. Thus, they are still needed to be presented in the model. The surface plots (Figure 6) indicated that the maximum TiO$_2$ dosage yielded the maximum direct dye photodegradation rate. The equation used to predict the rate constant of direct dye photodegradation is shown in Equation (1) with $R^2$ and adjusted $R^2$ values of 79.98 and 66.21, respectively.

$$\text{Rate constant (}k\text{)} = 0.0692 + 0.1121(\text{TiO}_2) - 0.1113(\text{pH}) - 0.2496(\text{Dye})$$
$$+ 0.0196(\text{TiO}_2 \times \text{TiO}_2) - 0.0204(\text{pH} \times \text{pH}) + 0.1821(\text{Dye} \times \text{Dye})$$
$$- 0.0906(\text{TiO}_2 \times \text{pH}) - 0.0806(\text{TiO}_2 \times \text{Dye}) - 0.0331(\text{pH} \times \text{UV})$$
$$+ 0.1119(\text{pH} \times \text{Dye}) - 0.0406(\text{UV} \times \text{Dye})$$ (1)

where $k$ = rate constant (min$^{-1}$), TiO$_2$ = TiO$_2$ dosage (g/L), UV = UV-A intensity (µW/cm$^2$) and Dye = dye concentration (mg/L). It was also found that an increase in the photocatalyst dosage could increase the photodegradation rate due to the increase of active sites of the photocatalyst. According to previous studies, the nanoparticle TiO$_2$ (P25) had a better level of color removal performance (76–93% at 4 h) [11,23] than when TiO$_2$ was coated on the substrate. While many active sites were lost in comparisons from the interface between the catalyst and the substrate, the coated substrate offered less efficiency than the discrete
TiO₂ nanoparticles in terms of surface area per gram of the catalyst [11]. However, surplus amounts of the photocatalyst dosage could reduce the photodegradation rate as the light penetration is lessened [24].

Figure 6. Surface plots showing the effects of the process parameters on the photodegradation rate of organic dyes.

Table 3. Analysis of variance of the photodegradation rate of organic dyes under UV-A light using TiO₂-coated glass beads as a catalyst.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>p-Value</th>
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</thead>
<tbody>
<tr>
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<td>0.319</td>
<td>5.81</td>
<td>0.001</td>
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<td>Linear effects</td>
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<td>2.094</td>
<td>0.698</td>
<td>12.71</td>
<td>0.000</td>
</tr>
<tr>
<td>TiO₂</td>
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<td>0.302</td>
<td>0.302</td>
<td>5.49</td>
<td>0.032</td>
</tr>
<tr>
<td>pH</td>
<td>1</td>
<td>0.297</td>
<td>0.297</td>
<td>5.41</td>
<td>0.034</td>
</tr>
<tr>
<td>Dye conc.</td>
<td>1</td>
<td>1.495</td>
<td>1.495</td>
<td>27.22</td>
<td>0.000</td>
</tr>
<tr>
<td>Square effects</td>
<td>3</td>
<td>0.936</td>
<td>0.312</td>
<td>5.68</td>
<td>0.008</td>
</tr>
<tr>
<td>TiO₂×TiO₂</td>
<td>1</td>
<td>0.010</td>
<td>0.010</td>
<td>0.18</td>
<td>0.678</td>
</tr>
</tbody>
</table>
The result also showed that the direct dye photodegradation rate was improved when the initial pH value was low (Figures 5 and 6) [25]. This was because, at a low pH value, the TiO₂ surface was positively charged, while Direct Blue was sulfonated to provide aqueous solubility and became negatively charged due to its anionic state in nature. This helped the adsorption rate of the dye to occur more efficiently and resulted in the degradation rate being increased [26]. The TiO₂ surface charges in the acidic and alkali media are shown in Equations (2) and (3), respectively.

\[
\text{TiOH} + H^+ \rightarrow \text{TiOH}_2^+
\]  
\[
\text{TiOH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O}
\]

The results indicated that the dye removal rate decreased when the dye concentration was increased (Figures 5 and 6). This result contradicted the pseudo-first-order reaction principle, possibly because the high dye concentration reduced the amount of light penetration to the photocatalyst. Another study showed that increasing the initial dye concentration could result in a decrease in the overall photodegradation rate due to the fact that the degree of light penetration was lessened [24]. This, in turn, reduced the photodegradation rate and degree of efficiency. However, the dye removal rate was increased with the amount of dye higher than 180 mg/L (Figure 5). This result occurred possibly due to the changing of dye adsorption behavior at a high dye concentration, resulting in an increase of the adsorbed dye on the photocatalyst surface, rendering a high degree of photocatalytic activity as enough light was able to penetrate the closest surface during the process [27].

With the predicted equation generated from the CCD and RSM optimization experiments, the parameters in the equation can be used for designing the direct dye wastewater treatment systems in order to achieve the desired effluent concentration and dye removal rate by varying the value of parameters in the equation to predict the outcome. The predicted equation should also work with any working volume of direct dye wastewater, which will help with the design of a direct dye wastewater treatment system on a larger scale in future studies. However, any exceeded values for each parameter outside the scope in this study need further study to validate the predicted equation in order to increase the accuracy of the equation. Moreover, the reduction of the photodegradation efficiency in the continuous system could be expected due to the differentiation of the water velocity and bed thickness of the batch and continuous systems.
3.2.2. Validation of the Prediction Equation

TiO$_2$ dosage of 3 g/L was selected due to its potential to generate the highest photo-degradation rate. A direct dye concentration of 50 mg/L was selected based on the average concentration detected in the real dyeing wastewater according to personal communication with the dyeing company staff [22], while the UV-A intensity was fixed at 2500 and 3000 µW/cm$^2$. The direct dye removal efficiencies were equal to 94.7 ± 0.2 and 93.3 ± 0.3% (rate constant -0.0020 and -0.0019 min$^{-1}$) at pH values of 4.0 and 5.0, respectively, when UV-A intensity was 2500 µW/cm$^2$. These values were remarkably close to those calculated by the predicted equation (-0.0027 min$^{-1}$). The direct dye removal efficiency at pH 5.0 was increased slightly to 93.7 ± 0.3% (rate constant -0.0020 min$^{-1}$) when UV-A intensity was 3000 µW/cm$^2$.

3.3. Effect of Light Source on Photodegradation Rate

A higher color removal rate, which consumed half of the reaction time (92.3 ± 0.3% at 12 h) in the photocatalytic process, was achieved when sunlight was used instead of a UV-A lamp (93.7% at 24 h). The sunlight had a higher light intensity (approximately 5800 µW/cm$^2$) than UV-A lamp experiments (2500 and 3000 µW/cm$^2$). Although the UV-A light intensity in the range of 1000–4000 µW/cm$^2$ was found to have no effect on color removal efficiency, further study of the effect of other ranges of the UV-A light intensity on color removal is required. However, it was found that the temperature of the solution in the batch reactor was higher than that when the UV-A lamps were used. This was because sunlight contains other types of radiant energy which also emits invisible heat. Thus, further experiments were conducted using UV-A lamps with a reaction temperature of 40 °C to compare the results with those when sunlight was used. The results from the comparison experiments using different light sources (sunlight: 92.3 ± 0.3% at 12 h, UV-A lamps at 40 °C: 95.4 ± 0.2% at 12 h) showed a similar range of color removal efficiency, while the experiments using UV-A lamps at different temperature (ambient temperature: 74.7% at 12 h, 40 °C: 95.4 ± 0.2% at 12 h) showed a significant increase in the color removal rate when the temperature was increased, as is shown in Figure 7.

![Figure 7. Direct Blue dye photodegradation efficiency using batch experiments (● = Prediction, ■ = Sunlight, ▲ = UV-A at 40 °C and X = UV-A at ambient temperature).](image)

3.4. Fixed-Bed Photocatalysis Reactor for Treatment of Textile Dye Dyeing Wastewater

The outcomes of this study indicated that up to 80.2% of the direct dye could be removed (the average direct dye removal efficiency: 67.8%) when a fixed-bed photocatalysis reactor was used during 30 d of operation at the initial pH value, UV-A intensity and a dye concentration of 5.0, 3000 µW/cm$^2$ and 50 mg/L, respectively under ambient temperatures (Figure 8). As the operation continued, the initial pH slowly increased to around
5.0–6.0 during the process. According to the other study, the photodegradation efficiency of the fixed-bed reactor could be reduced from the calculated value 10–20% [21]. In addition, an increase in the bed layer thickness in the reactor (5 cm) might reduce the light penetration than that in the bed layer of the batch experiments (1 cm). The photodegradation effectiveness was lowered by approximately 25% in this investigation, owing to differences in water velocity and bed thickness between batch and continuous systems. In this situation, the higher the water velocity and bed thickness in the continuous system, the less light penetrates the water sample.

![Figure 8. Direct Blue dye photodegradation efficiency using fixed-bed photocatalysis reactor.](image)

A study of the photodegradation of the direct dye at high temperatures was also investigated. Synthetic textile dyeing wastewater at 60 °C was fed to the fixed-bed photocatalysis reactor (40 °C when reaching the reactor). It was found that the degree of dye degradation efficiency was increased from 67.8 to 78.2% when the operating temperature was increased from 27 to 40 °C. (Figure 8). This is in accordance with the study of Chairungsri et al. [11], which found that the dye degradation efficiency increased from 64.4 to 82.3% when increasing the operating temperature from 25 to 40 °C. Normally, a large storage tank is often needed to reduce the temperature of the dyeing wastewater before it is introduced into the system, such as in biological treatment. The size of the storage tank can be reduced if the dyeing wastewater is immediately fed into the reactor. With this technique, the dyeing wastewater, which typically has a high temperature (around 80 °C), could directly feed to the reactor and also accelerate the color removal efficiency.

While the dye degradation efficiency of the fixed-bed photocatalysis reactor of this study could make it to 82.3%, it could be noted that the fixed-bed photocatalysis reactor using TiO$_2$-coated glass beads prepared by modified spray method has a dye degradation efficiency higher than the photocatalytic fixed-bed bioreactor system using TiO$_2$ as a catalyst. From the study of Tiwari et al. [28], the integrated photocatalytic fixed-bed bioreactor system had an Acid Blue 113 removal rate of around 68.0% according to the graph provided in the study using photocatalyst dosage 2.0 g/L and pH 7.5 indicating the TiO$_2$-coated glass beads fixed-bed reactor is the alternative choice while provided the simpler and more efficiency in term of dye removal.

Remarkably, the reused catalyst was not significantly changed in terms of degradation efficiency and the binding between the glass bead surface and the immobilized TiO$_2$ particles (Figure 4a,b) during 45 d of operation in this present study revealing its capability to be reused. However, the leaching of catalytically active particles from the surface substrate could have possibly happened after multiple uses [29]. In this case, the used immobilized TiO$_2$ catalyst on the fixed substrate, which has less TiO2 (after leaching),
could be reused as a starting substrate for preparing TiO$_2$ nanoparticle immobilization. The deactivated catalyst is usually recovered through the simple regeneration process (re-calcination), which makes it unnecessary to dispose of the used photocatalyst after its exhaustion [29,30]. However, the further study about regeneration of the used catalyst is required.

The study of Chairungsri et al. [11] indicated that the as-synthesized catalyst offered a 3.6 times cheaper alternative in regards to the cost of achieving photocatalytic degradation efficiency when compared with P25. Additionally, P25 presents the problem of not being available for reuse. This occurs because certain difficulties exist with regard to separating TiO$_2$ from the treated wastewater [31,32]. The TiO$_2$-coated glass beads fixed-bed reactor employed in this study also represented a better alternative choice in terms of cost, with no additional costs accrued by the addition of other chemical substances used during the operation. With regard to the UV-A light source, the reactor could be exposed to sunlight in order to reduce the operational costs of running the UV-A lamps.

The results of this study showed that immobilized TiO$_2$ on a glass bead prepared using the simplified procedures of spraying and calcination had considerable levels of direct dye degradation efficiency when exposed to UV-A radiation. This research determined the optimum conditions for textile dyeing wastewater photocatalysis in order to further develop the prototype of a low-cost wastewater treatment system that could effectively be used in the small-scale dyeing industry. This wastewater treatment system seems to be a sustainability treatment system due to its simple operation, and as-prepared TiO$_2$-coated glass beads indicate excellent stability and can be reused for a long period of time. Furthermore, sunlight can be employed as a source of UV-A, which saves energy. Thus, this low-cost treatment technology could be afforded by the owners of small dyeing facilities. To avoid any other potential influences on color removal efficiency, synthetic textile dyeing wastewater was applied only to the direct dye in this study. Thus, future experiments should evaluate the effects of other ions, particularly sodium chloride and other organic chemicals that are typically introduced during the dyeing process. Moreover, further studies into textile dyeing wastewater photocatalysis (other direct dyes and other types of dyes) would still be necessary. Utilization of sunlight instead of a UV lamp should also be employed in further investigations for the purposes of energy conservation and to establish the potential benefits achieved from infrared heat that could enhance the degree of photodegradation efficiency. The real textile dyeing wastewater should be treated at the pilot scale using this treatment system. In addition, further study about the possibility of reusing the treated wastewater in the dyeing processes to achieve zero waste discharge is required.

4. Conclusions

The outcomes of the study indicated that the process of photocatalysis using TiO$_2$-coated glass beads as a catalyst could be employed in the treatment of textile dyeing wastewater. A direct dye photodegradation efficiency of 93.7% was achieved under optimum conditions from the batch-type experiment (TiO$_2$: dosage, initial pH, UV-A intensity, and dye concentrations of 3 g/L, 5.0, 3000 µW/cm$^2$, and 50 mg/L, respectively). Over a 30 d of operation, the average direct dye removal efficiency value of 67.8% was achieved when a fixed-bed photocatalysis reactor was used in the optimum condition with an initial pH value, UV-A intensity, and a dye concentration of 5.0, 3000 µW/cm$^2$, and 50 mg/L, respectively. The results indicated the capability of the glass beads to be reused and the excellent stability of the as-prepared TiO$_2$-coated glass beads. Additionally, it was found that a high temperature could accelerate the direct dye removal efficiency.

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