



Synthesis of TiO₂ Nanofiber-Nanoparticle Composite Catalyst and Its Photocatalytic Decolorization Performance of Reactive Black 5 Dye from Aqueous Solution

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Abstract. In this study, synthesis of TiO₂ nanofiber-nanoparticle composite photocatalyst was carried out and its photocatalytic decolorization performance was investigated. TiO₂ nanofibers were developed by electrospinning. The TiO₂ nanoparticle films were prepared by dipping the glass substrates into a sol solution made by sol-gel method. The TiO₂ nanofiber-nanoparticle composite was immobilized on glass plates and annealed at 500 °C. The effects of pH and catalyst loading were studied during a photocatalytic decolorization experiment using simulated dyeing wastewater containing Reactive Black 5 (RB5). The photocatalytic decolorization performance with 60 min of UV-irradiation time using the TiO₂ nanofiber-nanoparticle composite was found to be higher (94.4%) than that of the TiO₂ nanofibers (75.5%) and the TiO₂ nanoparticle catalyst (74.1%). An alkaline condition and high catalyst loading were found to be preferable to achieve optimum photocatalytic decolorization of Reactive Black 5 (RB5). The TiO₂ nanofiber-nanoparticle composite could be recovered after reusing multiple times through re-annealing at a high temperature. TiO₂ nanofibers based on a composite catalyst that is strongly immobilized on glass plates enlarges the prospect of the photocatalytic method as a compact, practical and effective advanced treatment process for effluents from textile wastewater.

Keywords: *decolorization; nanofiber-nanoparticle composite; photocatalytic; textile dyeing wastewater; TiO₂.*

1 Introduction

Reactive azo dyes are extensively used in cotton dyeing processing industries since recent years due to their superior performance. Unfortunately, the use of these dyes can pose a hazard to the environment due to aromatic rings in their azo molecular structure. It is known that 1-20% of azo dye is lost during the end

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processes of the dyeing and discharged in textile dyeing wastewater [1]. Textile dyeing wastewater usually contains 10-50 mg L⁻¹ of dyes in solution and has a black color. Such high concentrations could induce color problems in water streams [2]. The existence of color from textile wastewater treatment effluents in water streams is a major environmental issue, specifically in West Java, Indonesia [3] due to its non-aesthetical appearance and non-biodegradable characteristics, which can cause difficulties in biological treatment processes. In some cases, dyes are adsorbed onto biomass without being successfully degraded [4]. Coagulation-flocculation, a physico-chemical process, has been proven to be particularly effective in removing dye substances from water [5-6]. However, the aforementioned methods only transform the pollutants into a sludge, thus further treatment is needed, which may be costly.

Alternatively, advanced oxidation processes (AOPs) have been demonstrated to be effective in degradation and mineralization of organic dye pollutants through the generation and subsequent reaction of hydroxyl radicals ($\bullet\text{OH}$) [7-8]. Photocatalytic degradation by combining titanium dioxide (TiO₂) and UV light is considered a promising AOP for decolorization processes [9]. TiO₂ is a semiconductor with a high photocatalytic activity, is non-toxic, relatively inexpensive and has good stability in aqueous solution [10]. The advantages of utilizing a degradation process employing photocatalytic phenomena have been mentioned in several research publications. These advantages include: rapid reaction, less production of sludge, high reproducibility, and relatively low cost [7,11].

The past three years, the application of photocatalytic processes to remove dyes from water has been a topic of interest for several researchers. In 2014, photocatalytic degradation of Mordant Black 11 using ZnO nanoparticles and ultraviolet irradiation was studied by Miao, *et al.* [12]. A study in 2015 on removal of Reactive Black 5 using ozone as an oxidant showed promising results by an additional enhancement through the application of nano-sized copper oxide as catalyst [13]. This catalyst was attached to an amorphous carbon aerogel. Fenton reaction under UV light is another AOP technique that is commonly used in degrading dye in water. Fe-based amorphous alloys have high stability and can remove methylene blue [14] and Cibacron Brilliant Red 3B-A dyes [15] from water within 20 minutes. Jia, *et al.* [16] investigated methyl orange degradation using this material as catalyst combined with simulated solar light. A recent research on a photocatalytic method is ozonation with WO₃ as catalyst. The experiment showed that with this method also an active compound in an insect repellent, i.e. N,N-diethyl-meta toluamide (DEET), could be effectively removed from water [17].

The photocatalytic process is commonly performed in a batch slurry photoreactor operated with a TiO₂ suspension. Although several results on the effectivity of the TiO₂ suspension's performance have been reported [8,18], the use of this suspended photocatalyst remains unpractical due to the need of TiO₂ particle separation at the end of the photocatalytic processes. Another concern in employing a photocatalytic method is the limited depth of UV penetration after intense light absorption by the catalyst particles [9]. To overcome these issues, immobilization of the catalyst in various inert media is being developed intensively (e.g. carbon material and steel [19-20]). However, the fixation of TiO₂ on solid materials may reduce its photocatalytic efficiency [21]. Two known methods to increase photocatalytic efficiency are: (i) by decreasing the size of the catalyst particles to nanometer size to widen its contact area [21]; and (ii) by employing a composite technique using polymers [23] or nanofibers [24] to enhance the photocatalytic reaction.

In this study, a catalyst immobilization method employing a composite technique using TiO₂ nanofibers on glass plates as media was carried out. Application of TiO₂ nanofiber-based composite photocatalyst enlarges the active catalytic surface area and provides massive structures. Therefore, this method is considered an effective technique for enhancing the photocatalytic process and making it suitable for practical application [24-25].

The aim of this study was to explore the photocatalytic degradation performance of TiO₂ nanofiber-nanoparticle composite catalyst on the decolorization of simulated textile dye wastewater using Reactive Black 5 (RB 5) in a range of initial concentrations (10-50 mg L⁻¹). The kinetic behavior of the decolorization process, which follows the Langmuir-Hinshelwood model, was also investigated.

2 Materials and Methods

2.1 Preparation of TiO₂ Nanofibers, TiO₂ Nanoparticle Film and Composite Photocatalyst

TiO₂ nanofibers were prepared by electrospinning and immobilizing them on a surface of glass plates (25 mm x 75 mm). Optimization of the nanofiber structures was obtained by adjusting the operational parameters of the electrospinning technique (electric potential, flow rate and spinneret-collector gap). The electrospinning solution was made by mixing several compounds: titanium tetraisopropoxide/TTIP (1 g), ethanol (4 ml), acetic acid (1 g) and polyvinylacetate (1 g). The TiO₂ nanofibers on glass plates were covered by silicon rubber and annealed at a temperature of 500 °C for 60 min.

The TiO₂ nanoparticle films were prepared by dipping the glass substrates into a sol solution made by sol-gel method. The sol solution (3.5%) was composed of TTIP (58.6 ml) and ethanol (200 ml), then nitric acid (100 ml, pH 1.5) was added drop by drop to acidify the solution, which was stirred for 1 h and then continued at a slow stirring rate for 12 h. The TiO₂ nanofiber-nanoparticle composite catalyst was produced by slow dipping on glass plates annealed with the nanofibers into the nanoparticle solution, after which it was dried at 80 °C. The TiO₂ nanofiber-nanoparticle composite catalyst was re-annealed at a temperature of 500 °C for 60 min.

2.2 Characterization and Analysis

The surface morphologies and structures of the TiO₂ nanofiber, nanoparticle film and composite nanofiber-nanoparticle catalysts were characterized by scanning electron microscopy (JEOL, JSM 6360 LA). The composition and distribution of the TiO₂ nanofiber-nanoparticle catalyst composite was determined by energy dispersive X-ray spectroscopy (JEOL, JSM 6360 LA). Absorbance measurements for dye degradation analysis were performed using a UV-Vis spectrophotometer (Perkin Elmer Lambda 35). The pH of the solution was monitored using a calibrated pH meter (Schoot Gerate Handylab 1).

2.3 Photocatalytic Experiments

The photocatalytic experiments were performed in a laboratory scale photocatalytic batch reactor. The system consisted of a wastewater container with a size of 400 mm x 100 mm x 25 mm, completed with 3 x 15 W UV-C lamps (Vilbert and Lourmat) with wavelength (λ) of 245 nm (Figure 1). The glass plates (25 mm x 65 mm x 2.5 mm) covered with catalysts were arranged horizontally on the bottom of the wastewater container. The solution of simulated wastewater was pumped into the reactor through a peristaltic pump. C.I. Reactive Black 5 (RB5) azo dye (Sigma Aldrich) was used as dye reagent.

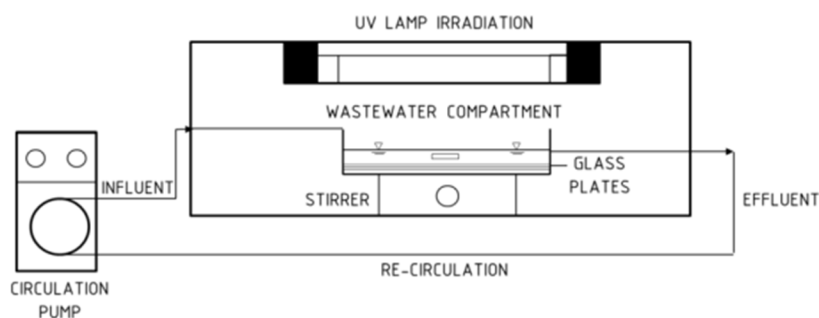


Figure 1 Illustration of the photoreactor.

The simulated dye wastewater solution was synthesized by diluting Reactive Black 5 dye in boiled deionized water (90 °C) for 30 min and then cooled at room temperature for 12 h as a hydrolysis process. A bare glass plate (blank) and glass plates covered with catalyst were submerged briefly in the wastewater compartment and kept in a dark room for 1 h to establish a state of adsorption-desorption equilibrium. A magnetic stirrer and a recirculation pump were used to homogenize the samples during the experiment.

2.4 Decolorization Kinetic Study

The pseudo-first order kinetic model as described in Equation (1), also known as the Langmuir-Hinshelwood model, is commonly used to represent decolorization kinetics. This model describes a heterogen photocatalytic process based on electron production by photoexcitation on a catalyst. The mathematical model in Eq. (1) is used to calculate the dye degradation reaction constant (k') [22].

$$\ln\left(\frac{C_0}{C}\right) = k't \quad (1)$$

where C_0 is the initial dye concentration (mg L^{-1}), C is the dye concentration at t (mg L^{-1}), t is the irradiation time, and k' is the degradation reaction rate constant (min^{-1}).

2.5 Effects of pH, Initial Dye Concentrations and Catalyst Loading

In order to investigate the effects of pH on the photocatalytic decolorization of RB5 using the TiO_2 nanofiber-nanoparticle composite catalyst, the photocatalytic experiment was performed at different pH values (3, 7, and 11). The contact time for this experiment was 120 min. The initial RB5 dye concentration was 10 mg L^{-1} and the TiO_2 loading was 2 g L^{-1} .

A test to describe the effects of initial dye concentration was carried out with 5 different initial concentrations of RB5 (10, 20, 30, 40, and 50 mg L^{-1}). The pH and the TiO_2 loading were adjusted to 11 (as optimum pH) and 2 g L^{-1} , respectively. The contact time was 120 min. Catalyst loading also plays a major role in the photocatalytic decolorization process. In order to examine its effect, the RB5 photocatalytic decolorization experiment using TiO_2 nanofiber-nanoparticle composite catalyst was carried out with TiO_2 loading at 2 g L^{-1} , an initial dye concentration of 10 mg L^{-1} and an initial pH of 11. A series of experiments on different amounts of catalyst loading of 0.5 to 2.5 g L^{-1} was also conducted.

2.6 Reuse of Catalyst Experiment

Additionally, the performance of reused catalyst was observed in this study. The TiO₂ nanofiber and composite (nanofiber-nanoparticle) catalyst were used repeatedly in a recirculation photoreactor. The catalysts were reused every 2 h for multiple cycles. The pH was adjusted to 11, the initial concentration of dye wastewater was 10 mg L⁻¹, and the TiO₂ loading was 2 g L⁻¹.

2.7 Mechanisms of RB5 Decolorization

To investigate the mechanisms of RB5 decolorization in water, an experiment using Gas Chromatography-Mass Selective (GC-MS) Detector Hewlett Packard HP 6890, MSD: Hewlett Packard 5973 was performed. The possibility of RB5 degradation pathways was analyzed by detection of existing compounds during the photocatalytic process.

3 Results and Discussion

3.1 Characteristics of the TiO₂ Photocatalysts

The TiO₂ nanofiber structure characteristics were varied depending on several parameters, including electrical potential, flow rate, and spinneret-collector gap adjusted for the electrospinning process (Table 1). The optimal condition, which produced a continuous and thin fiber of TiO₂ nanofibers, was obtained with electrical potential, flow rate, and spinneret-collector gap at 20 kV, 4 mL h⁻¹ and 15 cm, respectively. Achieving thin and continuous fibers, as shown in Figure 2a, was the objective of the nanofiber synthesis process. However, due to limitations of the electrospinning process conducted, the diameter of the TiO₂ fibers was adjusted from 500 nm to 1200 nm (Figure 2(a)). After annealing at 500 °C for 1 h, the diameter of the fibers decreased due to the volatilization of organic substances contained in the crystalline phases of the TiO₂ nanofibers.

An SEM image of the annealed TiO₂ nanofibers (Figure 2(b)) shows that the diameter of the fibers ranged from 200 nm to 500 nm. According Subbiah *et al.* [27], fibers with diameters in the range of 100-500 nm can be generally referred as nanofibers. The nanofibers were observed to be composed of rows of connected nanoparticles and formed chains. The annealed nanofibers contained many cross-links of chains, which presumably could enhance the mechanical stability of its structure on a micron scale [26]. The EDXS analysis showed that crystalline compounds of TiO₂ (up to 85%) and SiO₂ (up to 27%) dominated the nanofiber structure. Based on a stoichiometric calculation, the TiO₂ nanofibers on the glass plate surfaces were found to contain 2.13 mg TiO₂ cm⁻². The TiO₂ nanoparticles were densely distributed and created a film layer on the glass plate

surfaces (Figure 2(c)) with particle diameters smaller than 50 nm. The process of dip coating five times formed a dense nanoparticle structure. Based on the gravimetric measurement of the distribution of the TiO₂ nanoparticles on the glass plate surfaces, it was found there was an addition of 0.43 mg TiO₂ cm⁻² after each dip coating procedure.

Table 1 Electrospinning condition settings.

Electric potential (kV)	Flowrate (ml hr ⁻¹)	Spinner-collector gap (cm)	TiO ₂ nanofiber characteristic
10	1	15	Continuous slow
10	4	15	Discontinuous
15	4	15	Discontinuous
15	8	15	Not formed
20	1	15	Discontinuous
20	4	20	Discontinuous
20	4	15	Continuous, thin fiber
20	4	10	Continuous, thick fiber
20	8	15	Not formed

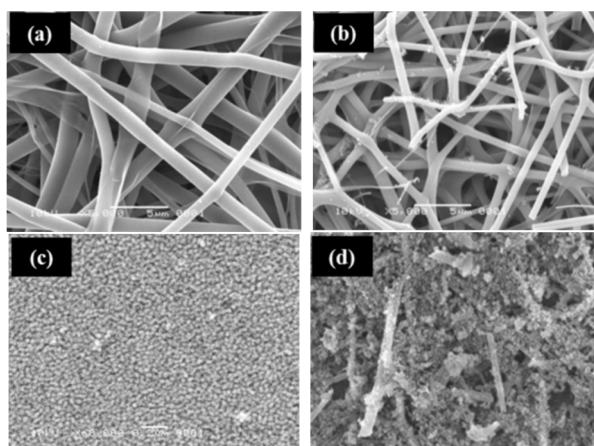


Figure 2 SEM images: (a) TiO₂ nanofibers as spun nanofibers (5000x); (b) TiO₂ nanofibers as annealed nanofibers (5000x); (c) TiO₂ nanoparticles (60000x); (d) TiO₂ nanofiber-nanoparticle composite (5000x).

The SEM image of the annealed TiO₂ nanofiber-nanoparticle composite catalyst in Figure 2(d) shows the dense TiO₂ nanoparticle structure on the surface of the TiO₂ nanofibers. The attachment of the TiO₂ to the glass plate, nanofibers and nanoparticles creates the composite structure of the catalyst. The TiO₂ and the SiO₂ as the major compounds in the catalyst structure create a TiO₂-SiO₂ composite system that provided excellent support for attachment of the catalyst material to the glass surfaces.

3.2 Photocatalytic Decolorization Experiments

The photocatalytic dye decolorization experiments were performed with UV irradiation, using the TiO₂ nanofibers, nanoparticle film and composite as catalysts. The experimental setup was: catalyst loading at 2 g L⁻¹, initial dye concentration at 10 mg L⁻¹ and pH of the simulated wastewater adjusted to 11. The peak absorbance for RB5 was found at 592 nm, which was hence considered the optimum wavelength (λ_{\max}) for the maximum band to determine the concentration of the dye using UV-Vis spectrophotometry.

As shown in Figure 3, the decolorization of the RB5 dye by adsorption without UV radiation did not significantly reduce the dye concentration in the simulated wastewater. It can be seen from the result that when UV was not utilized, the bare glass plate (blank) adsorbed 0.91% of the RB5 dye. The TiO₂ nanofiber and the nanoparticle film catalyst both adsorbed 1.82% of the dye, while the TiO₂ nanofiber-nanoparticle composite adsorbed 2.73%, i.e. more than the other catalysts.

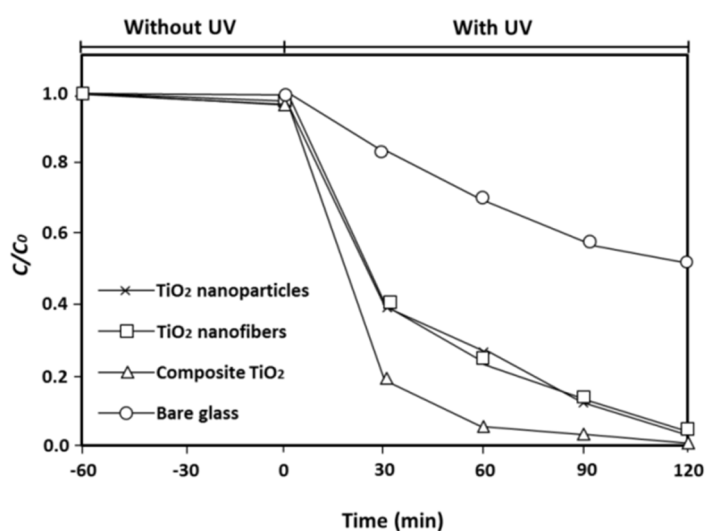


Figure 3 Photocatalytic dye (RB5) adsorption and degradation at time interval of UV irradiation (dye: 10 mg L⁻¹, pH: 11, TiO₂ loading: 2 g L⁻¹, C_0 : initial dye concentration, C : dye concentration at time t).

The adsorption capacities of a catalyst are affected by the number of reactive sites on the surface of the catalyst and the type of its pore structure [23,28]. Photocatalytic decolorization or dye degradation is an electron photoexcitancy in a semiconductor, followed by electron-hole pair production on the catalyst surface [29]. The SEM images in Figure 2 show that the TiO₂ nanofibers

created macropore structures, while the TiO₂ nanoparticles created nanopore structures. Macropores can induce a faster adsorption rate of the dye molecules, followed by diffusion of molecules into the nanopores for a longer time. The TiO₂ nanofiber-nanoparticle composite has a greater amount of macropores and nanopores, which may yield a higher dye adsorption rate than the other catalysts. On the other hand, the nanopore structure provides a wider surface area that could induce an excellent photocatalytic process. The greater amount of semiconductor area engages a more intensive process of photoexcitancy, which generates more oxidative species that play a major role in the organic dye degradation process [7].

As illustrated in Figure 3, after 60 min of contact time of UV irradiation, the bare glass plate (blank) without catalyst reduced the dye color in the simulated wastewater by 29.4%, while the TiO₂ nanofiber and TiO₂ nanoparticle film catalysts achieved 75.5% and 74.1% dye removal, respectively. A higher percentage of dye degradation was obtained by the composite catalyst with a removal efficiency of 94.4%, which was achieved in only 60 min. After 120 min of UV irradiation, all of the catalysts showed a significant dye decolorization (more than 95%).

The Langmuir-Hinshelwood model in Equation 1 can be used to describe the photo-oxidation kinetics of dyes as the adsorption of the dye materials that is considered in a heterogeneous photocatalytic oxidation process [22]. In this model it is assumed is that the oxidant sorption and the reductant sorption are both in a rapid equilibrium process. The rate-determining step of the reaction involves both species to be present in a monolayer at the interface [30]. The calculated kinetic rates (k') of the decolorisation process of RB5 are summarized in Table 2.

Table 2 Kinetic rates of decolorization process of RB5 for each catalyst variation.

Catalyst	Kinetic rate k' (min ⁻¹)
Without catalyst (bare glass)	5×10^{-3}
TiO ₂ nanoparticles	2.5×10^{-2}
TiO ₂ nanofibers	2.6×10^{-2}
TiO ₂ nanofiber-nanoparticle composite	3.9×10^{-2}

The kinetic rate of RB5 decolorization using the TiO₂ nanofiber-nanoparticle composite catalyst was $3.95 \times 10^{-2} \text{ min}^{-1}$, i.e. higher than that of the TiO₂ nanofiber catalyst ($2.60 \times 10^{-2} \text{ min}^{-1}$) and the TiO₂ nanoparticle film catalyst ($2.52 \times 10^{-2} \text{ min}^{-1}$). These results reveal that the composite of nanofibers and nanoparticles greatly enhanced the rate of decolorization process. The higher rate of the decolorization process indicates higher photocatalytic activity of the

TiO₂ nanofiber-nanoparticle composite due to its high active surface area. This finding also suggests that nanofibers are very useful as a basic structure for catalyst immobilization, which could improve the mechanical strength of the catalyst attachment.

3.3 Effects of pH

The experiment on the photocatalytic decolorization of RB5 by TiO₂ nanofiber-nanoparticle composite catalyst was performed at different pH values (3, 7, and 11). As shown in Figure 4, after 60 min of UV irradiation time, the RB5 dye concentrations at pH 3, 7 and 11 were decreased to 71.3%, 63.9% and 94.4% of their initial concentrations, respectively. The optimum RB5 dye degradation was obtained in alkaline condition (99.1%) after 2 h of contact time. It is clear that pH significantly affects the photocatalytic activity and in this experiment higher decolorization efficiencies were achieved in the following sequence: pH 11 > pH3 > pH7.

Photocatalytic degradation performance is affected by the charge on the TiO₂'s surface, the ion charge of the dye molecules, the adsorption of the dye into the surface of the TiO₂ and hydroxyl radicals formed [28]. Similar studies found that photocatalytic decolorization efficiency was increased at acidic pHs, which is strongly related to the increase in adsorption capacity, which is affected by the positive charge of the surface of the TiO₂ [26,31-32]. However, several studies [28,33] mention that the adsorption of a dye in an aqueous solution is not the only determinative factor in a photocatalytic degradation process.

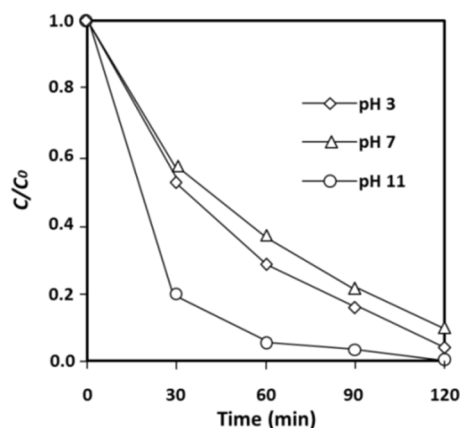


Figure 4 Effect of pH on photocatalytic decolorization of RB 5 at time intervals of the UV irradiation using TiO₂ nanofiber-nanoparticle composite catalyst (dye: 10 mg L⁻¹, TiO₂ loading: 2 g L⁻¹, C₀: initial dye concentration, C: dye concentration at time *t*).

The photocatalytic degradation process of RB5 investigated in this study was mainly due to hydroxyl radicals reacting with dye molecules. In a recent experiment, an alkaline solution yielded an effective condition for the decolorization of RB5. The production of hydroxyl radicals in an acidic condition is different from that in an alkaline condition. At an alkaline pH, the negative surfaces of the TiO_2 and OH^- ions in the solution act as efficient traps for the photogenerated holes and produce hydroxyl radicals [28]. The results of this study suggest that an alkaline pH is more favorable to enhance the reaction between $\bullet\text{OH}$ and RB5 dye molecules, which leads to an efficient decolorization process.

3.4 Effects of Initial Dye Concentration Variation

Figure 5 describes the effects of the initial dye concentration on the photocatalytic activity against interval of contact time of UV irradiation. The dye removal efficiencies decreased with the increase of the dye concentration in the simulated wastewater. When the dye concentration in the solution increased, more organic substances were adsorbed onto the TiO_2 surface, which may reduce the catalytic activity of the TiO_2 [8].

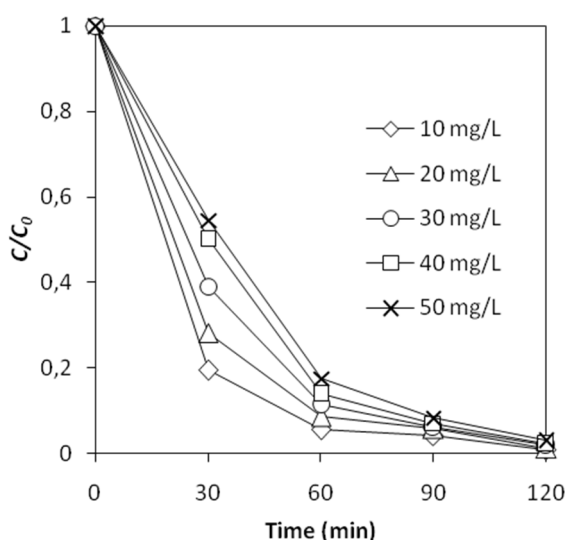


Figure 5 Photocatalytic decolorization of RB5 with different initial dye concentrations against time intervals of UV irradiation using TiO_2 nanofiber-nanoparticle composite catalyst (pH 11, TiO_2 loading: 2 g L^{-1} , C_0 : initial dye concentration, C : dye concentration at time t).

Increasing the dye concentration in the solution decreased the path length of the UV irradiation and decreased the quantity of photons accepted by the catalyst

surface to inhibit the formation of •OH. Due to the small portion of •OH formed, the dye degradation performance slightly decreased. A certain amount of UV-light photons could be absorbed into the dye molecules rather than into the catalyst, which may also reduce catalytic activity [28]. Another possibility is the intervention of by-products that may be formed during the degradation process of the dye molecules [8].

3.5 Effects of Catalyst Loading Variation

Variation of the catalyst loading affected dye degradation efficiency as shown in Figure 6. The efficiency of the dye degradation process was increased, while the catalyst loading was also increased. The higher photocatalytic decolorization efficiency was achieved by the enhancement of the active photocatalytic surface area and the formation of hydroxyl radicals. As the formation of active surface area increases, more hydroxyl radicals can be produced and thus the reaction site between organic matters and these hydroxyl radicals also increases. These intense reactions therefore accelerate the dye degradation process. This phenomenon could be an advantage of immobilized catalyst systems compared to suspended systems. In a suspended system, a higher catalyst concentration does not contribute to an increase of reactive sites.

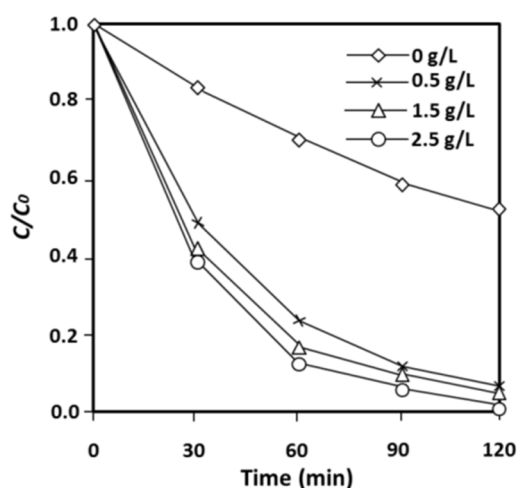


Figure 6 Photocatalytic decolorization of RB5 with different TiO₂ nanofibers-nanoparticles composite catalyst loadings against time intervals of UV irradiation (pH 11, dye concentration 10 mg L⁻¹, C₀: initial dye concentration, C: dye concentration at time *t*).

High opacity of the solution due to a high catalyst concentration reduces the light penetration and could lead to the reduction of the availability of active sites. Furthermore, the increase of the catalyst concentration favors

agglomeration of the catalyst particles, hence some parts of the catalyst surface become unavailable for photon absorption and dye adsorption, and the decolorization rate subsequently decreases [1,28,33].

3.6 Effects of Reusing on Catalyst

Reusing of the catalyst for five cycles was performed to test the decline of catalyst performance after multiple reuses. In this experiment, the TiO₂ nanofibers and the TiO₂ nanofiber-nanoparticle composite catalyst were used repeatedly in a recirculation photoreactor. Initially, the catalysts were used for 2 h to treat the RB5 contained in the dye wastewater. The catalyst was then recirculated and reused to treat a fresh batch of simulated wastewater with an initial dye concentration of 10 mg L⁻¹ for 5 cycles.

Figure 7 shows that photocatalytic performances of both recycled catalysts were slightly decreased after being reused. During the photocatalytic processes, the hydroxyl radicals form oxidized organic matters that are then adsorbed on the surface of the catalyst. Some undegraded organic matters remain, which accumulate on the surface of the catalyst and will reduce the photon absorption efficiency of the catalyst surface. Removal of organic substances on the surface of the catalyst through reannealing at temperature 500 °C for 30 min was found to be effective in recovering photocatalytic degradation performance of the catalyst, as shown in the last cycle.

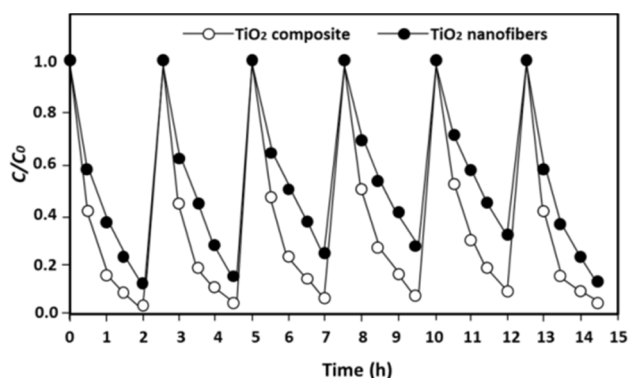


Figure 7 Photocatalytic decolorization of RB5 by reusing catalysts against time intervals of UV irradiation (pH: 11, dye concentration: 10 mg L⁻¹, TiO₂ loading: 2 g L⁻¹, C₀: initial dye concentration, C: dye concentration at time *t*).

3.7 Photocatalytic Degradation Mechanisms

Dye degradation processes commonly begin with the formation of radicals of O₂⁻, HOO• and OH•. When a catalyst is exposed to UV radiation with energy higher than the band gap energy (3.14 eV), the material will be electrically

conductive. Oxygen as an electron acceptor will be reduced by the promoted electrons to the conductivity band and forms pairs of electrons and holes. Identification of the main compounds produced in the RB5 degradation process was conducted using a GC-MS instrument. The chromatogram data in Figure 8 represent several compounds as fraction of the initial dye molecule structure. Figure 8 predicts the existence of at least 7 different compounds as degradation products of RB5. Compounds with a higher molecule weight only emerged in the early phase of the photocatalytic process and did not form for a longer time phase.

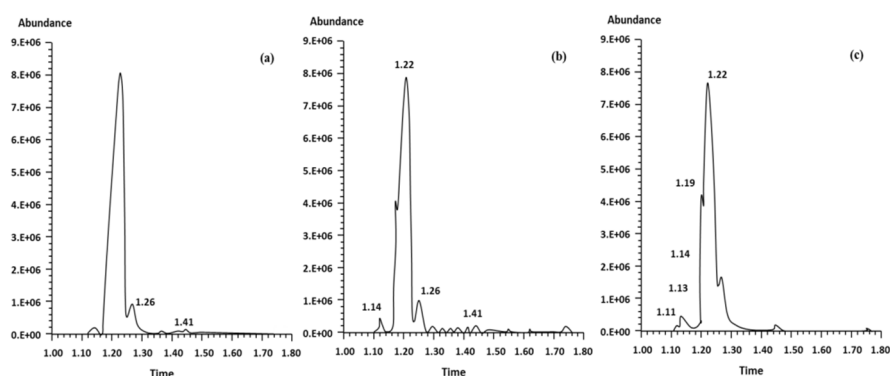


Figure 8 Photocatalytic decolorization of RB5 using TiO₂ nanofiber-nanoparticle composite catalys against time intervals of UV irradiation (a) 1 h, (b) 3 h, and (c) 5 h (pH: 11, dye concentration: 10 mg L⁻¹, TiO₂ loading: 2 g L⁻¹, C_0 : initial dye concentration, C : dye concentration at time t).

The intermediate or transformation products formed were naphthalene derivatives (as 2,7-diamino, 3,6,7-trihydroxy naphthalene and 1-sulfonate, 2-(4-aminobenzenesulfonyl), ethanol and benzene derivatives (3,6,8-trihydroxy naphthalene). Meanwhile, compounds with a lower molecule weight appeared to form in 3 to 5 h of irradiation time, indicating that the larger molecules were broken down into smaller ones through this photocatalytic process. The final transformation products formed were organic acids with a smaller molecular weight (i.e. phthalic anhydride, benzoate acid, phenol, and oxalate acid).

4 Conclusions

TiO₂ nanofibers (diameter 200-500 nm) developed by electrospinning and immobilization techniques on glass plates were found effective for use as photocatalyst for photocatalytic decolorization of simulated textile dyeing wastewater containing RB5. Immobilized TiO₂ nanofiber-nanoparticle composite catalyst was found to significantly enhance the decolorization process ($k' = 3,95 \times 10^{-2} \text{ min}^{-1}$) compared to TiO₂ nanofiber catalyst ($k' = 2,60 \times$

10^{-2} min^{-1}) and TiO_2 nanoparticle film catalyst ($k' = 2,52 \times 10^{-2} \text{ min}^{-1}$). Optimum process conditions for the photocatalytic decolorization of the simulated dye wastewater containing RB5 were obtained at high pH, with low initial dye concentration and high catalyst loading. The TiO_2 nanofiber-nanoparticle composite catalyst was found to be recoverable after several cycles of reuse through reannealing at a high temperature ($500 \text{ }^\circ\text{C}$). The experiment using GC-MS suggested that the final products of RB5 decolorization through this photocatalytic process were organic acids with low molecular weight.

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