PHOTOCATALYTIC DEGRADATION OF TEXTILE WASTEWATER CONTAINING REACTIVE BLACK 5 AZO DYE BY USING IMMOBILIZED TiO_2 NANOFIBER-NANOPARTICLE COMPOSITE CATALYST ON GLASS PLATES

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The photocatalytic degradation of textile wastewater containing Reactive Black 5 (RB5) azo dye was investigated by using immobilized TiO_2 nanofiber-nanoparticle composite catalyst on glass plates. The process was studied by monitoring the change in RB5 concentration, depletion in total organic carbon (TOC) and by determining the intermediate products using UV-visible spectrophotometry and gas chromatography-mass spectrometry (GC-MS) techniques. After immobilization, the composite shows higher photocatalytic activity for degradation of RB5 than that of nanoparticle thin-film layer under UV irradiation. Complete decolorization was achieved in 120 min, corresponding to organic degradation with a reduction in TOC after 300 min of UV irradiation by 91%. The photocatalytic degradation mechanism of RB5 was proposed based on the identified compounds by GC-MS technique, showing the destruction of the azo dye structure, which became smaller molecular mass compounds. The degradation slightly decreased after multiple reuse of composite catalyst during photocatalytic treatment. The recovery of its photocatalytic performance was obtained through reannealing.

Key Words : decolorization TiO_2 , nanofibers, photocatalytic, textile dyeing wastewater

1. INTRODUCTION

Textile dyeing wastewater has been known to contain considerable amounts of dyes, especially azo dyes and surfactants. Azo dyes with aromatic moieties linked by azo ($-\text{N}=\text{N}-$) chromophores, represent the largest class of dyes used in the textile dyeing industry¹. Around 1%–20% of dyes are lost during dyeing finishing process and discharged as textile dyeing wastewater². The existence of color from textile wastewater effluent in receiving water body has become a major environmental issue for a long time due to non-aesthetical appearance and unbiodegradable characteristics, which generate some difficulties in biological treatment processes. Coagulation, adsorption, and membrane filtration processes suc-

cesses fully remove dye substance^{3),4),5)}. However, these systems remove the color without destroying dye compound, and therefore cause further problems with sludge.

Photocatalytic technology has been widely studied since 1970 and is proposed as an effective method for rapid treatment of dyeing wastewater, it does not produce sludge, has high reproducibility and relatively low cost⁶⁾. Photocatalytic reactions are activated by absorption of a photon with an energy level that is equal to or higher than the band-gap energy of the catalyst⁷⁾. The reactions are initiated by charge separation due to the promotion of an electron (e^-) from the valence band of the catalyst to the conduction band, thus generating a hole (h^+) in the valence band. The photogenerated electrons could reduce the dye

or react with electron acceptors such as O_2 adsorbed on the catalyst surface or dissolved in water, to form superoxide radical anion ($O_2^{\cdot-}$). The photogenerated holes can oxidize the organic molecule or react with OH^- or H_2O producing $OH^\bullet$. The $O_2^{\cdot-}$ and $OH^\bullet$ are very strong agents that are able to degrade most azo dyes to the mineral end-products. Equations (1)–(8) summarize the general mechanism of photocatalysis^{2,7}.

In the literature reports, the most commonly used photocatalytic process is carried out in a slurry photoreactor that uses titanium dioxide suspensions^{8,9}. However, suspended photocatalyst systems have functional and economic disadvantages. The main problem with slurry photoreactors is the separation of TiO_2 nanoparticles after treatment. To solve this problem, immobilization of catalyst has been developed intensively by using various inert solid media. Different types of substrates such as glass¹⁰, zeolite¹¹, polymer¹² and activated carbon¹³ have been tested. Several common immobilization techniques have been studied including dip-coating, spray coating, sputtering and electrophoretic deposition⁶. This study attempts to apply a different immobilization approach, by using nanofiber structure as a tough base on glass plates and TiO_2 nanoparticle coating layer.

In our previous work, the synthesis of an immobilized TiO_2 nanofiber composite photocatalyst has been studied¹⁴. In this study, the photocatalytic degradation performance of the photocatalyst was investigated for the treatment of textile dyeing wastewater containing Reactive Black 5 azo dye in a laboratory photocatalytic reactor. The photodegradability of the catalyst, identification of intermediate products, photocatalytic degradation mechanism and reuse of photocatalyst were investigated.

2. MATERIALS AND METHODS

(1) Materials

Reactive Black 5 azo dye obtained from Sigma Aldrich, Germany was used. Titanium tetraisopropoxide, zinc acetate, polyvinylacetate, acetic acid, ethanol and nitric acid were supplied by Merck, Germany. Silicone rubber was obtained from Kleber-

mann, Germany. Demineralized water was purchased from PT. Brataco Indonesia. H_2SO_4 and $NaOH$ were obtained from Merck, Germany.

(2) Preparation of TiO_2 -immobilized nanofiber composite catalyst

Photocatalyst materials used in this study were developed based on a previous research¹⁴. The TiO_2 nanofibers were prepared by using electrospinning, attached on the configuration of glass plates (25 mm $\times$ 65 mm $\times$ 2.5 mm) as immobilization media. The optimized electric potential, flow rate and spinneret-collector gap in electrospinning were 20 kV, 4 mL/hr and 15 cm, respectively. The electrospinning solution was composed of titanium tetraisopropoxide (precursor), ethanol, acetic acid and polyvinylacetate. The TiO_2 nanofibers on glass plates were covered by silicon rubber and annealed at 500°C for 60 minutes. The dip coating technique was applied by dipping the glass plate into the nanoparticle solution made by the sol-gel method (composition: titanium tetraisopropoxide, ethanol, acetic acid and nitric acid) to create the immobilized TiO_2 nanoparticles film on glass plate. Similarly, the TiO_2 nanofiber-nanoparticle composite was made by dipping the glass plates containing annealed nanofibers into the nanoparticles solution. All developed catalysts above were again annealed at 500°C for 60 minutes.

(3) Photocatalytic experiment

Photocatalytic degradation experiments were carried out in a laboratory batch photoreactor with a volume of 500 cm³, using 3 $\times$ 15 watt UV-C lamps (Vilbert Lourmat, VL-315G), with 254 nm wavelength (Fig. 2). Glass plates covered with catalyst were arranged horizontally at the bottom of a wastewater chamber (400 mm $\times$ 100 mm $\times$ 25 mm). Magnetic stirrer and circulation pump were applied for aeration and homogenization of wastewater during the experi-

Fig.1 Molecular structure of Reactive Black 5.

Fig.2 Photoreactor.

ment.

Experimental conditions such as initial dye concentration (10 mg/L), pH (11), UV intensity (45 W) and catalyst loading (2 g/L) were applied in this study following the optimized parameters obtained in a previous research¹⁴.

(4) Kinetic analysis

Pseudo-first-order equation, which was simplified from the Langmuir-Hinshelwood equation (Eq. (9)), was used to calculate dye degradation reaction rate (k')¹⁰.

$$\ln\left(\frac{C_0}{C}\right) = kKt = k't \quad (9)$$

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

Fig. 3 shows the $\ln C_0/C$ of RB5 versus irradiation time. It also shows that decreasing the dye concentration follows a linear pattern towards the lapse of irradiation time, indicating that the pseudo-first-order kinetics is operative for the estimation of decolorization rate constant.

(5) Characterization and analysis

Surface morphologies and structures of immobilized TiO_2 nanofiber composite were characterized by *Scanning Electron Microscope/ SEM* (JEOL, JSM 6360 LA). Composition and distribution of composite TiO_2 nanofibers was determined by *Energy Dispersive X-ray Spectroscopy/ EDXS* (JEOL, JSM 6360 LA). UV spectral analysis was done by using a UV-Vis spectrophotometer (Perkin Elmer Lambda 35). Total organic carbon (TOC) measurements were carried out by Automatic TOC Analyzer (TORAY-TOC 100). The pH of the solution was measured by using digital pH meter (Schoot Gerate Handylab 1).

Hewlett Packard 6890 gas chromatograph with a 30 m (length) - 0.25 mm (diameter) - 0.25 μm (film thickness) HP-5MS capillary column coupled with

Fig.3 Pseudo-first-order decolorization rate of RB5.

a Hewlett Packard 5973 mass spectrometer (Hewlett Packard, US) was used for the GC-MS analysis. The GC-MS analysis was carried out using the following temperature program: 100°C for 2 min, 15°C min^{-1} up to 300°C and hold time of 2 min. The temperature of the injector and detector were 260°C and 230°C, respectively.

3. RESULTS AND DISCUSSION

(1) Characteristics of TiO_2 composite photocatalyst

The scanning electron microscope (SEM) image of the TiO_2 nanofibers on glass plate (**Fig. 4 A**) shows

Fig.4 SEM images: (A) TiO_2 nanofibers on glass plate (5000 $\times$); (B) TiO_2 nanoparticles on glass plate (60.000 $\times$); (C) TiO_2 nanofiber-nanoparticle composite on glass plate (5000 $\times$).

the predicted diameter of fibers ranging from 200 nm to 500 nm. The TiO₂ distribution on glass plates was determined stoichiometrically. The glass plates with TiO₂ nanofibers contain 2.13 mg TiO₂/cm².

The SEM image of TiO₂ nanoparticles attached on the surface on glass media (**Fig. 4 B**) shows a homogeneous structure and morphology, with the particle diameter in the range of 10–50 nm. The SEM image of the annealed TiO₂ nanofiber-nanoparticle composite (**Fig. 4 C**) shows TiO₂ nanoparticles attached to the surface of TiO₂ nanofibers. A dense structure of nanoparticles was formed by dip coating five times during its development. Based on gravimetric measurement, a catalyst distribution on the glass plate was found to be 0.43 mg TiO₂/cm² after a single dipping process. Therefore, the total TiO₂ mass distribution in the composite was 4.26 mg TiO₂/cm². The main composition according to EDXS analysis (data not shown) was TiO₂ (84%) and SiO₂ (12%) rather than other compounds, suggesting the formation of TiO₂-SiO₂ composite as the main catalyst structure on the glass media.

(2) Photocatalytic process performance of catalyst

The UV-Vis absorbance spectra of RB5 aqueous solution show that absorbance peak was found at 592 nm, hence it is considered as the optimum wavelength ($\lambda_{\max}$) in this experiment. Initial experiments were carried out along 2 hrs of 45 W-UV irradiation to evaluate decolorization of RB5 influenced by: (i) adsorption on catalyst without UV-light, (ii) self photolysis with UV-light and (iii) photocatalytic process by using immobilized TiO₂ nanoparticle and composite catalysts. The results are shown in **Fig. 5**.

Decolorization efficiency of RB5 caused by adsorp-

Fig.5 Decolorization of RB5: (1) Adsorption by composite (2) Self photolysis (3) Photocatalysis by TiO₂ nanoparticle catalyst (4) Photocatalysis by TiO₂ nanofiber catalyst (5) Photocatalysis by composite (Dye conc.: 10 mg/L, TiO₂ loading: 2 g/L, pH: 11, UV irradiation: 1 hr)

tion on composite catalyst surface without UV irradiation was only 2.7%. Self photolysis of RB5 achieved 47.2% of decolorization ($k' = 0.005 \text{ min}^{-1}$). Photocatalytic decolorization by using composite catalyst was found to be faster ($k' = 0.039 \text{ min}^{-1}$) than nanoparticles film ($k' = 0.025 \text{ min}^{-1}$) and nanofiber ($k' = 0.026 \text{ min}^{-1}$). Complete decolorization was achieved by using composite catalyst in 2 hours of 45 W - UV irradiation.

Adsorption of dye molecule on the surface of the TiO₂ catalyst was affected by the effective surface area and pores structure type¹⁶. Adsorption of dye on the catalyst surface seems to be higher in suspended catalyst than in conventional immobilized catalyst due to the larger surface area as reported in some research^{8,17}. However, the immobilized TiO₂ nanofiber-nanoparticle composite has the unique pores structure. The combination of macropores and nanopores in nanofiber-nanoparticle composite, gives a better adsorption of dye molecules compared to single nanofiber or nanoparticles layer. Whereas, the photolysis plays an important role in the decolorization of dyes when sufficient oxygen is available for photolysis reaction. During photolysis, the dye and the excited dye can be decomposed by homolytic cleavage into radicals. Therefore, oxygen can act as a photogenerated electron scavenger to provide O₂•⁻ for the decolorization of RB5 in the absence of a photocatalyst²⁰. The immobilized TiO₂ catalysts greatly show a high photocatalytic activity for the decolorization of RB5. The nanofiber-nanoparticle composite catalyst clearly exhibits an enhancement of photocatalytic decolorization performance compared to nanoparticle or nanofiber catalyst. High photocatalytic activity of the composite catalyst was also related to the larger active surface area.

Photocatalytic degradation process was then evaluated for the total duration of 5 hrs and measured by UV-Vis spectrophotometer at a wavelength 200–700 nm. The changes in the absorption spectra of RB5 dye solution during the photocatalytic process at different irradiation times are shown in **Fig. 6**. The absorbance spectra of RB5 shows a decline of the absorbance peak at wavelength around 590–610 nm, 300–320 nm and below 250 nm.

The decline of the absorbance peak at visual color wavelength indicates decolorization of azo dyes, which was accomplished faster compared to that of the absorbance peak at UV wavelength. Decoloration of azo dyes was related to the cleavage of nitrogen double bond of azo dyes, as the most reactive site from oxidative attack positive hole, hydroxyl radical and reduced by electron in the conduction band¹⁸. RB5 contains two azo bonds, therefore rapid decolorization of RB5 indicated that the chromophoric azo bond of dye molecule was destroyed immediately.

Fig.6 UV-Vis absorbance spectra of RB5 dye solution by time interval of UV irradiation (Dye conc.: 10 mg/L, TiO_2 loading: 2 g/L, pH: 11, UV: 45 W).

Under UV intensity of 45 W, complete decolorization was achieved at 120 min of irradiation while complete degradation occurred at more than 240 min. The degradation of the aromatic part of the dye molecule produced a number of intermediate compounds and the removal of these intermediates took a longer time.

The color of RB5 azo dye is the result of the interaction between an azo function ($-\text{N}=\text{N}-$) and two aromatic species. The decline in the absorbance peak at 590–610 nm may be attributed to the decolorization of RB5 due to the cleavage of azo bond. Whereas, the decline of the absorbance peak in the lower wavelength (300–320 nm and below 250 nm) could be attributed to the aromatic ring destruction attached to the $-\text{N}=\text{N}-$ group in the dye molecule²¹.

Fig. 6 shows that during the photocatalytic process, aromatic degradation in RB5 decreased more slowly than that of decolorization. The dye molecular structure of RB5 gives the characteristics of organic decolorization and mineralization kinetics. The numbers of azo bond in the dye molecular structure is known to affect the reaction rate of decolorization process; therefore the decolorization of RB5 was noticeably faster than that of mineralization. Mineralization of organic dye substances into CO_2 and H_2O required a longer time, due to the formation of reaction intermediates in the solution during the degradation of the dye. Generally, the degradation of dye is represented by the typical wavelength of naphthalene and condensed ring aromatics at wavelength of 300 nm and the benzene group at about 254 nm¹⁸.

The intermediates of some organic dye compounds can exist for a long time in nature and are toxic to aquatic life²⁰; thus complete destruction of dye intermediates is important. It is necessary to analyze the degree of mineralization of the azo dye to evaluate the degradation level applied under photocatalytic treatment. In this study, photocatalytic mineralization of RB5 by means of TiO_2 composite photocatalyst was monitored by TOC removal and changes in UV-Vis

Fig.7 Change in TOC of RB5 dye solution during photocatalytic treatment by time interval of UV irradiation (Dye conc.: 10 mg/L, TiO_2 loading: 2 g/L, pH: 11, UV: 45 W).

Fig.8 Change in pH of RB5 dye solution during photocatalytic treatment by time interval of UV irradiation (Dye conc.: 10 mg/L, TiO_2 loading: 2 g/L, pH: 11, UV: 45 W).

spectra. The change in TOC value reflects the degree of mineralization at the end of the photocatalytic process. As can be seen in **Fig. 7**, the TOC gradually decreased during interval of irradiation due to the time-related photocatalytic degradation to cleave intermediate compounds.

TOC removal after 300 min of 45 W-UV irradiation was 91%. It indicates that there is still a residual amount of organic compounds, consisting of low mass molecules such as aldehydes and carboxylic acids in the treated solution. As shown in **Fig. 8**, the depleted pH during the experiments revealed that at the end of the photocatalytic reaction, the dye was degraded to small molecules such as organic acids. The identification of degradation products during time interval of photocatalytic reaction in the next section may further explain further the mechanism of photocatalytic degradation of organic dye compounds.

(3) Identification and mechanism of degradation products and mechanism

The intermediates generated during the photocatalytic degradation process were analyzed by GC-MS

Table1 Degradation products identified by GC-MS during photocatalytic process.

Symbol	Compounds	Structure	Molecular weight	Sampling time (min)		
				60	180	300
A	2,7-diamino,3,6,8-trihydroxy naphthalene		207	√	√	
B	1-sulfonic,2-(4-aminobenzenesulfonyl) ethanol		281	√	√	
C	3,6,8-trihydroxy naphthalene		178		√	√
D	Phthalic anhydride		148		√	√
E	Benzoic acid		122			√
F	Phenol		94			√
G	Oxalic acid	(COOH) ₂	90			√

and identified by comparison with commercial standards and by interpretation of their molecular ions and mass spectrometric fragmentation peaks. Identifying the main aromatic metabolites resulting from RB5 decomposition was attempted. The species given in **Table 1** were considered as possible degradation products found by means of GC-MS analysis of samples collected after different times of reaction. It is obvious that by opening the aromatic rings of RB5, a wide range of cleavage compounds can be expected. Some intermediates could not be identified for various reasons: the limitations of the analytical technique, the insignificant accumulation in the medium or the quick oxidation of their derivatives⁶⁾.

Since decolorization happens very fast, the RB5 molecules were first decolorized in the bulk solution by photolysis and/or $O_2^{\bullet-}$. The fragments produced by the cleavage of the azo bond of the dye molecule must be the primary reaction intermediates. Then the process could shift from a decolorization reaction in the bulk solution to a surface degradation reaction, cleaving the naphthalene and benzene rings. The intermediates formed by the cleavage of azo bonds were adsorbed on the surface of the catalyst and then rearranged. The dye molecules adsorbed onto the catalyst

surface might be excited by positive holes. The photogenerated conduction band electrons were trapped by water or oxygen molecules, leading to the formation of radicals such as $O_2^{\bullet-}$, $HO_2^{\bullet}$ and $OH^{\bullet}$. These free radicals with a high oxidation potential were the predominant species that contributed to the degradation of the dye.

The possible mechanistic steps in the photocatalytic degradation of RB5 at pH 11 are proposed as follows: Cleavage of the azo bond seemed to occur first on the dye molecule and led to the formation of compounds A and B. The naphthalene derivatives (product A and C) could have been attacked by $OH^{\bullet}$ and when further oxidized became benzene derivative (product D) by the breakdown of the aromatic ring. On the other hand, product B could have been cleaved by the $h\nu$ mechanism and $OH^{\bullet}$ reactions to form benzene derivatives (product F). Benzene derivatives (product D and F) were degraded to smaller molecular organic acids such as benzoic acid (product E), and oxalic acid (product G) with further reaction. Finally, these aromatic and aliphatic by-products were mineralized to CO_2 and H_2O .

Fig.9 Effect of multiple reuse of photocatalyst on photocatalytic decolorization (120 min irradiation) and TOC removal (300 min irradiation) of RB5 at dye conc.: 30 mg/L, pH 11, TiO₂ loading: 2 g/L, Run 1: fresh catalyst, Run 2–5: reused catalyst, Run 6: reactivated catalyst.

(4) Effect of multiple reuse of catalyst on photocatalytic performance

The reuse of photocatalyst was investigated to evaluate its efficiency after multiple treatment use. TiO₂ composite catalyst was applied in a series of photocatalytic experiment to evaluate decolorization (120 min of UV irradiation) and TOC removal (300 min of UV irradiation) of RB5 dye solution. The result of the experiment (**Fig. 9**) shows that photocatalytic decolorization and TOC removal efficiency had average decrease of 1.3% and 2.2%, respectively. Decolorization rate constant (k') changed from 0.018 min⁻¹ to 0.015 min⁻¹ after 5 runs. Although photocatalytic performance slightly deteriorated during repeated use, it still remained sufficiently high in terms of decolorization.

The recorded catalyst deactivation could be explained as follows: The deposition of photo-insensitive hydroxides on the photocatalyst surface would cover its active sites and inhibit the transfer of photon, and therefore affects the production of active photocatalytic species. Moreover, the presence of adsorbed species would possibly change the dimension of the catalyst particles and reduce its performance²⁰. The reactivation of TiO₂ composite photocatalyst through heat treatment at 500°C for 30 minutes was found effective in recovering its performance close to the initial condition.

4. CONCLUSION

The photodegradation of textile wastewater containing RB5 azo dye in the presence of the immobilized TiO₂ nanofiber-nanoparticle composite catalyst under UV light irradiation was investigated. The immobilized TiO₂ nanofiber-nanoparticle composite on glass plates exhibited higher decolorization activity ($k' = 0.039$ min⁻¹) than that of the TiO₂ nanopar-

ticles film ($k' = 0.025$ min⁻¹) during the photocatalytic process. The results of UV-vis spectra changes, TOC depletion and formation of intermediates confirm that the photocatalytic process was effective for the complete decolorization and mineralization of the azo dyes. The attack of the (–N=N–) azo bonds contributes to the decolorization of RB5 as the initiative mechanism, followed by the cleavage of naphthalene and benzene rings. The degradation of RB5 to small molecules such as organic acids was indicated by the decline of pH during the photocatalytic experiments. TiO₂ nanofibers-based composite photocatalyst was reusable after several cycles of treatment through catalyst reactivation at high temperature.

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