PENENTUAN MASSA FOTOKATALIS DAN SUHU OPTIMUM PADA PROSES FOTODEGRADASI ZAT WARNA RHODAMIN B MENGGUNAKAN FOTOKATALIS TiO_2

DETERMINATION OF OPTIMUM TEMPERATURE AND PHOTOCATALYST MASS OF RHODAMINE B PHOTODEGRADATION PROCESS BY TiO_2 PHOTOCATALYST

Rizzha Arvian Diputra* and Rusmini
Chemistry Department, Faculty of Mathematical and Natural Sciences-Universitas Negeri Surabaya
correspondent : email : new.creator2008@gmail.com

Abstrak *Telah dilakukan penelitian tentang penentuan massa fotokatalis dan suhu optimum pada proses fotodegradasi zat warna Rhodamin B menggunakan fotokatalis TiO_2. Massa fotokatalis dan suhu optimum pada proses fotodegradasi zat warna Rhodamin B ditentukan dengan variasi massa 0 mg sampai 100 mg dan variasi suhu 30 ^oC sampai 60 ^oC. Fotodegradasi dilakukan dalam reaktor tertutup yang dilengkapi dengan lampu UV. Konsentrasi zat warna yang tersisa setelah fotodegradasi diukur dengan spektrofotometer UV-Vis. Kondisi maksimum pengukuran adalah pada panjang gelombang 553,40 nm. Hasil penelitian menunjukkan bahwa massa fotokatalis optimum pada proses fotodegradasi zat warna Rhodamin B sebesar 70 mg dan suhu optimum pada 50 ^oC.*

Kata kunci: massa fotokatalis, suhu larutan, Rhodamin B, TiO_2.

Abstract *The determination of optimum temperature and photocatalyst mass of Rhodamine B photodegradation process was studied using TiO_2 as catalyst. Optimum temperature and photocatalyst mass of Rhodamine B photodegradation process was determined by variation of mass 0 mg to 100 mg and variation of temperature at 30 ^oC to 60 ^oC. Photodegradation carried out in a closed reactor completed with UV lamp. The remaining of Rhodamine B concentration after photodegradation was measured by UV-Vis spectrophotometer. Maximum condition of measurement was at wavelength of 553,40 nm. The result showed that optimum photocatalyst mass of Rhodamine B photodegradation process was 70 mg and optimum temperature was 50 ^oC.*

Key Words: photocatalyst mass, solution's temperature, Rhodamine B, TiO_2

INTRODUCTION

The textile industry produces large quantities of non – biodegradable compound that contaminate the water environment. Rhodamine B is one of the dyes used in textile industry [1]. Rhodamine B ($C_{28}H_{31}N_2O_3Cl$) is one of the most important dyes of the xanthene group and is used in many industrial processes, such as paper dyeing and the production of dye laser [2]. This dye can interact with DNA [3] and cause damage in single strand of DNA in Chinese Hamster Ovary cells [4].

Because of the characteristic of Rhodamine B that show mutagenity, waste water treatment need to done. In an Environmental Protection Agency (EPA) study, eleven of the eighteen azo dyes passed through Activated Sludge Process untreated. While the physical processes, such as coagulation and adsorption, merely only transfer the pollutant from wastewater to another media and cause a secondary pollution [5].

One of the other waste water treatment is photodegradation using TiO_2 photocatalyst [6]. Photocatalytic degradation is considered a favoured, promising, cleaner, and greener technology for the removal of toxic organic and inorganic pollutants from water and wastewater [7]. Organic compounds such as halogeno-aliphatic hydrocarbon, halogeno-aromatic hydrocarbon, organic acid, coloring matter, nitro-aromatic hydrocarbon, substitute aniline, muhiring aromatic hydrocarbon, heterocyclic compound, hydrocarbon, hydroxybenzene, surface-active agent and pesticide can be changed into non-poisonous, decolored, inorganic compounds and then ultimately eliminated as pollutants [8]. Many semiconductor materials have been tested as photocatalysts but it is generally accepted that TiO_2, due to its low cost and high activity and stability under irradiation, is the most reliable material [9]. There are three types of crystal structure in TiO_2: anatase, rutile and brookite type. The band gap value for the anatase type is 3.2 eV, for the rutile type is 3.02 eV and for the brookite type 2.96 eV [10]. Photocatalysis over a semiconductor oxide such as TiO_2 is initiated by the absorption of a photon with energy equal to, or greater than the band gap of the semiconductor, producing electron-hole (*e*-/*h*+) pairs [11].

$$TiO_2 + h\upsilon \rightarrow e^-_{cb}\,(TiO_2) + h^+_{vb}\,(TiO_2) \quad (1)$$

Reactions involving conduction band e^-

$$TiO_2(e^-) + O_2 \rightarrow TiO_2 + \bullet O_2^- \quad (2)$$

$$TiO_2(e^-) + \bullet O_2^- + 2H^+ \rightarrow TiO_2 + H_2O_2 \quad (3)$$

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + \bullet OH + OH^- \quad (4)$$

$$\bullet O_2^- + H_2O_2 \rightarrow \bullet OH + OH^- + O_2 \quad (5)$$

$$\bullet O_2^- + H^+ \rightarrow HO_2\bullet \quad (6)$$

$$TiO_2(e^-) + HO_2\bullet \rightarrow TiO_2 + HO_2^- \quad (7)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \quad (8)$$

$$2\,HO_2\bullet \rightarrow O_2 + H_2O_2 \quad (9)$$

Reactions involving valence band h^+

$$TiO_2(h^+) + H_2O_{ads} \rightarrow TiO_2 + \bullet OH_{ads} + H^+ \quad (10)$$

$$TiO_2(h^+) + 2H_2O_{ads} \rightarrow TiO_2 + 2H^+ + H_2O_2 \quad (11)$$

$$TiO_2(h^+) + OH^-_{ads} \rightarrow TiO_2 + \bullet OH_{ads} \quad (12)$$

Mass photocatalyst and solution temperatures is the variable that affect photodegradation process. Photodegradation process will decrease if run at lower temperatures and there is less of mass photocatalyst added. If there is a lot of mass photocatalyst added and run at the higher temperatures, it also decrease the photodegradation process [2]. So it is important to determine the optimum temperature and photocatalyst mass in the photodegradation process.

EXPERIMENTAL SECTION

Instruments

Some instrument than used in this research was: photodegradation reactors completed with UV lamp, magnetic stirrer, Whatman filter paper no. 42, UV-Vis spectrophotometer Shimadzu UV-1700, sentrifuge.

Materials

In this research, we use pure Rhodamine B, Rhodamine B sample was 10 mg/L, Aquademin as solvent and anatase TiO_2 powder.

Procedure

Rhodamine B Solution

Rhodamine B 1000 mg/ L in this research was made by solving 25 mg of Rhodamine B powder into 25 ml aquademin in volumetric flask. The amount of 25 ml of Rhodamine B 1000 mg/ L diluted until 50 ml with aquademin to make Rhodamine B 500 mg/ L. Rhodamine B 250 mg/ L was made by dilute 25 ml of Rhodamine B 500 mg/ L until 50 mL in volumetric flask. The amount of 100 ml of Rhodamine B 250 mg/ L diluted with aquademin until 250 ml to make Rhodamine B 100 mg/ L. From Rhodamine B 100 mg/ L, sample solution 10 mg/ L and Rhodamine B 1,2,3,4 and 5 mg/ L was made to make calibration curve.

Maximum Wavelength of Rhodamine B Determination

Maximum wavelength determination was made by measured 10 mg/ L Rhodamine B in UV-Vis spectrophotometer at wavelength between 400 – 600 nm.

Calibration Curve

Calibration curve of Rhodamine B dye was made with 1, 2, 3, 4 and 5 ppm of Rhodamine B dye. Maximum absorbance of Rhodamine B at 553,40 nm.

Determination Of Optimum Temperature And Photocatalyst Mass Of Rhodamine B Photodegradation Process

Photodegradation process was placed in closed reactor with UV lamp completed with magnetic stirrer and temperature regulator. Mass photocatalyst variation were 0, 30, 40, 50, 60, 70, 80, 90 and 100 mg. Every mass variation was running at 30, 40, 50 and 60^{o}C. After running until 4 hours, the solution was sentrifuge and filter by Whatman filter paper no. 42. The filtrat from filtration was measured by UV-Vis spectrophotometer Shimadzu UV-1700.

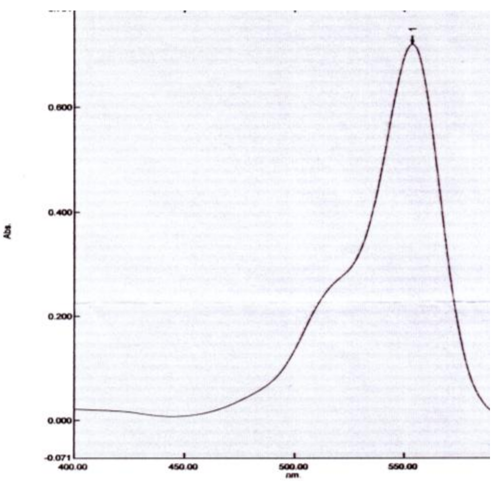
Measurement of Rhodamine B Concentration After Photodegradation Process

The measurement of Rhodamine B concentration was measured with UV-Vis spectrophotometer Shimadzu UV-1700 that plotted by calibration curve. The equation of calibration curve is Y = aX + b. Y is absorbance and X is concentration.

RESULT AND DISCUSSION

This research aim were studied the determination of optimum temperature and photocatalyst mass of Rhodamine B photodegradation process catalysis by TiO_2 photocatalyst. Variable at this research were photocatalyst mass and solution temperature, because both of this factor influence photodegradation process. This research was divided to some phase, maximum wavelength determination of Rhodamine B, making of standard calibration curve and photodegredation process of Rhodamine B. The results of maximum wavelength determination and the standard calibration curve further used to measure the concentration of Rhodamine B after photodegradation process.

The determination of maximum wavelength was needed because each solvent have different wavelength, in order not to be obtained two absorbance value at two wavelength and also minimized a big deviation. Besides, maximum wavelength could improve analysis effectivity. The result of measurement with UV-Vis spectrophotometer Shimadzu UV-1700 at wavelength between 400 – 600 nm was obtained wavelength like at picture 1.

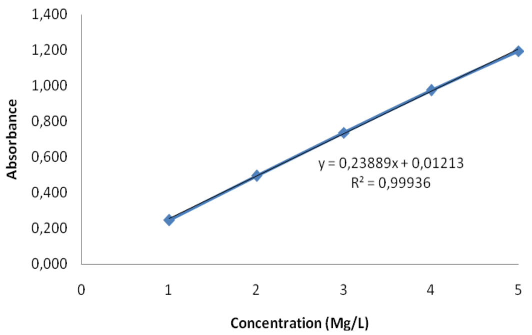


Picture 1. Spectrum of Rhodamine B

From the picture 1, it was known that maximum absorbance of Rhodamine B happened at wavelength 553.40 nm. the maximum indicate that Rhodamine B had green colour (as absorbent colour) and purple as complementary colors with wavelength range 500 – 560 nm.

This maximum wavelength (553.40 nm) had near result with Vasu research [12]. In his research, Vasu get maximum wavelength at 555 nm. Other research which support this result were research by Barka [13] and Jiao [2] which in its research yield maximum wavelength at 554 nm and 553.9 nm.

Standard calibration curve of Rhodamine B with measuring absorbance of Rhodamine B standard concentration 1 ppm, 2 ppm, 3 ppm, 4 ppm and 5 ppm at maximum wavelength 553.40 nm result the linear regression y = 0.23889x + 0.01213 with correlation coefficient 0.99936. Standard calibration curve of Rhodamine B shown in picture 2.



Picture 2. Standard Calibration Curve of Rhodamine B

The concentration of Rhodamine B before photodegradation process was 10.088 mg/L. Photodegradation process was placed in closed reactor with UV lamp completed with magnetic stirrer and temperature regulator. We use mass photocatalyst variation 0, 30, 40, 50, 60, 70, 80, 90 and 100 mg. Every mass variation was running at 30, 40, 50 and 60^{o}C. The concentration of Rhodamine B decreased by photodegradation process shown in table 1.

Table 1 show that photodegradation process has running without photocatalyst TiO_2 but less effective, only a few of Rhodamine B which was degradated. This matter indicate that photodegradation process of Rhodamine B can be done under UV light but the process was slowly. At this process, hydroxyl radicals formed by water photolysis process [14].

$$H_2O + h\upsilon \rightarrow H\bullet + \bullet OH \quad (13)$$

Photodegradation of Rhodamine B without photocatalyst TiO_2 has running in the presence of oxygen. The reaction mechanism in absence of titania and presence of oxygen includes the following possible steps [15].

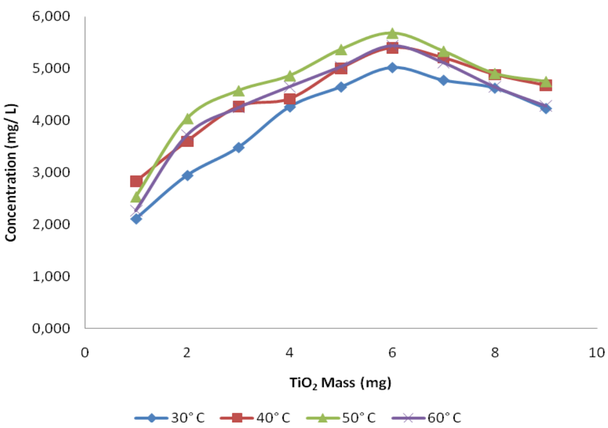
$$RhB + h\upsilon \rightarrow RhB^{*} \quad (14)$$

$$RhB^{*} + O_2 \rightarrow \bullet RhB^{*} + \bullet O_2^{-} \quad (15)$$

$$\bullet O_2^{-*} + H^{+} \rightarrow \bullet OOH \quad (16)$$

$$\bullet RhB^{*} + O_2 \rightarrow \text{Rhodamine} \rightarrow \text{Product} \quad (17)$$

In the mass variation, at all of temperature variation, concentration of degradated Rhodamine B increased till 70 mg of photocatalyst mass and then decreased shown in picture 3.



Picture 3. Concentration of Rhodamine B that photodegradated in photodegradation process with mass photocatalyst variation

Increasing of photocatalyst mass causes a lot of hydroxyl radicals was formed in photodegradation process [16].

$$TiO_2 + h\upsilon \rightarrow e^{-}_{cb}\,(TiO_2) + h^{+}_{vb}\,(TiO_2) \quad (18)$$

Hidroxyl radicals was formed when hole in valence bond react with water and hydroxide ion [17].

$h^{+}_{vb,s} + H_2O_{ads} \rightarrow \bullet OH_{ads} + H^+$ (19)

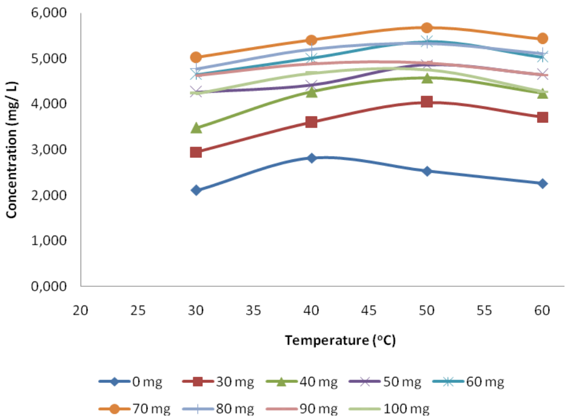
$h^{+}_{vb,s} + OH^- \rightarrow \bullet OH_{ads}$ (20)

Usage of greater TiO_2 cause concentration of degradated Rhodamine B was decreased. The decreased of Rhodamine B which was degradated because high vicosity of solution blocked of UV light by photocatalityc powder on the surface. So the formed of hydroxyl radicals at photodegradation process was decreased.

Table 1. Concentration of Rhodamine B degradated by photodegradation process

Temp (°C)	Photocatalyst Mass (mg)								
	0	30	40	50	60	70	80	90	100
30	2,109	2,945	3,483	4,264	4,647	5,021	4,777	4,625	4,233
40	2,822	3,599	4,270	4,418	5,006	5,405	5,210	4,888	4,678
50	2,536	4,040	4,574	4,864	5,368	5,681	5,334	4,905	4,751
60	2,264	3,717	4,242	4,648	5,032	5,434	5,109	4,644	4,277

Photocatalysis process with temperature variation shown in picture 4. Based to the picture, the concentration of degradated Rhodamine B was increase from temperature 30 - 50°C and decrease at temperature 50 - 60°C in general.



Picture 4. Concentration of Rhodamine B that photodegradated in photodegradation process with temperature variation

The increasing of Rhodamine B concentration that photodegradated because more collision possibility between molecule that happened. At the higher temperature, collision possibility between Rhodamine B molecule and hydroxyl radicals produced on photodegradation process was higher than lower temperature. The decreasing of Rhodamine B concentration that photodegradated because formation of H_2O_2 from hydroxyde radical was faster than the forming of hydroxyl radicals.

$H_2O \rightarrow H\bullet + \bullet O$ (21)

$H\bullet + O_2 \rightarrow HO_2\bullet \rightarrow \bullet OH + \frac{1}{2}O_2$ (22)

$2 \bullet OH \rightarrow H_2O_2$ (23)

$2 HO_2\bullet \rightarrow H_2O_2 + O_2$ (24)

The increasing and decreasing of Rhodamine B concentration that degradated in the photodegradation process with temperature variation shown at picture 4.

CONCLUSION

The conclusion from the research data and analysis were the optimum photocatalyst mass on photodegradation of Rhodamine B by TiO_2 photocatalyst was 70 mg and the optimum temperature on photodegradation process of Rhodamine B by TiO_2 photocatalyst was 50 ^oC.

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