CHEESA: Chemical Engineering Research Articles
ISSN **2614-8757 (Print)**, ISSN **2615-2347 (Online)**
Available online at: http://e-journal.unipma.ac.id/index.php/cheesa

Research Article

Photocatalytic Activity and Kinetic Study of Methylene Blue Degradation using N-Doped TiO_2 with Zeolite-NaY

Aktivitas Fotokatalitik dan Studi Kinetika pada Degradasi Metilen Biru menggunakan Material TiO_2 Doping N berpendukung Zeolit-NaY

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Received: 16/10/2020; Revised: 20/07/2021; Accepted: 28/07/2021; | ***doi:*** *10.25273/cheesa.v4i2.7646.75-81*

Abstract

Methylene blue is the most widely used dye in the industry and it is difficult to be degraded by the microorganism. This research aims to investigate the photocatalytic activity and effects of contact time on the photocatalytic degradation rate of methylene blue by TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY material based on the kinetic study. The Advanced Oxidative Process (AOP) method was used to degrade methylene blue. Furthermore, the AOP is a degradation process that uses semiconductor material such as TiO_2 or modification catalyst of TiO_2 to be TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY. The degradation of methylene blue with catalyst TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY were tested under UV light for 5, 20, 30, 40, and 50 minutes. The result showed that TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY had an excellent activity for degrading the dye, which reached up to 99% after 20 and 30 minutes reaction, respectively. Also, a kinetic study of methylene blue degradation on TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY showed the kinetic models were according to pseudo-second-order.

Keywords: kinetic; methylene blue; photocatalytic; TiO_2/Zeolite-NaY; TiO_2-N/Zeolite-NaY.

Abstrak

Salah satu zat warna yang banyak digunakan dalam industri adalah metilen biru yang sulit didegradasi oleh mikroorganisme. Penelitian ini bertujuan untuk mengamati pengaruh doping N pada material TiO_2 berpendukung zeolite-NaY dalam degradasi metilen biu. Metode yang digunakan untuk mendegradasi metilen biru adalah Advanced Oxidative Proccess (AOP). AOP adalah proses degradasi yang menggunakan material semikonduktor seperti TiO_2 atau modifikasi katalis TiO_2 seperti TiO_2/zeolit-NaY dan TiO_2-N/zeolit-NaY. Degradasi metilen biru dengan katalis TiO_2/Zeolit-NaY dan TiO_2-N/Zeolit-NaY diuji menggunakan sinar UV selama 5, 20, 30, 40, dan 50 menit. Hasil penelitian menunjukkan bahwa katalis TiO_2/zeolit-NaY dan TiO_2-N/zeolit-NaY memiliki aktivitas yang sangat baik untuk mendegradasi metilen biru yaitu mencapai 99% setelah 30 menit pada reaksi TiO_2/zeolit-NaY dan 20 menit pada reaksi TiO_2-N/zeolit-NaY. Studi kinetika pada degradasi metilen biru menggunakan TiO_2/Zeolit-NaY dan TiO_2-N/Zeolit-NaY menunjukkan model kinetika yang sesuai yaitu pseudo-second-order.

Kata kunci*: fotokatalitik; kinetika; metilen biru; TiO_2/Zeolit-NaY; TiO_2-N/Zeolit-NaY.*

1. Introduction

Dyes are used by textile industries to degrade naturally, although it may cause problems in the environment and contaminate the water ecosystems [1]. The most widely used dye in the industry is methylene blue. Although methylene blue is not strongly hazardous, it causes harmful effects in humans such as increased heart rate, vomiting, shock, Heinz body for motion, cyanosis, jaundice, quadriplegia, and tissue necrosis. Moreover, this dye in water affect plant life and is aesthetically unpleasant [2].

However, a promising method for dye removal is adsorption by porous material [3]. This method has limited adsorption capacity, unreusable adsorbent, and may release new waste to the environment. Also, the Advanced Oxidative Process (AOP) method, known as the photocatalytic degradation, is employed and a semiconductor is used to degrade the dye compounds. In addition, the AOP consist of reusable catalyst, low energy and cost, and the use of sunlight at low band gap energy catalyst as a source of irradiation [4][5].

The photocatalytic degradation method was conducted using a semiconductor as a catalyst. Therefore, methylene blue was degraded using TiO_2 as the semiconductor. Titanium Dioxide (TiO_2) is relatively inert compared to other compounds and has a band gap of 3.3 eV[6]. Also, it serves as a photocatalyst with a high photoactivity and stability [7], and the particle size affects the performance for the degradation of dye compound [8]. Furthermore, the photocatalytic activity of TiO_2 can be increased by reducing the band gap of TiO_2 [9]. Ansari *et al.* [8] showed that nitrogen doping on TiO_2 decreases band gap energy from 3.2 eV to 2.46 eV. Therefore, this research uses TiO_2 with N-doped as material to degrade methylene blue.

According to the study, addition of porous material can increase the photocatalysis of TiO_2. Furthermore, Andari & Wardhani [9] synthesized TiO_2-Zeolite which showed an increase in the photodegradation activity of methylene blue. Setyaningsih *et al.* [10] modified MnO_2 with Zeolite-NaY to obtain MnO_2/Zeolite NaY composite in order to develop catalyst in a catalytic converter system. The zeolite-NaY, with a pore size of 7.4 Å [11], is a promising porous material to combine with TiO_2-N because it is suitable with methylene blue molecules with a length and width of 13.82 Å and 9.5 Å, respectively [12]. The research aims to investigate the application of TiO_2 material with N-doping and zeolite-NaY in degradation of methylene blue.

The effects of contact time on the removal rate of methylene blue are important factors to consider during the photocatalysis process [12]. Behnajady *et al.* [13] investigated the contact time using the kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO. Consequently, the kinetic study on the degradation of methylene blue was achieved using pseudo-first-order, pseudo-second-order and diffusion with the equation as stated in a previous research by Kurajica *et al.* [14]. Therefore, the aim of this research is to investigate the photocatalytic activity and effects of contact time on the photocatalytic degradation rate of methylene blue by TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY material based on the kinetic study.

2. Materials and Method

2.1 Materials

The materials used in this research include sodium aluminate, sodium silicate, NaOH, TiO_2 anatase, ethanol 98%, and urea.

2.2 Synthesis of TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY material using impregnation method

Firstly, zeolite-NaY was synthesized using the hydrothermal method according to Setyaningsih *et al.* [10]. Furthermore, 1.2 g of TiO_2 or TiO_2-N was mixed with Zeolite-NaY and 10 mL of ethanol 96% was added as a dispersant and stirred for 5 hours. TiO_2/Zeolite-NaY or TiO_2-N/Zeolite-NaY was dried at 120 °C and both materials were calcined at 500 °C for 5 hours. Also, a photodegradation test was carried out at room temperature and at different times.

2. 3 Photocatalytic activity test

The photocatalytic activity testing was carried out on the TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY. Subsequently, 50 mg of each catalyst (TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY) was added to 20 mL methylene blue 20 ppm solution in 2 beakers. The methylene blue and catalyst were given a UV radiation (UV lamp 8 W) for 3 hours.

After UV radiation, the performance of TiO_2/zeolite-NaY and TiO_2-N/zeolite-NaY were tested at different times. The photocatalytic activity was tested during 5, 20, 30, 40, and 50 minutes under UV radiation to determine the kinetic reaction. Figure 1 showed the reactor design for the photocatalytic activity test. The concentration of methylene blue was measured using a UV-Vis spectrophotometer with a maximum wavelength of 664 nm at room temperature (30 °C). However, equation (1) was used to determine the efficiency of methylene blue degradation with C_0 and C_t as the initial concentration and residual concentration, respectively.

$$Efficiency\ (\%) = \frac{C_o - C_t}{C_o}\ x\ 100\% \quad \textbf{.....(1)}$$

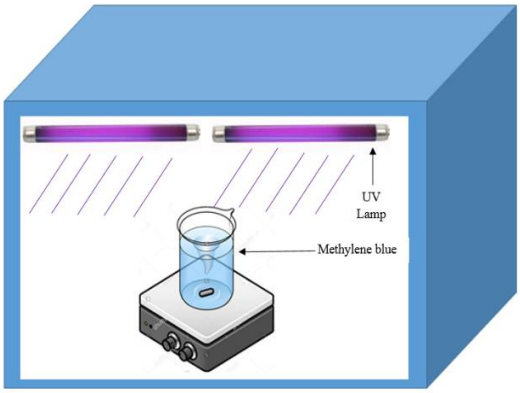

Figure 1. Reactor design of photocatalytic test

3. Result and Discussion

TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY were used as catalysts in methylene blue degradation. The purpose of the research was to observe the effect of contact time in the degradation of methylene blue. Figure 2 represents the degradation efficiency of methylene blue as a function of contact time using TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY. During 5 minutes reaction, TiO_2/zeolite-NaY and TiO_2-N/zeolite-NaY degraded methylene blue upto 96.40 and 97.20%, respectively. Moreover, it is promising in the industrial sector where dye treatment is very fast and cheap. Consequently, after 20 and 30 minutes of reaction for TiO_2-N/Zeolite-NaY and TiO_2/Zeolite-NaY, respectively, up to 99% degradation efficiency was reached. Therefore, the degradation efficiency

increases with reaction time until the dye is completely degraded.

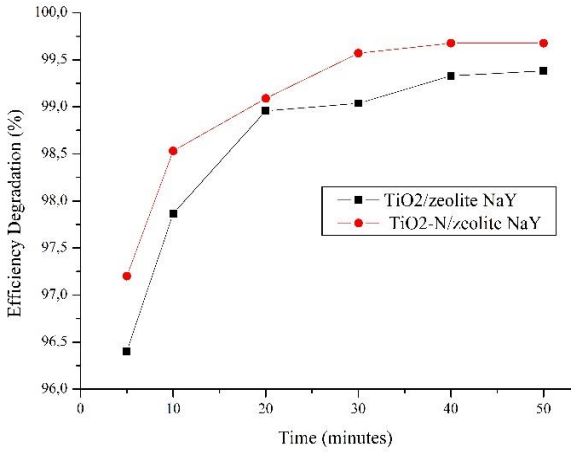

Figure 2. Degradation efficiency of methylene blue at different time

The kinetic study of methylene blue degradation was simulated using the pseudo-first-order with equation (2) [15], pseudo-second-order with equation (3) [16], and intraparticle diffusion with equation (4) [17]. Where, k_f is pseudo-first-order constant (min^{-1}), k_s is pseudo-second-order (g/mg.min), k_{id} is intraparticle diffusion constant, q_t is the amount of methylene blue taken up by each sample per unit mass (mg/g) at any time t and q_e is the amount of methylene blue at equilibrium (the total removal amount).

$$ln(q_e - q_t) = ln\, q_e - k_f\, t \quad \text{.....(2)}$$

$$\frac{t}{qt} = \frac{1}{k_s q_e^2} + \frac{t}{q_e} \quad \text{.....(3)}$$

$$q_t = k_{id} t^{1/2} + C \quad \text{.....(4)}$$

Furthermore, the kinetic models of pseudo-first-order, pseudo-second-order, and intraparticle diffusion were shown in Figures 3, 4, and 5, respectively. Based on the kinetics model, methylene blue degradation was suitable with the kinetic model of pseudo-second-order. In addition, it causes the correlation number (R^2) of pseudo-second-order to be larger than the pseudo-first-order and diffusion intraparticle. Table 1 shows the kinetic parameter from 3 models.

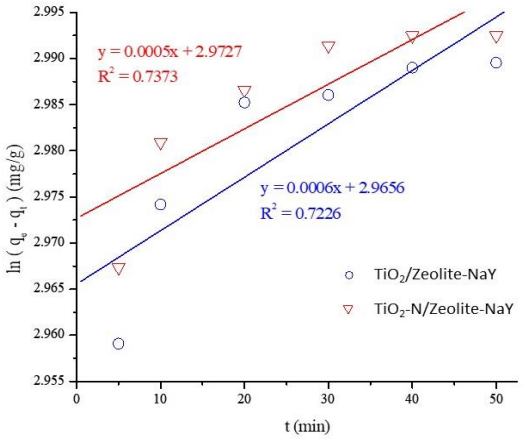

Figure 3. Kinetic model of pseudo-first-order of methylene blue degradation on TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY.

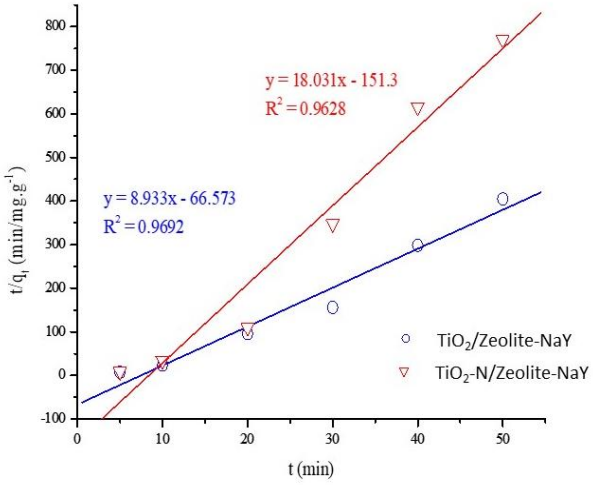

Figure 4. Kinetic model of pseudo-second-order of methylene blue degradation on TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY

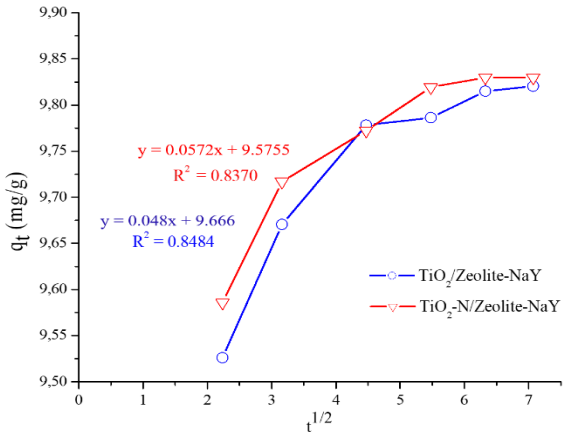

Figure 5. Kinetic model of intraparticle diffusion of methylene blue degradation on TiO_2/Zeolite-NaY and TiO_2-N/Zeolite-NaY.

In pseudo-second-order, the removal rate of methylene blue on TiO_2N/Zeolite-NaY (-0.0066 mg/g.min) was more than TiO_2/Zeolit-NaY (-0.0150 mg/g.min). However, this indicated that the removal of methylene blue was easier on the TiO_2-N/Zeolite-NaY than TiO_2/Zeolite-NaY due to the greater attachment of methylene blue molecules to the surface of TiO_2N/Zeolite-NaY. This lead to a decrease in contact distance and time between methylene blue molecules and the composite material leading to rapid diffusion and progression of the photocatalytic reaction.

In addition, the amount of residual methylene blue after degradation on TiO_2-N/Zeolite-NaY (0.0555 mg/g) was lower than TiO_2/Zeolite-NaY (0.1119 mg/g). This shows that the removal of methylene blue on TiO_2-N/Zeolite-NaY is greater than TiO_2/Zeolite-NaY. Furthermore, it showed that the photocatalytic performance of TiO_2-N/Zeolite-NaY was greater than TiO_2/Zeolite-NaY. The kinetic study also confirms degradation efficiency in Figure 2, which showed that the degradation efficiency of photocatalytic of TiO_2-N/Zeolite-NaY is greater than TiO_2/Zeolite-NaY. Moreover, this indicates that methylene blue enters TiO_2/Zeolite Na-Y and TiO_2-N/Zeolite-NaY through 2 stages namely external diffusion through TiO_2 and internal diffusion through micropore of zeolite Na-Y.

4. Conclusion

The degradation of methylene blue was tested using UV radiation at different times. Furthermore, the degradation efficiency showed that TiO_2-N/zeolite-NaY was excellent material for the degradation of methylene blue and could degrade the dye up to 99% for 20 minutes of reaction under UV radiation and a longer reaction time would increase the degradation efficiency. Therefore, it can be concluded that impregnation of TiO_2-N/zeolite-NaY increases the surface area of its material and lead to improved performance of the catalyst. The kinetic study of methylene blue degradation was suitable with the kinetic model of pseudo-second-order and it causes the correlation number (R^2) of this order to be larger than pseudo-first-order and intraparticle diffusion.

Acknowledgments

The author is grateful to the Ministry of Research and Technology for research grant under PDP Scheme with contract No 059/SP2H/LT/DRPM/2020.

Table 1. Kinetic model in methylene blue degradation

Kinetic Model	**Parameter**			
Pseudo-first-order	**k_f**		**q_e**	**R^2**
TiO_2/ Zeolite-NaY	0.0006		19.4063	0.7226
TiO_2-N/ Zeolite-NaY	0.0005		19.5446	0.7373
Pseudo-second-order	**k_s**	**h**	**q_e**	**R^2**
TiO_2/ Zeolite-NaY	1.1986	-0.0150	0.1119	09692
TiO_2-N/ Zeolite-NaY	2.1488	-0.0066	0.0555	0.9628
Intraparticle Diffusion	**k_{id}**	**C**	**R^2**	
TiO_2/ Zeolite-NaY	0,048	9,666	0,8484	
TiO_2-N/ Zeolite-NaY	0,0572	9,5755	0,8370	

Where,
k_f = pseudo-first-order constant (min^{-1})
q_e = amount of MB at equilbrium (mg/g)
h = initial rate of pseudo-second-order (mg/g.min)
k_s = pseudo-second-order constant (g/mg.min)
k_d = rate of intraparticle diffusion constant ($mmol/g.min^{1/2}$)
C = Intercep to explain of layer boundary thickness

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