Jurnal Kimia Valensi, Vol 8(1), May 2022, 54-59
Available online at Website: http://journal.uinjkt.ac.id/index.php/valensi

Photodegradation of Indigosol Blue Dye Using TiO_2/Natural Zeolite Photocatalyst

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Received: January 2022; Revision: February 2022; Accepted: March 2022; Available online: May 2022

Abstract

Indigosol blue is one of the dyes that has not been widely studied for photodegradation. This study aims to determine the photodegradation activity of indigosol blue using TiO_2/Natural zeolite. TiO_2 embedded in natural zeolite was synthesized using the sol-gel method. The synthesis results were characterized using X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), and UV-Vis Diffuse Reflectance Spectroscopy (DRS). The characterization of TiO_2-zeolite obtained a bandgap energy of 2.62 eV that could be seen in the UV-Vis DRS spectra. UV light is used during the photodegradation process to irradiate TiO_2-zeolite photocatalyst. The results show that the optimum mass of natural TiO_2-zeolite photocatalyst was 0.02 g with a degradation percentage of 58.3%. The optimum radiation time was 30 min with a degradation percentage of 58.7%, and the optimum concentration of blue indigosol was 600 ppm with a degradation percentage of 58.7%. TiO_2/Natural zeolite photocatalyst could degrade indigosol blue dye effectively at the optimum condition.

Keywords: Indigosol blue, Natural zeolite, Photodegradation, Sol-gel, TiO_2.

DOI: *10.15408/jkv.v8i1.24558*

1. INTRODUCTION

Nowadays, synthetic dyes are increasingly used, particularly in the textile industry. The number of textile industries in Indonesia is increasing from year to year. The most textile industry uses synthetic dyes because it is cheap, durable, easy to obtain, and easy to use (Andari et al., 2014). However, the general dye waste is a non-biodegradable organic compound that negatively impacts the environment, especially the aquatic environment. One of the synthetic dyes widely used in the textile industry is indigosol blue, an essential basic dye in the dyeing process (Dewi et al., 2018). Indigosol blue is one of the dyes that has not been widely studied for photodegradation. Only some research discusses this dye, especially in Indonesia, because this dye is usually used in the batik industry. Batik is one of Indonesia's cultural statements. These synthetic dyes are difficult to break down in the environment. If wastewater containing synthetic substances is discharged into the environment, it can last a long time, so a treatment process is needed before releasing it into the environment. One alternative treatment for dye waste is the photocatalytic principle (Alinsafi et al., 2007).

Photocatalyst is a material that can increase the rate of oxidation and reduction reactions induced by light. Several studies say that photocatalytic processes can use semiconductor photocatalysts (Neppolian et al., 2002). The most commonly used semiconductor is TiO_2. TiO_2 has a relatively more significant energy gap (3.28 eV) compared to other photocatalysts, making it excellent for photocatalysts. It also has long-term chemical stability, good photon stability, and high photocatalyst activity. In addition, photocatalyst activity using the semiconductor TiO_2 in degrading pollutants can be increased in the presence of adsorbent material (Ramadhani et al., 2017).

TiO_2 embedded in adsorbents such as zeolite can increase its photocatalytic ability. Natural zeolite is abundant in Indonesia; however, its potential uses have been confined

P-ISSN: 2460-6065, E-ISSN: 2548-3013

to its nature as an adsorbent and ion exchanger. Due to the adsorbent and catalyst qualities of natural zeolite and the photocatalyst properties of TiO_2 semiconductor, TiO_2-natural zeolite photocatalyst can be employed in wastewater treatment. Utubira studied that TiO_2 added to the zeolite can be decreased COD number up to 57.85% for textile wastewater (Utubira et al., 2010).

This study uses natural zeolite from Bandung, West Java, Indonesia. To the best of our knowledge, there is no sufficient research report about utilizing natural zeolite as material support of photocatalyst for indigosol blue photodegradation. Therefore, our focus is to observe the application of TiO_2/natural zeolite for the photodegradation process of indigosol blue. This research also studied the optimum photocatalyst dosage, irradiation time, and blue indigosol concentration in the photodegradation process.

2. MATERIALS AND METHODS

Materials and Instrumentation

Natural zeolite was used from Bandung, West Java (Indonesia). Titanium (IV) isopropoxide (Sigma Aldrich) was used as a precursor. Indigosol blue O4B, isopropanol (Merck), hydrochloric acid 6 M (Merck), glacial acetic acid (Merck), sodium nitrite (Merck), and all the reagents used were analytical grade.

The stirring hot plate Thermo Scientific Cimarec (SP 131320-33Q), the electronic oven Memmert UF 55, and the electric furnace were used for synthesizing TiO_2/natural zeolite. X-Ray Diffraction (XRD) PANalytical X'Pert Pro, X-Ray Fluorescence (XRF) PANalytical Minipal 4, and UV-Vis Diffuse Reflectance Spectroscopy (DRS) Thermo Scientific Evolution 220 were utilized for characterization of synthesis result. A set of photoreactors with a xenon UV lamp with the power of 10 watt was used for the degradation process of indigosol blue. In contrast, indigosol blue concentration was determined using Varian Cary® UV-Vis Spectrophotometer.

TiO_2/Natural Zeolite Synthesis

Natural zeolite was sieved to get 250 meshes of particle size. First, 100 grams of sieved zeolite was soaked using 400 mL of 6 M HCl for 4 hours. Then the precipitate was filtered using Whatman 42 paper and washed with distilled water while stirring until the pH was neutral. Finally, the zeolite was dried for 12 hours at 80 °C and calcined at 550 °C for 5 hours.

The synthesis of TiO_2/natural zeolite (10:90%) was accomplished by mixing 5.72 mL Titanium (IV) isopropoxide (TIP) precursor with 34.32 mL isopropanol for 30 minutes. The TIP solution in isopropanol was added to 5.71 mL of glacial acetic acid, then stirred until the solution became a gel. Then the gel was added to 13.5 grams of natural zeolite in 100 mL of distilled water while stirring for 4 hours. The solution is soaked for 24 hours for the aging process. Then the solution is filtered and then dried at 100 °C in the oven for 3 hours. The drying results were calcined at 550 °C for 4 hours. The photocatalyst product was characterized by XRD, XRF, and UV-Vis DRS.

Photodegradation of Indigosol Blue

25 mL indigosol blue (600 ppm) were filled into erlenmeyer. Then, 0, 10, 20, 40, and 80 mg of TiO_2/natural zeolite were added. Then, all Erlenmeyer is irradiated in a photoreactor using a UV lamp for 60 minutes while magnetically stirred. The photodegradation process was carried out in triple. A UV-Vis Spectrophotometer set to 625 nm was used to determine the photodegraded concentration of indigosol blue. A similar procedure was used to assess the effect of irradiation time and indigosol blue concentration.

3. RESULTS AND DISCUSSIONS

Preparation of Natural Zeolite

The elemental content and percentage of impurities in the framework and surface of natural zeolite were determined using XRF on zeolite before and after activation. The result of XRF characterization is presented in Table 1.

In Table 1, the main content of natural zeolite is Si/Al, with Fe as the main impurity metal. According to the results of the XRF analysis, activation without immersion in a hydrochloric acid solution was able to reduce the amount of Fe metal content (iron) with a percentage of Fe from 15.3% to 13.1%. Several other metals such as Mn, Eu, Cr, V, Zn, and Cu are also known to have decreased in percentage. It confirmed that the activation could reduce the number of metals in the natural zeolite.

Table 1. The result of XRF characterization

Element	Before activation (% mass)		After activation (% mass)	
	without Helium	with Helium	with Helium	with Helium
Si	58.6	57.3	71.3	65.3
Al	-	7.28	-	9.44
K	11	10.6	7.78	6.56
Mg	-	0.3	-	-
Ca	11.3	11.1	3.95	3.08
Ti	1.3	0.96	2.70	2.33
V	0.02	0.28	0.03	0.26
Cr	-	1.1	0.085	0.63
Mn	-	7.1	0.14	4.5
Ba	0.08	4.0	-	-
Fe	15.3	-	13.1	-
Cu	0.13	-	0.14	-
Zn	0.04	-	0.15	-
Eu	0.3	-	0.4	-
Re	0.2	-	0.2	-

Characterization of TiO_2/Natural Zeolite

The synthesis results were grey-white before calcination, and after 4 hours of calcination at 550 °C, they were brownish-white. A brownish white color is produced because iron is still present as a contaminant in a natural zeolite (Sariman, 2005). The synthesis results were characterized by XRD, XRF, and UV-Vis DRS.

The diffractogram of TiO_2/natural zeolite can be seen in Figure 1. The typical peak of TiO_2 was identified with the highest peak intensity at position 2θ: 25.29°, while the relatively high peak intensity at 2θ: 27° was the typical peak of mordenite (zeolite).

The characterization indicates the typical peak of TiO_2 anatase and modernite (zeolite) based on the TiO_2/natural zeolite diffractogram interpretation in Figure 1. The usual peak of modernite (zeolite) is more dominant than the TiO_2 anatase peak. Furthermore, due to the lower content of TiO_2 than modernite (zeolite) on this TiO_2/natural zeolite, several TiO_2 anatase peaks were low in intensity.

Characterization using XRF was carried out on zeolite before and after activation to determine the elemental content and percentage of impurities in the framework and surface of natural zeolite. The result of XRF characterization is presented in Table 1. In Table 1, the main content of natural zeolite is Si/Al, with Fe as the main impurity metal. According to the results of the XRF analysis, activation without immersion in a hydrochloric acid solution was able to reduce the amount of Fe metal content (iron) with a percentage of Fe from 15.3% to 13.1%. Furthermore, several other metals, including Mn, Eu, Cr, V, Zn, and Cu, have also been shown to have decreased in proportion, implying that activation can lower the number of metals in the natural zeolite.

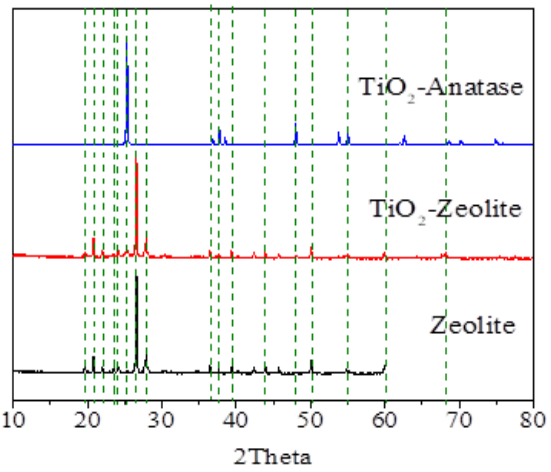

Figure 1. Diffractogram of TiO_2, TiO_2/natural zeolite and natural zeolite

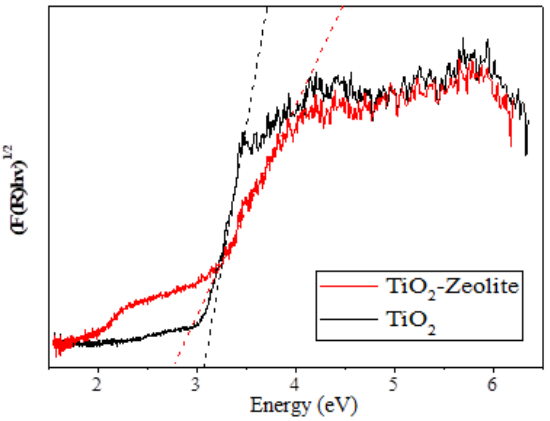

Figure 2. UV-Vis DRS spectra of TiO_2 and TiO_2/natural zeolite

The bandgap energy of the photocatalyst can be changed by adding natural zeolite; the bandgap energy of pure TiO_2 is 3.28 eV (Gunlazuardi, 2000), whereas the bandgap energy of TiO_2 synthesis is 3.07 eV, according to other studies (Sakti *et al.*, 2013). Therefore, the bandgap energy of the TiO_2/natural zeolite photocatalyst was obtained is 2.62 eV. The bandgap energy decreases because of the localized states near the

conduction or valence band of the modified TiO_2 (Wang *et al.*, 2012). Therefore, TiO_2/natural zeolite has lower bandgap energy than TiO_2, making electron excitation simpler and producing •OH radicals, resulting in increased photodegradation activity (Wardhani *et al*., 2016). The result of the characterization of TiO_2/natural zeolite is shown in Figure 2.

Effect of TiO_2/Natural Zeolite Mass on Photodegradation of Indigosol Blue

The percentage of degradation was calculated using a Spectrophotometer UV-Vis. The maximum wavelength of indigosol blue was first established, and it was found to be 625 nm. The calibration curve is then generated using the determined maximum wavelength. Finally, the concentration of indigosol blue is obtained using this calibration curve, and the degradation percentage is calculated using the difference in concentration before and after the degradation process.

The mass of the photocatalyst TiO2/natural zeolite 10:90%, which was utilized as a photocatalyst in the degradation process of indigosol blue dye, was varied to establish the optimum catalyst mass. Using the irradiation time of each sample for 60 minutes, mass changes of 0, 10, 20, 40, and 80 mg were carried out. The optimum result was 20 mg, which reduced the concentration of indigosol blue solution from 600 to 250 ppm with a 58.3% degradation. Figure 3 shows the result of determining the optimum catalyst mass.

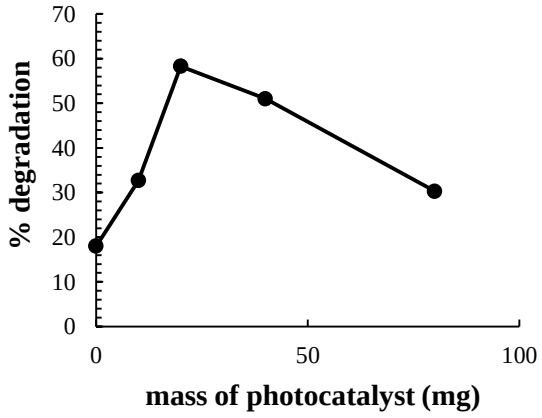

Figure 3. Correlation of mass of photocatalyst on %degradation

In the Figure 3, the photodegradation process without photocatalyst shows a percent degradation even though it does not use a photocatalyst because H_2O in the indigosol blue solution can form •OH radicals in the presence of light or photons (Equation 1 and 2).

$$H_2O + h\upsilon \rightarrow H^+ + \bullet OH + e^- \quad (1)$$

$$H^+ + \bullet OH \rightarrow HO_2\bullet \rightarrow \bullet OH + \tfrac{1}{2}\, O_2 \quad (2)$$

The more photocatalyst used the more percentage of the degradation process. This was because the more catalysts included, the more •OH radicals formed. However, more photocatalyst (over 20 mg photocatalyst mass used) will decrease the percentage of degradation because the excess photocatalyst will make the turbid solution. So, the light will be prevented from carrying out the photodegradation process.

Effect of Irradiation Time on Photodegradation of Indigosol Blue

The optimum irradiation time was determined by varying the irradiation time of 15, 30, 60, 120 and 240 minutes using 20 mg of photocatalyst TiO_2/natural zeolite 10:90% for each sample.The result of the determination of the optimum irradiation time is shown in Figure 4.

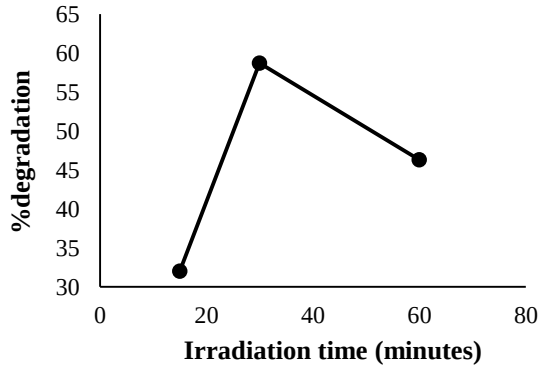

Figure 4. Correlation of irradiation time

The irradiation time in the photodegradation process describes the interaction or contact between the photocatalyst and light (hυ) in producing •OH radicals and the contact between •OH radicals and indigosol blue solution. In Figure 4, the optimum irradiation time obtained is 30 minutes, decreasing the blue indigosol solution from 600 ppm to 248 ppm with a percent degradation of 58.7%. At the 15 minutes to 30 minutes irradiation time, the degradation

percentage increased. The longer the irradiation time, the more •OH radicals formed. The interaction between the indigosol blue dye and the catalyst will intensify, resulting in increased degradation. However, the degradation percentage will decrease after 30 minutes of irradiation time (Pratama & Artsanti 2019).

Effect of Concentration of Indigosol Blue on Photodegradation Process

The optimum blue indigosol concentration was determined by varying the indigosol blue concentration of 200, 400, 600, 800 and 1000 ppm using the optimum mass of photocatalyst TiO_2/natural zeolite 10:90% determination of the optimum indigosol blue concentration is shown in Figure 5.

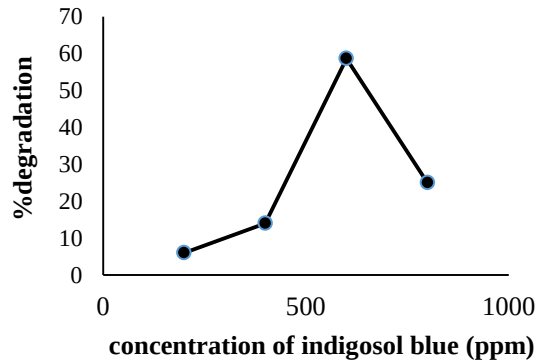

Figure 5. Correlation of concentration of indigosol blue on %degradation

At Figure 5, the optimum concentration of indigosol blue is 600 ppm, the concentration of indigosol blue solution decreased from 600 ppm to 248 ppm with a percent degradation of 58.7%. The degradation percentage increased as the concentration varied from 200 ppm to 600 ppm. This was due to the fact that the more solutes dissolved in a blue indigosol solution, the more photocatalyst TiO_2/natural zeolite could perform photodegradation. The percentage of degradation decreased after a concentration of 600 ppm. This is due to the generated •OH radicals are incapable of resuming the photodegradation process. As a result, the increased concentration of blue indigosol slowed the breakdown process. Similarly, an excess of dyes lowered the potential for organic molecules to decompose.

Effect of Different Treatment on Photodegradation Process

The indigosol blue photodegradation effectivity was evaluated using various treatments, including UV light without photocatalyst, TiO_2, zeolite, and TiO_2/natural zeolite-UV light. The result is shown in Figure 6.

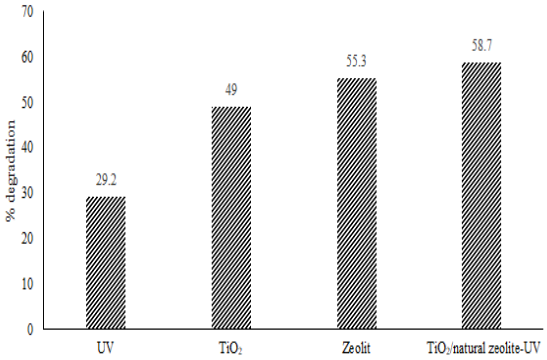

Figure 6. Degradation of indigosol blue on different treatment

Figure 6 shows that the treatment of indigosol blue dye exclusively irradiated by UV lamps for 60 minutes resulted in the lowest percentage degradation value of 29.2%. This occurs because, despite the presence of energy in the form of photons from UV lamps, there is no photocatalyst capable of producing hydroxyl radicals (•OH) and adsorbents capable of absorbing blue indigosol. As a result, the photolysis process is responsible for a significant portion of the degradation. Furthermore, TiO_2 has a percentage degradation value of 49% in the absence of UV light, while zeolite has a percentage degradation value of 55.3% in the absence of UV light. Because there is no energy in the form of photons from UV light, TiO_2 is unable to generate hydroxyl (•OH) in this circumstance. Simultaneously, the zeolite is an adsorbent that may adsorb the indigosol blue, resulting in a higher percent of degradation than TiO_2.

When TiO_2 was treated with TiO_2/natural zeolite and UV radiation, the highest percentage of degradation occurred, with a value of 58.7%. This demonstrates that the TiO_2/natural zeolite photocatalyst has high efficiency for degrading indigosol blue dye.

4. CONCLUSIONS

The TiO_2/natural zeolite was synthesise using the sol-gel method with the bandgap energy of 2.62 eV. The optimum mass of TiO_2/natural zeolite photocatalyst required to degrade indigosol blue is 20 mg. The optimum irradiation time required in indigosol blue degradation is 30 minutes. The optimum concentration of indigosol blue that can be degraded by photocatalyst TiO_2/natural zeolite is 600 ppm. Some efforts are necessary to improve the photodegradation activity for more prolonged photocatalyst use.

ACKNOWLEDGMENT

Authors would like to thank the Ministry of Religious Affairs of the Republic of Indonesia for funding this research through *Penelitian, Publikasi dan Pengabdian kepada Masyarakat* (LITAPDIMAS) program.

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