

Photocatalytic Degradation of Methylene Blue Using TiO₂-Natural Zeolite as A Photocatalyst

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ABSTRACT

TiO₂-zeolite photocatalyst has been prepared by impregnation of TiO₂ onto acid-activated natural zeolite. The XRD data confirmed that natural zeolite used in this work is predominated with mordenite and clinoptilolite types, whereas anatase type can be attributed to TiO₂. The highest performance of TiO₂-zeolite, which is indicated by the surface area of 13.304 m²/g and band gap energy of 3.15 eV, is obtained when 10 mmol of TiO₂ is impregnated onto the zeolite. The ability of this photocatalyst is evaluated by examining degradation of methylene blue (MB) in the presence of UV source. The effects of MB concentration, pH and UV irradiation time on the degradation are studied in a batch reactor. It is interesting since the addition of H₂O₂ can improve the degradation efficiency of MB. The optimum result is achieved at pH 11, duration of UV irradiation of 50 min, showing degradation amount of 98.25%. Surprisingly, the chemical oxygen demand (COD) in the degraded MB aqueous solution can be reduced about 77.9%, exhibiting the improvement of water quality. No loss of the activity of the degradation efficiency after reusability of this TiO₂-zeolite photocatalyst for at least 4 times.

Keywords: TiO₂, zeolite, methylene blue, photocatalyst, UV irradiation, H₂O₂

INTRODUCTION

Photocatalysis, well-known as advanced oxidation processes (AOPs), is one of the techniques that frequently used to degrade organic pollutants into harmless inorganic materials i.e CO₂ and H₂O [1]. Photocatalyst can facilitate the degradation of organic waste along with eliminating COD in wastewaters. Vinu and Madars [2] have established TiO₂ as a photocatalyst for degradation and mineralization of various toxic organic compounds such as chlorophenols, dyestuffs, pesticides, phenolic and pharmaceutical compounds. Ibadon and Fitzpatrick [3] found that the TiO₂ photocatalyst efficiently degrades organic waste in a water system due to the strong oxidizing ability of TiO₂ when illuminated with light. This ability corresponds to the band gap energy of TiO₂ [3]. The use of TiO₂ semiconductor as a photocatalyst requires combination with UV radiation. Sources of UV radiation can come from sunlight or use UV radiation with a wavelength corresponding to the energy gap of the semiconductor. UV light from the sun is only about 5-8% [3]. Therefore, the use of sunlight as an UV energy source becomes less efficient although it is coupled with TiO₂ photocatalytic process.

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Semiconductor catalytic activity can be enhanced through the developing of a porous material, for instance, is zeolite [4-6]. Distribution of TiO₂ in the inner and outer surface of zeolite resulted in increasing specific surface area and total pore volume [4]. Bahranifard studied that the loading TiO₂ onto zeolite can improve the degradation percentage of safranin-O by 69% compared with only TiO₂ as a photocatalyst [5].

As located in volcanic areas, Indonesia has abundant source of natural zeolites and our group has put much efforts to utilize this worthwhile material. In this study, we use natural zeolite from Turen, Malang, East Java (Indonesia). To the best of our knowledge, there is no adequate information dealing with the utilization of natural zeolite as a material support for photocatalyst. Our work focus in modification of natural zeolite through impregnation of various concentration of TiO₂ (TiO₂-natural zeolite), which include preparation, characterization, and application to the photodegradation of methylene blue (MB). Some parameters affecting degradation efficiencies, such as the effects of MB concentration, pH and UV irradiation time are investigated in detail. Additionally, H₂O₂ is added to the system, improving degradation efficiency of MB.

EXPERIMENT

Chemicals and instrumentation

Natural zeolite was obtained from Turen, Malang, East Java (Indonesia). Pharmaceutical grade of TiO₂ was used as impregnating agent. All other reagents used in this work were of analytical grade. Methylene blue was purchased from Uni Chem (Indonesia), whereas silver nitrate, hydrochloric acid, ethanol, hydrogen peroxide, and phenol were obtained from Merck (Germany).

The shaker rotator model H-SR-200 (HEALTH®, China), the electronic oven model 655F (Fisher scientific, UK), and the electric furnace were used for preparation of TiO₂-natural zeolite. Surface area analyzer and X-Ray Diffraction (XRD) PANalytical, Expert Pro (Netherlands) are employed for characterization of resulted photo-catalysts. A set of photoreactor with dimension of 45 cm length x 40 cm width x 40 cm height and UV lamp 325 nm equipped with the power of 10 watts were used for degradation process of MB. The band gap energy of the TiO₂-natural zeolite was investigated using UV-Vis diffuse reflectance, while MB concentration was estimated using the spectronic UVmini-1240 (Shimadzu, Japan).

Procedure for preparation of TiO₂-natural zeolite

A total of 300 g of natural zeolite was crushed into powder to obtain the particle size of 150 to 200 meshes. This zeolite was then washed with 600mL of distilled water while stirring. The suspension was filtered using a filter paper and dried in an oven for 2 hours at a temperature of 110°C. A total of 150 grams of zeolite laundering proceeds put into a 250 mL Erlenmeyer flask and added with 750 mL of 0.4 M HCl. The Erlenmeyer was covered with aluminum foil and followed by shaking for 4 h at a speed of 100 rpm. The zeolite was filtered and washed with distilled water until the filtrate is free from chloride ion. Cl⁻-ion-free test was performed by the addition of 0.1 M AgNO₃ in the filtrate until no white precipitate formed. Zeolite residue was dried in an oven at 110°C for 2 h, and then weighed to obtain a constant mass. This treated natural zeolite is now ready for further modification through the impregnation of TiO₂.

The preparation of TiO₂-natural zeolite photo-catalyst was carried out by impregnating various concentration of TiO₂ (5, 10, 12.5, 15, 20, and 25 mmol per gram zeolite) onto the treated natural zeolite in the medium of 96% ethanol. This mixture is stirred for 5 h. The

TiO₂-natural zeolite formed was dried in an oven at a temperature of 120°C for 5 h. Once dried, it was crushed into powder and then sieved using a 150 mesh filter. Then, TiO₂-natural zeolite was calcined at temperatures of 400-500°C for 5 h. The final product obtained was characterized by UV diffuse reflectance, XRD, and SAA.

Procedure for photo-degradation of Methylene Blue

Five of the 50-mL beaker glasses are filled with each 25 mL of 20 mg/L methylene blue. Then, a 50 mg of TiO₂-natural zeolite was added to each beaker followed by UV irradiation for 10, 20, 30, 40, and 50 min inside the photo-reactor. This photo-degradation process was repeated twice. The concentration of degradation products of methylene blue was determined spectrophotometrically at 664 nm. The similar procedure was carried out to examine the effects of MB concentrations, pH, and the addition of H₂O₂ towards photo-degradation efficiency.

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RESULT AND DISCUSSION

Characterization of TiO₂-natural zeolite

Surface area analyzer followed by BET method calculation was applied to estimate the specific surface area, the radius and pore volume of the resulted TiO₂-natural zeolites at various concentrations of impregnating agent as shown in Table 1. It can be seen that the natural zeolite impregnated with TiO₂ showed a significant decrease in its surface area, confirming the successful loading process of the impregnating agent into internal and external surface of natural zeolite.

Table 1. Surface area, pore volume, and radius of the zeolite and TiO₂-zeolite

Photocatalyst	Surface Area (m ² /g)	Pore Volume (mm ³ /g)	Pore Radius (Å)
Natural zeolite	113,689	0.054	15.245
TiO ₂ -natural zeolite A	13,304	0.030	21.602
TiO ₂ -natural zeolite B	12,423	0.030	28.058
TiO ₂ -natural zeolite C	10,861	0.027	24.483

Natural zeolite impregnated with 10 mmol (A), 15 mmol (B), and 20 mmol (C) of TiO₂

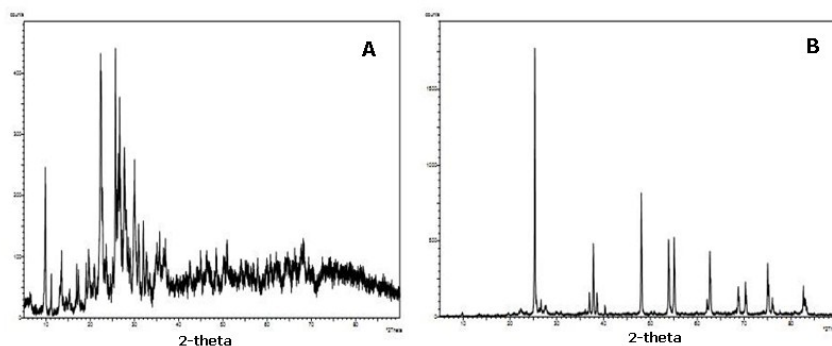


Figure 1. Diffractogram of natural zeolite (A) and TiO₂-natural zeolite (B)

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The diffractogram of natural zeolite and TiO₂-natural zeolite obtained by XRD were displayed in Fig 1. As given in Figure 1 (A), peaks at 2θ 9.872; 11,171; 17.345; 26.058, and 28.176 could be attributed to the clinoptilolite type of natural zeolite according to a JCPDS 47-1870 library, while the peaks of 2θ 22.205 and 27.680 represent the existence of the natural zeolite mordenite type as confirmed by JCPDS 29-1257 library. Figure 1 (B) showed that the TiO₂ entrusted into the activated natural zeolite possess anatase structure as identified by peaks of 2θ 25.281; 37.800; 48.049; 53.890 and 55.060 according to a JCPDS 21-1272 library [7].

The edge wavelength as well as band gap energy of natural zeolite, TiO₂, and TiO₂-natural zeolite obtained by the UV-Vis diffuse reflectance, and then processed by the Kubelka-Munk equation [8] were presented in Table 2. The decrease in band gap energy of TiO₂-natural zeolite in comparison to TiO₂ itself may result in electron excitation occurs more easily. This phenomenon will produce more •OH radicals, contributing higher photodegradation efficiency.

Table 2. Edge wavelength and band gap (E_g)

	Edge wavelength (nm)	Band gap (E _g) (eV)
Zeolite	405	3.06
TiO ₂	378	3.28
TiO ₂ -natural zeolite	395	3.15

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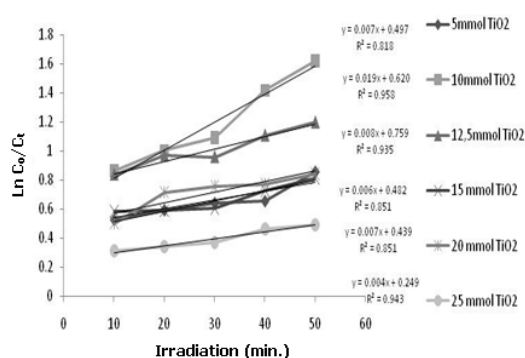


Figure 2. Correlation of irradiation time to Ln C₀/C_t (TiO₂ concentration of 5 to 25 mmol/g)

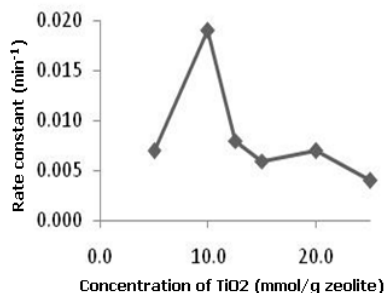


Figure 3. Concentration effect of TiO₂ on the degradation rate constant of MB

Effect of TiO₂ concentration impregnated onto natural zeolite to the degradation rate constant of MB

The photocatalytic degradation of MB using TiO₂-natural zeolite and UV irradiation follows the pseudo-first-order reaction since correlation coefficients of irradiation time vs Ln C₀/C_t were close to 1 as shown in Figure 2. [It means that the rate constant is only influenced by the concentration of MB]. Several studies have also described that the reaction rate of photocatalytic degradation of dyes can be explained by the model using the kinetic rate constants in a pseudo-first order [9-11].

As illustrated in Figure 3, TiO₂ concentration of 10 mmol/g zeolite provides the highest MB degradation rate constant. Probably, at this concentration, adequate amounts of TiO₂

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could be dispersed evenly throughout the surface of the zeolite, leading to higher surface area as well as enabling to absorb and degrade MB more efficiently greater than other TiO₂ concentrations.

Sintering process [12] led to the natural zeolite surface areas impregnated with TiO₂ 15 and 20 mmol/g becomes smaller so that the adsorption energy is reduced. This phenomenon results in decreasing adsorption and photocatalytic reaction. Additionally, increasing the amount of TiO₂ led to decrease the amount of oxidant generated on the active side of the photocatalyst as a depreciation catalyst occurred due to the lowering of sintering atmospheres adsorption capability. Lower amounts of TiO₂ exposed on the surface of natural zeolite causes the amount of •OH generated also decreased, which result in a decreased rate constant.

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Effect of UV irradiation time

Duration of UV irradiation strongly affect the degradation of MB as shown in Fig. 4. MB has been degraded by the photocatalyst increase if the longer exposure. This is due to the number of photons, which interact with the system (TiO₂-natural zeolite – UV light), excite more electrons to the conduction band (from the TiO₂ valence band). This condition produces higher electron numbers and hole in the conduction and the valence bands, respectively. Then electrons and holes react with dissolved OH⁻ and O₂ to produce active oxygen species, such as hydroxyl radicals and superoxide radicals that can degrade organic compounds. The longer the process of degradation, the higher amount of OH⁻ generated, so that the interaction intensity between the adsorbate and the catalyst will increase, causing the degradation efficiency raise and finally tend to constant.

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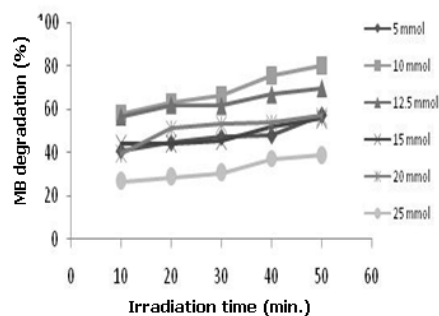


Figure 4. Effect of irradiation time on the degradation of MB

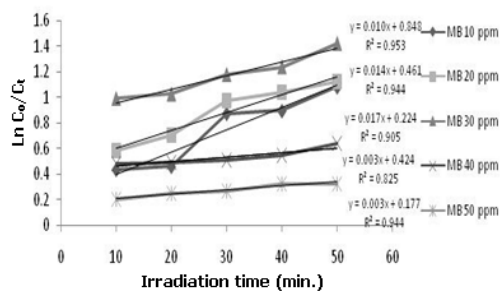


Figure 5. Effect of irradiation on Ln C₀/C_t (MB concentration 10 to 50 mg/L)

Effect of MB Concentration

Figure 5 and 6 shows that the rate constants change regularly when the concentrations of MB are varied. As MB concentration is raised, the rate constants decrease because of increasing in color intensity of MB. The color intensity will effect to the incoming light, which may reduce interaction of the light with the photocatalyst. Moreover, it will hinder •OH radical generation so that the degraded amount of MB is diminished.

The similar result was obtained by Ling [13], in which photodegradation of MB with TiO₂ gave the highest constant rate at the lowest concentration of MB. Photons are not able to penetrate surface of the photocatalyst at high concentration of MB, resulting in a decrease of degradation products. According to Chong [14], an increase in the concentration of the dye

resulted in a decrease of the formation of $\cdot\text{OH}$ on the catalyst surface due to the ionic dye hindrance.

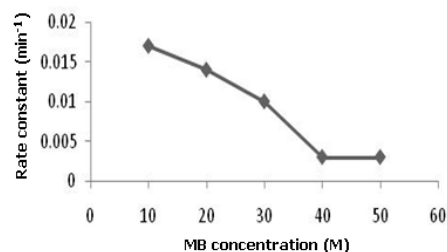


Figure 6. Correlation of methylene blue concentration on rate constant value

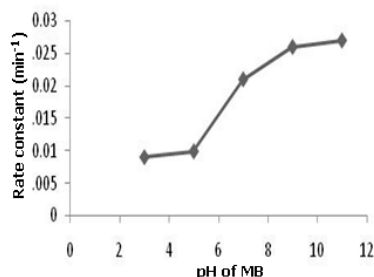


Figure 7. Correlation of initial pH on the MB degradation rate constant

Effect of pH MB

MB alkaline pH adjustment is done by adding a solution of NaOH. As shown in Fig 7 and 8, pH strongly affects to the rate constant of MB degradation. At high pH, TiO_2 is negatively charged whereas MB is positively charged. For degradation of MB, the higher pH results in the increase of the degradation rate constant. This is because MB is a cationic dye, which tends to be positively charged at high pH.

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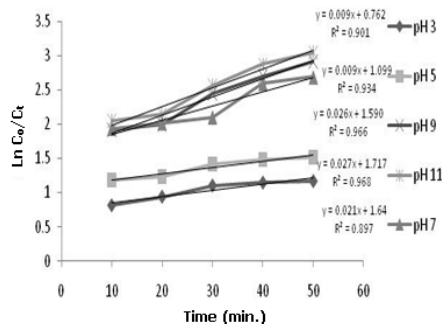


Figure 8. Correlation of irradiation time and $\text{Ln } C_0/C_t$ at various initial pH of MB

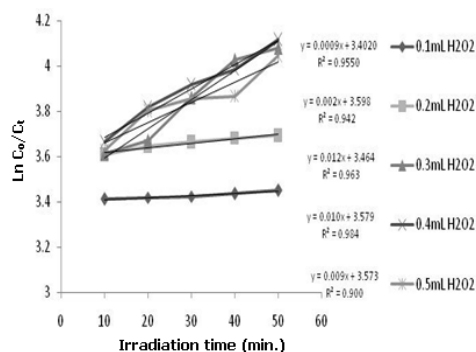


Figure 9. Correlation of irradiation time and $\text{Ln } C_0/C_t$ with addition of H_2O_2 to MB 25ml.

Effect of the H_2O_2 addition

Fig. 9 shows that the addition of H_2O_2 improves the photodegradation rate constant along with the increase in H_2O_2 concentration ranging from 0.1 to 0.3 mL. This is because the more H_2O_2 is used, the more $\cdot\text{OH}$ produced via reduction reaction in the conduction band. The more $\cdot\text{OH}$ is generated, causing a rise of degraded MB. However, the rate constant of photodegradation decreased when ≥ 0.4 mL of H_2O_2 is added due to the formation of $\cdot\text{HO}_2$ radicals, which is less reactive than $\cdot\text{OH}$ radicals (Reaction 1) and partly reshaping H_2O_2 (Reaction 2). The $\cdot\text{HO}_2$ radical is undissolved gas molecule, but it adheres to the photocatalyst surface, which will hinder the transfer of photon energy [15]. In addition, $\cdot\text{HO}_2$ radical formed from the reaction of $\cdot\text{OH}$ with H_2O_2 reduces the amount of $\cdot\text{OH}$ radical itself.

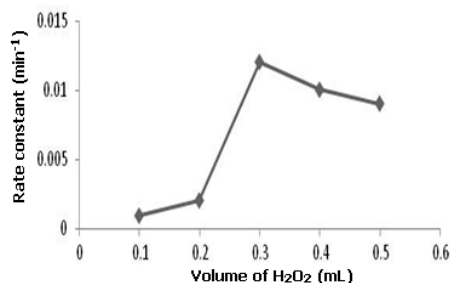
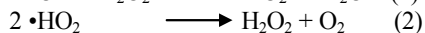
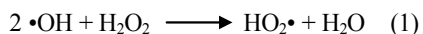


Figure 9. Correlation H₂O₂ volume to the MB degradation rate constants

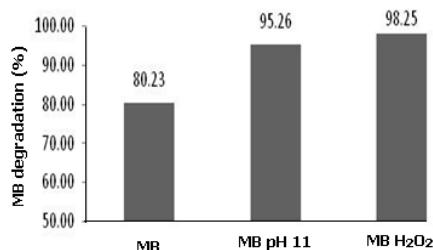


Figure 10. Effect of degradation conditions the degradation of MB

Fig. 10 shows the degradation percentages of MB with and without pretreatment. It can be seen that MB added with H₂O₂ generates the highest degradation efficiency. This is because the more H₂O₂ is used, the more •OH produced via reduction reaction in the conduction band. The more •OH is generated, causing a rise of degraded MB. MB adjusted at pH 11 provides higher degradation efficiency than that of without pH adjustment. Alteration of the TiO₂ charge along with positively charged MB at pH 11 improves the adsorption of MB onto the catalyst, leading to higher degradation efficiency due to the strong interaction of MB with •OH radicals generated by the photocatalyst.

Table 3. Effect of photocatalyst reusability on the degradation efficiency of MB

Cycle	Degradation of MB (%)	Loss of efficiency (%)
1	79.91	0.00
2	77.31	3.25
3	76.38	4.42
4	72.06	9.82

Table 4. The COD value before and after degradation of aqueous MB solution

Sampel	COD (mg/L)	Decrease in COD concentration (%)
Initial aqueous MB solution	2168	-
Aqueous MB solution after the 1 st irradiation	480	77.86
Aqueous MB solution after the 2 nd irradiation	152	92.99

Table 3 shows the reusability of the photocatalyst for the degradation efficiency of MB. It should be noticed that the degradation efficiency declines for about less than 10% after four cycles. Such results indicate that TiO₂ catalyst bound rather strongly on the surface of natural zeolite, which agree well with the result reported so far [16]. However, we still attempt to

improve immobilization techniques of catalyst onto material supports to achieve more satisfactory results. After degradation, chemical oxygen demand (COD) in aqueous MB solution was measured. As given in Table 4, COD remarkably diminished for about 92.3 % after the 2nd irradiation, indicating improvement of water quality.

CONCLUSION

Newly photocatalyst prepared by the impregnating TiO₂ onto natural zeolite (TiO₂-natural zeolite) was successfully produced, and further applied to the degradation of MB dye with satisfactory results. Such efforts are still necessary to improve the immobilization techniques of catalysts onto natural zeolite for prolonged use of the photocatalyst without losing its activity. Chemically binding catalysts onto natural zeolites via chelating agents may offer better solution.

ACKNOWLEDGMENT

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