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Research Article

The Composite of ZrO_2-TiO_2 Produced from Local Zircon Sand Used as A Photocatalyst for The Degradation of Methylene Blue in A Single Batik Dye Wastewater

Ita Permadani[1], Dhini A. Phasa[1], Andini W. Pratiwi[1], Fitria Rahmawati[1*]

[1]Research Group of Solid State Chemistry & Catalysis, Chemistry Department, Sebelas Maret University, Jl.Ir. Sutami 36 A Kentingan Surakarta, Indonesia 57126

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Abstract

In this research, a composite of ZrO_2-TiO_2 was used as a photocatalyst in the degradation of dye wastewater. The dye waste water is a single Methylene Blue, MB, waste water from Batik industry. The ZrO_2 was prepared from zircon sand founded from Bangka Island, Indonesia. The composite was prepared at various weight ratios and heat treated at 500 ^oC. The result shows that the purity of ZrO_2 from zircon sand is only 66.46 %. However, the addition of ZrO_2 into TiO_2 is able to increase the photocatalytic activity which proven by 88.75 % degradation of MB at a ZrO_2-TiO_2 weight ratio of 1:1. The degradation result is higher than that with anatase TiO_2; that is only 62.67 %. The kinetics study found that the photocatalytic degradation of MB with single TiO_2 has the rate constant of 1.85×10^{-2} $minutes^{-1}$. Meanwhile, the rate constant of the MB degradation with the composite ZrO_2-TiO_2 is 16.73×10^{-2} $minutes^{-1}$.

Keywords: Photocatalytic; Methylene Blue; Zirconia; Titania; Batik Waste Water

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1. Introduction

Industrial developments almost always have a negative impact on the environment, especially the generation of waste and wastewater. Batik industry might be a small scale industry. However, the large number of it have generated impacts on the environmental due to their waste water from dyeing process. Many attempts have been conducted to handle the waste, including absorption and activated sludge. However, those treatments are less effective because of the dye adsorbed accumulated in the absorbent become a new problem. The activated sludge method is also not effective for some types of dye wastewater, especially for dyes that resists to biologically degradation [1]. Photocatalytic degradation is a proximity alternative due to some reasons such as less expensive, saving the use of chemicals, faster process, non-toxic, and long usage capability [2]. Photocatalytic degradation is a process that became importance in the area of wastewater treatment; especially for wastewater containing small amounts of refractory organic substances [3]. This photocatalytic treatment can be very inexpensive when the

* Corresponding Author.
E-mail: fitria@mipa.uns.ac.id (F. Rahmawati)

sunlight become the photon source. However, some well-known photocatalyst such as TiO_2 has high gap energy that made TiO_2 only active under ultraviolet radiation. Also, the possibility of recombination of the excited electrons-hole also become another disadvantage of photocatalytic degradation. Many attempts have been conducted such as by combining TiO_2 with metal [4], doping of TiO_2 with metals [5], and also combining TiO_2 with another semiconductor material, such as ZrO_2 [6]. Study on the composite photocatalyst found that the ZrO_2 might increase the photoactivity of TiO_2 catalyst [6].

On the other side, the sustainability of raw materials must be considered to guaranty the sustainability production of the composite material. The availability of raw materials in Indonesia is very promising due to the very large content of minerals that spread over the islands. Bangka Island is one of the islands with a large content of mineral sand, especially Tin. Zircon, $ZrSiO_4$, sand is the side product of some tin mining industries in Bangka Island. XRF results indicate the content the tin mines of Bangka island-sand zircon ($ZrSiO_4$) are ZrO_2, SiO_2, Al_2O_3, Na_2O, MgO, and SO_3 [7]. On the other side, the demand on pure ZrO_2 becomes high due to the development of materials for energy conversion devices, such as fuel cells [8], semiconductor and semiconductor photocatalyst [9], etc. Therefore, the economic value of zircon sand can be increased by converting this zircon sand into zirconia powder.

This paper discuss the conversion of high-grade zircon sand into ZrO_2 and then applied it as a raw material for photocatalyst composite of ZrO_2-TiO_2. The research study the characteristics of the prepared material including the diffraction pattern, the content of functional groups and the ability to adsorb molecules. Also, the prepared composite was used as photocatalyst for methylene blue degradation. The methylene blue solution was found from a single dyeing treatment of batik processing.

2. Materials and Methods

Synthesis of zirconia (ZrO_2) was conducted by caustic fusion method from zircon concentrates ($ZrSiO_4$). The zircon concentrate was destructed by mixing with NaOH, then followed by acid leaching with HCl and water leaching [10]. In this research, the water leaching was conducted twice to minimize the content of sodium.

The prepared zirconia powder then was mixed with titania at various weight ratios. The weight ratio of ZrO_2:TiO_2 were 0.5:2; 0.75:2; 1:2; 1.5:2; and 2:2 (in grams). The mixture then was press into a pellet and heated to 500 ^oC for 3 hours. XRD analysis (Shimadzu, XRD-6000) was conducted to analyse the phases existed in the prepared materials based on their comparison with the standard. The standard diffraction of anatase TiO_2 from ICSD #9852, rutile TiO_2 from ICSD#9161 and the standard diffraction of ZrO_2 from ICSD#66786. FTIR analysis (Shimadzu, Prestige 21) was conducted to investigate the functional groups existed in the prepared materials. Meanwhile, SEM analysis (JEOL, JSM-6510LA) investigated the surface morphology and the particle size estimation.

The photodegradation of MB solution (model solution) and MB batik wastewater were conducted under ultraviolet light and sunlight during 50 minutes. In every 10 minutes, the solution was analyzed by UV-Vis spectrophotometer (PerkinElmer Lambda 25). The photodegradation was conducted without catalyst or named as photolysis and with the photocatalyst. The photocatalysts are anatase TiO_2 and the composite ZrO_2-TiO_2 at a various weight ratio.

The intensity of sunlight was measured by a Lightmeter (Krisbow KW06-288; measure range 200, 2000, 20000, 50000 Lux/fc, accuracy ± 5 % rdg ± 10 dgt). The photodegradation with sunlight as photon source was conducted simultaneously in a day for 100 minutes, which was started at 11.30-13.10, West Indonesian time (GMT +7). Meanwhile, the UV light used in this research was monochromatic UV (GNB-9W BLB, Lamp Holder E27, 9 watts).

The photodegradation efficiency was determined by calculating the percentage of degradation, %D, (Equation (1)).

$$\%D = \frac{C_0 + C_t}{C_0} \times 100\% \quad (1)$$

C_0 is the initial concentration and C_t is the concentration after t minute.

Kinetics of photodegradation was investigated by plotting the result based on the first order and second order, as written in Equation (2) and (3), respectively.

$$\ln A = -k.t + C \quad (2)$$

$$\frac{1}{A} = k.t + C \quad (3)$$

A is absorbance; k is the rate constant, and C is the intercept. The linearity constant, R, of linear regression, was used as a parameter to de-

termine the kinetics order of reaction.

3. Results and Discussion

Synthesis of zirconia was conducted by caustic fusion methods with NaOH as destruction agent. The process was then followed by HCl and water leaching. Ammonium hydroxide was used to precipitate zirconium hydroxide, $Zr(OH)_4$. The reactions of every step are listed in Equation (4), (5) and (6).

$$ZrSiO_4 + 4\ NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2\ H_2O \quad (4)$$

$$Na_2ZrO_3 + 4\ HCl \rightarrow ZrOCl_2 + 2\ NaCl + 2H_2O \quad (5)$$

$$ZrOCl_2 + 2NH_4OH \rightarrow Zr(OH)_4 + 2NH_4Cl + 2H_2O \quad (6)$$

The XRF analysis of the prepared ZrO_2 found the zirconia content is 66.46 %. The impurities are still existed i.e Na_2O, SiO_2, MgO, and others. List of elemental composition is depicted in Table 1. Meanwhile, The diffraction pattern is described in Figure 1. The pattern is compared to the standard diffraction of ZrO_2 from ICSD#66786. It can be seen that the peaks are broad representing the small crystalline size, and the peaks are in agreement with the standard diffraction, except a peak at 2θ of 28.36° which is indentified as monoclinic zirconia. The peak was identified by compare it with the standard diffraction of monoclinic ZrO_2 from ICSD#157403. It indicates that reaction of zirconium oxide production might produce the monoclinic structure, beside of tetragonal as a major phase.

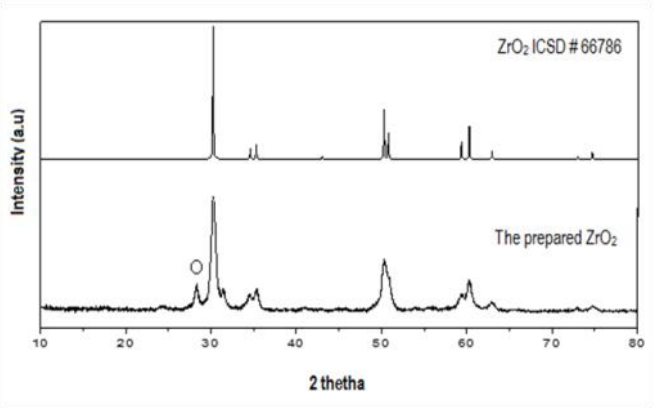

Figure 1. The diffraction pattern ZrO_2 compared to standard ICSD#66786. O is an unidentified peak

Table 1. The elemental analysis results on Zirconia

Material	Content In Materials (%)
ZrO_2	66.46
Na_2O	17.38
SiO_2	4.04
MgO	2.52
Other materials	9.66

The XRD patterns of ZrO_2-TiO_2 composites at various ratio are depicted in Figure 2. The anatase peaks are at 2θ ~ 25.27°; 37.87°; 48.20°; 54.02° and 62.73°. Meanwhile, zirconia peaks at 2θ ~ 30.30°; 34.70°; 35.24°; 50.34° and 60.26°. A peak at 2θ~ 28.36° refers to a peak of monoclinic zirconia. The diffraction of various composition shows a similar pattern with different intensity. The peak intensity was changed based on the weight content in the prepared composite.

Figure 3 shows the FTIR spectra of the ZrO_2-TiO_2 at the various ratio and its comparison to the single initial materials. A broad peak at 3395-3470 cm^{-1} and a sharp band at 1635 cm^{-1} shows the bending vibration of the hydrogen bonding -OH group. The peak at 900-400 cm^{-1} indicates the presence of Zr−O and Ti−O vibrations. Meanwhile, a peak at 470 cm^{-1} indicates the presence of ZrO_2.

Figure 3 shows that the intensity of -OH peaks at 1635 cm^{-1} and 3395-3470 cm^{-1} decreased. Meanwhile, the Ti−O stretching and Zr−O at 500-900 cm^{-1} increased. Those results are consistent with the previous report that investigated the effect of the increasing of calcination temperature on the disappearance

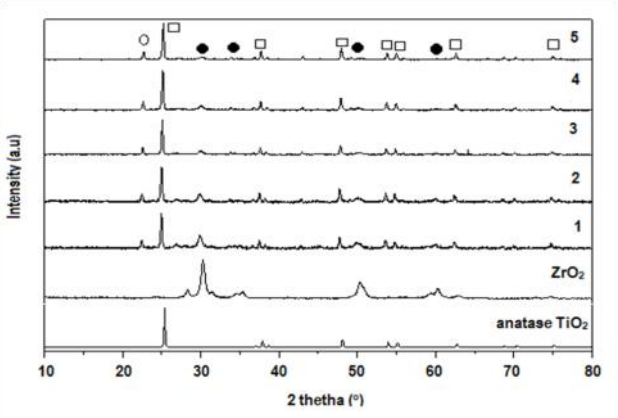

Figure 2. The diffraction pattern of TiO_2 anatase, ZrO_2, 1 is TiO_2-ZrO_2 = 1:1; 2 is TiO_2-ZrO_2 = 1.5:2; 3 is TiO_2-ZrO_2 = 1:2; 4 is TiO_2-ZrO_2 = 0.75:2 and 5 is TiO_2-ZrO_2 = 0.5:2. The sign refers to anatase peaks, □, ● refers to ZrO_2 peaks and O is an unidentified peak.

of water molecules to produce a link of metal-oxygen-metal. Morphological analysis of the prepared material as described in Figure 4(a), shows that the material is in spherical form with the average particle size of 159 nm. Elemental mapping (Figure 4(b)) confirms that the prepared material consist of Ti, O and Zr atoms with detailed spreading of atoms as described in Figure 4(b). It indicates that Ti and O are homogeneously spread over the material. Meanwhile, the Zr atoms are presented non-homogenously. EDX analysis (Figure 4(c)) found that the mass percentage of O is 35.85%; Ti is 42.03%, and Zr is 22.11%. Even though, the composite was prepared at 1:1 ratio, non-homogenous spreading of Zr atoms might cause a lower mass percentage of ZrO_2 detected by spot analysis such as EDX.

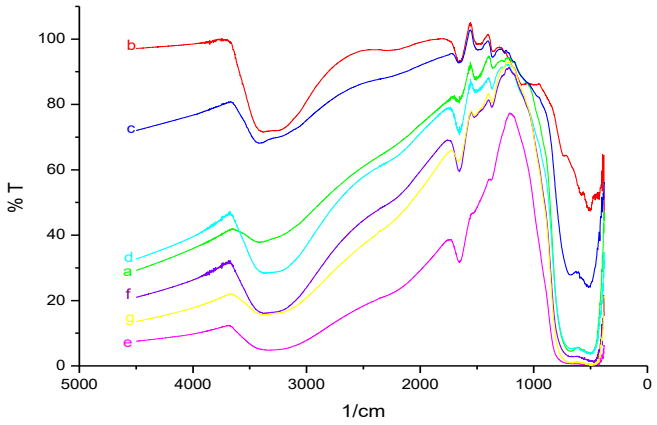

Figure 3. The FTIR spectrum of (a) TiO_2 anatase, (b) ZrO_2, (c) ZrO_2-TiO_2 = 1:1, (d) ZrO_2-TiO_2 = 1.5:2, (e) ZrO_2:TiO_2 = 1:2, (f) ZrO_2-TiO_2 = 0.75:2, (g) ZrO_2:TiO_2 = 0.5:2

Photodegradation plots of methylene blue with various ratio of ZrO_2-TiO_2 are described in Figure 5. The catalytic activity was increased with the increasing of ZrO_2 content, and the result is optimum at a ratio of 1:1. Such high reactivity occurs due to the easy transfer of the photo-formed electrons. The transfer occurs from the conduction band of ZrO_2 to the conduction band of TiO_2 through a strong chemical interactions. Those electronic transfer might prevent the radiative recombination of the photo-formed electrons and holes [11].

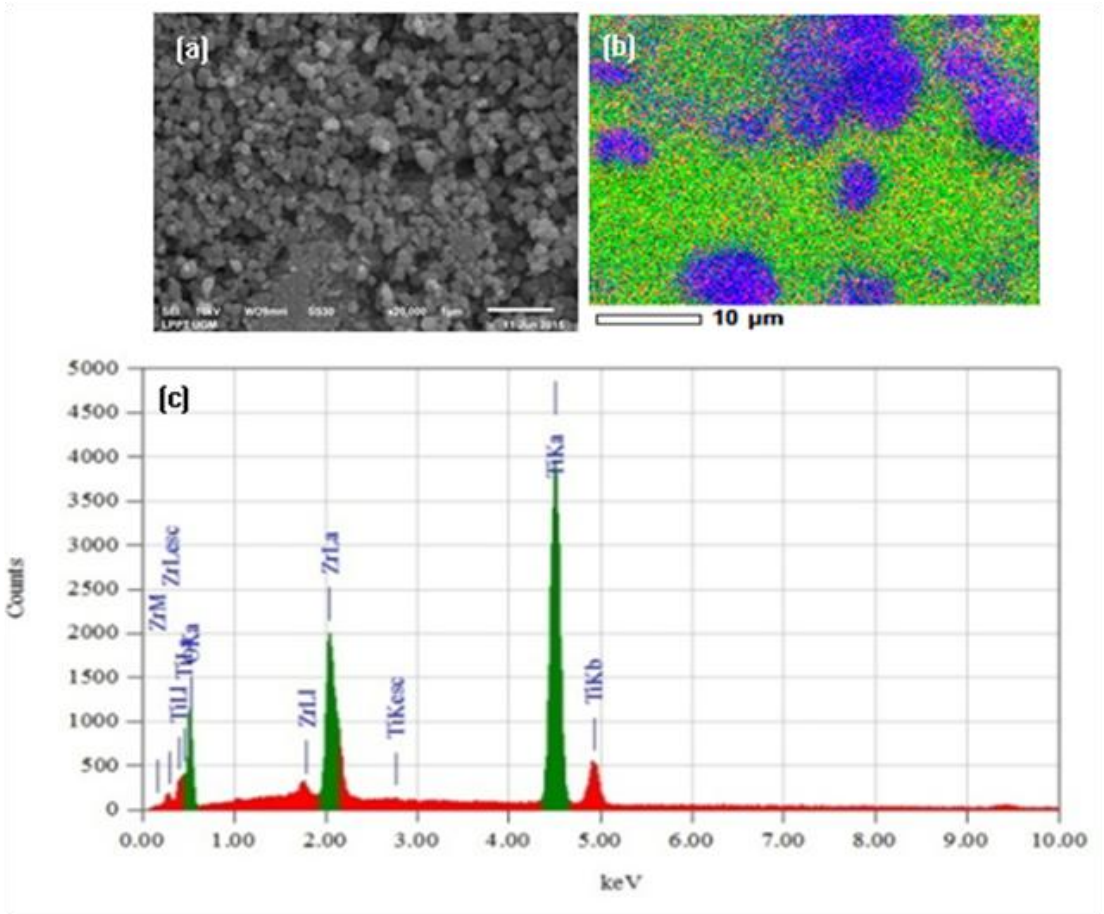

Figure 4. SEM image of ZrO_2-TiO_2 (1:1) (a), the elemental mapping result, the green color refers to Ti, blue refers to Zr, black points refer to O atoms (b), EDX result (c)

Also, Figure 6 shows that the photocatalyst plays a significant role in the degradation proven by the increasing of %degradation when the photocatalyst was used. ZrO_2 has not served only as a substrate for TiO_2. It also served as a secondary functional catalyst since the ZrO_2 itself has a contribution to the degradation through the photocatalytic mechanism and also the ability to engineer the material properties. The addition of small amounts of ZrO_2 into TiO_2 can decrease the particle size of TiO_2 due to the similar nuclei, coordination geometry and increase in the surface area [12]. The addition of ZrO_2 to TiO_2 can prevent phase transformation from anatase to rutile thus promoting the stability of the catalyst [13]. Anatase phase is metastable and has the greater photocatalytic activity; meanwhile, rutile has a high chemical stability but is less active [14, 15]. However, a mixture of a large quantity anatase TiO_2 and a small amount of rutile phase could exhibit a higher photocatalytic activity than in the pure anatase or rutile phase [16, 17].

The degradation during 50 minutes is 62.67 % with TiO_2 as a photocatalyst, and it is 88.75 % with the composite of ZrO_2-TiO_2 at

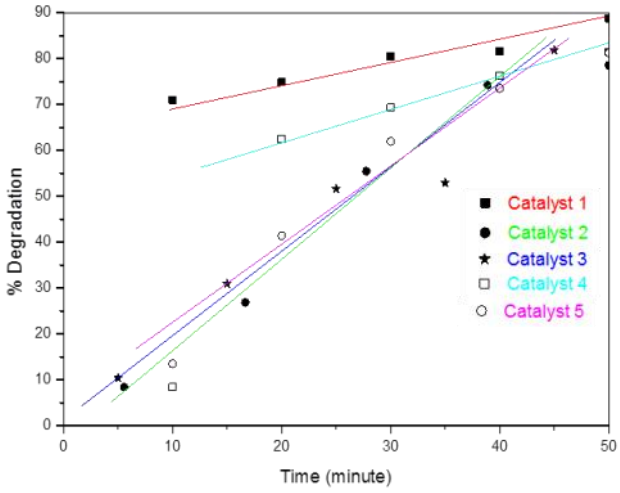

Figure 5. % Degradation of methylene blue with various ratio of ZrO_2-TiO_2 under UV light radiation. The catalyst 1 is TiO_2-ZrO_2 = 1:1; Catalyst 2 is TiO_2-ZrO_2 = 1.5:2; Catalyst 3 is TiO_2-ZrO_2 = 1:2; Catalyst 4 is TiO_2-ZrO_2 = 0.75:2 and Catalyst 5 is TiO_2-ZrO_2 = 0.5:2

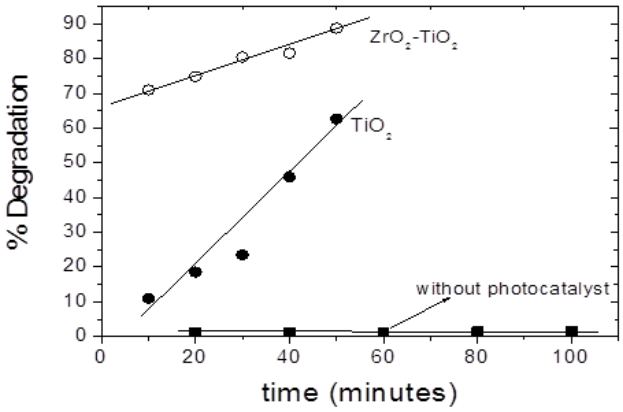

Figure 6. % Degradation of methylene blue under UV light radiation

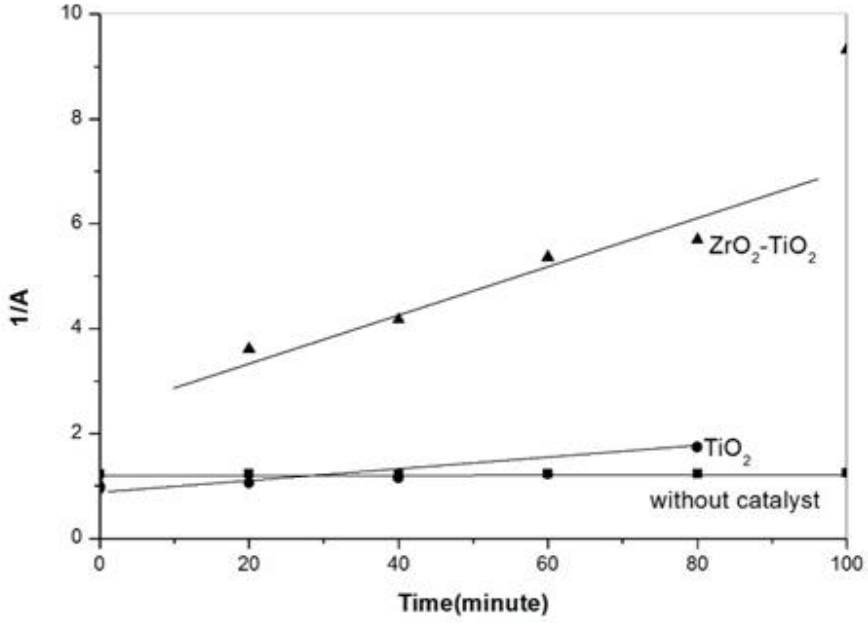

Figure 7. The second-order plots of photocatalytic degradation under UV radiation with and without photocatalyst

Table 2. Rate constant (k), linear regression coefficient (R^2) of methylene blue solution by using catalyst tablet of ZrO_2-TiO_2

No	Materials	Rate Constant for 1st order		Rate Constant for 2nd order	
		k_1 (min^{-1})	R^2	k_2 (min^{-1})	R^2
1	Without catalyst UV	0.0001	0.7298	0.0002	0.7314
2	Catalyst TiO_2 UV	0.0185	0.8874	0.0343	0.8069
3	Catalyst 1 UV (1:1)	0.0358	0.8228	0.1673	0.9093

1:1 as a photocatalyst. The degradation ability of ZrO_2-TiO_2 catalyst increased with an increase of ZrO_2 loadings to TiO_2, and the highest degradation percentage was found at a ratio of 1:1. The presence of zirconia known to stabilizes the anatase phase and elevates the temperature at which the phase transformation to rutile occurs [18]. Both ZrO_2 and TiO_2 are n-type semiconductors with excellent catalytic properties for various reactions. Mixed of them have superior properties than the single phase, as the mixture exhibits high surface area, powerful surface acid-base properties, high thermal stability and strong mechanical strength [19, 20, 21]. The mixed oxide provides not only active catalyst from TiO_2 and the acid-base properties of ZrO_2 but also generate new catalytic sites due to a strong interaction between them [21].

Kinetics study on the MB photo-degradation found that the photodegradation of Methylene Blue with the mixture of ZrO_2-TiO_2 follows the second order. It means that the reaction rate or degradation rate will increase in equal to the square of the MB concentration. The trend also occured for the MB degradation with TiO_2 and also without photocatalyst. However, the rate constant of degradation with the ZrO_2-TiO_2 composite is 1.673×10^{-1} min^{-1}, which is ten times higher than the rate constant of photodegradation with TiO_2. It indicates the significant role of ZrO_2 addition. The rate constant values are listed in Table 1. Meanwhile, the kinetics plots are described in Figure 7. The photocatalytic degradation of dyes such as Remazol Yellow 120 [22] is a heterogeneous process. The reaction involves decomposition of dye molecules on the surface and the surface reaction assumption between dye molecules with the OH• [22]. Both reactions may have a different order, i.e. the first order of decomposition reaction of dye on the surface and the second order of the reaction between adsorbed dye molecules with the hydroxyl radical, OH•. As water as a solvent is in large excess. Therefore, the concentration of OH• radicals is also very large. The surface concentration of OH• may be assumed to be constant [22].

4. Conclusions

The zirconium dioxide from locally zircon sand can be used as a component in a composite catalyst of ZrO_2-TiO_2. The result shows that even though the purity of ZrO_2 that was prepared from zircon sand is only 66.46%, however, the addition of ZrO_2 into TiO_2 increased the photocatalytic activity. It is proven by 88.75% degradation of MB at a ZrO_2-TiO_2 weight ratio of 1:1. The result is higher than the degradation with anatase TiO_2, which is only 62.67%. The kinetics study found that the photocatalytic degradation of MB with single TiO_2 has the rate constant of 1.85×10^{-2} $minutes^{-1}$. Meanwhile, the rate constant when the degradation was conducted with the composite ZrO_2-TiO_2 is 16.73×10^{-2} $minutes^{-1}$.

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