



Degradation of Methyl Violet Using TiO₂-Bayah Natural Zeolite Photocatalyst

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Abstract

Degradation of methyl violet using photocatalysis method has been investigated. In this study TiO₂ was superimposed on the surface of the Bayah natural zeolite with two solvents, ethanol, and distilled water. The activation of the Bayah natural zeolite used HCl. In this study, the effect of zeolite size (60, 80 and 100 mesh), the composition of TiO₂-Zeolite (2, 4 and 6), and intensity of photon energy on the degradation of methyl violet have been evaluated. The samples were characterized by means X-ray powder diffractometer (XRD). The specific surface area of each sample was determined by the BET nitrogen gas adsorption/desorption method. The measurement of methyl violet concentration used UV, Vis spectrophotometry. The results showed that optimum composition of TiO₂ in zeolite (80 mesh) was 4 grams with a solvent of distilled water. The use of this sample could reduce methyl violet by 94.5% for 4 hours with UV light intensity of 1340 μW /cm².

Keywords: Degradation, Photocatalysis, TiO₂, *methyl Violet*, Bayah Natural Zeolite

1. Introduction

One of the negative effects in textile industry is contamination by wastewater which contains dyes, such as methylene violet. Methylene violet is synthetic dyes frequently used in the industries of textile, leather, plastic, cosmetics, pharmacy, paper, and printing (Ikhsan, 2014). This waste of methylene violet can be dangerous pollutant since its synthetic compound structure is large and stable; it is not easy to be degraded (Ikhsan, 2014), so it requires more effort to reduce the effect of waste.

Some methods have been used to degrade this organic waste, such as photocatalysis (Kustiningsih, I., et al., 2016), adsorption, fenton oxidation (Jayanudin, et al., 2017), coagulation, ozonation (Sulaiman, F., et al., 2017), sonication, and electro-oxidation, but there are some weaknesses in fenton oxidation method, such as low capability in degrading waste from dyes; it only works optimally at low pH and requires many chemicals and high cost (Sholeh, 2014). One of effective methods to degrade this waste is photocatalysis.

The advantages of photocatalysis over other methods are strong oxidizer, inert trait in biological and chemical way, stability toward light (photostable), being affordable and easy to find, and insoluble in the reaction (Litter,

M.I., 1999). One of the semiconductor materials which can be photocatalyst is titanium dioxide (TiO₂), with its photoactivity capability and chemical stability which are high (Kocl, 2009; Kustiningsih, I., et al., 2018), non-toxic, capable of oxidizing organic pollutant and reducing metal ion (Dugandzic, 2012, Kustiningsih, I., et al., 2018). However, photocatalysis method is less effective in managing waste with high concentration (Takeda, 1995). TiO₂ is more effective using adsorbent (Naimah, 2014). The activities of TiO₂ photocatalysis can be improved by carrying out the supporting material, such as adsorbent (Damayanti, 2014). Zeolite is an adsorbent which is frequently used since it has active side and can be found abundantly in 46 locations in which its total capacity is billions of ton according to Mineral Technology Development Centre (Suyitno, 2000). Locations which have been commercially mined are Bayah, Lebak, and Banten, but the use is not yet optimal, so this research is conducted to exploit Bayah natural zeolite to be more optimal.

Some researches about dye degradation using TiO₂-zeolite have been frequently conducted, by Damayanti et al. (2014) who degraded methylene blue up to 80.23% using Turen natural zeolite, Wenjie Zhang et al. (2010) who tested capability of TiO₂-zeolite in degrading methyl orange using HZSM-5 synthetic zeolite with the degradation result

of 99.5%, Cheng-Cai Wang (2008) who researched the loading performance of TiO₂ in degrading *methyl violet* using Y zeolite (zeolite with Si/Al = 5.1). The best result of TiO₂ loading is 20% with the photodegradation efficiency of 58%. Furthermore, Hardeli et al. (2014) used TiO₂ to get degradation percentage of 81% in methyl violet with optimum time of 6 hours (Hardeli, 2014). Therefore, this research was conducted to optimize the degradation of methyl violet using TiO₂-Bayah natural zeolite, to get better result.

2. Methodology

This research used TiO₂ Degussa P25 and natural zeolite from Bayah, Banten. To activate Bayah natural zeolite, HCL pro analyst from Merck was used. The waste used was artificial waste from methyl violet of sigma Aldrich. This research was conducted in four phases, namely activating Bayah natural zeolite, fusing TiO₂ and Bayah natural zeolite, characterization of the resulted catalyst, and adsorption and degradation tests of methyl violet.

2.1. Activating Bayah Natural Zeolite

In this stage of zeolite activation, the initial step to be conducted was to reduce zeolite into a finer shape using ball mill tool; the solid was sifted to get zeolite sizes of 60, 80, and 100 mesh to be made variation. 100 gram of zeolite was prepared and mixed using HCl 0.3 M into beaker glass to activate zeolite since this concentration was an optimal condition for HCL to activate zeolite (Wenjie, 2010). Mixture was stirred for 2 hours at a temperature of 92–95°C with the aim of accelerating the zeolite-activating reaction to be filtered using filter paper, so the zeolite solid can be separated. Zeolite solid was then heated in oven for 2 hours at a temperature of 110°C with the aim of vaporizing water left in zeolite, so the width of pore surface in zeolite can be expanded. After that, calcination was performed to zeolite which was activated at a temperature of 500°C for 3 hours. Zeolite calcination was done to improve the special traits in zeolite by eliminating pollutants and vaporizing water trapped in zeolite crystal pore. Surface in final result was measured using BET analysis.

2.2. Fusing TiO₂ and Bayah Natural Zeolite

The preparation stage of TiO₂-zeolite used 200 mL of distilled water solvent, mixed with

a number of TiO₂ P25 Degussa (2, 4, and 6 gram), and 10 gram of zeolite. The mixture was then stirred using agitator for 45 minutes, so the dissolved TiO₂ catalyst can stick to zeolite, and it was filtered using filter paper to get the solid of TiO₂-zeolite. The solid was then heated at a temperature of 110° C for 3 hours, so the solvent can be completely dissolved and structure of TiO₂-zeolite was expected to remain undamaged (Maraschi Federica, 2014).

2.3. Characterization stage of catalyst

In this stage, some tests have been performed for the resulted catalyst (TiO₂-zeolite), such as test of area surface width using BET analysis and catalyst crystallinity analysis using XRD. BET analysis was conducted for zeolite sample before and after activation, TiO₂, and catalyst from fusion of TiO₂ and zeolite. Meanwhile, XRD analysis was conducted on the catalyst of TiO₂-Zeolite, TiO₂, and zeolite after activation.

2.4. Stage of Adsorption and Degradation Test for Methyl Violet

In this stage, TiO₂-zeolite which has been prepared was tested to degrade methyl violet. Meanwhile, 0.25 gram of TiO₂-zeolite was mixed with 500 mL of synthetic methyl violet into beaker glass of 1 L and put into photoreactor equipped with UV lamp while mixed for 4 hours using magnetic stirrer. The mixture was then taken as sample every 15 minutes and analyzed using UV-VIS spectrophotometer to calculate the concentration of methyl violet in sample. For adsorption test, UV lamp was switched off, so the decrease of methyl violet concentration was only caused by adsorption, not photocatalysis reaction.

3. Result and Discussion

3.1. Result of BET analysis test

The specific surface width of zeolite catalyst, TiO₂ P25 Degussa and TiO₂-zeolite can be identified with Brunauer Emmett and Teller (BET) analysis in Table 1. Table 1 shows the surface width of Bayah natural zeolite after activation was 27.119 m²/g, while the value without activation was 34.75 m²/g. The decrease of this surface width shows the structural change in zeolite in calcination process, so the activation process, which should be capable of increasing the surface width, decreased surface width. Low zeolite surface width indicated that zeolite pores had more pollutants, such as Al₂O₃, SiO₂, Fe₂O₃,

CaO, K₂O (Kunarti, 2015 and Pamungkas, 2011). Besides, the decrease of BET value was caused by some factors, such as zeolite washing.

Table 1. Result of BET analysis

Material Type	Surface area, m ² /g
Non-Activation Zeolite	34.75
Activation Zeolite	27.119
TiO ₂ P25	54
TiO ₂ - Bayah natural zeolite (4 gram of TiO ₂ -10 gram of zeolite)	18.276

Another cause of the decrease of this surface area was possibly the lack of time for washing zeolite after activation process; long washing process resulted in secretion of H⁺ ion in zeolite, so the surface width was larger. Based on the data, it is known that the carrying out of TiO₂ in zeolite caused the decrease of specific surface width; the possible cause was the closing of zeolite pores by TiO₂ particles. This result is similar to a research by Fatimah (2006) in which the carrying out of TiO₂ into zeolite resulted in the decrease of surface width, based on the research. Based on the research, its cause was a sintering process of TiO₂ particles in external and internal surfaces of zeolite. Sintering is fusion or clumping of particles at high temperature (Fatimah, 2006). Because of sintering, its specific surface width was relatively smaller.

3.2. XRD Characterization Result

Figure 1 shows XRD analysis data about zeolite crystal phase, TiO₂, and TiO₂ - zeolite. In zeolite data, many sharp peaks were found at angles around 100, 220, 250, 260 and 270 which show mordenite and clinoptilolite phases. These data show mordenite phase on peaks at angles of 220, 250, 260, and 270, while clinoptilolite phase was shown on peak at angle of 100 with the shaping percentage of 64.92% for mordenite phase and 35.08% for clinoptilolite phase. This clinoptilolite zeolite can be used well in ion exchange, while mordenite zeolite can be used well as catalyst (Jayanudin, et al. 2017). Many mordenite phases in zeolite were caused by high zeolite-heating process which resulted in unstable clinoptilolite phase. In TiO₂ data, anatase phase was frequently found, compared with rutile phase; anatase phase was shown on sharp peak at angles of 25, 38, 48, 54, and 56, while its rutile phase was found at angle of 27.5.

According to Malldoti (2000), anatase and rutile structures are quite stable in terms of existence, compared with brookite structure. In the photocatalysis reaction, TiO₂ in anatase shape showed its activeness, compared with rutile phase. Besides, energy of band gap in anatase energy was larger than rutile, which was 3.23 eV for anatase phase and 3.02 eV for rutile phase, so anatase phase had high photocatalysis activity.

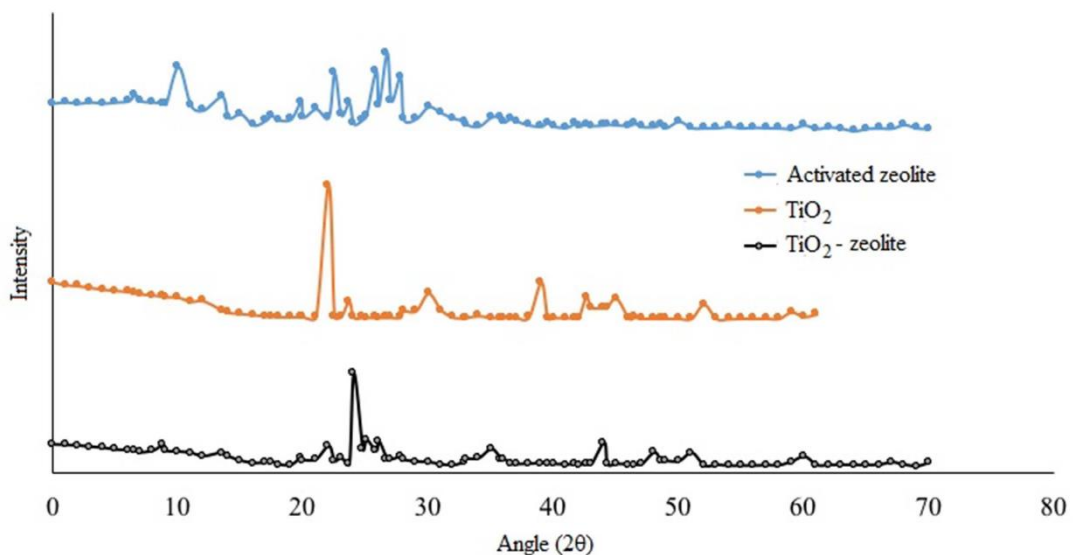


Figure 1. Result of XRD characterization in zeolite, TiO₂ and TiO₂-Zeolite

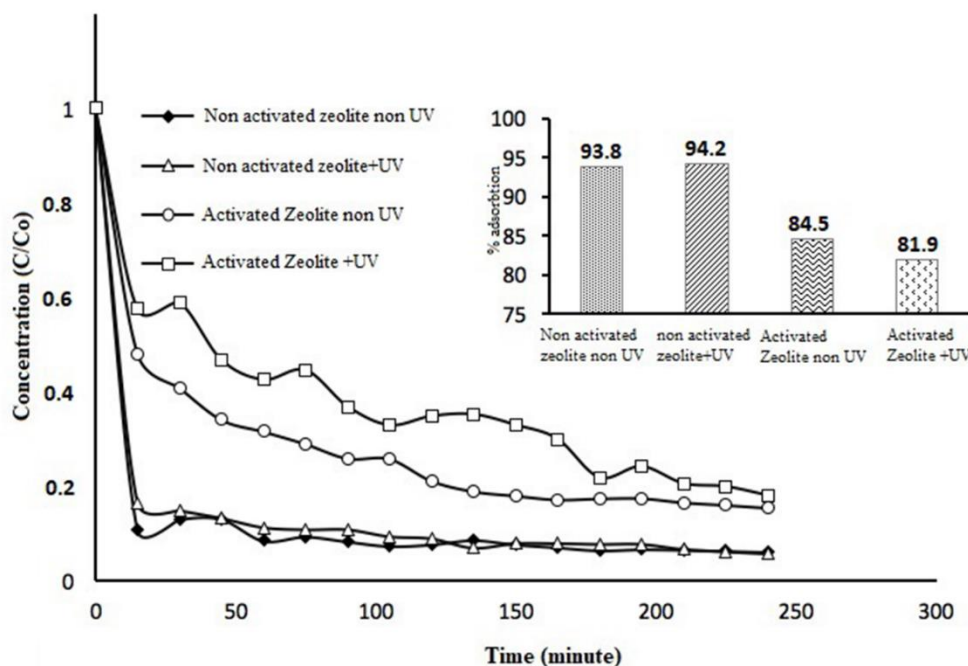


Figure 2. Effect of initial treatment in zeolite for adopting methyl violet

Table 2. Anatase crystal size

Sample	Crystal size (nm)
TiO ₂ P25 Degussa	21.06
Acid activation zeolite	-
TiO ₂ -zeolite	18.89

Table 3. Percentage of methyl violet adsorption using zeolite

Sample	% adsorption without UV lamp	% adsorption with UV lamp
Non-activated zeolite	93.8	94.2
Acid activated zeolite	84.5	81.89

Data of TiO₂-zeolite show some peaks at angles of 25°, 38°, and 48° which were similar to peak of TiO₂. According to the result of analysis, the peak was anatase phase of TiO₂. Peak in graphic also shows that TiO₂ stuck to zeolite, so it formed peak graphic which was similar to TiO₂ graphic. XRD data can be used to identify the size of anatase crystal in TiO₂ catalyst. Size of anatase crystal was one of the parameters in activeness of TiO₂ catalyst in degrading organic compounds. Measurement result of crystal size is shown in Table 2. One of the parameters for photocatalyst activeness in TiO₂ for degrading

organic compounds was size of anatase crystal.

3.3. Zeolite adsorption test

Effect of initial treatment in zeolite on methyl violet adsorption is shown in Figures 2 and 3. This stage was performed with and without UV lighting.

Non activated zeolite shows a sharp decrease of concentration in methyl violet at first point; it can be caused by some factors which affected the absorption. Zeolite is a porous mineral, when some molecules penetrate the zeolite micro pore system, molecule can be absorbed based on polarity or interaction between molecule and zeolite (Buchori, 2003). Besides, absorption effectiveness also depends on the absorbed species trait, ion exchange capability, zeolite solid acidity, and system moisture.

Factor of ion exchange capability causes the decrease of concentration value at first point in non-activation zeolite. One of the basic requirements in ion exchange is adequate hydrophilic to allow ion diffusion through its structure at the measured rate. Zeolite activated by acid can have hydrophobic trait, while inactivated zeolite has hydrophilic trait (Lestari, 2010). Therefore, when activation zeolite absorbs methyl violet, its absorption process tends to be long, compared with zeolite without activation.

Figure 2 and Table 3 show non-active zeolite absorption value which is larger than the activated zeolite; another cause of activation zeolite absorption which is lower than non-activation zeolite is surface area value of activation zeolite which has smaller value, 27.119 m²/g, compared with non activated zeolite with surface area value of 34.075 m²/g. Surface area value will affect absorption capacity in zeolite itself; the more larger the surface area, the more higher the capacity for its absorbed material will be. Besides, the factor affecting a decrease in active zeolite absorption process is capability of ion exchange. In previous result of XRD analysis, clinoptilolite phase played role in ion exchange of 35.08%, so zeolite capability in absorbing decreased.

3.4. Zeolite effect as TiO₂ support

This research compared effectiveness of zeolite catalyst, TiO₂, and TiO₂- zeolite, with and without UV lamp, in degradation process of methyl violet. Test result is shown in Figure 3 and Table 4. Figure 3 shows analysis result with zeolite, TiO₂, and TiO₂ - zeolite with artificial methyl violet concentration of 20 ppm, degraded in photocatalytic reactor for 4 hours.

The decrease of methyl violet concentration on TiO₂ material without lighting can reduce 25.5% in 240 minutes, while concentration decrease with TiO₂ using lighting was 91.9%.

This difference in decrease was caused by lighting on TiO₂ using UV lamp. When TiO₂ was illuminated by UV light, TiO₂ actively formed radical OH to oxidize methyl violet, so the concentration decrease was large. When TiO₂ was illuminated by UV light, TiO₂ reacted to form electron (e⁻) and hole (h⁺); these electron and hole reacted again to form radical OH, while TiO₂ without UV light did not react to form electron (e⁻) and hole (h⁺), so the ongoing process was only adsorption process.

Table 4. Percentage of methyl violet elimination for 4 hours

Sample	% of elimination without UV light	% of elimination with UV light
Non-activation zeolite	93.8	94.2
Acid activation zeolite	84.5	81.89
TiO ₂ P25 Degussa	25.5	91.9
TiO ₂ -zeolit	71.35	94.75

Concentration of methyl violet was reduced by TiO₂-zeolite the most in which the percentage was 94.75%. Methyl violet concentration did not decrease too much, compared with the concentration decrease using zeolite without activation. Zeolite before activation had wider area, compared with other catalysts.

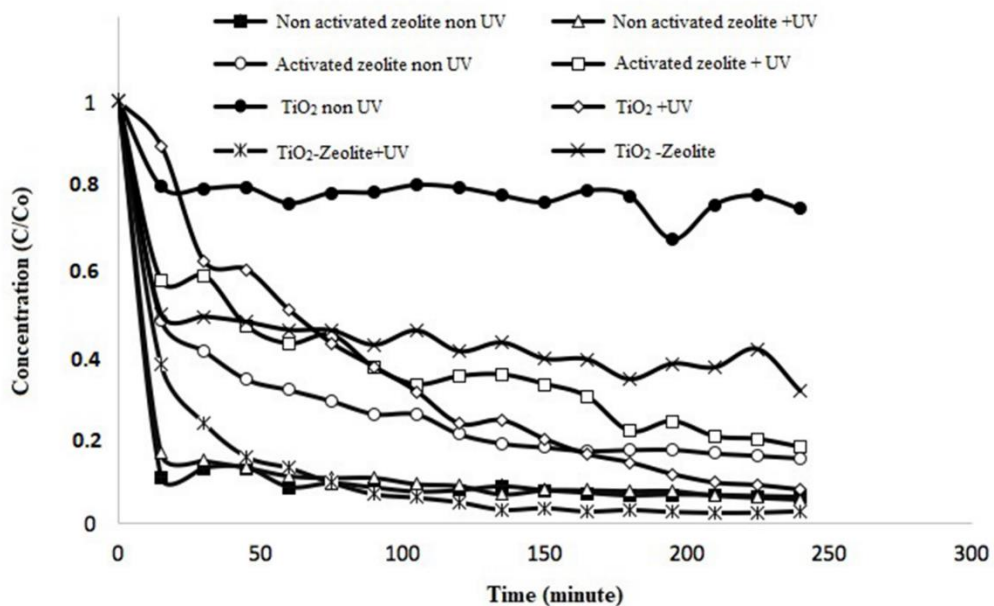


Figure 3. Effect of catalyst variation on methyl violet degradation.

However, methyl violet concentration was decreased only because of adsorption. It was different from condition when using fusion of TiO₂ and zeolite. When methyl violet was absorbed in zeolite, methyl violet was simultaneously degraded by photocatalyst fused in zeolite, so concentration of methyl violet was moved from solution to zeolite and then degraded into CO₂ and H₂O.

Methyl Violet concentration was decreased using fusion of TiO₂ and zeolite. Degradation process performed by TiO₂ used energy from UV lamp. Energy from UV lamp was used by TiO₂ to form hole and radical OH; this radical OH reacted to degrade methyl violet. For reaction in TiO₂-zeolite and TiO₂, they were almost the same since degradation process of methyl violet reacted more frequently than TiO₂.

In mechanism of TiO₂ reaction on methyl violet, TiO₂ absorbed UV light to form electron (e⁻) and positive hole (h⁺). When the surface of TiO₂ came in contact with methyl violet solution, oxidation mechanism process occurred because of positive hole (h⁺); this positive hole oxidized water (H₂O) to form a radical OH which had capability to decompose the organic compounds. Simultaneously, reduction process was performed by electron (e⁻); this reduction process affected O₂ and changed it into superoxide anion (O₂⁻). Superoxide anion (O₂⁻) underwent reaction oxidation to form hydrogen peroxide which changed into H₂O. This H₂O was used by positive hole (h⁺) to form radical OH which affected N element with positive charge from methyl violet molecule, so the structure of methyl violet molecule was broken into NH₂ compounds which changed these organic compounds into carbon dioxide and water. Photocatalysis reaction mechanism for methyl violet degradation is illustrated in Figure 4.

For TiO₂-zeolite mechanism with methyl violet, its reaction mechanism was almost the same with TiO₂ reaction using methyl violet, but the difference was its additional zeolite in supporting the methyl violet absorption process to pull methyl violet compounds, so the performance of TiO₂ can be faster.

Mechanism of TiO₂-zeolite and methyl violet refers to Figure 5; methyl violet was absorbed by zeolite to form pull force which pulled methyl violet compounds toward zeolite. With this pull force, when methyl violet approached TiO₂, the degradation reaction of methyl violet occurred and some of them, which were not degraded at that time, were absorbed by zeolite. Besides, TiO₂ illuminated by UV lamp

was excited very quickly, so the use of zeolite here was quite helpful in reducing concentration.

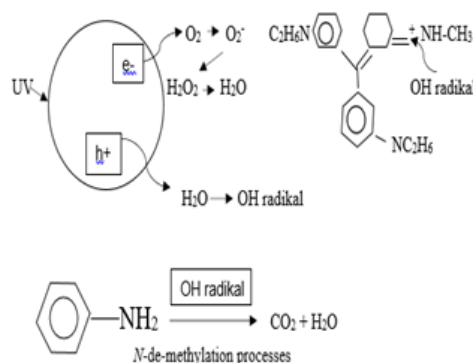


Figure 4. Illustration of TiO₂ mechanism using Methyl Violet

Comparison of concentration value performed by fusion of TiO₂-zeolite was larger with the decrease of 94.75%, while the decrease by TiO₂ was 91.9%. In other words, TiO₂ photocatalyst reaction with zeolite to degrade methyl violet dyes can be written as follows:

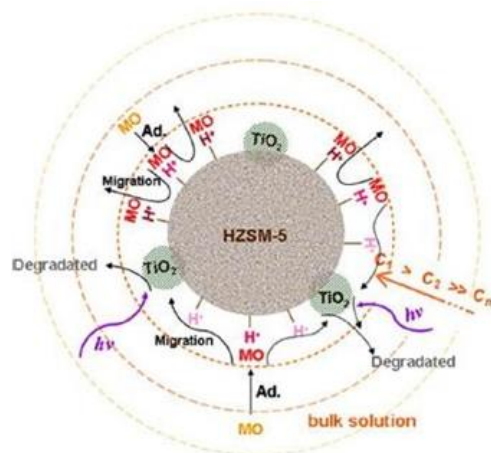
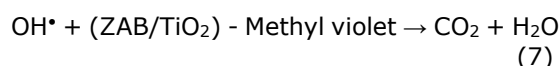
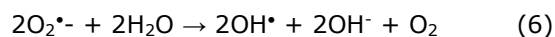
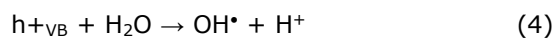
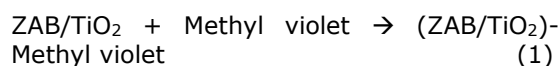


Figure 5. Mechanism of TiO₂ - zeolite (Mahalakshmi, 2008)



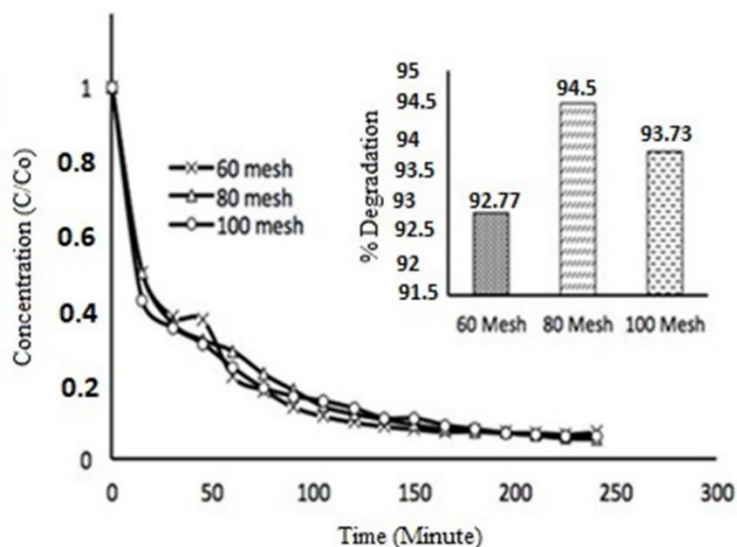


Figure 6. The effect of zeolite mesh size on methyl violet degradation

3.5. Effect of Zeolite Mesh Size

Figure 6 shows the effect of zeolite size used for fusing TiO_2 -zeolite. The result shows TiO_2 -zeolite fusion using zeolite with a size of 80 mesh to reach the lowest concentration decrease, compared with zeolite with sizes of 60 mesh and 100 mesh. The more small the zeolite size, the more large the capability of zeolite adsorption found at size of 80 mesh, methyl violet adsorption was the best since it had composition structure suitable with TiO_2 to be fused into zeolite, compared with other sizes.

The result of this research is in accordance with previous research (Kustiningsih, I and Sari DK., 2017). Zeolite with a size of 80 mesh was capable of providing space for TiO_2 (compared with zeolite of 100 mesh). Although a smaller zeolite size will theoretically provide many pores, TiO_2 which will penetrate into zeolite requires pores and strong support to support TiO_2 at large quantity (Kustiningsih, I, and Sari DK., 2017).

3.6. Effect of mass comparison in TiO_2 and zeolite

In order to identify the effect of TiO_2 mass in zeolite toward degradation process of methyl violet dyes, test was conducted by varying amount of TiO_2 (2 gram, 4 gram, and 6 gram) in which zeolite mass used in every variation was 10 gram. Variation of TiO_2 amount was tested in methyl violet solution at concentration of 20 ppm for 4 hours.

The effect of TiO_2 mass in zeolite on methyl violet degradation is shown in Figure 7.

Figure 7 shows that more TiO_2 carried in zeolite mean more possibility of hole and superoxide ion. Hole in TiO_2 reacted with H_2O or OH^- ion-molecule and resulted in hydroxyl radical ($\bullet\text{OH}$), in which hydroxyl radical degraded the methyl violet dyes, so an increase of hole number resulted in the increase of methyl violet degradation.

Figure 7 shows that TiO_2 -zeolite photocatalyst activity was improved along with the increase of TiO_2 in Zeolite and TiO_2 fusion. The best degradation of methyl violet was obtained at mass of 4 gram in TiO_2 (40% on Zeolite). Using this photocatalyst, methyl violet concentration was decreased by 94.5%. Optimal TiO_2 loading was different from a research conducted by Slamet et al. (2007). In the research, optimal TiO_2 mass was obtained at 30% on zeolite. It was possibly caused by different type of zeolite used.

3.7. Effect of solvent variation

In fusing zeolite and TiO_2 , this research used two different solvents, namely distilled water and ethanol, for comparison, to identify the best solvent in fusing TiO_2 -zeolite. Figure 8 shows graphic about the use of solvent to fuse TiO_2 and zeolite. The use of ethanol and distilled water as solvent was almost the same in terms of quality in the process of fusing TiO_2 -zeolite, by considering the data of concentration decrease in this research. Based on the result, ethanol and distilled water show the best solvent to fuse TiO_2 -zeolite, but the process of fusing TiO_2 -zeolite with distilled water shows precipitation which was faster than ethanol solvent.

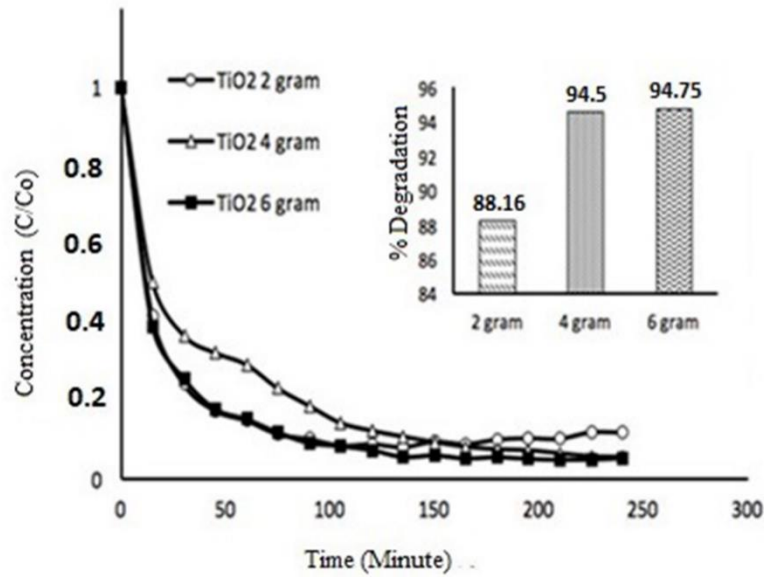


Figure 7. The effect of TiO₂ mass in zeolite on methyl violet degradation

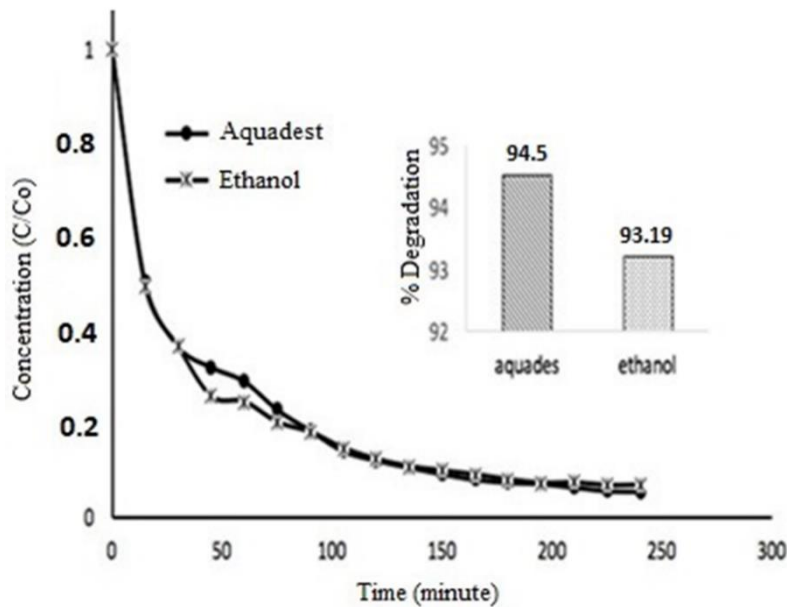


Figure 8. The effect of solvent variation in fusing TiO₂-zeolite on its capability to degrade methyl violet

3.8. Effect of UV Lamp Intensity

This test was conducted using 6 gram of TiO₂ photocatalyst, 10 gram of Bayah natural zeolite, distilled water solvent, and UV lamp with variation of 2, 4, and 6 units. The measurement result of UV light intensity is shown in Table 5. The effect of UV light intensity on methyl violet degradation is shown in Figure 9.

The highest elimination percentage was in the use of 6 lamps (1,340 μW/cm²), which was 94.75%. Semiconductor material can result in electron pair and hole when semiconductor was exposed to photon with energy which was the same or larger than its energy band gap ($h\nu \geq E_g$), in which hole can react with H₂O and form hydroxyl radical ($\cdot\text{OH}$). Radical hydroxyl had important role in degrading organic compounds. Intensity of UV light on semiconductor surface can affect number of the formed hydroxyl radical. Meanwhile,

when the forming of hydroxyl radical was higher, photocatalysis process was easier and amount of the degraded dyes was larger. When intensity of UV light increases, the possibility of electron excitation will improve and increase degradation rate (Mehrotra, 2003). It shows that degradation level is directly proportional to value of UV light intensity (Sun, 2015).

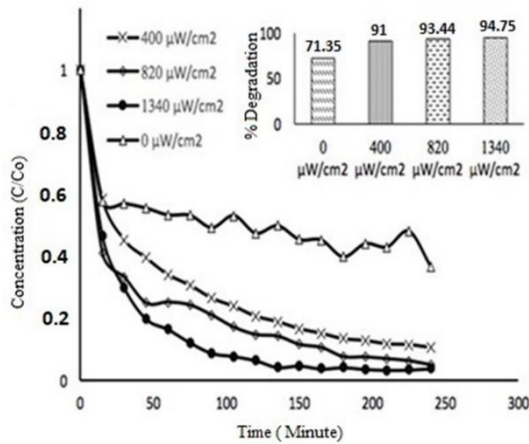


Figure 9. The effect of UV light intensity on methyl violet degradation

Table 5. Intensity of UV Light on lamp number

Number of Lamp	UV Intensity (μW/cm²)
2	400
4	820
6	1,340

Figure 9 shows that the more high the intensity of UV light, the more large the concentration of degraded methyl violet will be.

4. Conclusion

Zeolite activation failed, marked by decrease of zeolite surface width from 34.075 m²/g to 27.119 m²/g. The best zeolite size was at 80 mesh. Intensity of UV lamp also affects the degradation of methyl violet. The more high the intensity of UV lamp, the more large the degradation of methyl violet will be. Optimal TiO₂-Zeolit photocatalyst was obtained at composition of 4 gram of TiO₂ with solvent using distilled water. Using this photocatalyst, methyl violet degradation was 94.5%.

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