

## Effect of Aeration Treatment on Methylene Blue Removal Using TiO<sub>2</sub>-Zeolite

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**Abstract.** Effect of aeration treatment on *Methylene Blue* (MB) removal using TiO<sub>2</sub>-Zeolite has been investigated. The TiO<sub>2</sub>-Zeolite was prepared by mixing activated zeolite and TiO<sub>2</sub> in absolute ethanol. This composite was characterized using *Fourier Transform Infrared* (FT-IR) and *X-Ray Diffraction* (XRD). The MB removal was monitored spectrophotometrically. The effect of contact time, composite mass, and aeration treatment on MB removal was observed. Characterization results showed that there was interaction between TiO<sub>2</sub> and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of zeolite. The observation of aeration treatment using oxygen exhibited significant improving on MB removal.

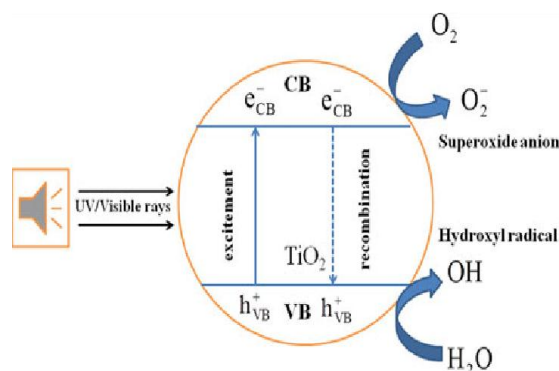
**Keywords:** Aeration, Composite, Methylene Blue, Removal, TiO<sub>2</sub>-Zeolite

### INTRODUCTION

Along with the increase in population, the textile industry in Indonesia continues to grow. The rapid development of the textile industry has a positive impact on increasing employment. In addition to providing many benefits for human life, the development of the textile industry has a negative impact on the environment. This is because in textile production it always produces waste. The waste of textile industry has a high content of dye. Dyes in the textile industry are organic compounds that are not biodegradable and toxic (Manurung et al., 2004).

Reactive dyes are dyes which are widely used for dyeing of textile products. Various methods have been carried out to treat the waste and the results are quite effective. Some of the methods are adsorption, biodegradation, chlorination and ozonation. However, this method requires large operational cost making it is less effective to implement in Indonesia. Another method that is widely used is a combination of coagulation, oxidation, electrochemistry, osmosis and adsorption. However, these methods have a weakness, which basically only acts to transfer pollutants from wastewater to other media, causing new problems (Wijaya et al., 2006).

Fujishima and Honda (1972) showed that photodegradation using photocatalyst emerged as one of the alternative of waste treatment technology. Photocatalyst is a chemical process involving light and a catalyst. TiO<sub>2</sub> which can function as a semiconductor is often used as a photocatalyst because it is available and safe to use. However, the high photocatalytic activity of TiO<sub>2</sub> does not appear to be compatible with its ability to absorb the target compounds. According to Fatimah et al (2005), the photocatalytic activity of TiO<sub>2</sub> can be enhanced through the use of the supporting materials, one of which is acid-activated natural zeolite.



**Figure 1.** The photocatalytic activity of TiO<sub>2</sub> under UV irradiation (Krishna et al., 2013).

Upon UV irradiation, TiO<sub>2</sub> mainly absorbs UV photons leading to the generation of electrons and holes on the surface. A photon having energy equal to or higher than that of the band gap moves an electron from the valence band to the conduction band leaving behind a hole in the valence band. The photogenerated electrons and holes either recombine or migrate to the surface to react with contaminant adsorbed on the surface. The hole in the valence band (VB) reacts with H<sub>2</sub>O adsorbed on the surface to produce hydroxyl radicals, and the electron in the conduction band (CB) reduces O<sub>2</sub> to produce superoxide ions (O<sub>2</sub><sup>-</sup>). Hydroxyl radicals and superoxide ions are particularly reactive to decompose organic compounds present on the TiO<sub>2</sub> surfaces because of their strong oxidation power (Krishna et al., 2013).

Aeration is one way to enhanced the dissolved oxygen of water. In theory, the use of pure oxygen aeration will help in the process of photodegradation of organic compounds. According to the theory of photocatalytic activity of TiO<sub>2</sub> under UV irradiation (Figure.1), the more oxygen around TiO<sub>2</sub>, the more anionic superoxide will be produced. This will increase

the degradation of MB as a target compound and lead to improve on MB removal.

## MATERIALS AND METHODS

### Materials

The tools that using for  $\text{TiO}_2$ -Zeolite preparation are glassware, analytical scale, buchner pump, hot plate, magnetic stirrer, spoon glass, pH meter, regulator, oxygen tube, centrifuge, furnace, UV- blacklight reactor, and 106 micron sieve. While the characterization of the composite using X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR). The monitoring of MB removal is using UV-Vis Spectrophotometer and 20-D Spectronic.

The natural zeolite used in this research was obtained from Wonosari, Gunung Kidul, Yogyakarta. The other materials using for research are  $\text{TiO}_2$  p.a Merc, Hydrochloric acid (HCl) p.a Merc, whatman-42 filter paper, millipore paper, oxygen, distilled water and Methylene Blue (MB).

### Zeolite Activation

Fifty grams of natural zeolite which passed the sieve with a 106 micron diameter was soaked in 100 mL of 3M HCl, then stirred the mixture for 24 hours using magnetic stirrer at  $90^\circ\text{C}$ . After that, the mixture was filtered using filter paper and washed using distilled water until the pH of filtrate is equal to the pH of distilled water. Then zeolite was calcined on  $450^\circ\text{C}$  for 3 hours and characterized using XRD and FT-IR.

### The Preparation of $\text{TiO}_2$ -Zeolite Composite

Eight grams of activated zeolite and 1.4 g  $\text{TiO}_2$  were mixed in beaker glass. The mixture was dissolved in 10 mL of absolute ethanol and stirred for 5 hours. This mixture was then dried by heating in oven at  $120^\circ\text{C}$  for 5 hours. The solid then grinded and sieved with 106 micron sieve. Finally, the solid was calcined at  $500^\circ\text{C}$  for 5 hours. By using this procedure, the solid obtained was assigned to as composite of  $\text{TiO}_2$ -Zeolite. This composite was characterized using *Fourier Transform Infrared* (FT-IR) and *X-Ray Diffraction* (XRD).

### Photodegradation of Methylene Blue

Photodegradation experiments were conducted in a batch reactor under UV light. Photodegradations were engaged by dispersing a certain amount of  $\text{TiO}_2$ -Zeolite composite into MB solution followed by stirring and UV irradiation.

#### 1. Optimum contact time determination.

The determination of optimum contact time was conducted by dispersing 40 mg of  $\text{TiO}_2$ -Zeolite composite into 25 mL of 40 ppm MB solution. The experiments were observed at 30, 45, 60, 75, and 90 minutes contact time with UV irradiation. This experiment was also performed a control by dispersing the same amount of  $\text{TiO}_2$ -Zeolite

composite into the same volume and concentration of MB solution at the same varied of contact time without UV irradiation. Another control was performed by dispersing 40 mg of activated zeolite into the same volume and concentration of MB solution at the same varied of contact time with UV irradiation. The MB removal was determined using UV-Vis Spectrophotometer and 20-D Spectronic.

#### 2. Optimum composite mass determination.

The determination of optimum composite mass was conducted by dispersing 20, 40, and 60 mg of  $\text{TiO}_2$ -Zeolite composite into 25 mL of 40 ppm MB solution. The experiments were observed at the optimum contact time. This observation was also performed the controls using  $\text{TiO}_2$ -Zeolite composite (without UV irradiation) and activated zeolite (with UV irradiation). The MB removal was determined using UV-Vis Spectrophotometer and 20-D Spectronic.

#### 3. Aeration treatment effect.

The effect of aeration was observed by diffusing of oxygen into 25 mL of 70 ppm MB solution at varied of oxygen diffusing time; 10, 20, and 30 minutes, respectively. These experiments were conducted using the optimum mass of  $\text{TiO}_2$ -Zeolite for 30 minutes contact time with UV irradiation. The MB removal was determined using UV-Vis Spectrophotometer.

## RESULTS AND DISCUSSION

### Materials Characterization

Pattern of X-ray diffraction provides information about the type of the mineral arrange in materials (natural zeolite (ZA), activated zeolite (ZH), and  $\text{TiO}_2$ -Zeolite composite) and the cristallinity of the materials. Figure 2 showed the characteristics of ZA, ZH, and  $\text{TiO}_2$ -Zeolite composites.

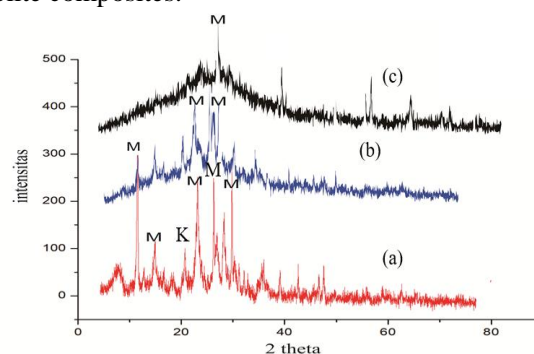


Figure 2. Diffractogram (a) ZA and (b) ZH (c) Composite  $\text{TiO}_2$ -Zeolite.

Figure 2 shows that the main composition of the natural zeolite (ZA) is mordenite. This is indicated by specific peak of material that appear on the  $2\theta = 9,75^\circ$ ;  $13,37^\circ$ ;  $19,48^\circ$ ;  $22,20^\circ$ ;  $25,54^\circ$ ;  $26,16^\circ$ ;  $27,60^\circ$  dan  $29,81^\circ$ . These specific peaks are confirmed by Wijaya (2006). The diffractogram of activated zeolite (ZH) shows no significant difference with ZA, but it shows a

decrease in intensity, that means decreasing of crystallinity of ZH. It apparently due to the activation process using 3M HCl that escalate dealumination process resulting increasing the ratio of Si/Al (Lestari, 2010).

To ensure the presence of TiO<sub>2</sub> in the TiO<sub>2</sub>-Zeolite composite, the X-ray diffraction analysis on TiO<sub>2</sub> and TiO<sub>2</sub>-Zeolite composite was made. The diffraction pattern of TiO<sub>2</sub> and TiO<sub>2</sub>-Zeolite composite are shown in Figure 3. X-Ray diffraction provides information about the types of TiO<sub>2</sub> crystals. The diffractogram of TiO<sub>2</sub> (a) was compared with the XRD data of various types of crystals such as anatase, rutile and brookite in JCPDS (2001). Figure 3, especially the specific peaks that appear on the  $2\theta = 37,55^\circ$ ;  $47,80^\circ$ ; and  $53,61^\circ$  shows the reflection of TiO<sub>2</sub>. In the TiO<sub>2</sub>-Zeolite composite (b), it can be observed that the high diffraction intensity appeared at peak on the  $2\theta = 25,06^\circ$ , indicate the specific peak of mordenite.

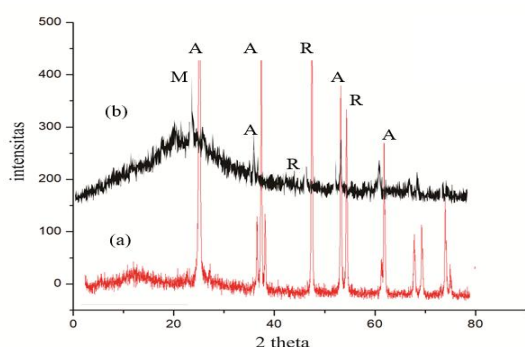


Figure 3. Diffractogram (a) TiO<sub>2</sub> Degussa and (b) Composite TiO<sub>2</sub> zeolite.

The functional groups that present in activated zeolite and TiO<sub>2</sub>-Zeolite composite were studied using the FTIR spectroscopy. Figure 4 shows the comparison of FTIR spectra of activated zeolite and TiO<sub>2</sub>-Zeolite composite. From Figure 4, it can be observed that the samples of activated zeolite and TiO<sub>2</sub>-Zeolite composite exhibited similar FTIR spectra characteristics of zeolite. This indicated that zeolite is high suitable to act as TiO<sub>2</sub> immobiliser, as the structure is not affected by impregnating of TiO<sub>2</sub>.

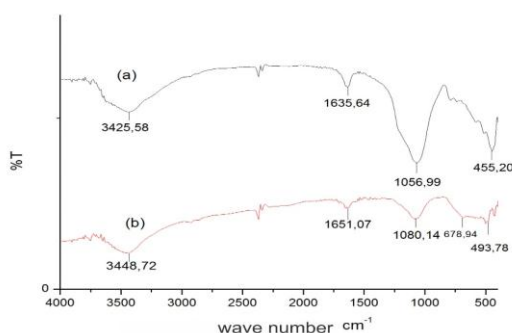


Figure 4. FT-IR spectra (a) Activated Zeolite and (b) Composite TiO<sub>2</sub>-Zeolite.

In Figure 4 there is a spectral difference between the spectra of TiO<sub>2</sub>-Zeolite composite (b) and activated zeolite (a). The difference is pointed out at the presence of the band at  $678.94\text{ cm}^{-1}$  in TiO<sub>2</sub>-Zeolite composite spectra which were not observed in activated zeolite spectra. The band is probably associated with TiO<sub>2</sub> as reported by Chamidah (2016) that TiO<sub>2</sub> band showed at  $694.37\text{ cm}^{-1}$ . This characterization results indicated that there was interaction between TiO<sub>2</sub> and SiO/AlO of zeolite.

## Photodegradation of Methylene Blue

### Optimum Contact Time Determination

The contact time is an important point in photocatalytic water treatment processes. The optimum contact time enables the maximum photocatalytic activity. The results of the optimum contact time determination are showed in Figure 5. The results of the treatment using TiO<sub>2</sub>-Zeolite composite with UV irradiation (Figure 5(a)) show that the percentage removal of MB increases with the increasing of contact time and significantly decreases in the removal of MB when passing the optimum point of contact time. The highest percentage removal is pointed at 75 minutes contact time resulting in 91.10% removal.

Control experiment (Figure 5(b)) shows that in the absence of UV irradiation, the removal of MB was relatively low. The optimum contact time of this control experiment was 45 minutes resulting 80.91% MB removal. According to Wijaya (2006), this phenomenon indicates the adsorption process, since there is no source of light (photons). In the other control experiment with the absence of TiO<sub>2</sub>, the activated zeolite reached the optimum contact time at 45 minutes resulting 86.13% MB removal. Both of these control experiments show the evidence of lower MB removal in comparison with the MB removal using TiO<sub>2</sub>-Zeolite composite in the presence of UV irradiation.

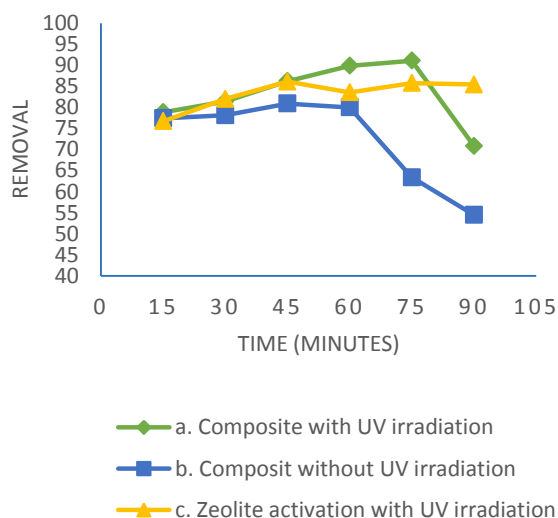


Figure 5. The results of MB removal at the optimum contact time determination.

In order to ensure that MB removal by TiO<sub>2</sub>-Zeolite composite was caused by photodegradation mechanism, spectrophotometric analysis to the treated MB solution was conducted. Figure 6 shows that the absorbance of characteristic spectra are decreased as indication of adsorption process. Furthermore, the UV-Visible spectra of treated MB solutions by using TiO<sub>2</sub>-Zeolite composite at the presence of UV irradiation

(Figure 6 (a)) exhibit the lowest absorbance. This observation also brings out the change in color of the treated solution, becomes clearer (data not shown). It can be stated that apparently both of these phenomenon indicate the adsorption and degradation process of MB molecule. This is confirmed by Wang S.L et.al., (2011) that observed the similar phenomenon.

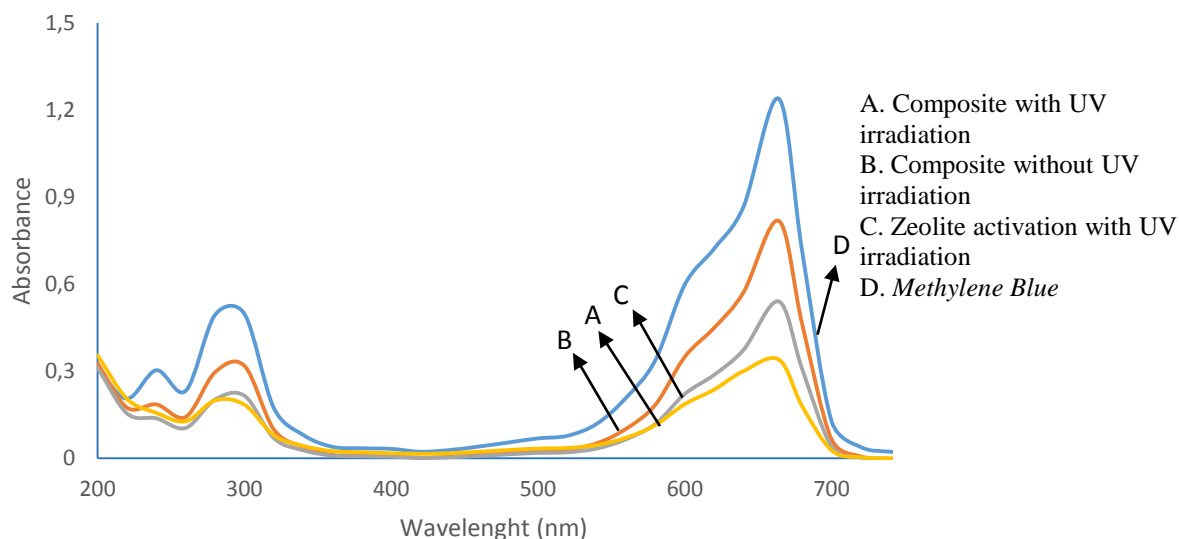


Figure 6. UV-Visible spectra of treated MB solutions at the optimum time.

### Optimum Composite Mass Determination

The optimum composite mass enables the maximum photoactivity while preventing the unnecessary excess

use of composite. The results of the optimum composite mass determination are showed in Figure 7.

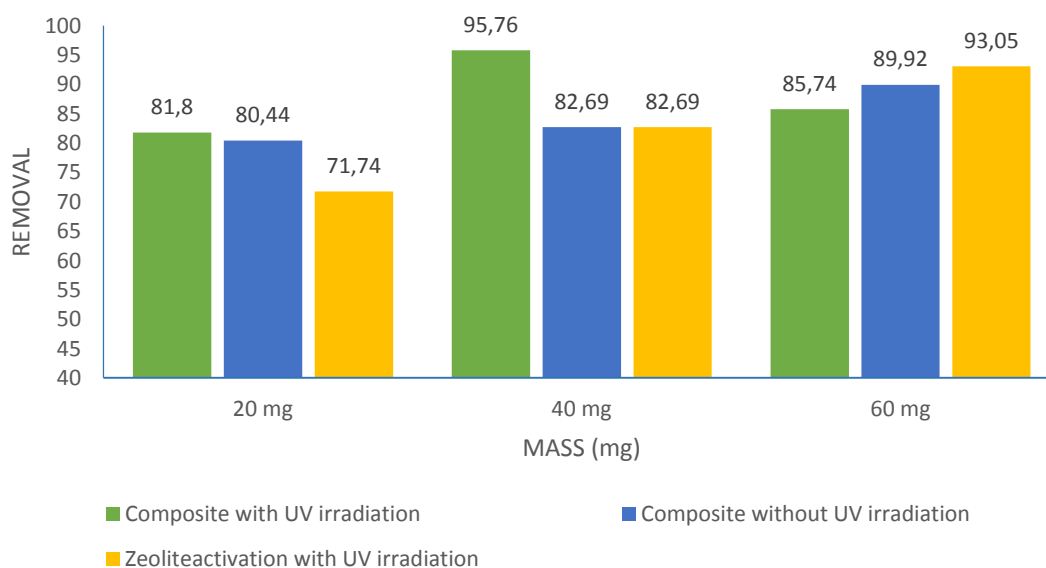
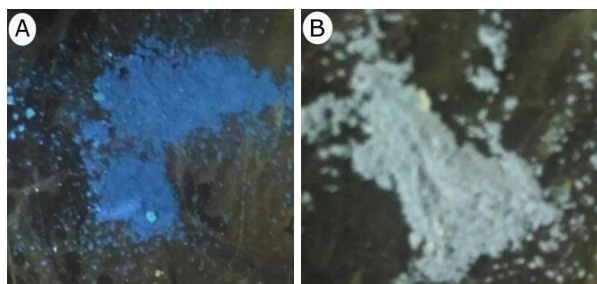


Figure 7. The results of MB removal at the optimum mass determination.



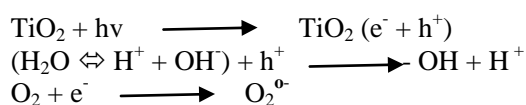
Primarily the increase in MB removal when the TiO<sub>2</sub>-Zeolite composites loading was increased from 20 mg to 40 mg was attributed to the higher number of active sites and more reactive radicals available for surface reaction. However, the reduction in MB removal of TiO<sub>2</sub>-Zeolite composites was observed at higher composite loadings (60 mg) owing to the increasing cloudiness in the reaction solution that prevents penetration from UV irradiation. Similar phenomenon was observed by M.N. Chong et al (2014). The calculation of maximum MB removal that obtained in this experiment was 0.023 mg per 1 mg of composite material.



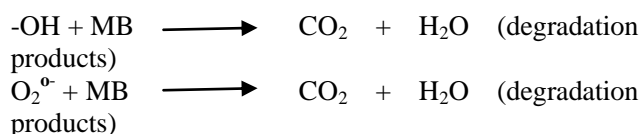
**Figure 8.** The color of the materials that had been used to treat the MB solution in this experiment (a) Activated Zeolite with UV irradiation (b) TiO<sub>2</sub>-Zeolite composite with UV irradiation.

The color of the materials that have been used to treat the MB solution in this experiment were compared and photographed as data, Figure 8. In the photograph (Figure 8), it is clear that activated zeolite exhibits a strong blue color while TiO<sub>2</sub>-Zeolite composite exhibits significant different color, white with a bluish color. The blue color of activated zeolite after been used to treat the MB solution indicates that MB molecules was adsorbed, changing the brownish color of activated zeolite into blue color. In contrast, the composite of TiO<sub>2</sub>-Zeolite exhibits white with a bluish color. This significant different color of the materials that had been used to treat the MB solution reveals a strong evidence of degradation process of MB molecule when treated using TiO<sub>2</sub>-Zeolite composite at the presence of UV irradiation. Similar phenomenon was observed and confirmed by Wang S.L et al (2011). In conclusion, it can be stated that both adsorption and photodegradation process contributed on MB removal in this experiment.

On the whole, it is clear that photodegradation process in this experiment requires both, photocatalyst material (TiO<sub>2</sub>) and photon source (UV irradiation). The absence of photocatalyst material or photon source reveals no photodegradation process. Degradation of MB by using TiO<sub>2</sub> is refer to reduction-oxidation reactions generated from absorption of photons by TiO<sub>2</sub> that leads photoexcitation: the formation of electron–positive hole pairs. If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially,  $h^+_{vb}$  may react with surface-bound H<sub>2</sub>O or OH<sup>-</sup> to produce the hydroxyl radical and  $e^-_{cb}$  is picked up by oxygen to generate superoxide radical anion (O<sub>2</sub><sup>•-</sup>), as indicated in the following reaction (Haque et al., 2012):



It has been suggested that the hydroxyl radical (·OH) and superoxide radical anions (O<sub>2</sub><sup>•-</sup>) are the primary oxidizing species in the photocatalytic oxidation processes.



#### Aeration Treatment Effect

Aeration treatment was done to increase the amount of dissolved oxygen in the MB solution. Pure oxygen was diffused into a solution of MB before the photodegradation process was carried out. This treatment was expected to improve the performance of TiO<sub>2</sub>-Zeolite composites to degrade MB when photodegradation was carried out. Dissolved oxygen would interact with  $e^-_{cb}$  on the surface of TiO<sub>2</sub>-Zeolite and produce superoxide radical anion (O<sub>2</sub><sup>•-</sup>). The more dissolved oxygen, the more superoxide radical anion (O<sub>2</sub><sup>•-</sup>) formed. The synergy of this condition was highly expected to maximize the process of MB photodegradation resulting greater MB removal. The results of this experiment are showed in Table 1.

**Table 1.** Aeration treatment - methylene blue photodegradation.

Diffusing Time	Absorbance	C final (ppm)	Removal (%)	MB initial (mg)	MB removal (mg)
10	0,908	8,405	87,99	1,75	1,53
20	0,657	6,075	91,32	1,75	1,59
30	0,441	4,0696	94,18	1,75	1,64

According to Tabel 1, it is clear that the enhancement of photodegradation process can be attained using aeration treatment. The total time used in

the maximum MB removal in this type of experiment was 60 minutes consisting of 30 minutes of oxygen diffusing time plus 30 minutes of contact time for

photodegradation process using  $\text{TiO}_2$ -Zeolite composite at the presence of UV irradiation, resulting 0.041 mg MB removal per 1 mg composite. This is much more effective and efficient in compare to the former experiment (I and II). The total time consumed in the former experiment that resulting maximum MB removal was 75 minutes (optimum time) using  $\text{TiO}_2$ -Zeolite composite with UV irradiation. The former experiment was only removed 0.023 mg of MB per 1 mg composite. In conclusion, it can be stated that aeration treatment using oxygen bringing out significant improving on MB removal.

## CONCLUSIONS

Composite of  $\text{TiO}_2$ -Zeolite was successfully prepared. Characterization results of  $\text{TiO}_2$ -Zeolite composite using XRD and FT-IR show that there was interaction between  $\text{TiO}_2$  and  $\text{SiO}/\text{AlO}$  of zeolite. The results of MB photodegradation demonstrated that the MB treatment using  $\text{TiO}_2$ -Zeolite composite with UV irradiation showed an increase in the percentage of MB removal with increased contact time and significantly decreased in MB removal when it passed the optimum contact time. The optimum composite mass was also enabling the maximum photoactivity while preventing the unnecessary excess use of composite. The observation of aeration treatment using oxygen in this experiment revealed significant improving on MB removal.

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