Synthesis of TiO2/Zeolite-A Composite for the Removal of Methylene Blue on Direct Sunlight

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Abstract—**Wastewater generated from textile industry contains azo dye, (e.g., methylene blue), which is inefficient to decompose by using biological processes, and requires long treatment time. TiO2 is the most widely used adsorbent for industrial applications and photocatalytic degradation of various azo dyes in textile wastewater. Its anatase is the most effective and widely used photocatalyst, however the wide band gap of TiO2 has limited its widespread application in industry since it needs to be excited by ultraviolet (UV) light. In order to overcome this issue, combination of adsorbent zeolite and TiO2 into the composite was used in this study so that TiO2 can adsorb methylene blue under direct sunlight. Composition of 1 g TiO2 and 1 g Zeolite composite was used in batch method to eliminate different methylene blue concentrations, i.e., 25; 50; 75; 100; 125; 150; 200; and 250 ppm by means of adsorption process under direct sunlight. The experimental result showed that addition of zeolite was able to considerably improve adsorption capacity of TiO2 on direct sunlight in the range of 97.2 – 99.3 % of methylene blue removal. The highest removal was observed in the case of lower concentrations of methylene blue, i.e., in the range of 25-50 ppm.**

Keywords*— *Azo dye, Direct Sunlight, TiO2/Zeolite-A.

I. INTRODUCTION

Textile industry wastewater contains various kinds of dyes. Among those, azo dyes are the most important class and the largest commercial coloring agent and contribute to almost 75% of all textile dye products[1]. Azo dyes have reactive and acidic characteristics, these substances and their decomposition products are also toxic, mutagenic and carcinogenic. Textile industry wastewater contains azo dye, which is prone to biological treatment, and thus ineffective for shorter treatment time[2]. Disposal of azo dye in the water bodies without proper treatment is a threat to the environment. Azo dye used in this study is methylene blue. Methylene blue is one of the cationic dyes used in the textile industries for purposes. It is also a basic dye used extensively in the dyeing and printing of cotton, silk, etc[3]. Methylene blue is a heterocyclic aromatic compound with a molecular formula of $C_{16}H_{18}N_3SCl$ and has a molecular weight of 319.85 g/mol. This compound may pose various harmful effects. For example, high concentrations of azo dye can cause corneal injury if in contact with the eye. A concentration of 500 mg azo dye dose or above can also cause anemia, dizziness, headache, abdominal pain, nausea, profuse sweating and mental confusion[4]. There are currently a various physical and chemical processes for the treatment of effluent containing dyes discharged from the textile industries. The physical treatments includes membrane – filtration, reverse osmosis, electrolysis and adsorption method. Nevertheless, filtration method has some disadvantages such as limited lifetime before membrane fouling occurs and the cost of periodic replacement that must be included in any analysis of their economic viability. Among all the physical treatments, adsorption process has been reported to be the most effective method for pollutant removal in water[4]. Moreover, a chemical method shows high treatment efficiency, however the high cost of chemical substances and the possible production of sludge at the end of the treatment which is pH dependent lead to other water pollution challenges[5]. Biological treatment of wastewater is an alternative and most economical method compared to physical and chemical methods. Microorganisms such as yeasts, bacteria, fungi and algae are able to accumulate and degrade different water pollutants. However, due to some technical, their applications are often limited. Neverthelss, the major drawsback are substantial land area requirement and sensitivity obstacle toward diurnal variation as well as toxicity of chemicals and incapable of obtaining satisfactory color reduction[4]. Table 1 presents the advantage and disadvantages of azo dye removal methods.

Basically among all the available treatment methods, adsorption is the most effective process in removing azo dye from textile wastewater. The adsorption process is desired as an environmentally friendly and cost effective among variety of wastewater treatment methods. It has high purification yield and the choice of adsorbent plays very essential role in determining its cost efficiency[6]. Titanium dioxide is the most widely used adsorbent for industrial applications and several studies of the photocatalytic degradation of various azo dyes in textile wastewater[7]. TiO_2 also has the highest stability, the lowest cost, high oxidative power, and its anatase is the most effective and widely used photocatalyst but the wide band gap of TiO_2 has limited its widespread application in industry since it needs to be excited by ultraviolet (UV) light due its large band gap has restricted the utilization of solar energy to the UV portion, which is only ~4% of the solar energy [8]–[11]. Therefore, various support materials and coating methods have been studied to overcome that issue[9]. Many studies have been proposed the improvement of solar light utility by extending the photo-response of TiO_2 to the visible light. For example, Zhou et al. reported that TiO_2 can be used as adsorbent in visible light by forming a heterostructure with Ag_2O nanoparticles[10]. Another study by Gu et al. also reported the visible photocatalytic degradation of Rhodamine B using a novel TiO_2-Polyaniline composite[11]. Adsorbents, such as zeolite

[12], activated carbon [12]–[14], silica [14], and alumina [14] are often used as a disposable material for the removal of diluted organic contaminants in water and air. Many studies reported the combination of adsorbent and TiO_2 into composite for increasing the efficiency of photocatalytic systems with specific functions. In the case of composite system, photocatalytic process in water and air purification relies on the surface properties particularly can be enhanced by the addition of high-surface area adsorbent materials[15], [16]. In this study, zeolite was used as a material support to form composite materials with TiO_2 in azo dyes adsorption and degradation. Zeolite is a porous aluminosilicate material with a unique three-dimensional structure. It is widely used as a specific catalyst, adsorbent, and ion exchanger for specific application particularly specific recovery material in wastewater industry [17], [18]. In order to analyze the ability of zeolite towards TiO_2 that may increase surface area of TiO_2, a novel process which is applied in the adsorption process of methylene blue under visible light was carried out in this present research[19]. The composite characterization and effect of reaction such as absorbance were investigated in detail.

Table 1.
Comparison of Azo Dye Removal

Treatment	Advantage	Disadvantage
Biological	Economically feasible and eco-friendly process for dye degradation[20].	Dyes are generally toxic and very resistant to bio-degradation, only can be applied at a constant pH value. Poor adsorption ability to acid and reactive dyes due to their high water solubility[21], [22].
Coagulation	Economically feasible, excellent colour removal[23].	pH dependent, production of sludge, may not remove highly soluble dyes [22], [23].
Adsorption	Excellent removal of wide azo dye variety[24].	Expensive due to regeneration, adsorbent loss, and disposal[22], [24].
Ion Exchange	Adsorbent can be regenerated without adsorbent loss, dye recovery conceptually possible[25].	Expensive in regeneration and operation, Poor removal of wide azo dye variety due to dye-specific resins[22], [25].
Chemical Oxidation	Not produce chemical or biological sludge in high amount and possible in almost comple demineralization of organics[26].	Thermodynamic and kinetic limitations along with secondary pollution are related to different oxidants, possible in negligible mineralization, suspected in releasing aromatic amines and additional contaminants with chlorine[22].
Photocatalyst	The occurrence of photocatalytic degradation on the surface of the catalyst has resulted in this method being more selective. And the costs used are more effective because they use sunlight[27].	If there is no sunlight, this process does not occur. In addition, dyes containing more sulfonate substituents are less reactive in the photocatalytic process[27].
Biochemical	Possible to reduce COD, and not depend on the presence of salt in waste water [22].	In terms of cost, it is less effective because it requires high electrical energy. In addition, for the level of efficiency, it depends on the type of dye[22].

II. METHODS

A. Materials Used

All chemicals used in this study were analytical grade reagents. Materials used were titanium (IV) oxide (Supelco, Germany), sodium aluminate chemical structure being $NaAl_2O_3{\cdot}H_2O$ (Sigma Aldrich, Germany), sodium silicate chemical structure being $NaSiO_2{\cdot}H_2O$ (Sigma Aldrich, Germany), powder NaOH (99% p.a), distilled water and methylene blue (Sigma-Aldrich, dye content ≥ 82%).

B. Synthesis Zeolite A

Synthesis zeolite in this study was obtained from molar ratio of 3.165 Na_2O : 1 Al_2O_3 : 1.926 SiO_2 : 128 H_2O. Sodium silicate and sodium aluminate were dissolved in separate NaOH solutions to give molar ratios of 2:1 SiO_2/NaOH (solution A) and 2:1 Al_2O_3/NaOH (solution B) respectively and these mixtures were stirred about 10 min. Mixed solution A and B were stirred again for 12 hours. A volume of solution A was combined with one half volume of solution B and stirred for 12 hours, forming a slurry solution. The slurry solution was transferred to an autoclave and heated for 18 hours at 100^{o}C. The resulting material was filtered to separate the filtrate and solid, and then washed with distilled water until the pH value of the wash liquor was decreased up to 9. The materials were then dried for 12 hours at 100^{o}C.

C. Adsorption of Methylene Blue (MB)

For adsorption studies, the batch method was used because of its simplicity. To understand the mechanism of adsorption of methylene blue on the surface of the biomass, solutions were prepared with initial concentrations of 25, 50, 75, 100, 125, 150, 200, and 250 ppm of this contaminant. The pH value of the prepared solutions in the initial concentration was not adjusted. The mixtures were agitated on magnetic stirer continuously for 180 min, as the equilibrium time at room temperature. After 180 min, wait about 1 hour until the suspension was formed as filtrate (top layer). The filtrates were then analyzed by using UV-Visible spectrophotometer (Genesys 10S Spectrohotometer) at 665 nm. The dye removal percentage (%) was calculated using the following equation:

$$Removal\ (\%) = \frac{Co - Ce}{Co} \text{x } 100 \qquad (1)$$

where, C_0 and C_e are the initial and final dye concentrations ($mg.L^{-1}$).

D. Characterization

The results of zeolite-A/TiO_2 composites were characterized by BET, XRD, FTIR analyses as shown in Figure 1 and 2.

III. RESULTS AND DISCUSSION

A. Characterization of Composite

The effect of crystallinity of the addition of TiO_2 on zeolite was carried out with XRD. The results are presented in Figure 1. Peaks generated from the XRD analysis are categorized as a value of 2Θ (°) which is the angle of the incoming light and reflected light. As seen, there is a typical peak shift from zeolite in area 2 but 29 to 2Θ 25.3°, the shift is characteristic of TiO_2. The presence of TiO_2 decreases the crystallinity of the zeolite so that the 2Θ shifts towards the lower area. This result is in accordance with that reported by JCPDS No. 39-0222 (Joint Committee on Powder Diffraction Standards) that is a typical peak 25 which indicates a typical area for TiO_2 composite material Changes in the structure of zeolite graphality by the presence of TiO_2 result in the formation of new pores which can support the adsorption process.

The functional group testing contained in the composite was carried out by using FTIR instrument. The results are shown in Figure 2. Based on these results, the obtained wave number data of 3368 cm^{-1} shows spectra of strain O-H groups. The O-H group is indicated to originate from zeolite, and thus it can be concluded that the zeolite is a type of zeolite hydrate. At wave number 1654 cm^{-1} and 976 cm^{-1} show the peak of the strain of the buckling O-H and O-Si-O groups, respectivelt. Therefore, it can be concluded that there is a bond between TiO_2 and zeolite.

The ability of Zeolite-TiO_2 composites can be influenced by the specific surface area and pore volume of the composite. In zeolite or zeolite-TiO_2 composites the result of measurements of surface area and pore volume were carried out by nitrogen gas adsorption-desorption method according to the BET Theory (Brunauer-Emmet-Teller). Nitrogen gas acts as an adsorbate that can close the pore so that it can be used as a medium in determining the surface area of composite or zeolite solids. The results of measuring surface area and pore volume are given in Table 2. The results of the measurement of specific surface area indicate that the addition of TiO_2 decreases the specific surface area and pore volume in pure zeolite-A. The decrease in S_{BET} (BET surface area) and pore volume in both the total pore volume and the micropore caused by TiO_2 has partially closed the pore in zeolites. This result is in accordance with the study reported by Chong et al. that at the same synthesis temperature conditions, composites with a greater TiO_2 ratio will reduce the value of surface area and pore volume in zeolites[19].

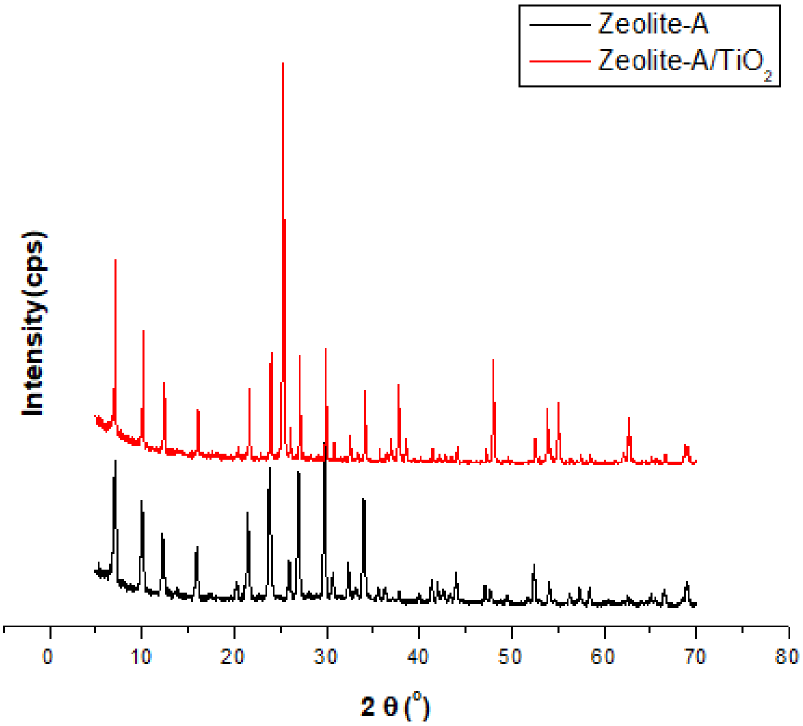

Figure 1. X-ray Diffractogram of Synthesized Zeolite A

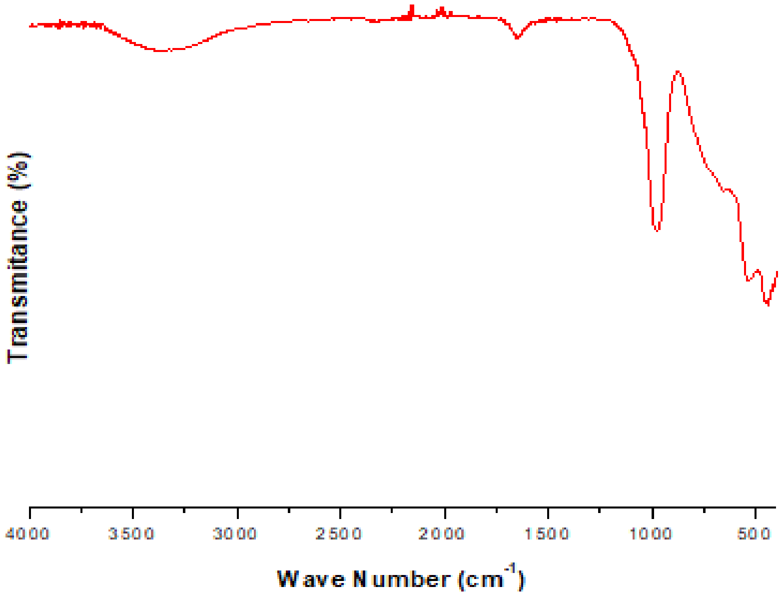

Figure 2. Fourier Transformation Infrared of Composite Zeolite A-TiO_2

Table 2.
The Results of Surface Area and Pore Volume

Sample	S_{BET} (m^2/g)	V_{Total} (cm^3/g)	V_{micro} (cm^3/g)
Zeolite-A	189.0091	0.0319	0.0304
Zeolite A-TiO_2	101.7891	0.0292	0.0189

B. *Adsorption of Methylene Blue*

The TiO_2/zeolite composite was carried out to determine the methylene blue adsorption capacity using batch method. Methylene blue was used because its interaction with water that would produce ions from methylene blue which are positively charged. Moreover, zeolites have a negative charge due to the substitution of Al^{3+} ions to Si^{4+} in their tissue structure and neutralized by alkali or alkaline earth cations. These cations can be exchanged with the methylene blue cation so that methylene blue is absorbed[28]. The adsorption process procedure was initialized by determining the maximum wavelength of methylene blue using a UV-VIS spectrophotometer and obtaining the maximum methylene blue wavelength in the region of 665 nm, with an absorbance value of 0.775. The obtained wavelength is used as the reference wavelength in determining the absorbance value on the standard curve as well as after the methylene blue adsorption process was carried out. These results are in accordance with previous studies confirming the maximum absorbance in methylene blue solution was detected in the area of 665 nm, i.e., in the range of visible area[29]. Determination of methylene blue adsorption capacity begins with the determination of standard curve in the concentration range of 1 to 5 ppm which is shown in Figure 3.

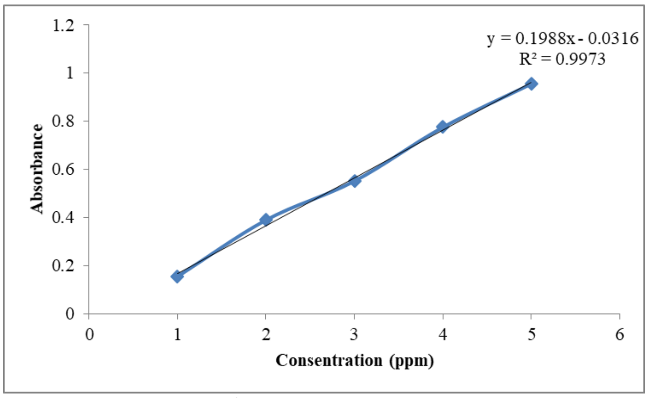

Figure 3. Standard Curve of Methylene Blue

Table 3.
The Results of Methylene Blue Adsorption by TIO_2/Zeolite Composite.

Initial Concentration (ppm)	Final Concentration (ppm)	% Removal
25	0.3	98.8 %
50	0.3	99.3 %
75	1.8	97.5%
100	3.1	96.9 %
125	3.5	97.2 %
150	3.9	97.4 %
200	4.3	97.9 %
250	4.6	98.2 %

The equation obtained from the standard curve is used in determining the final concentration of methylene blue after adsorption, where y value is absorbance while x is the concentration value obtained. Methylene blue solution was prepared at various concentrations to determine the largest methylene blue adsorption capacity by TiO_2/Zeolite composite. Those various methylene blue adsorption capacity are 25, 50, 75, 100, 125, 150. 200, and 250 ppm. The results of methylene blue adsorption shown as absorbance are presented in Table 3.

In Table 3 shows that all absorbance values obtained by adsorption using TiO_2/zeolite composite were increased in the increase in methylene blue concentration along the experiments. The greater the absorbance value, the higher the maximum adsorption capacity (qe) and the value of the equilibrium concentration (Ce) obtained is lower (Table 4). TiO_2/Zeolite adsorption data shows that concentration of 25 ppm and 50 ppm have very small absorbance value and great % removal of methylene blue which indicates that the composite can work effectively within the concentration range using 1g : 1g composition so that the filtrate obtained low absorbance value. In this study, the adsorption process was carried out directly on the direct sunlight of the city of Surabaya without the help of ultraviolet light not as was done in the previous studies using ultraviolet light for adsorption systems using TiO_2 material.

In the same comparison of TiO_2, the previous research found that the degradation process of methylene blue using sol TiO_2 under UV Irradiation resulted in absorbance values after adsorption is 0.146 in the concentration of methylene blue 50 ppm[30]. This value is higher than the absorbance obtained in this study and indicates that the TiO_2/zeolite composite in this study has a higher adsorption capacity than pure TiO_2 in the presence of UV Irradiation. Another previous research found that the degradation efficiency of methylene blue using poly(azomethine)/ TiO_2 nanocomposites in the presence of natural sunlight for 5 hrs is 95% [31]. This value is lower than the degradation efficiency in this study.

Results of analysis shows that the addition of zeolite can improve the adsorption ability of TiO_2 in visible light. Zeolite is an aluminosilicate material that has a higher surface area than TiO_2 and specific ability[17], [18]. The characteristic of this porosity which causes the methylene blue adsorption process can occur spontaneously in the visible light region compared to TiO_2 material only which is generally active in UV light. The absorbance data obtained were used to determine other parameters, namely the equilibrium oncentration (Ce) and adsorption capacity (qe) shown in Table 4. Adsorption kinetics is obtained from the data in the Table 4 which is determined by the Langmuir and Freundlich equation.

Table 4.
Adsorption Kinetics of Methylene Blue

Methylene Blue Concentration (ppm)	qe (mmol/gram)	ce (mM)
25	0.026	0.001
50	0.052	0.001
75	0.075	0.011
100	0.098	0.018
125	0.116	0.041
150	0.141	0.047
200	0.174	0.103
250	0.224	0.110

Langmuir equation[32].

$$\frac{Ce}{qe}=\frac{1}{Kb}+\frac{1}{b}\times Ce \qquad (2)$$

Information :
Ce = final concentration (mM)
qe= equilibrium capacity (mmol/g)
K = Langmuirconstant (L/mmol)
b = maximum adsorption capacity (mmol/g)

Freundlich equation[33].

$$\log \log qe = \log \log K + \frac{1}{n} \times \log \log Ce \qquad (3)$$

Information :
Ce = final concentration (mM)
qe = equilibrium capacity (mmol/g)
K = Freundlich constant
n = empirical constant

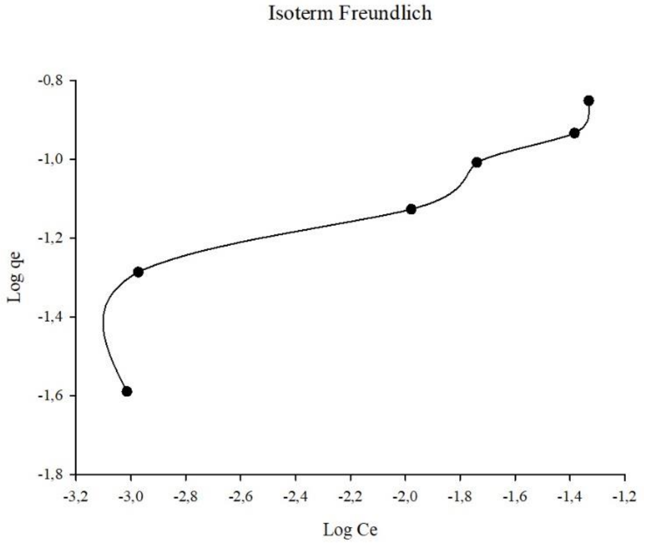

Figure 4. Isoterm Freundlich Adsorption Process by TiO_2/Zeolite Composite.

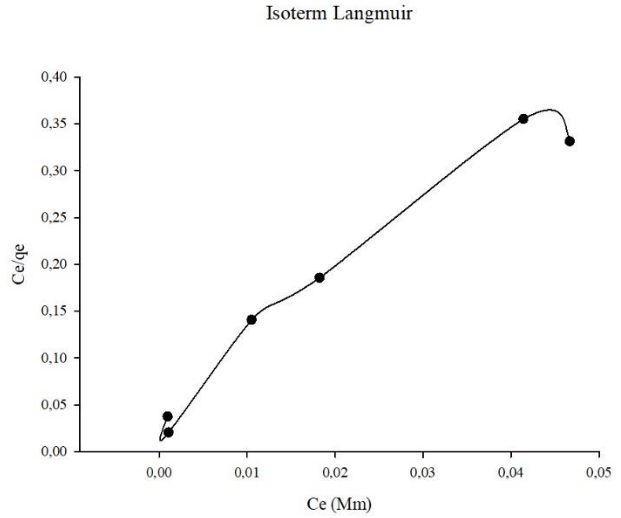

Figure 5. Isoterm Langmuir Adsorption Process by TiO_2/Zeolite Composite

From the data substitution using the equation above, a regression value is obtained shown in Figure 4 and 5 which indicates that this adsorption process is based on the Langmuir kinetic model. The Langmuir kinetic model is one model of adsorption kinetics which is mainly related to the absorption of monolayer[33]. Therefore, the adsorption process that occurs in the combination of TiO_2/zeolite for methylene blue occurs in full with low binding energy. These results are in accordance with the data of previous studies which stated that the physicosorption process is one of the adsorption processes with low binding energy, on average 10 kJ/mol, according to result experiment by Barrow in Masruhin et al. [34]. With low binding energy, the adsorption process takes place quickly. It can also be confirmed from the BET test results that after adding zeolite, a smaller composite surface area is produced. As a result, this adsorption process affects the nature of composite porosity. Therefore, it can be concluded that most of the adsorption process is dominated by physical adsorption processes.

IV. CONCLUSIONS

In this paper TiO_2/Zeolite composite with 1g : 1g composition was treated for different methylene blue concentrations,i.e., 25, 50, 75, 100, 125, 150, 200, and 250 ppm in adsorption process in the presence of direct sunlight for 180 min. The experimental result showed that the addition of zeolite can improve the adsorption capacity of TiO_2 on direct sunlight in the range of 97.2 – 99.3 %. The highest removal was observed in the case of lower methylene blue concentrations i.e., 25-50 ppm in 180 min.

ACKNOWLEDGEMENT

The authors would like to acknowledge the Ministry of Research, Technology and Higher Education for supporting this study through the "Program Kreativitas Mahasiswa" Grant scheme 2019.

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