

Adsorption and Photocatalytic Activity of Bentonite–Titanium dioxide on the Degradation of Methylene Blue Dyes

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Abstract

The aim of this research is to determine the effect of bentonite-titanium dioxide (Bentonite-TiO₂) composite on the degradation process of methylene blue. Synthesize of composite carried out through the impregnation of Titanium dioxide (TiO₂) on bentonite and then characterizing the obtained compound using XRD and SEM-EDX. The results of the XRD characterization showed that there was a shift in the diffraction angle (2θ), which indicated the success of the impregnation procedure. The morphology of the composite showed that the bentonite surface had been filled with TiO₂, as evidenced by the results of the EDX analysis, which showed a 7.03% increase in Titanium. Furthermore, the degradation process was carried out using various variables, including contact time, the ratio of composite weight to dye, and by irradiation with a UV lamp at a wavelength of 352 nm UV. It was discovered that the best degradation in the concentration of methylene blue occurred at a maximum contact time of 90 minutes and at a maximum weight of 10 mg of benonite-TiO₂, with an effectiveness of 99.91% after irradiation and 92.26% without irradiation

Keywords: Bentonite, Bentonite-TiO₂, methylene blue, photodegradation

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Penelitian ini bertujuan untuk mengetahui pengaruh komposit bentonit-Titanium dioksida (Benonit-TiO₂) terhadap proses degradasi metilen biru. Penelitian ini dilakukan dengan mensintesis komposit melalui impregnasi Titanium dioksida (TiO₂) pada bentonit dan kemudian mengkarakterisasi senyawa yang diperoleh dengan menggunakan XRD dan SEM-EDX. Hasil karakterisasi XRD menunjukkan adanya pergeseran sudut difraksi (2θ) yang mengindikasikan keberhasilan prosedur impregnasi. Morfologi komposit menunjukkan bahwa permukaan bentonit telah terisi oleh TiO₂, yang dibuktikan dengan hasil analisis EDX yang menunjukkan peningkatan Titanium sebesar 7,03%. Selanjutnya, proses degradasi dilakukan dengan menggunakan berbagai variabel, antara lain waktu kontak, rasio berat komposit dengan dye, dan dengan penyinaran dengan lampu UV pada panjang gelombang 352 nm. Ditemukan bahwa degradasi terbaik pada konsentrasi metilen biru terjadi pada waktu kontak maksimum 90 menit dan pada berat maksimum 10 mg benonit-TiO₂, dengan efektivitas 99,91% setelah penyinaran dan 92,26% tanpa penyinaran.

Kata Kunci: Bentonit, Bentonit-TiO₂, metilen biru, fotodegradasi

INTRODUCTION

Textile is also part of modern industries and uses advanced technology in its production process, starting from spinning yarns from natural and synthetic fibers, weaving traditional fabrics, to embroidering yarn into fabrics [1]. Traditional dyeing techniques used in weaving and batik, including modern technology for dyeing fabrics with synthetic dyes, have provided innovations in the modern textile industry. However, this industry has a negative impact on the environment. In the dyeing industry, for instance, liquid waste from the dyeing, washing, printing, and finishing processes has a negative impact on the environment [2]. Due to the content of dyes and heavy metals. Liquid dye waste that is not seriously treated could also pollute and poison aquatic ecosystems.

Many dyes and other organic contaminants are tough to degrade in nature and require more advanced techniques for their removal, which can be a serious challenge for many researchers to find methods to degrade the dye as a pollutant [3]. Some methods have been developed to treat dyed wastewater, including physical, chemical and biological processes [4]. Various treatments have been used to reduce the concentration of dye waste, either by conventional means or through modern processing technology, such as coagulation, flocculation, reverse osmosis, adsorption, and photodegradation [5]. One of the treatments is the adsorption method, and it is often used due to the advantages of having high efficiency in minimizing the concentration of unwanted compounds. It is also used due to its ability to overcome various toxic organic compounds, it is easy to use, and has many variations of types [6].

In this research, bentonite, also called clay minerals, was used as an adsorbent because it contains 85% montmorillonite with the chemical formula $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4 \cdot nH_2O$. Other contents in bentonite are impurities from several minerals such as quartz, illite, calcite, mica, and chlorite. The Montmorillonite structure consists of one layer of alumina (AlO_6) octahedral in the middle flanked by two layers of silica (SiO_4) in a tetrahedral shape [7]. The effect zeolite addition in natural rubber polypropylene composite on mechanical, structure, and thermal characteristics [8]. The montmorillonite is classified as a clay mineral that is easy to expand, as well as has easily exchanged cations and a large surface area according to the particle size. Due to these properties, it could be used as an adsorbent [9]. To improve the performance of the adsorbent from bentonite or montmorillonite, activation is necessary, either physically or by the acidification method.

The adsorption process of bentonite occurs without the degradation process because waste particles are only trapped in pores. Therefore, to accelerate the degradation process with the help of UV light, this research tried to combine the adsorbent with a photocatalyst of metal oxides. According to Subramani et al. [10], the decomposition of dye waste could also be carried out through the photodegradation method, using photocatalysis of titanium dioxide (TiO_2). The photocatalyst properties of TiO_2 are functional as solar cells, adsorbent, self-cleaning, anti-fogging, and antibacterial [11]. This photocatalysis process breaks down a large number of different organic compounds in wastewater into simpler compounds, including CO_2 , mineral salts and water [12].

According to Zaleska [13], TiO_2 semiconductors have been used for a long time as photocatalysts because they are relatively cheaper and have high effectiveness. Therefore, to increase the ability of bentonite, TiO_2 is applied as an impregnator to form bentonite- TiO_2 composites [9]. The movement of electrons and holes in semiconductor nanomaterials depends on the effects of quantum confinement, size, and geometry of the material. The specific surface area and surface-volume ratio increase as the material size decreases [14]. Bentonite is a mineral that could be used as an adsorbent with a large absorption capacity. Furthermore, this capacity could be increased with the impregnation of metal oxide into the bentonite structure. In this research, a bentonite- TiO_2 composite was synthesized with the insertion of TiO_2 as a dye photodegradator into the bentonite structure. The resulting compound was then characterized using X-Ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) and Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX). The observed parameters include the time and weight of bentonite- TiO_2 variables.

MATERIALS AND METHODS

Materials

Material used in this research is Titanium dioxide powder (Merck), bentonite technical, distilled water (H_2O), sulfuric acid (H_2SO_4) (Merck), and methylene blue ($C_{16}H_{18}N_3SCl$) (Merck).

Methods

Bentonite Preparation and Activation

Bentonite preparation and activation was carried out according to Zheng *et al.* [15] with modifications. The activation was carried out by adding 50 grams of natural bentonite into 500 ml of 0.6 M H_2SO_4 solution and stirring the mixture for 24 hours at 70 °C. The solution was then cooled, filtered using a separator

funnel and a vacuum device. The precipitate was washed using hot distilled water until it was clean of residual acid ions. Subsequently, the acid-activated bentonite was dried in an oven at 100-110 °C. After drying, it was ground until smooth and sieved using a 200 mesh sieve. Furthermore, the activated bentonite was characterized using XRD and SEM-EDX instruments. The bentonite was considered successfully activated when there was a shift in the diffraction angle when analyzed using the XRD instrument. The shift occurs due to the addition of hydroxyl groups between the bentonite layers.

Impregnation Process of Bentonite-TiO₂ Composite

Bentonite Preparation and activation was carried out according to Laysandra *et al.* [2] with modifications. A total of 10 g of activated bentonite was dispersed in 200 mL of distilled water and stirred. Furthermore, 5 grams of desperate TiO₂ was added to the bentonite mixture. The bentonite-TiO₂ mixture was stirred for 24 hours, then precipitated, and the precipitate obtained was subsequently heated in an oven at 100 °C for 12-24 hours until it dried up. The resulting composites were then characterized using XRD and SEM.

Application and Test of Bentonite-TiO₂ photocatalytic activity

A 100 mL glass beakers were prepared and added with 5 mg of bentonite-TiO₂ and 20 mL of 50 ppm methylene blue solution. The beakers were then put in a radiation box and their contents were stirred using a magnetic stirrer. They were subsequently irradiated with a 10 watt UV lamp at a wavelength of 352 nm for 15, 30, 45, 60, and 90 minutes. The obtained solution was then precipitated by centrifugation for 20 minutes to separate bentonite-TiO₂ from the degraded methylene blue solution. About 1 mL of the solution was taken to measure the absorbance value at its maximum wavelength using a UV-Vis spectrophotometer. The dye degradation was carried out without irradiating UV lamps or in a dark room, as a comparative control treatment. The weight variation of the composite was also carried out with the same procedure with weight variations of 2, 4, 6, 8, and 10 mg with the maximum time obtained from the previous procedure.

Analysis of Data

Characterization of synthesis was characterize using some instrument like X-Ray Diffraction (XRD) to get the 2θ angle and the shape of the crystal lattice from Bentonite-TiO₂, Scanning Electron Microscopy-Energi Dispersive X-Ray (SEM-EDX) obtained data in

the form of surface morphology images of Bentonite-TiO₂ with the composition element of material synthesis, and Brunauer-Emmett-Teller (BET) analysis for physical characterization specific surface area and porosity distribution of synthesis materials. Data of degradation has been collected and can be determined percentage of Degredation (%) and adsorption capacity (Q_e) value with equation :

$$\text{Removal Effectivity}(\%) = \left(\frac{C_0 - C_t}{C_0} \right) \times 100\% \quad (1)$$

$$\text{Adsorption Capacity } (Q_e) = \frac{(C_0 - C_t) \times V_{\text{solution}}}{m_{\text{adsorbent}}} \quad (2)$$

Note :

C₀ = concentration before degredation

C_t = concentration after degredation

V_{solution} = solution volume

m_{adsorbent} = mass of adsorbent.

RESULTS AND DISCUSSION

Characterization of Activated Bentonite and Bentonite-TiO₂ using XRD

The characterization of bentonite-TiO₂ using XRD aimed to determine the changes in the bentonite material after being added with TiO₂ dopants. The success of the characterization procedure was indicated by a change in the x-ray diffraction angle. This showed that the bentonite-TiO₂ composite could be used as a photocatalyst in the photodegradation of methylene blue dye. The activated bentonite and bentonite-TiO₂ were then characterized using XRD to determine the shift in the diffraction angle (2θ). The results of the characterization are shown in **Figure 1**.

Figure 1 shows that there has been a shift in the x-ray diffraction angle in the diffractogram patterns of activated bentonite and bentonite-TiO₂. The difference is presented by the presence of diffractogram peaks that appear and disappear at certain angles. In **Figure 1(a)**, activated bentonite shows a characteristic diffraction angle (2θ) around 6.99, 19.674, 28.43, and 34.97°, while in **Figure 1(b)**, bentonite-TiO₂ shows a diffraction angle (2θ) around 19.71, 25.235, 37.70, 47.97, 53.82 and 62.57°. This data is related according to Widi *et al.* [17] and Laysandra *et al* [2], which diffraction angle (2θ) at 25.50°, 37,69°, 48,15°, and 54,99° is the unique intensity of TiO₂ and 5.40°, 19.82°, 27.70°, and 34.79° is the intensity of Bentonite. Based on the results of XRD characterization, it was concluded that bentonite-TiO₂ has a characteristic of increasing changes in diffraction angle. This indicates a change that occurs after the impregnation of bentonite with metal oxide TiO₂ [18].

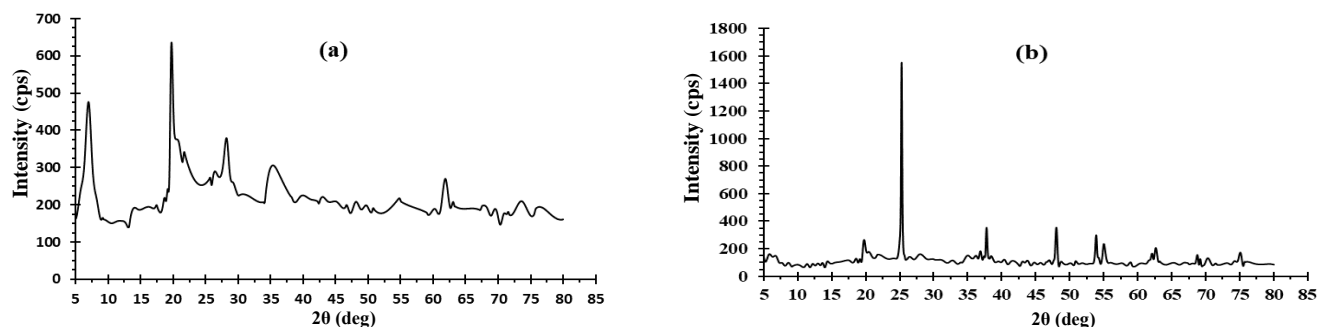


Figure 1. XRD diffractogram pattern : (a) activated bentonite (b) bentonite-TiO₂

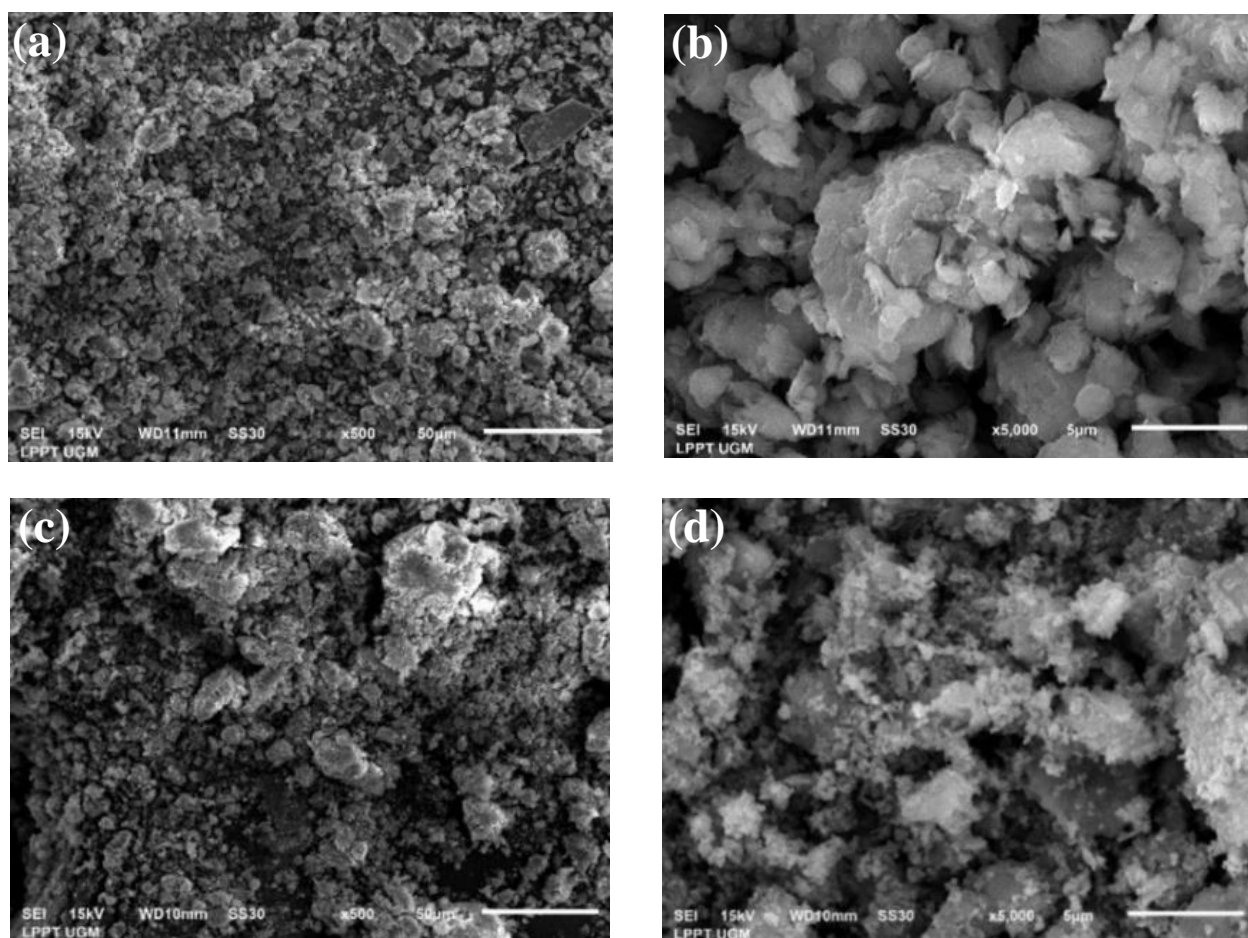


Figure 2. SEM image of activated bentonite with (a) 500x magnification (b) 5000x magnification; and Bentonite-TiO₂ with (c) 500x magnification (d) 5000x magnification

In **Figures 2(a)** and **(b)**, the activated bentonite still has many gaps, while in **Figures 2(c)** and **(d)**, the existing gaps are starting to be covered. Furthermore, many small particles could be seen sticking to the surface of the bentonite. This shows that the gaps on the surface have been filled with TiO₂. According to Surya *et al.* [18] the natural bentonite shows massive, aggregated morphology, some large flakes and a layer structure which after modification with TiO₂ species,

the bentonite surface changed, resulting in a large number of small particles with a barely observable layer structure.

Data from the EDX results are presented in **Table 1**, which shows that there was a decrease in the percentage of certain elements in bentonite-TiO₂, especially Al and Si as the main constituent. Moreover, the EDX results show that the TiO₂

impregnation process increased the percentage of Ti metal oxide from 0 to 7.03%.

The data from Table 1 shows a decrease in the percentage of Al from 9.54 to 8.41% and Si from 23.13 to 20.15%. It also shows the emergence of Ti by 7.03 and an increase in Na from 0.22 to 0.30% and Mg from 1.29 to 1.33%. Consequently, from the SEM-EDX data, it was concluded that the metal oxide, TiO₂ has been successfully impregnated into the bentonite structure [20].

Table 1. Result of elemental analysis using EDX

Composite	Al (%)	Si (%)	Na (%)	Ti (%)
Activated bentonite	9.54	23.13	0.22	-
Bentonite-TiO ₂	8.41	20.15	0.30	7.03

Characterization of activated bentonite and bentonite-TiO₂ using BET

Activated bentonite and bentonite/TiO₂ were characterized through nitrogen adsorption-desorption, so that data on surface area, pore volume and pore size were obtained through calculations using BET which would be directly obtained from the measurement data. Nitrogen adsorption-desorption isotherms for activated bentonite and bentonite/TiO₂ can be seen in Figure 3

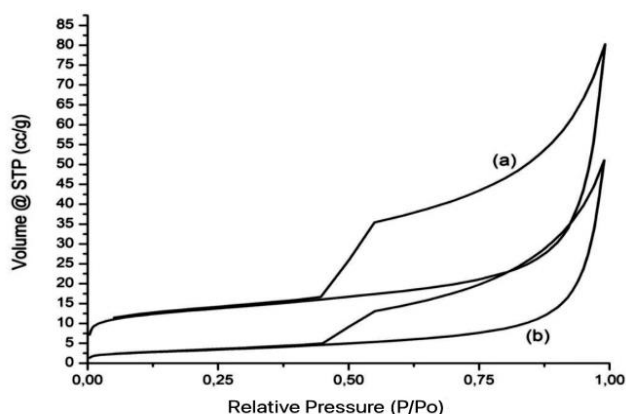


Figure 3. Nitrogen adsorption and desorption isotherm curves: (a) activated bentonite (b) Bentonite/TiO₂

Hysteresis pattern of adsorption-desorption isotherms in Figures 3 (a) and (b) for activated bentonite and TiO₂/bentonite show the isotherm in type IV. This type usually occurs in porous adsorbents with a size of 1.5 – 100 nm, which includes pore sizes in the form of mesopores to macropores, at high pressures it shows an increase in absorption of the adsorbate which makes the pores large [21]. The two lines on the isotherm curve Figure 3 show the adsorption and

desorption processes of nitrogen gas on activated bentonite and Bentonite/TiO₂. Surface morphological data measured for natural bentonite, activated bentonite and Bentonite/TiO₂ can be seen in Table 2.

Table 2. Surface morphology data from MBET and BJH desorption isotherms

Isotherm BET	Surface area (m ² /g)	Diameter Pore _{BJH} (nm)	Volume Pore _{BJH} (cm ³ /g)
Activated bentonite	6.464	13.211	0.105
Bentonite/TiO ₂	21.993	2.131	0.113

Effect of Contact Time in Bentonite-TiO₂ photocatalytic activity

The effectiveness of dye degradation with the influence of contact time variations is shown in Figure 4. The presence of ionized TiO₂ metal in bentonite when receiving UV light makes it easier to bind and trap methylene blue, while the negatively charged bentonite compound attracts dye particles that are more positively charged [22]. Based on the graph above, it was found that at 60 minutes there was a decrease in the dye concentration. The percent of effectiveness increases from 73.36% to 89.05%. In the photodegradation process, the percent of effectiveness increases from 59.61% to 83.44%. This shows that the photodegradation process (with irradiation) and the adsorption process without irradiation have no significant effect on the treatment of photodegradation and degradation without irradiation at 60 minutes. Moreover, it also shows that the longer the contact time, the more degraded the methylene blue is due to the more contact between composite and dye particles. Figure 4 shows that bentonite-TiO₂ treated with UV light has a higher ability to degrade methylene blue than without UV treatment.

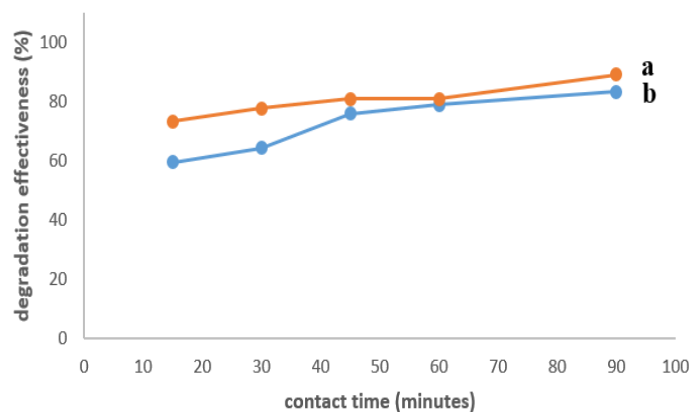


Figure 4. Effect of contact time (a) with UV irradiation, (b) without UV irradiation

Effect of Composite Weight Variation

Composite weight is one of the factors affecting the success of the dye degradation process as shown in **Figure 5**. Due to this condition, there was an increase in the percentage of effectiveness of the photodegradation process from 58.33 to 99.91% with irradiation and 54.61 to 92.26% without irradiation when the composite weight was increased from 2 to 10 mg. Photodegradation occurs when bentonite-TiO₂ is irradiated with UV light. Therefore, when the TiO₂ band gap was transverse by UV light, TiO₂ experienced electron excitation or shell displacement, causing an electron vacancy and attracting methylene blue to its bond [23]. The curve obtained then showed that there was a gradual decrease in the concentration of methylene blue.

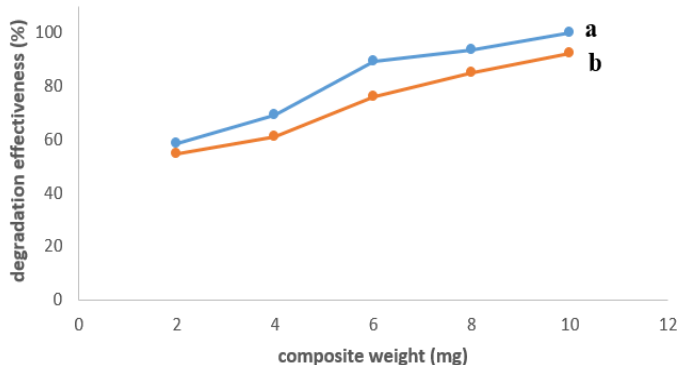


Figure 5. Effect of composite weight: (a) with UV irradiation, (b) without UV irradiation

Bentonite is an adsorbent that is often used because its adsorption process is generally related to the area phenomenon and its selectivity. Furthermore, it is a negatively charged material, while methylene blue is a positively charged compound. Due to this condition, there would be an attractive force between both particles, leading to the formation of a bentonite-methylene blue bond [24]. The effect of bentonite composition: TiO₂ during synthesis also affects the photocatalytic effect of degradation. The Research that has been done by Mahmooda and Ismail [24], The higher bentonite ratio and decrease in dye removal efficiency can be attributed to excessive bentonite particles contacting with TiO₂, therefore, reducing the number of potential photoactive sites on the TiO₂ surface. At higher TiO₂ ratios, the explanation of lower dye removal efficiency may lie in the formation of an interface between bentonite and TiO₂ where excessive TiO₂ particles surround bentonite, which results in limiting the availability of active sites to the adsorption process [25].

CONCLUSION

The results of XRD characterization showed a shift in the diffraction angle (2θ) at 47.971, 53.82, and 62.570°, which indicated the success of the TiO₂ impregnation against bentonite. However, the SEM results showed that the activated bentonite still had many gaps compared to TiO₂ impregnated bentonite. While the results of EDX proved a decrease in the elemental composition of Al and Si in Bentonite-TiO₂ compared to activated bentonite, which decreased from 9.54 and 23.13% to 8.41 and 20.15%, respectively, and contained about 7.03% of Ti elements. The most effective degradation of the concentration of methylene blue at 50 ppm (99.91%) occurs at the maximum weight of 10 mg and at a maximum time of 90 minutes.

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