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Titanium Dioxide (TiO_2)-modified Bentonite for Photodegradation of Methylene Blue

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Abstract

Dye is one of the water contaminants which, if the amount exceeds the threshold, might cause environmental issues. A modification of bentonite with titanium dioxide into a composite used to adsorb methylene blue has been conducted. In addition, this study also aimed to examine the effect of bentonite-TiO_2 photocatalyst mass, and determine the effect of variations in pH and irradiation time on the adsorption of methylene blue. The composite was synthesized by mixing bentonite (20 grams) with TiO_2, whose mass varied from 0% to 100%, into distilled water and heating it in a furnace at 550°C for 5 hours. Bentonite-TiO_2 composites were characterized using Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), and Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX). Photodegradation of methylene blue using composites was performed by varying the mass of the composites (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, and 0.08 grams), the pH of the dye (1, 3, 5, 7, 9, and 11), and UV irradiation time (30, 60, 90, and 120 minutes). FTIR analysis showed the presence of Ti-O-Ti vibrations at 1419 cm^{-1}, while Si-O-Si at 780 cm^{-1} and 799 cm^{-1}. XRD results on the composite with a TiO_2 mass of 20% revealed rutile, anatase, and montmorillonite phases. From the SEM analysis, bentonite-TiO_2 produced some small particles with a layered structure, with TiO_2 particles clumping and forming agglomerates. Moreover, EDX indicates chemical composition, such as C, Na, Mg, Al, Si, K, Ca, Fe, and Ti. The adsorption results showed that the highest activity of the bentonite-TiO_2 composite was achieved by BT-20% photocatalyst with a mass of 0.08 grams, pH 1, and UV irradiation time of 120 minutes with 99.942% of methylene blue adsorbed.

1. Introduction

Water contamination by organic molecules is a severe problem of industrial wastewater treatment, such as in the textile and dyeing industry [1]. Typically, the dyes in wastewater from the textile industry are organic compounds with an aromatic structure that makes them difficult to degrade naturally and not environmentally friendly [2]. Methylene blue is a dye used in the textile industry, and about 5% of methylene blue is used in dyeing. In comparison, the remaining 95% will be discharged into water, which can pollute the environment [3].

Methylene blue compound has a benzene structure which is difficult to decompose and is toxic, carcinogenic, and mutagenic. Additionally, the abundance of dye molecules in water will obstruct photosynthesis [4]. Many technological methods are used to overcome this problem, such as chlorination, biodegradation, and ozonation methods. However, this method is less effective in dealing with dye waste and often raises new environmental problems [5]. Photodegradation is one method that is relatively inexpensive, easy to implement, and currently suitable as an alternative to be developed for treating dye waste. The photodegradation method is effective because the dyes are broken down into simpler compounds and become harmless compounds such as H_2O and CO_2 [4]. The dye approaches the surface of the photocatalyst, which then undergoes degradation with the help of UV light [6].

Photocatalyst performance can be optimized by adding a supporting material. Using semiconductor photocatalysts is expected to be a choice, one of which is using TiO_2 material. Titanium dioxide is one of the photocatalysts with high activity. TiO_2 photocatalyst has various advantages, including high stability, corrosion resistance, abundant natural availability, and relatively low price. Titanium dioxide or Titania (TiO_2) is a semiconductor that has wide bandgap energy (3.2 eV-3.8 eV) [7]. However, the high photocatalyst activity of TiO_2 (Titanium (IV) oxide) is not matched by its ability to adsorb the target compound, so the photocatalytic degradation process does not work well because there are not enough opportunities for TiO_2 to come into contact with pollutants. TiO_2 can be added to a supporting material with a fairly high adsorption capacity to cover this deficiency. Several porous materials used as adsorbents include silica gel, activated carbon, zeolite, and bentonite. Adding TiO_2 to bentonite is expected to increase the number of photocatalytic active sites resulting in increased photodegradation performance [8].

Bentonite has a large surface area, the ability to swell, and ion exchange properties. In the presence of bentonite, the interaction surface area on the catalyst will be larger, so the use of photocatalyst oxide will be more efficient. Bentonite also has excellent adsorption properties, so the use of bentonite as a solid will facilitate and speed up the mass transfer process of the adsorbate. The contact between the photocatalyst metal oxide and organic compounds occurs more easily, and the reaction will occur more quickly [6].

Surya *et al.* [9] researched modified bentonite into bentonite-TiO_2 composites using the sol-gel method to degrade naphthol blue-black. The photocatalytic activity of the bentonite-TiO_2 composite was achieved at the initial pH of the dye solution of 3. The photocatalyst dose was 0.4 grams, and the initial dye concentration was 5 mg/L, 120 minutes for UV irradiation and 90 minutes under sunlight. This result shows that the bentonite-TiO_2 composite is an effective photocatalyst for removing naphthol blue-black under UV light and sunlight.

Aji *et al.* [8] studied the bentonite-TiO_2 composite, which was applied to reduce BOD and COD in pond water. The largest BOD and COD values decrease for BOD is 18.40 ppm and COD at 10.05 ppm. The ability of the TiO_2- bentonite composite is greater than that of the TiO_2 and bentonite catalysts. The XRD results showed that the crystalline phase of the bentonite-TiO_2 composite was an anatase crystalline phase. Mishra *et al.* [10] researched synthesizing TiO_2/bentonite nanocomposites by adding g-C_3N_4. Nanocomposites are highly porous with a uniform distribution. They were applied for RBX-3B dye degradation with optimal results of 90% in 100 minutes.

In this research, the modification of bentonite with titanium dioxide (TiO_2) was conducted using a simple chemical agitation method to photodegradation methylene blue. This study aims to synthesize bentonite material modified with TiO_2. The purpose of adding TiO_2 here is to improve its photocatalytic performance. In this study, the researchers also wanted to determine the effect of variations in mass, pH, and activity test time using variations of bentonite-TiO_2 composition on the photodegradation of methylene blue.

2. Materials and Methods

In this study, the synthesis and characterization of bentonite-TiO_2 were carried out using the agitation method because of its ease and simplicity in degrading methylene blue dye. The purpose of adding TiO_2 was to improve the performance of bentonite.

2.1. Materials and Instruments

The materials used in this study were bentonite, titanium dioxide (TiO_2) (P-25 Degussa), 1 M hydrochloric acid (HCl), sodium hydroxide (NaOH), distilled water, and methylene blue dye. The instruments were X-Ray diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX), UV-Vis Spectrophotometer, and Fourier Transform Infrared (FTIR).

2.2. Preparation of Bentonite

One L of distilled water was put into a 2 L beaker glass containing 250 grams of bentonite, stirred for 2 hours, and then allowed to stand for 24 hours. The bentonite suspension was then filtered and dried in an oven at 110°C for 2 hours. The dried bentonite was ground and sieved using a 100-mesh sieve [11]. To activate bentonite, 10 grams of sieved bentonite was activated with 100 mL of 1 M HCl solution under stirring for 24 hours. Then the mixture was filtered, and the residue was washed with distilled water until the filtrate was neutral and chloride ions-free. The residue obtained was then dried at 110°C for 2 hours using an oven. After that, the dried activated bentonite was stored [12].

2.3. Fabrication of Bentonite-TiO_2 Composites

The composite was prepared by dissolving 20 grams of bentonite in 500 mL of distilled water and stirring for 24 hours. The solution was added slowly with 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100% TiO_2 from 20 grams of bentonite. The mixture was stirred again for 8 hours, and after that, it was centrifuged for 15 minutes. The product obtained was dried at 110°C for 2 hours. The dried samples were furnaced at 550°C for 5 hours [13].

2.4. Characterization of Photocatalyst (Bentonite- TiO_2)

Bentonite-TiO_2 was characterized using FTIR to identify the functional groups. XRD analysis was utilized to determine the structure and crystallinity of bentonite-TiO_2. The surface morphology of the composite was investigated using SEM-EDX.

2.5. Photodegradation of Methylene Blue

2.5.1. Mass Variation of Bentonite-TiO_2 Composite

The experiment was started by putting 100 mL of 20 ppm methylene blue into a 250 mL glass beaker and then adding the photocatalyst BT-10%, BT-20%, BT- 30%, BT-40%, BT-50%, BT-60%, BT-70%, BT- 80%, BT-90%, and BT-100% by varying the mass of bentonite-TiO2 (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, and 0.08 grams). Then it is stirred with a magnetic stirrer for 30 minutes then put in a photodegradation device called a photoreactor, where it is irradiated with a UV lamp for 120 minutes. The mixture was centrifuged for 20 minutes at 2000 rpm [12]. The process was repeated without using a photoreactor or irradiating it with a UV lamp. Furthermore, methylene blue levels were tested with a UV-Vis spectrophotometer.

2.5.2. Effect of Bentonite-TiO_2 Composite pH

A 100 mL of 20 ppm methylene blue was put into a 250 mL beaker glass and added with photocatalyst BT- 10%, BT-20%, BT-30%, BT-40%, BT-50%, BT- 60%, BT- 70%, BT-80%, BT-90% and BT-100 % with optimum mass. The mixture was stirred with a hotplate stirrer for 30 minutes, and afterward, the pH was measured at intervals of 1, 3, 5, 7, 9, and 11. After that, the sample was exposed to UV light for 120 minutes and then centrifuged for 20 minutes at 2000 rpm [12]. Methylene blue levels were measured with a UV-Vis spectrophotometer.

2.5.3. The Effect of Irradiation Time

A 100 mL of 20 ppm methylene blue was put into a 250 mL beaker glass and added with photocatalyst BT- 10%, BT-20%, BT-30%, BT-40%, BT-50%, BT- 60%, BT- 70%, BT-80%, BT-90% and BT-100 %. The mixture was stirred with a hotplate stirrer for 30 minutes at the optimum pH. After 30 minutes, the mixture was irradiated under a UV lamp for 2 hours. Samples were tested for levels at 30, 60, 90, and 120 intervals [12]. For comparison, the procedure was repeated without using a photoreactor. Methylene blue levels were measured with a UV-Vis spectrophotometer.

3. Results and Discussion

3.1. Characterization of Bentonite-TiO_2

3.1.1. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analysis was performed to identify the functional groups of the compounds in bentonite and bentonite-TiO_2 materials. The results of this study appear as peaks that indicate the existence of functional groups in a certain absorption range.

Based on the characterization results in Figure 1, the bentonite spectrum has absorption at 3229 cm^{-1}, indicating the presence of stretching vibrations of the OH group from the hydrated layered structure of the adsorbed water molecule. This result is comparable to a study conducted by Sari *et al.* [14], where an OH functional group (3700-3200 cm^{-1}) exists. This result is reinforced by an absorption band at 1617 cm^{-1}, which indicates bending vibrations from H–OH from water adsorbed in bentonite [15]. Sharp absorption bands with high intensity at wavenumbers 1008 cm^{-1} and 1017 cm^{-1} indicate the characteristics of the Si–O asymmetric stretching vibration [16]. The absorption peaks at 780 and 799 cm^{-1} result from Si-O-Si symmetrical vibrations [16].

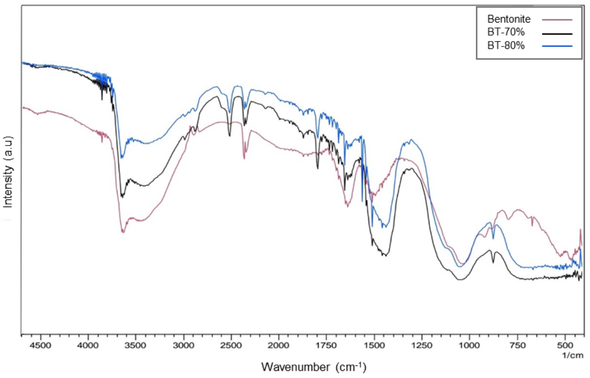

Figure 1. FTIR spectra of bentonite and bentonite-TiO_2

Table 1. Functional groups of bentonite and bentonite-TiO_2

No.	Bentonite	Bentonite-TiO_2	Interpretation	Reference wavenumber
1	3229	3656, 3625	OH stretching vibration	3700-3200 [14]
2	-	2362, 2515, 2512	Ti-O uptake	2302-2520 [14]
3	-	512, 594, 667	Ti-O-Ti vibrations	800-400 [14]
4	1008, 1017	1043, 1053	Si-O stretching vibration	1009-1036 [16]
5	873, 918	874, 943	O-Al-O stretching vibration	800-900 [14]
6	780, 799	-	Si-O-Si symmetrical vibration	825-700 [14]
7	-	404,413, 512,563, 594, 631, 667,668, 874, 930, 943	Si-O-Ti bond	930-400 [15]

Bentonite-TiO_2 has an absorption peak on its spectrum that experiences a decrease in intensity at 3656 cm^{-1}, corresponding to the OH group. The absorption peaks at 2512, 2515, and 2362 cm^{-1} indicate the presence of Ti-O absorptions, and at 512, 594, and 667 cm^{-1} indicate the presence of Ti-O-Ti vibrations [14]. O- Al-O stretching vibrations appear at 874 and 943 cm^{-1} [14]. A Si-O-Si stretching vibration exhibits an increase in intensity at 1043 and 1053 cm^{-1}. This is similar to research by Fauziyati [16] that at 1030, 1048 cm, and 1055 cm^{-1} indicate Si -O-Si stretching vibrations.

Based on the absorption comparison of the functional groups in Table 1 shows that there is a change in wavenumber, which indicates an interaction that occurs between bentonite and bentonite-TiO_2. Changes in absorption intensity and peaks that appear indicate the success of the TiO_2 embedding process on bentonite.

3.1.2. X-Ray Diffraction (XRD)

XRD is used to identify crystalline phases in materials by determining lattice structure parameters and to obtain particle sizes, determine single crystals and determine crystal structures of unknown materials. This study analyzed the synthesized product as a whitish-brown powder. The analysis results are particle diffraction patterns that will be adjusted to the diffraction patterns in the Joint Committee on Powder Diffraction Standard (JCPDS) database.BasedThe best test results for methylene Blue photocatalyst are found in the BT-10% and 20% BT Composites which will be characterized.

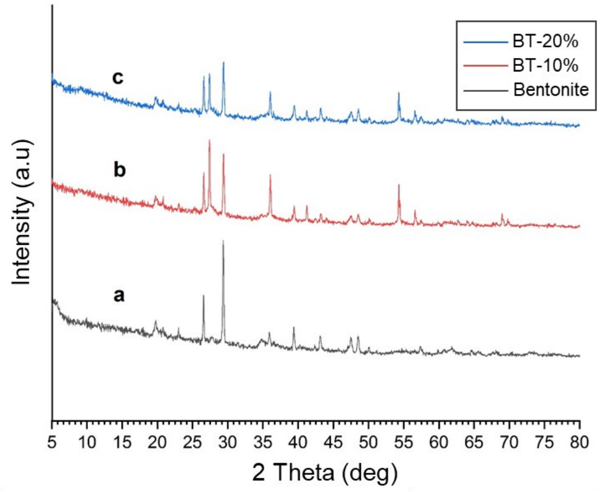

Figure 2. Diffractogram of (a) bentonite, (b) BT-10%, (c) BT-20%

The bentonite-TiO_2 composite X-ray diffraction pattern is shown in Figure 2. The bentonite diffraction pattern lies at the peak 2θ = 5.25° (16.80 Å) shown in Figure 2(a) corresponding to the d001 basal distance of the layered structure (JCPDS file number: 03-0019), which is characteristic montmorillonite minerals on bentonite [10]. This peak was not observed in the Bentonite-TiO_2 composite pattern due to the insertion of TiO_2 on the bentonite surface, showing an irregular structure. Apart from the characteristic peak indicating that the constituent element of bentonite is montmorillonite, there are also other diffraction peaks other than montmorillonite, namely at peak 2θ = 19.74° (d = 4.49 Å) according to JCPDS 06-0911, namely d_{111} = 4.44 Å, 27.83 (d=3.20 Å), 35.93 (d=2.49 Å) according to JCPDS No. 24.0495 which is characteristic of illite minerals.

A peak at 2θ = 26.55° (d=3.35 Å) appears due to the presence of quartz in bentonite, according to JCPDS:01-083-2466. Peaks at 2θ = 23.01° (d=3.86 Å) and 39.39° (d=2.28 Å) appear due to the presence of calcite minerals in bentonite [17]. According to JCPDS No.14-0164, the kaolin is the yield at peak 2θ = 50.06° (d=1.82 Å). Bentonite, characterized by XRD at an angle of 2θ, mainly consists of montmorillonite supported by other minerals, including quartz, calcite, illite, and kaolin [18].

After adding TiO_2 to the bentonite surface, the d spacing decreased from 4.49 Å to 4.48 Å, from 3.86 Å to 3.85 Å and from 1.82 Å to 1.81 Å. The decrease in d spacing indicates that the interaction between bentonite and TiO_2 most likely occurs in the out-layer region [3] and is caused by the collapse of the layered structure of bentonite [19]. In addition to a decrease in d spacing, the XRD results also show a shift at an angle of 2θ between unmodified bentonite and modified bentonite, namely the peak suitable for bentonite is 19.74° (d=4.49 Å) shifted to 19.79° (d=4.48 Å) on bentonite-TiO_2. Likewise, changes occurred at the peak of 23.01 (d=3.86 Å), shifted towards 23.04 (d=3.85 Å), the peak at 26.55 (d=3.35 Å) shifted to 26.59, the peak at 27.83 (d=3.20 Å) shifted to 27.41 (d=3.25 Å), a peak at 39.39 (d=2.28 Å) shifted to 39.42 (d=2.28 Å), and peak at 50.06 (d=1.82 Å) shifted to 50.13 (d=1.81 Å). The occurrence of a shift at an angle of 2θ indicates that there has been an interaction between bentonite and TiO_2.

The peak shift of BT-20% occurred due to the formation of TiO_2 rutile with a peak position at 27.41° (110), which has an interplanar distance of 3.2 Å (0.32 nm) according to JCPDS No.21-1276. According to JCPDS No. 21-1272, another rutile TiO_2 diffraction peak appears at 36.08°, 41.25°, and 54.33°, which is in the region of points (111), (211), and (002). The bentonite peak at 2θ = 26.55° also shifted to 26.59° due to the formation of anatase TiO_2 with a peak position at 25.30°. Other diffraction peaks of anatase TiO_2 appear at 48.55° and 62.76°. Likewise, there was a shift in BT-10% from 2θ=19.74° to 2θ=19.79° and similarly for other peaks, namely 2θ=26.55° to 2θ=26.59°, while at 2θ=29.37° it becomes 2θ=29.33° and 2θ=39.39° becomes 2θ=39.43°. An increase in the value 2θ indicates that TiO_2 has interacted with bentonite.

In addition to the 2θ value, the XRD data also shows a decrease in the value of the distance between planes (d), from 2θ=4.49° to 2θ=4.48°, and 2θ=3.04° to 2θ=30.3°. The increase in the 2θ value and the relatively small decrease in the distance between planes indicate that the interactions between bentonite and TiO_2 most likely occur in the outer layer [3]. Even anatase TiO_2 diffraction spots appear at 2θ=25.25° and 2θ=48.56° according to JCPDS No.010-72-7058. Meanwhile, according to JCPDS No.010-72-7058, at the rutile TiO_2 diffraction peaks, the peaks appeared at 2θ=27.45°, 2θ=41, 24°, 2θ=54.33°, and 2θ=69.03°. The reflection at 2θ reveals that rutile and anatase are the two crystalline phases in BT-20%. These results indicate that the formation of the bentonite-TiO_2 composite did not significantly change the crystallinity of TiO_2.

3.1.3. Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX)

Characterization using SEM aims to determine the difference in surface morphologies between unmodified and modified bentonites (bentonite-TiO_2). SEM analysis uses electrons reflected from the sample's surface to produce a three-dimensional image. The results of the SEM characterization can be seen in Figure 3, and the results of the photocatalyzed EDX analysis of unmodified and modified bentonites (bentonite-TiO_2) are shown in Table 2.

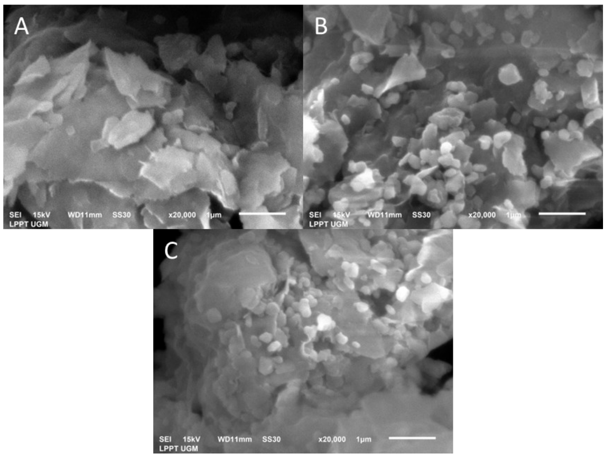

Figure 3. SEM images of (a) bentonite, (b) BT-10%, (c) BT-20% at 10,000-20,000× magnification

Based on Figure 3(a), bentonite particles have uniform morphologies, such as spherical, large flakes, layered structures [9], and irregular particle surfaces. These results are the same as those of previous research conducted by Suprihatin *et al.* [6]. After modification with the TiO_2 species shown in Figures 3(b) and 3(c), the bentonite surface changed, producing some small particles with a layered structure. This shows that the TiO_2 particles are agglomerated particles and are still in the form of agglomerates.

Table 2. The elemental composition of bentonite and bentonite-TiO_2

Element	% mass			% atom		
	Bentonite	BT-20%	BT-10%	Bentonite	BT-20%	BT-10%
C	19.65	16.00	12.99	56.74	51.96	44.30
O	36.26	38.31	35.55	-	-	-
Na	0.12	0.23	0.07	0.09	0.19	0.06
Mg	1.60	1.60	1.26	2.29	2.57	2.12
Al	8.46	8.87	6.51	5.44	6.41	4.94
Si	19.71	18.77	13.80	24.33	26.07	20.13
K	1.10	0.80	0.54	0.49	0.40	0.28
ca	10,11	3.09	20.57	8.75	3.01	21.02
Ti	0.17	7.95	6,19	0.13	6,47	5,29
Fe	2.82	2.62	2.52	1.75	1.83	1.85
Cu	-	1.77	-	-	1.09	-
Total	100	100	100	100	100	100

The results of photocatalyst analysis of unmodified bentonite and bentonite-TiO_2 using EDX can be seen in Table 2. The elemental composition of bentonite includes C, O, Na, Mg, Al, Si, K, Ca, Ti, and Fe. K and Fe elements are present due to the isomorphic substitution of metal cations K^+ and Fe^{2+} [13]. The spectrum of the bentonite-TiO_2 photocatalyst shows the chemical composition of C, O, Na, Mg, Al, Si, K, Ca, Fe, and Cu, including Ti. This result confirms the presence of Ti in this photocatalyst. Increasing the amount of TiO_2 on the modified bentonite surface compared to pure bentonite is based on the results of elemental analysis using the EDS spectrum shown in Table 2. These results indicate that the TiO_2 content increased from 0.17% in pure bentonite to 7.95% for BT- 20% and 0.17% to 6.

3.2. Application of Photocatalyst in Photodegradation of Methylene Blue

3.2.1. Effect of Bentonite-TiO_2 Composite Mass

In this study, photodegradation was carried out by varying the mass of the bentonite-TiO_2 catalyst (BT-10%, BT-20%, BT-30%, BT-40%, BT-50%, BT-60%, BT- 70%, BT-80%, BT-90%, and BT-100%). Figures 4 and 5 show the adsorption percentage increase with the mass of the ten bentonite-TiO_2 catalysts. The adsorption percentages of the ten consecutive catalysts were 99.68%, 99.87%, 99.64%, 99.78%, 99.45%, 99.55%, 99.63%, 97.85%, 99.57%, and 96.67%.

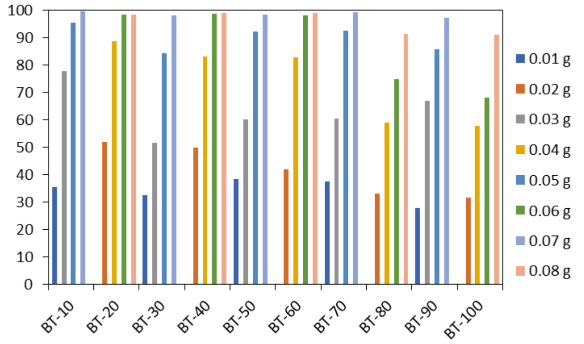

Figure 4. The effect of mass variation without a photoreactor

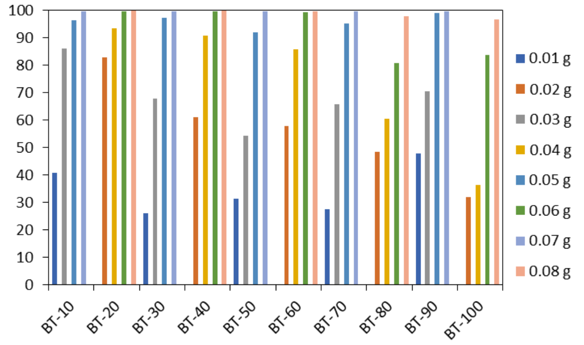

Figure 5. The effect of mass variation using a photoreactor

Based on mass optimization data, a catalyst mass of 0.08 grams was chosen as the optimum mass because the percentage of photodegradation of methylene blue has been relatively constant [6]. It indicates that the more catalyst mass used, the better the methylene blue dye degrades. This result follows the research of Fujishima *et al.* [20] that the photocatalyst plays a role in increasing the production of OH radicals in the TiO_2 valence band region so that the more OH radicals are formed, the degradation process will also run.

3.2.2. Effect of pH Variation

Differences in the pH conditions of the solution can cause changes in surface charge and shifts in the catalyst's reaction potential, thereby affecting the dye degradation process. This research conducted the pH variation to see the optimum catalyst at acidic or basic pH.

The pH of the solution was adjusted by adding HCl and NaOH solution to the methylene blue solution.

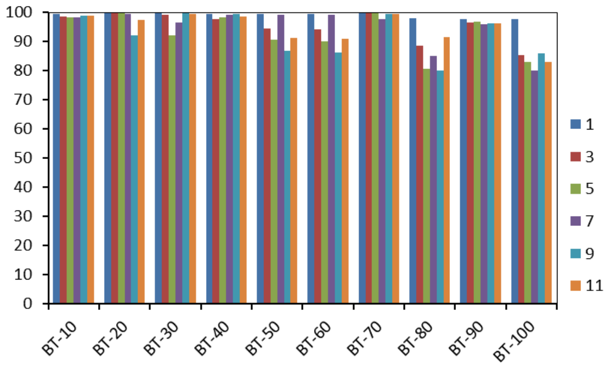

Figure 6. The effect of pH without a photoreactor

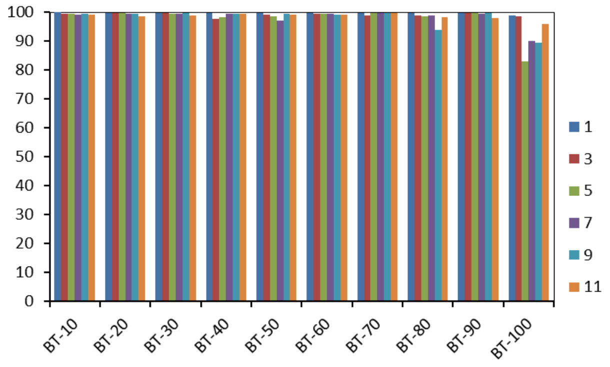

Figure 7. The effect of pH using a photoreactor

From Figure 7, it can be seen that the five catalysts have optimum conditions at pH 1, which percent degradations are 99.89%, 99.85%, 99.86%, 99.89%, 99.78%, 99.69%, 99.79%, 99.74%, and 98.83% for BT- 10%, BT-20%, BT-30%, BT-40%, BT-50%, BT- 60%, BT-70%, BT-80%, BT-90%, and BT-100%, respectively. However, BT-90% showed optimum conditions at pH 5 with a percent degradation of 99.76%. This is due to the repulsive forces caused by the negatively charged surface of the catalyst and pollutant so that methylene blue is more effectively adsorbed at acidic pH. The negative state can increase the adsorption of cationic dyes through electrostatic attraction, especially at high pH levels where the surface is more negatively charged. At low pH levels, the surface becomes relatively less charged. Adsorption of cationic dyes may be less favorable at low pH levels due to competition with excess H^+ ions, thus higher (lower) negative surface charge at higher (lower) pH explains higher (lower) adsorption of cationic dyes in terms of attractive electrostatic interactions.

From the results, the highest percentage of adsorption was obtained at pH 1 due to the difference in surface charge between the catalyst and the pollutant causing electrostatic interactions between the positively charged surface of the catalyst and the anions of methylene blue, which is negatively charged results in strong adsorption. This phenomenon causes methylene blue to be adsorbed more effectively at acidic than alkaline pH. From the test results on ten catalysts, it can be concluded that the BT-10%, BT-20%, BT-30%, BT- 40%, BT-50%, BT-60%, BT-70%, BT-80%, BT- 90%, and BT-100% are active at an acidic pH of 1 [6].

3.2.3. Effect of Irradiation Time

The effect of time variations with and without UV light irradiation on the catalyst was carried out to determine the optimum time conditions after determining the optimum pH conditions. This experiment aims to determine the optimum time required for the catalyst to achieve optimum adsorption of methylene blue. Results of methylene blue adsorption on BT-10%, BT-20%, BT-30%, BT-40%, BT-50%, BT- 60%, BT-70%, BT-80%, BT-90%, and BT-100% can be seen in Figure 6, which shows that the optimum time for each catalyst is 120 minutes with an adsorption percentage of 99.94%, 99.60%, 99.86%, 99.87%, 99.88%, 99.67%, 99.91%, 99.67%, 98.56%, and 99.48%.

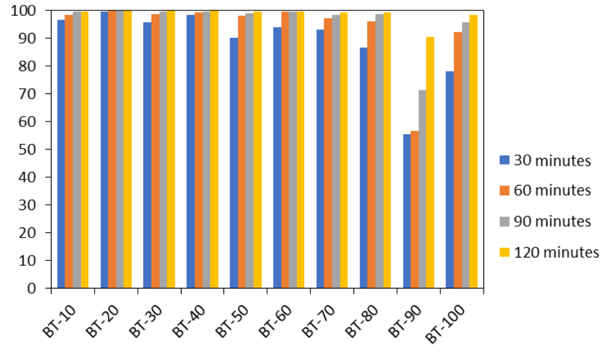

Figure 8. The effect of time without a photoreactor

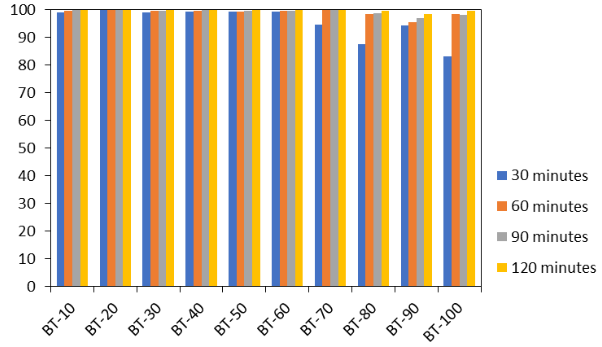

Figure 9. The effect of time using a photoreactor

Irradiation time affects the photodegradation of methylene blue. The longer the UV light irradiation time on the catalyst, the more methylene blue is degraded because the number of hydroxyl radicals (·OH) formed increases. However, the degradation rate of methylene blue by the composite slows down over time due to the adsorption process on the composite, thus inhibiting the photocatalytic reaction on the composite surface. This is in accordance with the study of Lestari *et al.* [21], where there was an increase in degradation as the irradiation time increased. Photodegradation of methylene blue is affected by irradiation time; the longer the UV light irradiation time on the catalyst, the more methylene blue is degraded because the number of hydroxyl radicals (·OH) produced increases. The longer the irradiation time, the more photon energy the surface catalyst absorbs, making methylene blue absorption easier.

Photon energy from ultraviolet light can cause the catalyst to generate more OH radicals than photon energy.

4. Conclusion

Based on the results of the research that has been done, it can be concluded that from the XRD results, bentonite-TiO_2 consists of rutile and anatase phases, while from the SEM-EDX results, bentonite-TiO_2 produces several small particles with a layered structure. In the adsorption process, the greater the mass amount used, the greater the adsorption % obtained and the time used. The higher the time used, the greater the adsorption ability of methylene blue dye. In this study of the catalystBT-10%, BT-20%, BT-30%, BT-40%, BT-50%, BT-60%, BT-70%, BT-80%, BT-90%, and BT-100%, which resulted in the best adsorption ability of methylene blue, namely on BT-20% catalyst with an optimum mass of 0.08 grams, pH 1 with an adsorption percentage of 99.4% within 120 minutes.

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