

Photodegradation of Methylene Blue Dye Using TiO₂/Zeolite with the Addition of Nitrate Ions (NO₃⁻)

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ABSTRACT

Purpose of the study: This study aims to determine the characterization of TiO₂/zeolite composites and determine the amount of TiO₂/zeolite, NO₃⁻ ion concentration, and optimum irradiation time for the photodegradation process of methylene blue in solution.

Methodology: This study used X-Ray Diffraction (XRD-6000 Shimadzu), UV-Vis spectrophotometer, UV lamp (Sankyo, 10 W, 352 nm), Teflon type hydrothermal reactor, and photocatalyst reactor (40×40×40 cm). The methods include zeolite activation, TiO₂ dispersion, hydrothermal synthesis, photodegradation test, and data regression analysis.

Main Findings: The TiO₂/zeolite composite showed characteristic peaks at $2\theta = 25.2737^\circ$, 37.6855° , and 48.0278° without any change in the crystal structure. The maximum degradation effectiveness of 29.94% was obtained by adding 75 mg of the composite. The optimum NO₃⁻ concentration was 0.5 M with an irradiation time of 100 minutes resulting in an effectiveness of 30.81%. NO₃⁻ has a dual role in the degradation process.

Novelty/Originality of this study: This study developed a photodegradation system with a combination of TiO₂/zeolite composite and nitrate ions. The novelty lies in the simultaneous analysis of the effects of catalyst amount, NO₃⁻ concentration, and irradiation time, as well as revealing the dual role of NO₃⁻ in enhancing and inhibiting degradation.

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1. INTRODUCTION

Photodegradation is one of the methods that has been widely developed to overcome dye waste pollution in aquatic environments [1], [2]. Synthetic dyes such as methylene blue are widely used in the textile industry, but they are difficult to decompose naturally [3], [4]. The accumulation of these substances can degrade water quality and harm aquatic organisms [5], [6]. Therefore, effective, efficient, and environmentally friendly methods are needed to decompose these dyes. One promising approach is the use of semiconductor-based photocatalysts.

Titanium dioxide (TiO₂) is known as a photocatalyst with high activity, good chemical stability, and non-toxicity [7], [8]. However, the use of TiO₂ in powder form has drawbacks, such as difficulty in separating it from the solution after the process. To overcome this, TiO₂ is often combined with supporting materials such as zeolite. Zeolite has a porous structure that can increase surface area and adsorption capacity [9], [10]. The TiO₂/zeolite combination is expected to increase the efficiency of the photodegradation process [11], [12]. Thus, this composite system is an attractive alternative for further study.

In addition to material factors, the presence of additional ions in the system can also affect the photodegradation process. Nitrate ions (NO_3^-) are known to act as electron acceptors or additional radical sources under certain conditions. The presence of these ions has the potential to increase the formation of reactive species that play a role in dye degradation [13], [14]. However, the effect of nitrate ion concentration on photocatalyst performance still requires systematic study [15], [16]. The interaction between nitrate ions, TiO_2 , and zeolite is a crucial aspect to understand. Therefore, research into the influence of nitrate ions in this system is relevant.

Another factor influencing the photodegradation process is irradiation time [17], [18]. The longer the irradiation time, the greater the chance of hydroxyl radical formation, which plays a role in the degradation of organic compounds [19], [20]. However, increasing irradiation time does not always directly correlate with degradation efficiency, as saturation can occur. Therefore, determining the optimum time is necessary to achieve maximum efficiency. Furthermore, light intensity and light source can also affect process results. Selecting the right operating conditions is key to the success of a photocatalytic system [21], [22].

Although various studies have been conducted on the photodegradation of methylene blue using TiO_2 , there are still research gaps that need to be filled [23], [24]. Some studies have focused solely on the use of pure TiO_2 without considering other supporting materials such as zeolite. Furthermore, studies on the influence of nitrate ions in the TiO_2 /zeolite system are still limited. Variations in TiO_2 /zeolite composition and optimization of reaction conditions have also not been comprehensively reported. This indicates a gap in understanding the synergy between the system's components. Therefore, further research is needed to fill this gap.

The novelty of this research lies in the combination of TiO_2 with zeolite and the addition of nitrate ions in a single photocatalytic system. This approach not only relies on photocatalytic activity but also utilizes the adsorption capacity of zeolite and the role of nitrate ions as a supporting agent [25], [26]. Furthermore, this study simultaneously examines several important parameters, such as material composition, ion concentration, and irradiation time. This combination of variables is expected to provide a more comprehensive understanding of the photodegradation mechanism. Thus, this research offers a new contribution to the development of photocatalyst-based wastewater treatment technologies.

The urgency of this research is based on the increasing water pollution caused by difficult-to-degrade dye industrial waste. Conventional methods are often ineffective or expensive. Therefore, more efficient and sustainable technological innovations are needed. The use of a TiO_2 /zeolite system with the addition of nitrate ions has the potential to be a more environmentally friendly alternative solution. Furthermore, the results of this study are expected to form the basis for the development of industrial-scale applications. Therefore, this research has significant value both scientifically and practically.

Based on this background, the objectives of this study were to determine the characterization of TiO_2 /zeolite, determine the effective addition amount of TiO_2 /zeolite, and determine the effective addition concentration of NO_3^- ions. In addition, this study also aimed to determine the effective irradiation time for the photodegradation process of methylene blue. This study is expected to provide comprehensive information regarding the performance of the developed photocatalytic system. The results of the study are expected to increase the efficiency of dye degradation in liquid waste. Thus, this study contributes to the development of more optimal waste treatment technology.

2. RESEARCH METHOD

2.1. Tools and Materials

The equipment used in this study included a set of laboratory glassware, an analytical balance, a magnetic stirrer, a desiccator, a porcelain dish, an oven, and a spatula. An electric heater and furnace were used for the heating process, and a pH meter was used to measure acidity. Sample analysis was performed using a UV-Vis spectrophotometer with a UV lamp (Sankyo, 10 watts, 352 nm) as the radiation source. This study also utilized a Teflon-type hydrothermal apparatus, a 40 cm × 40 cm × 40 cm photocatalyst reactor, and a 3 kW Shimadzu X-Ray Diffractometer (XRD)-6000 instrument for material characterization.

The materials used in this study included natural zeolite from Malang and anatase phase titanium dioxide (TiO_2) as the main component of the photocatalyst. Methylene blue was used as a test substance in the photodegradation process, while NaNO_3 (p.a.) served as a nitrate ion source. Additionally, ethanol, a universal pH indicator, and Whatman 42 filter paper were used as supporting materials. Aluminum foil is also used for certain purposes in the research process.

2.2. Research Stages

The stages of this research included several main steps. First, a preparation phase was carried out as the initial step to prepare the tools and materials to be used. Next, natural zeolite was activated to improve its adsorptive properties and reactivity. The next stage was the modification of TiO_2 -natural zeolite using a closed hydrothermal method to produce an optimal composite material.

After synthesis, the obtained material was characterized using X-Ray Diffraction (XRD) to determine its crystal structure and the phases formed. Next, a photodegradation process of methylene blue was carried out using the synthesized material. The final stage of this research was data analysis to evaluate the results obtained and determine the optimum conditions for the process.

2.3. Research Procedures

The research procedure began with the preparation of natural zeolite samples from Malang. A total of 250 grams of fine zeolite was soaked in 500 mL of deionized water (aquadest) while stirring with a magnetic stirrer for 24 hours at room temperature ($\pm 25^{\circ}\text{C}$). The mixture was then filtered using a 200-mesh sieve, and the resulting precipitate was dried in an oven at 100°C for 24 hours. The next step was zeolite activation using a 2 M NH_4NO_3 solution. The dried zeolite was mixed with the solution in a 1:2 ratio (weight/volume), then stirred continuously for 2–4 hours without heating. Afterward, the mixture was filtered and washed with aquadest until the filtrate reached a neutral pH (± 7). The resulting solid was then dried in an oven at 110°C for 12 hours.

Zeolite modification was carried out by dispersing TiO_2 into H-zeolite. A total of 10 grams of H-zeolite was mixed with 0.32 grams of TiO_2 and stirred for 2 hours until homogeneous. The mixture was then heated in an oven at 90°C for 12 hours, then cooled and filtered. The filtered solid was calcined at 500°C for 4 hours to produce TiO_2 -zeolite material. Material characterization was performed using the X-Ray Diffraction (XRD) method. Natural zeolite and TiO_2 -zeolite samples were ground into powder, then placed on a slide and pressed. The samples were then analyzed using X-rays at a 2θ angle of $5\text{--}60^{\circ}$, with a scanning speed of $0.02^{\circ}/\text{s}$ and a wavelength (λ) of 1.54 \AA .

The photodegradation process began with determining the maximum wavelength of methylene blue. The absorbance of a 5 ppm methylene blue solution was measured over a wavelength range of 600–680 nm at 5 nm intervals, and the wavelength with the highest absorbance was designated as the maximum λ . Next, the operating time was determined by measuring the absorbance of the solution from 0 to 6 minutes, and a curve was constructed relating the relationship between time and absorbance. The next step was to determine the standard curve by preparing a series of methylene blue solutions at concentrations of 1–8 ppm, measuring their absorbance, and constructing a curve relating the concentration to absorbance. The effect of varying the amount of TiO_2 -zeolite on the degradation percentage was then tested using masses of 12.5, 25, 50, and 75 mg, each of which was reacted with 15 ppm methylene blue solution and 5 mL of 2 M NO_3^- solution, then irradiated with a UV lamp (10 watts, 352 nm) for 100 minutes.

The final step was to test the effect of varying NO_3^- ion concentration and irradiation time on methylene blue degradation. The NO_3^- concentrations used were 0.5; 1; 1.5; and 2 M, each as much as 5 mL, then mixed with 25 mL of 15 ppm methylene blue solution at a constant pH of 11. The mixture was then irradiated with a UV lamp (10 watts, 352 nm) with variations in irradiation time of 20, 40, 60, 80, and 100 minutes, then analyzed to determine the degradation efficiency.

2.4. Data Analysis Techniques

Data analysis in this study was carried out in several stages. First, a standard curve was determined using a linear regression equation with the form $y = ax + b$, which was obtained from the relationship between the concentration of methylene blue solution and the absorbance value [27], [28]. This equation was used to calculate the sample concentration based on the data from spectrophotometric measurements. Next, the percentage of methylene blue degradation was calculated to determine the effectiveness of the photodegradation process. The calculation was carried out by comparing the initial concentration of the solution with the final concentration after treatment. The percentage of degradation (%D) was calculated using the following equation:

$$\text{Degradation Percentage (\%D)} = \frac{C_0 - C_t}{C_0} \times 100\% \dots (1)$$

Where C_0 is the initial concentration of methylene blue and C_t is the concentration at a certain time after the photodegradation process takes place.

3. RESULTS AND DISCUSSION

3.1. Characterization by X-Ray Diffraction (XRD)

Characterization using X-Ray Diffraction (XRD) was carried out on activated zeolite, TiO_2 /zeolite composite with a ratio of (97:3)%, and pure TiO_2 . Diffractogram analysis was carried out qualitatively to identify the crystal phase, crystallinity level, and the possibility of new phase formation before and after the modification process. Based on Figure 1, the diffraction pattern shows that the activated zeolite has distinctive peaks that are still clearly visible in the TiO_2 /zeolite composite. In addition, the characteristic peaks of the anatase phase of TiO_2 are also still observed in the composite material. This indicates that the modification process does not change the

main crystal structure of each component. Thus, it can be concluded that TiO₂ and zeolite form a composite system characterized by the presence of both diffraction patterns without the formation of new crystal phases.

Table 1. Diffractogram peaks of TiO₂/zeolite composite

TiO ₂ Anatas		Zeolit		Komposit TiO ₂ anatas-zeolit	
Peak	Intensity	Peak	Intensity	Peak	Intensity
		5.1777	11.11	6.2133	19.17
		12.6449	12.68	12.4252	13.98
		18.8799	5.49	17.6352	4.04
		19.8948	10.44	19.7179	11.61
		20.9708	19.31	20.8439	19.03
		22.1681	15.41	21.9987	15.60
		23.6713	7.43	23.0000	3.71
25.3578	100.00			25.2737	22.94
		26.7406	100.00	26.6004	100.00
27.5270	2.40			27.8956	40.45
		28.0096	34.68	28.2443	11.75
		30.6056	7.59	30.4345	8.59
		31.5651	3.20	31.2876	4.86
		35.1651	18.03	35.0797	8.36
		36.6451	18.19	36.5571	8.27
37.8307	19.64			37.6855	3.34
38.6168	6.83			39.4606	4.46
		42.5534	7.04	42.4643	6.78
48.0743	27.45			48.0278	5.75
		50.2414	13.90	50.1078	13.31
53.9225	16.17			53.8816	3.93
55.0839	16.08			54.8581	3.23

The process of dispersing anatase TiO₂ into zeolite does not cause changes in the crystal structure of either the zeolite or TiO₂ itself. This indicates that the TiO₂ particles are not dispersed deeply into the pores of the zeolite, but remain in its crystal structure. The diffractogram in Figure 1 shows that the typical peaks of anatase TiO₂ and activated zeolite are still detected. Thus, it can be concluded that the interaction between zeolite and TiO₂ produces a composite system without changing its crystal phase.

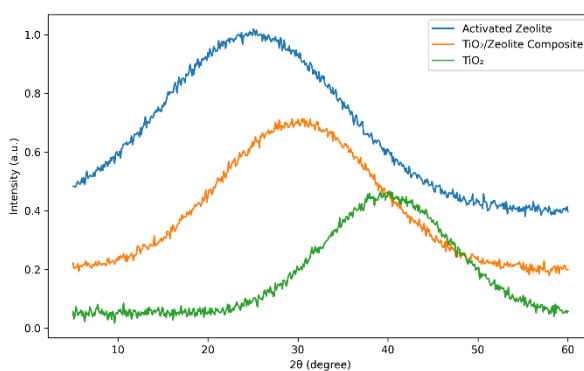


Figure 1. Diffractogram of TiO₂/Zeolite Composite

Zeolite dispersed with TiO₂ did not show significant peak changes, although there was a slight shift in its peak position. This shift could be influenced by several factors during the treatment process. One possible cause is the heating process in a furnace without the use of inert gas, thus providing no protection from the presence of other elements in the heating environment. This condition allows for interactions or the formation of chemical bonds between the material and the elements present in the furnace.

3.2. Effect of Variations in the Amount of Composite Addition on the Percentage of Degradation

Before determining the effect of increasing the amount of composite, a comparative treatment was carried out using 16 ppm methylene blue first, as shown in Table 2.

Table 2. Treatment of comparison samples irradiated with UV light for 100 minutes

Sample Treatment	Methylene blue concentration (ppm)		Degradation Percentage
	Beginning	End	
Methylene blue (blank)	10.1684	3.1343	69,17 %

Based on the data in Table 2, the methylene blue solution irradiated with UV light without the addition of TiO₂/Zeolite or NO₃⁻ ions showed a degradation percentage of 69.17%. This result indicates that the photodegradation process has occurred even without the presence of a catalyst, due to the direct influence of UV radiation. Therefore, in the test with variations in the addition of TiO₂/Zeolite composites and NO₃⁻ concentrations, the degradation value obtained was corrected by subtracting the blank degradation percentage. This correction was carried out to obtain a more accurate value of the degradation effectiveness of the developed system. In the variation of the amount of TiO₂/Zeolite composite, the masses used were 12.5; 25; 50; and 75 mg. Each variation was added with 5 mL of 2 M NO₃⁻ solution, then irradiated with a UV light for 100 minutes. The effect of variations in the amount of composite on the degradation of 16 ppm methylene blue is presented in Table 3.

Table 3. Effect of variations in composite addition on the percentage of methylene blue degradation with the addition of NO₃⁻ 2 M and UV light irradiation for 100 minutes

Variation in the addition of the amount of TiO ₂ /Zeolite composite (3:97) %	Methylene blue concentration		Degradation Percentage	Degradation Effectiveness
	Beginning	End		
0 mg + NO ₃ ⁻ 2 M	10.1684 ppm	3.8990 ppm	61.65%	-7.52%
12.5 mg + NO ₃ ⁻ 2 M	10.1684 ppm	3.8413 ppm	62.22%	-6.95%
25 mg + NO ₃ ⁻ 2 M	10.1684 ppm	1.3365 ppm	86.85%	17.68%
50 mg + NO ₃ ⁻ 2 M	10.1684 ppm	0.1938 ppm	98.09%	28.92%
75 mg + NO ₃ ⁻ 2 M	10.1684 ppm	0.0897 ppm	99.11%	29.94%

Based on the data in Table 3, the residual absorbance of methylene blue was obtained after treatment with various composite additions of 12.5, 25, 50, and 75 mg. In the condition without the addition of the TiO₂/zeolite composite, the degradation effectiveness was negative, at -7.52%. This indicates that the presence of 2 M NO₃⁻ ions actually inhibits the methylene blue degradation process. When the TiO₂/zeolite composite was added at 12.5 mg, the degradation effectiveness was still negative, at -6.95%. This value is lower than the blank degradation, indicating that the amount of composite added was still insufficient to offset the inhibitory effect of the NO₃⁻ ions. In other words, under these conditions, the role of NO₃⁻ was still more dominant than the photocatalytic activity of the composite.

As the amount of TiO₂/zeolite composite increased, the degradation effectiveness of methylene blue also increased. This was evident when the addition of 75 mg of the composite resulted in a degradation effectiveness of 29.94%. This increase indicates that a larger amount of catalyst can increase the formation of reactive species that play a role in the degradation process. The improved performance of the TiO₂/zeolite composite is due to its bifunctional nature. Zeolite acts as an adsorbent, accumulating methylene blue molecules on its surface, while TiO₂ functions as a photocatalyst, activating when exposed to UV radiation. Furthermore, the presence of zeolite also acts as a buffer, preventing agglomeration or sintering of TiO₂ particles, thus maintaining their catalytic activity.

The photodegradation mechanism occurs when TiO₂ absorbs light energy with sufficient energy to excite electrons from the valence band to the conduction band, resulting in the formation of electron (e⁻) and hole (h⁺) pairs. The resulting holes react with water molecules or hydroxide ions to produce hydroxyl radicals (•OH), while the electrons react with dissolved oxygen to form superoxide radicals. These reactive radicals then play a role in oxidizing and decomposing methylene blue molecules into simpler compounds. The resulting hydroxyl radicals play a key role in breaking chemical bonds in the methylene blue structure, including the C-S bonds and aromatic groups. This process occurs gradually through further oxidation reactions that produce intermediate compounds, ultimately resulting in the formation of end products such as sulfate, ammonium, and carbon dioxide. These reactions demonstrate that the degradation process not only breaks down the molecular structure but also leads to the mineralization of organic compounds.

Overall, the photodegradation of methylene blue using a TiO₂/zeolite composite is a heterogeneous photodegradation process that occurs on the semiconductor surface. This activity is influenced by the nature of the TiO₂ semiconductor, which has an energy band gap between the valence and conduction bands. With UV irradiation, this system is capable of producing reactive species that are effective in degrading dyes, especially when the composite quantity used is at optimum conditions.

3.3. The Effect of Variations in NO₃⁻ Concentration and Irradiation Duration on the Percentage of Methylene Blue Dye Degradation

The addition of inorganic anions in the form of NO₃⁻ in the photodegradation process of methylene blue can have two effects, namely inhibiting or increasing the percentage of degradation, depending on the conditions used. Therefore, variations in the concentration of NO₃⁻ were carried out by 0.5; 1.0; 1.5; and 2.0 M. Each concentration was combined with variations in irradiation time for 25; 50; 75; and 100 minutes. The percentage degradation value obtained from each treatment was then corrected by subtracting the blank degradation value, namely methylene blue which was only irradiated with UV light for 100 minutes by 69.17%. This correction aims to obtain a more representative value of the degradation effectiveness of the system being developed. The results of the effect of variations in NO₃⁻ concentration and irradiation time on methylene blue degradation are presented in Table 4.

Table 4. Effect of Variations in NO₃⁻ Concentration and Irradiation Time on The Degradation of Methylene Blue with The Addition of 75 mg TiO₂/Zeolite Composite

Variation of Concentration of Addition NO ₃ ⁻	Minute to-	Methylene Blue Concentration		Percentage of Degradation	Degradation Effectiveness
		Beginning	End		
75 mg composite + Without NO ₃ ⁻	100	10.1684	2,8383	72,08 %	2,91 %
	25	10.1684	0,0941	99,07 %	29,90 %
75 mg composite + 0,5 M	50	10.1684	0,098	99,03%	29,86 %
	75	10.1684	0,169	98,33 %	29,16 %
	100	10.1684	0,002	99,98 %	30,81 %
	25	10.1684	0,064	99,37 %	30,20 %
75 mg composite + 1,0 M	50	10.1684	0,0511	99,49 %	30,32 %
	75	10.1684	0,1835	98,19 %	29,02 %
	100	10.1684	0,0829	99,18 %	30,01 %
	25	10.1684	0,1186	98,83 %	29,96 %
75 mg composite + 1,5 M	50	10.1684	2,3141	77,24 %	8,07 %
	75	10.1684	1,3761	98,57 %	29,40 %
	100	10.1684	0,0829	99,18 %	30,01 %
	25	10.1684	0,3672	96,38 %	27,21 %
75 mg composite + 2,0 M	50	10.1684	0,0560	99,44 %	30,27 %
	75	10.1684	0,1489	98,53 %	29,36 %
	100	10.1684	0,1181	98,83 %	29,66 %

Based on the data in Table 4, each variation in NO₃⁻ concentration showed a maximum degradation percentage value at different irradiation times. Without NO₃⁻ addition, the degradation effectiveness was 2.91%. These results indicate that the use of a 75 mg TiO₂/zeolite composite without nitrate still performed better than the blank condition with only UV irradiation. With the addition of 0.5 M NO₃⁻, the highest degradation effectiveness was 30.81% at an irradiation time of 100 minutes. This indicates that the presence of a certain amount of NO₃⁻ can enhance the photodegradation performance of methylene blue. However, increasing the NO₃⁻ concentration does not always have a positive effect, as at higher concentrations it can actually decrease the degradation effectiveness.

This phenomenon occurs because NO₃⁻ ions can adsorb on the surface of the TiO₂/zeolite composite and interact with holes (h⁺), forming nitrate radicals (NO₃•). This interaction can inhibit the formation of hydroxyl radicals (•OH), which are the main reactive species in the degradation process. In addition, NO₃⁻ can also react with •OH radicals to form NO₃• which has a lower reactivity, thus reducing degradation efficiency. On the other hand, at certain concentrations, the presence of unadsorbed NO₃⁻ can undergo further reactions to form other radicals such as NO₂• and •OH. The formation of these radicals can accelerate the process of dye degradation. Thus, the role of NO₃⁻ in the photodegradation system is dual, namely it can enhance or inhibit the process depending on its concentration. In addition, the presence of TiO₂/zeolite composites and NO₃⁻ ions simultaneously greatly influences the formation of reactive species. Without the composite, the formation of hydroxyl radicals is limited, while without NO₃⁻ no additional radicals such as NO₂• are formed. The combination of the two under optimum conditions can increase the effectiveness of methylene blue photodegradation. Therefore, determining the appropriate NO₃⁻ concentration is an important factor in optimizing the performance of this photocatalytic system.

3.4. Utilization of TiO₂/Natural Zeolite from Malang as a Photodegradation Agent for Methylene Blue Dye

In an effort to degrade methylene blue dye using a TiO₂/zeolite composite with the addition of NO₃⁻ ions, each component exhibits a distinct role in the degradation process. The TiO₂/zeolite composite functions as

a photocatalyst that produces reactive species, while NO_3^- ions can act as either a supporter or an inhibitor depending on their concentration. The results showed that increasing the composite amount is directly proportional to the percentage of degradation, with the optimum value obtained at 75 mg. Conversely, increasing NO_3^- concentration does not always increase degradation efficiency. At low concentrations, NO_3^- can enhance the degradation process, but at high concentrations, it actually decreases effectiveness by inhibiting the formation of hydroxyl radicals.

This phenomenon indicates that each component in the system has specific limits and roles in supporting the photodegradation process. The interaction between $\text{TiO}_2/\text{zeolite}$ and NO_3^- must be in balance for optimal performance. An imbalance in the composition can lead to a decrease in the overall effectiveness of the system. Therefore, determining optimum conditions is a crucial aspect in the development of photocatalytic systems. In addition, the results of this study indicate that the photodegradation process is not only influenced by the presence of a catalyst, but also by the complex interactions between components in the system. The success of methylene blue degradation is highly dependent on the system's ability to generate and retain reactive species such as hydroxyl radicals. Thus, optimization of parameters such as the amount of composite and ion concentration is key to increasing degradation efficiency. In general, this study confirms that the combination of $\text{TiO}_2/\text{zeolite}$ composite and NO_3^- ions can improve photodegradation performance if used under appropriate conditions. These results provide an important basis for the development of more effective and efficient photocatalyst-based waste treatment technologies.

The photodegradation process of methylene blue using a $\text{TiO}_2/\text{zeolite}$ composite demonstrates a complex interaction between the photocatalytic properties of TiO_2 and the adsorption capacity of the zeolite. Zeolite plays a role in increasing the local concentration of dye molecules around the catalyst surface through an adsorption mechanism, thereby increasing the likelihood of a photocatalytic reaction [13], [29]. Meanwhile, TiO_2 functions as an active material capable of generating electron and hole pairs when exposed to UV radiation. The synergy between these two components is a crucial factor in improving overall system performance.

Furthermore, photodegradation efficiency is greatly influenced by the availability of reactive species formed during the process. Hydroxyl radicals ($\bullet\text{OH}$) are powerful oxidants that play a key role in breaking down the complex structure of methylene blue into simpler compounds [30], [31]. The formation of these radicals depends on the presence of holes on the TiO_2 surface and interactions with water molecules or hydroxide ions. Therefore, environmental conditions such as pH, light intensity, and the presence of other substances significantly influence the effectiveness of degradation [32], [33].

The presence of nitrate ions (NO_3^-) in the system has a complex effect, acting as both a promoter and inhibitor of the reaction. Under certain conditions, NO_3^- can contribute to the formation of additional radical species that support the oxidation process. However, under other conditions, these ions can compete with water molecules or hydroxide ions for holes, thereby reducing the formation of hydroxyl radicals [34], [35]. This indicates that the interactions between components in a photocatalytic system are dynamic and highly dependent on the composition used.

The irradiation time also plays a crucial role in determining the degradation rate. The longer the irradiation time, the more energy is absorbed by TiO_2 to generate electron-hole pairs, thus increasing the chance of reactive radical formation. However, increasing the irradiation time does not always directly correlate with increased degradation, as electron-hole recombination can occur, reducing process efficiency [36], [37]. Therefore, a balance between irradiation time and system conditions is necessary for optimal photodegradation.

Overall, the performance of the photodegradation system is influenced by the interaction between the $\text{TiO}_2/\text{zeolite}$ composite, NO_3^- ions, and operational parameters such as irradiation time. The right combination of these factors can increase degradation efficiency through a synergistic mechanism between adsorption and photocatalysis [38], [39]. Understanding this mechanism is crucial as a basis for developing more effective and applicable photocatalyst-based waste treatment technologies.

This research has a significant impact on the development of wastewater treatment technology, particularly in the treatment of organic dyes such as methylene blue. The use of a $\text{TiO}_2/\text{zeolite}$ composite demonstrates potential as an effective and relatively economical photocatalyst material due to the use of natural zeolite as a support. Furthermore, the use of a UV-based photodegradation system can be an environmentally friendly alternative to conventional methods that produce secondary waste [40], [41]. The results of this research can also serve as a basis for the development of larger-scale technology in the textile industry's wastewater treatment sector.

However, this research still has several limitations. The use of an artificial UV light source requires significant energy, which can be a barrier to industrial-scale application. Furthermore, the degradation efficiency obtained is still relatively low, requiring further optimization, both in terms of catalyst modification and operational conditions [42], [43]. The research variables are also limited to a few parameters, thus not reflecting more complex system conditions such as those encountered in real wastewater. Therefore, further research is needed to improve system performance and test its effectiveness in broader applications.

4. CONCLUSION

The results showed that the characterization of the TiO₂/zeolite composite had diffraction peaks at 2θ angles of 25.2737; 37.6855; and 48.0278°, which indicated that the TiO₂ dispersion process did not damage the crystal structure of either zeolite or TiO₂, so that both maintained their phase in the form of a composite. In addition, variations in the amount of the TiO₂/zeolite composite showed that the increase in the mass of the composite was directly proportional to the degradation effectiveness, with a maximum value of 29.94% at the addition of 75 mg. Meanwhile, variations in the concentration of NO₃⁻ ions showed that the optimum condition was achieved at a concentration of 0.5 M with an irradiation time of 100 minutes, which resulted in a degradation effectiveness of 30.81%. Further research is recommended to develop modifications to the TiO₂/zeolite composite, such as metal or non-metal doping, to improve photodegradation efficiency and broaden the response to visible light. Furthermore, testing on real wastewater and optimizing other operational parameters are necessary for more effective application of this system on an industrial scale.

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AUTHOR CONTRIBUTIONS

Conceptualization, E.; Methodology, E.E; Software, E.E; Validation, E.E; Formal Analysis, E.E; Investigation, E.E; Resources, E.E; Data Curation, E.E; Writing – Original Draft Preparation, E.E; Writing – Review & Editing, E.E; Visualization, E.E; Supervision, E.E; Project Administration, E.E; Funding Acquisition, E.E.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

USE OF ARTIFICIAL INTELLIGENCE (AI)-ASSISTED TECHNOLOGY

Not applicable.

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