Enhanced Photocatalytic Degradation Activity of Methyl Violet Dyes Utilizing TiO_2/Natural Zeolite Composite

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Abstract. For boosting the degradation activity of methyl violet employing photocatalyst, titanium dioxide modified by natural zeolite (TNZ) was successfully produced by sonication method. TiO_2 is a photocatalyst that can be used to degrade methyl violet. TNZ was characterized using XRD to determine crystal structure, XRF to determine the elemental composition, and Spectrophotometer UV-Vis/DRS to determine band gap energy and absorbance in the long wavelength region. Furthermore, TNZ was examined its photodegradation activity, including the effect of irradiation time, optimum catalyst mass, and optimum dye concentration for dye degradation. The XRD characterization results show that TiO_2 has an anatase phase, zeolite has a modernite phase. The XRF results indicate that some impurities in zeolite have been successfully removed after the activation process. Ti content in TNZ is 63.64%. Natural zeolite can decrease the band gap of TiO_2 from 3.31 eV to 3.29 eV. The optimum time for the photodegradation process is found to be 150 minutes with a degradation percentage of 98.27%. The optimum catalyst mass for the photodegradation process is 20 mg with a degradation percentage of 99.47%. The optimum dye concentration for the photodegradation process is 10 ppm with a degradation percentage of 99.74%.

Keyword : Methyl Violet, Natural Zeolite, Photodegradation, Titanium Dioxide

1. Introduction

The textile industry has a vital environmental impact due to the usage of dyes, which can cause severe ecological and health problems. The inappropriate disposal of dye effluents pollutes water bodies, endangering aquatic ecosystems and human health. The textile industry emits almost 8×10^5 tons of synthetic dyes annually, leading to significant water pollution [1]. Untreated effluents can contaminate soil, air, and water, leading various illnesses in humans and detrimental effects on aquatic life [1,2]. Numerous synthetic dyes are mutagenic and carcinogenic, directly endangering the health of textile workers and the people surrounding them [3]. The presence of toxic substances in wastewater can cause respiratory issues and skin diseases in those who are exposed [2]. While the textile industry is increasingly adopting sustainable practices, the reliance on synthetic dyes remains a critical challenge. The treatment technology and improved waste management practices is essential to mitigate these negative impacts.

Photodegradation employing TiO_2 photocatalysts has emerged as an applicable wastewater treatment technology, particularly for the degradation of dyes. This process leverages the photocatalytic properties of TiO_2 under UV or visible light to break down pollutants effectively. TiO_2 photocatalysts generate reactive oxygen species when exposed to light, which facilitate the degradation of organic pollutants like methylene blue (MB) and ciprofloxacin [4]. TiO_2 is the most effective semiconductor catalyst due to its non-toxic nature, affordable price, and abundance in nature. Its gap energy of 3.2 eV makes it appropriate for use as a photocatalyst [5].

Titanium dioxide photocatalysis is less effective in pure form due to its lowers surface area. Therefore, utilization of supporting materials may improve its activity. Studies highlight that TiO_2/zeolite composites could effectively degrade persistent organic pollutants including caffeine and methylene blue, at degradation efficiencies of up to 96% and 89.58%, respectively [6,7]. The combination of TiO_2 nanoparticles and zeolite not only enhances absorption but also accelerates the photocatalytic degradation of volatile organic compounds like toluene, achieving up to 70% decomposition efficiency [8].

The sonication approach for synthesizing TiO_2/zeolite composites provided promising outcomes in terms of photocatalytic activity and structural characteristics. This technology uses ultrasonic vibrations to increase the dispersion and interaction of TiO_2 with zeolite matrices, resulting in more effective composites. The sonication technique helps in the homogeneous distribution of TiO_2 nanoparticles, improving their interaction with the zeolite framework, which is essential for photocatalytic applications [9]. XRD and TEM characterization techniques confirm the structural integrity and high crystallinity of the TiO_2/zeolite composites, which are urgent for their photocatalytic effectiveness [10]. In addition, the incorporation of TiO_2 to zeolite matrices has been shown to increase light absorption and catalytic activity, making these composites appropriate for environmental applications [9].

The photodegradation process is significantly influenced by irradiation time, photocatalyst mass, and sample concentration. According to research, optimizing these parameters could increase degradation performance across various pollutants. Extended irradiation times commonly increase degradation rates. For instance, a study discovered that the optimal degradation of p-Cresol occurred around 280 minutes, through 94.7% efficiency [11]. In contrast, shorter irradiation intervals remain capable of results in significant degradation rates, as observed with indigosol blue, when 30 minutes resulted in 58.7% degradation [12]. A photocatalyst mass of 0.10 g/L has been shown to be optimal for formaldehyde degradation, with no significant enhancement detected above that level [13]. Higher initially concentrations of pollutants can enhance degradation rates, as seen with formaldehyde, whereby increased concentration led to greater degradation efficiency. However, excessive concentrations may lead to mass transfer limitations, suggesting a balance is necessary [13].

This study utilizes a sonication method to synthesize photocatalyst TNZ and determine the optimal TNZ effectiveness in degrading methyl violet by varying irradiation period, photocatalyst mass, and dye concentration. Additionally, various condition of degradation was conducted using different material of photocatalyst as a control test. The synthetic catalyst will be further characterized using XRD (X-Ray Diffraction), XRF (X-Ray Fluorescence), and a UV-Vis DRS (Diffuse Reflectance Spectroscopy).

2. Materials and methods

2.1 Materials

Titanium dioxide (SA), concentrated chloride acid, ethanol (96% pure), methyl violet 10B. Natural zeolite was collected from Bandung, West Java, Indonesia.

2.2 Preparation and activation of Natural Zeolite (NZ)

Natural zeolite preparation was carried out by weighing 150 grams of natural then mashed, the mashed NZ was then sieved through a 200 mesh. NZ (100 gr) was soaked in 200 mL of distilled water (1:2). This mixture was then stirred for 30 minutes, filtered and dried for 2 h in an oven at 100°C. Furthermore, the solid was placed in desiccator and weighed to achieve a consistent weight.

NZ activation using concentrated HCl, 30 grams of natural zeolite was soaked in concentrated chloride acid for 3 h. After that, the mixture was filtered and neutralized using distilled water. The NZ powder dried at 100°C for 2 h and calcined at 500°C for 4 h.

2.3 Synthesis of TNZ using sonication method

TNZ synthesis was carried out by mixing 4 grams of TiO_2 anatase and 10 grams of NZ (2:5) and added by 21 mL of 96% ethanol. Following that, the mixture was grinded by mortar agate and sonicated using probe-type sonication for 30 minutes. The sample was dried in an oven at 110°C for 3 h, and then calcined in a furnace at 550°C for 2 h. Following calcination, the sample was ground into powder form [14].

2.4 Characterization of TNZ

Powder XRD measurements were carried out on PANalytical X'Pert Pro for TiO_2 anatase, NZ and TNZ using Cu-Kα radiation with a wavelength of 1.5418 Å. The elemental content and its percentage of TiO_2 anatase, NZ before and after activation, and TNZ was characterized using XRF (X-Ray Fluorescence). Thermo Scientific Evolution 220 UV-Visible spectrophotometer was used to determine the catalyst's optical band gap through diffuse reflectance spectra (DRS). The sample reflectance ranged from 200 to 800 nm. In addition, the UV spectrum of the degraded and undegraded samples was also examined using the Varian Cary® UV-Visible spectrophotometer.

2.5 Photocatalytic degradation of methyl violet

A stock solution of 100 ppm methyl violet was generated by diluting 10 mg of methyl violet with distilled water in a 100 mL standard flask. The stock was diluted to a concentration of 10 ppm. Into a beaker glass, 25 mL of 10 ppm methyl violet solution (pH 7) was added along with 25 mg of TNZ photocatalyst. Photodegradation of methyl violet was conducted under UV light with different of time exposure ranged from 40, 80, 120 and 150 minutes each. Aliquots were collected and centrifuged to get rid of any catalyst particles from the solution before being analyzed with a UV-Visible spectrophotometer at the maximum wavelength that was determined first. The same procedure was followed for varying TNZ photocatalyst mass of 10, 15, 20, and 25 mg, using the previously determined optimum time. The optimum time and mass were then used to experiment with different concentrations of methyl violet (5, 10, 15, 20, and 25 ppm). Furthermore, control tests were conducted under various circumstances to assess the efficiency of photocatalytic degradation using optimum irradiation time, TNZ photocatalyst mass, and methyl violet concentration in the conditions of no catalyst at all, only TiO_2 photocatalyst, only zeolite, and TNZ photocatalyst.

3. Results and discussion

3.1 Characterization of TNZ

Material characterization was performed using X-Ray Diffraction (XRD), UV-Visible Diffuse Reflectance Spectroscopy (DRS), and X-Ray Fluorescence (XRF). The characterized materials were natural zeolite (NZ) and TiO_2 anatase precursors, as well as TiO_2/natural zeolite (TNZ) composites. TiO_2 and TNZ were analyzed by XRD, UV-Vis DRS, and XRF. Meanwhile, NZ has been assessed utilizing XRD and XRF.

3.1.1 X-Ray Diffraction (XRD)

The diffraction illustrates that a TNZ composite was formed (Figure 1a). The XRD pattern demonstrates that there is no chemical or structural alteration to NZ, as both TiO_2 and NZ peaks are visible. Furthermore, the absence of additional peaks in TNZ indicates that the composite contains no impurities. XRD analysis reveals that the TiO_2 phase generated during synthesis is anatase, while the zeolite phase is mordenite. Position shift resulting from TNZ modification and impregnation treatment. Increased particle size in TiO_2 and TNZ leads to a shift to the right.

Figure 1a demonstrates that the TNZ photocatalyst exhibits a typical peak with the maximum intensity value at position 2θ 25,326, and the top TiO_2 at position 2θ 25,342. The results align with the current zeolite ICDD standard no. 01-070-0232, which has a typical peak with the maximum intensity value at position 2θ 25.645. In prior research, XRD studies demonstrated that the TiO_2/Zeolite photocatalyst remained unaltered after nine cycles, indicating strong stability [15]. While the TNZ photocatalysts exhibit outstanding stability, problems such as potential catalyst deactivation over extended usage or under different environmental conditions may still need to be addressed to enhance their practical applicability.

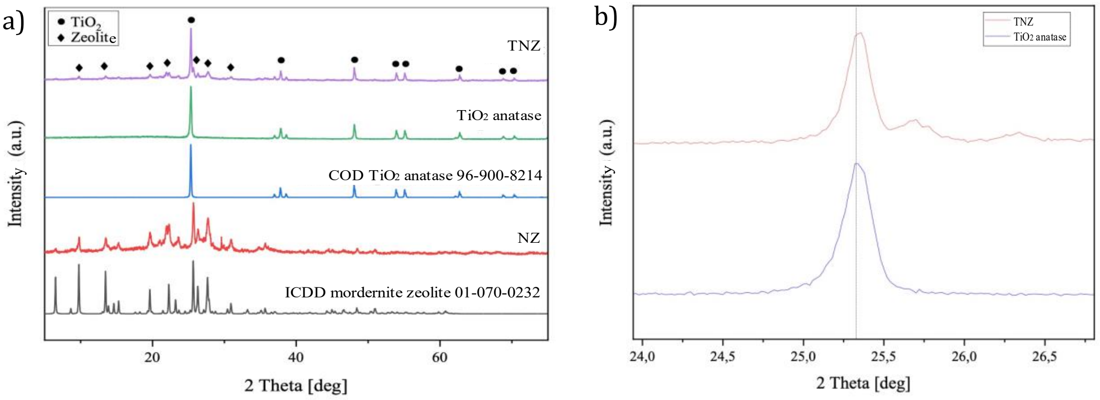

Figure 1. (a) XRD plots of TNZ and comparison with commercial TiO_2 anatase and natural zeolite and standard TiO_2 (96-900-8214-COD) and mordenite zeolite standard (01-070-0232-ICDD) samples; **(b)** Enlargement of XRD plots of the TNZ and TiO_2 anatase.

3.1.2 UV-Visible Diffuse Reflectance Spectroscopy (DRS)

The band gap of the synthetic composite TNZ was determined to be 3,29 eV using the Tauc plot of the UV-Visible DRS spectrum (Figure 2a) and the Kubelka-Munk function (Figure 2b). Incredibly, the band gap of the TNZ photocatalyst is lower than that of anatase TiO$_2$ (3.31 eV).

Figure 2a shows that there are differences to TiO$_2$ and TNZ in the visible light region. The shifts occur in wavelength 400-700 nm, indicating that TNZ has a lower percentage reflectance, leading it to be more effective in photodegradation assessment in the visible light region. In Figure 2b, the band gap energy can be calculated by plotting a straight line from the graph of the relationship between energy (eV) and $(F(R)*h\nu)^{1/2}$. TNZ photocatalyst has a lower band gap energy than TiO$_2$ anatase, making it a more effective photocatalyst for photodegradation process. When TiO$_2$ is dispersed in zeolite, it interacts with the zeolite at the interface, increasing the photocatalyst surface. These interactions modify the structure at the interface and affect the energy levels of internal electrons. This modification can alter the energy distribution of the inner band gap, leading to a reduction.

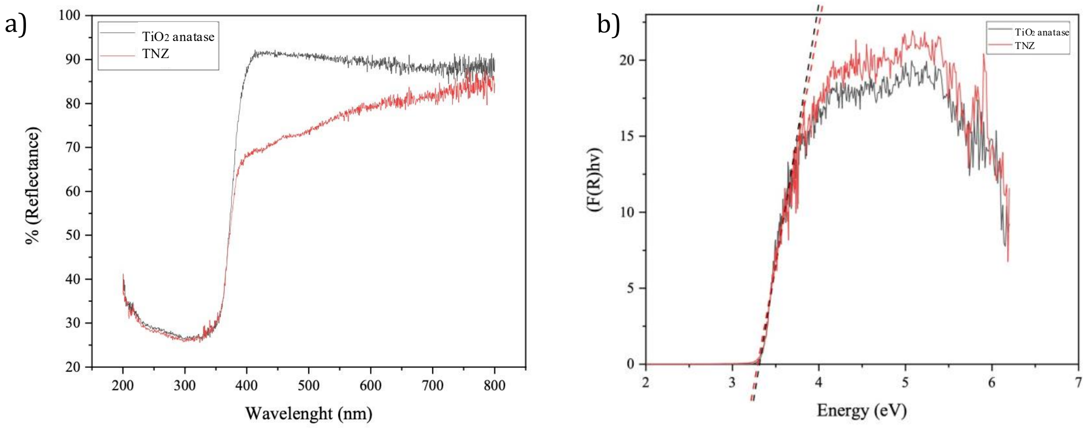

Figure 2. (a) Reflectance vs. wavelength plot; **(b)** Tauc plot of TNZ and TiO$_2$ anatase plotted using Kubelka-Munk function.

3.1.3 X-Ray Fluorescence (XRF)

The XRF analysis displayed the constituent components of the TiO$_2$ anatase, TNZ photocatalyst, NZ before and after activation (Table 1). Based on the XRF result, the zeolite activation procedure successfully removed impurities like Cr, resulting in successful TNZ synthesis with high percentages of Si and Ti (22.5% and 63.64%, respectively).

Table 1. Element content in TiO_2 anatase, TNZ, and NZ before and after activation

Element	Concentration (%)			
	NZ before activation	NZ after activation	TiO_2 anatase	TNZ
Al	8.4	-	-	3.6
Si	57.3	65	-	22.5
K	9.65	11.6	0.18	3.1
Ca	8.99	10.7	0.11	2.56
Ti	0.98	1.1	98.17	63.64
V	0.02	0.03	-	-
Cr	0.06	-	-	-
Mn	0.41	0.27	-	0.13
Fe	12.8	9.73	-	3.85
Cu	0.098	0.11	-	0.066
Zn	0.05	0.03	-	0.08
Sr	0.85	1	-	0.36
Ba	0.08	0.2	-	-
Eu	0.3	0.1	-	-
Re	-	0.2	-	0.1
Os	-	-	0.76	-

3.2 Photocatalysis

3.2.1 Effect of the irradiation time on the degradation

Further, to determine the optimal irradiation time for maximum methyl violet solution degradation, five different trials were conducted with stirring for 40, 80, 120, 150, and 180 minutes. The TNZ photocatalyst mass and the methyl violet concentration were kept constant at 25 mg/25 mL solution and 10 ppm, respectively. Figure 3 indicates that a 150-minute exposure duration resulted in the highest percentage of degradation (98.27%). As radiation exposure time increases, more hydroxyl radicals are created to breakdown methyl violet, leading to improved outcomes. The longer photons stay in contact with the catalyst, the more electrons and holes are produced [16].

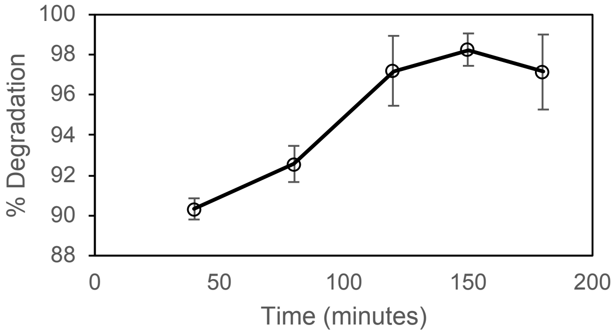

Figure 3. Degradation efficiency of TNZ photocatalyst to degrade 10 ppm methyl violet dye in five different irradiation time.

Longer exposure leads to greater results by producing more hydroxyl radicals (•OH) that degrade methyl violet. That was occurred because of longer contact time between photons and catalyst that leads to increased production of electrons and holes. As a result, more radicals are created. Exposure to the sample for a longer period increases the production of hydroxyl radicals (•OH), optimizing the degradation process [16].

3.2.2 Effect of the TNZ photocatalyst mass on the degradation

In addition, to identify the most efficient TNZ photocatalyst mass for maximum methyl violet solution degradation, five separate trials were undertaken with 5, 10, 15, 20, and 25 mg in 25 mL of solution. The irradiation time was kept constant at the optimum time (150 minutes), and the methyl violet concentration was maintained at 10 ppm. This investigation found that using a catalyst mass of 20 mg resulted in the highest degradation percentage of 99.48% (Figure 4). The more catalyst mass utilized, the higher the percentage of degradation. This is due to the formation of more •OH radicals, which increases the number of degraded dye molecules.

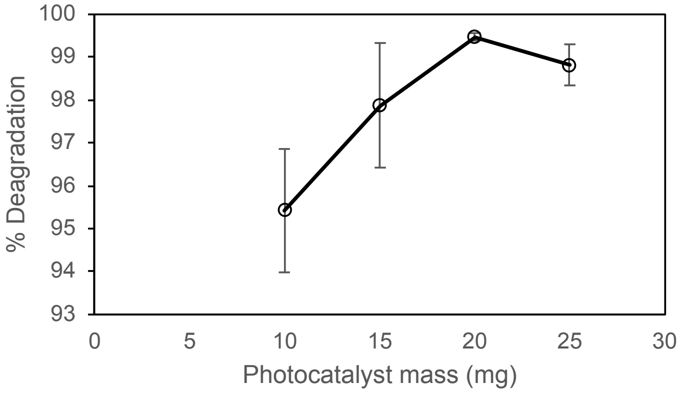

Figure 4. Degradation efficiency of TNZ photocatalyst to degrade 10 ppm methyl violet dye with mass variation of photocatalyst at optimum irradiation time.

The more catalyst mass utilized, the higher the percentage of degradation due to the formation of more OH radicals. This leads to an increase in the number of degraded molecules. At a catalyst mass of 25 mg, there was a slight decrease due to turbidity in the dye solution. Excess photocatalyst particles may block UV light access to the active surface, reducing photodegradation reaction. As the generation of hydroxyl radicals decreases, so does the intensity of the dye [17].

3.2.3 Effect of the methyl violet concentration on the degradation

Moreover, five different methyl violet concentrations (5, 10, 15, 20, and 25 ppm) have been investigated to determine the most efficient concentration for methyl violet solution degradation. The irradiation time and TNZ photocatalyst mass was kept constant at the optimum, 150 minutes and 20 mg. The investigation discovered that the percentage of degradation from 5 ppm to 25 ppm decreases as the concentration of dye molecules grows, covering the surface of the TNZ photocatalyst.

Figure 5 shows that the percentage of degradation decreases from 5 ppm to 25 ppm as the concentration of dye molecules increases, covering the surface of the TNZ photocatalyst. The vast number of dye molecules compete for adsorbed space on the photocatalyst, leading to decreased degradation.

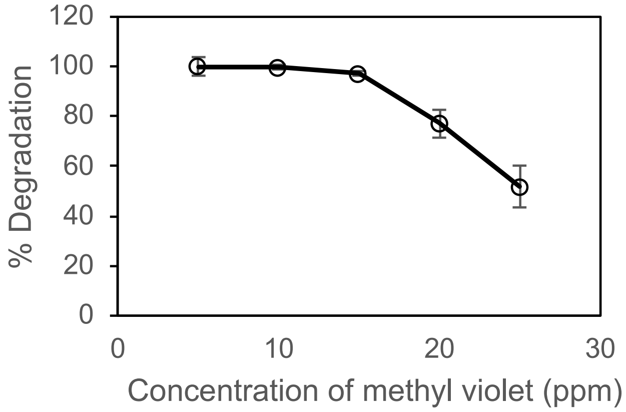

Figure 5. Degradation efficiency of TNZ photocatalyst to degrade methyl violet at different concentrations at optimum irradiation time.

3.2.4 Effect of the different condition on the degradation

Four different conditions of photocatalytic degradation have been investigated to determine the most efficient condition for methyl violet solution degradation. The conditions are no catalyst at all, only TiO_2 photocatalyst, only zeolite, and TNZ photocatalyst. The results suggest that utilizing TNZ photocatalyst was the most successful condition for methyl violet degradation, with a rate of 99.74%.

Figure 6 illustrates that the degradation of methyl violet without a catalyst resulted in the lowest degradation percentage, 14.42%. UV light could possibly degrade methyl violet, making this an important consideration. UV radiation interacts with the organic compounds like methyl violet, leading to degradation. The methyl violet molecule absorbs UV light energy, causing changes in its bonds and its structure. NZ and TiO_2 degradation rates were 92.18% and 98.7%, respectively. This is due to zeolite's ability to adsorb and TiO_2 photocatalyst properties. Whereas TiO_2 has a band gap of 3.31 eV, it is capable of degrading methyl violet, as seen by the high percentage degradation. When exposed to light, TiO_2 absorbs photons and forms pairs of holes (h^+, valence band) and electrons (e^-, conduction band), producing •OH.

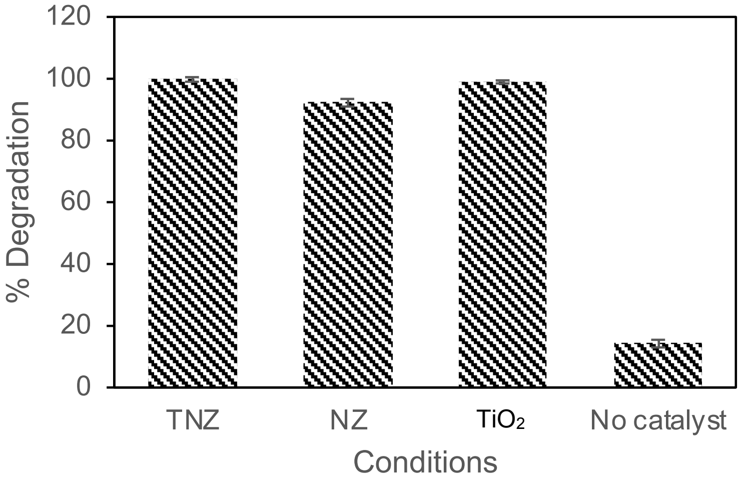

Figure 6. Degradation efficiency of TNZ photocatalyst to degrade methyl violet at different concentrations at optimum irradiation time.

The degradation percentages of TiO_2 and TNZ photocatalyst were not significantly different. However, TNZ photocatalyst has reuse potential, which is one of the most important qualities for establishing the economic viability of a material in actual water treatment systems. The TNZ photocatalyst demonstrates significant potential for reusability and stability across multiple cycles, making it a promising candidate for environmental applications. TiO_2/zeolite composites revealed no detectable leaching and maintained their structure over several cycles, with one study reporting effective reuse for at least nine consecutive cycles [15]. The TiO_2/zeolite filters exhibited over 90% regeneration efficiency in the first two cycles, decreasing to over 60% after five cycles [18].

During the degradation process, the •OH radical produced triggered the degradation of the methyl violet dyes. The methyl group of the methyl violet is attacked by the •OH radical, which functions as an oxidizing agent to produce aldehyde. The aldehyde group oxidizes the carboxylic acid group, which then decarboxylates producing CO_2 [19]. TNZ absorbed UV light to form electrons (e-) and positive holes (h+) during the methyl violet degradation. When the surface of TNZ encountered methyl violet solution, the oxidation mechanism process began because of the positive hole (h^+); this positive hole oxidized water (H_2O) to generate a radical •OH that had the capability to degrade organic compounds to form CO_2 and H_2O [20] [21]. This equation shows the reaction occurred during the photodegradation process.

$$\text{TNZ} + h\nu \rightarrow \text{TNZ}\ (e^-/h^+) \qquad (1)$$
$$h^+(\text{vb}) + OH^- \rightarrow OH^\bullet \qquad (2)$$
$$h^+(\text{vb}) + H_2O \rightarrow OH^\bullet + H^+ \qquad (3)$$
$$e^-\ (\text{cb}) + O_2 \rightarrow O_2^{\bullet -} \qquad (4)$$
$$OH^\bullet + \text{methyl violet} \rightarrow CO_2 + H_2O \qquad (5)$$

According to the findings of this study, TNZ photocatalyst has the potential for use in various pollutants, particularly organic pollutants such as dyes, pharmaceuticals, and surfactants. The capability of TNZ photocatalyst to degrade organic compounds makes it preferable because it is low-cost and environmentally beneficial.

4. Conclusion

The optimal irradiation time for TNZ photocatalyst to decompose methyl violet is 150 minutes, the optimal mass of TNZ photocatalyst for decomposing methyl violet was 20 mg/25 mL, and the optimal concentration for methyl violet dye degradation is 10 ppm, resulting in a maximum 99.74% degradation rate.

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