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Engineering and Application of Fe-TiO_2/MOR Zeolite Photocatalysts for the Photodegradation of Methylene Blue Dye Waste

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Abstract. The use of dyes such as methylene blue is widespread. However, if methylene blue is discharged without prior treatment, it can lead to pollution problems. In this study, the engineering of zeolites and the degradation mechanism of methylene blue using Fe-TiO_2/MOR zeolite as a photocatalyst were investigated. XRD characterization results revealed that Fe-TiO_2/MOR zeolite has a crystalline phase. Based on XRF characterization, the percentage of Fe and Ti significantly increased, indicating the successful immobilization of TiO_2 and doping of Fe^{3+} into the zeolite structure to form a composite. The morphological analysis of the Fe-TiO_2/MOR zeolite composite showed a rough surface, which could affect its surface area. The Fe-TiO_2/MOR zeolite photocatalyst has a band gap of 3.08 eV, allowing it to absorb visible light more efficiently. The study on the application of methylene blue photodegradation using Fe-TiO_2/MOR zeolite as a photocatalyst demonstrated higher degradation efficiency compared to using unactivated, non-immobilized, and undoped mordenite zeolite. With an optimal mass of 0.03 grams, a contact time of 90 minutes, and a pH of 10, the percentage of degraded methylene blue reached 98.91%. The Fe-TiO_2/MOR zeolite composite has the potential to be used as a photocatalyst in methylene blue photodegradation reactions.

Keywords: *immobilization, doping, photocatalyst, photodegradation, methylene blue*

Abstrak. Pengunaan zat warna seperti metilen biru sangat luas. Namun, apabila zat warna metilen biru langsung dibuang tanpa melalui pengolahan terlebih dahulu, maka akan menimbulkan masalah pencemaran. Pada penelitian ini telah dipelajari rekayasa zeolit dan mekanisme degradasi zat warna metilen biru menggunakan fotokatalis Fe-TiO_2/zeolit MOR. Hasil karakterisasi XRD menunjukkan bahwa Fe-TiO_2/zeolit MOR memiliki fase kristalin. Berdasarkan hasil karakterisasi XRF, persentase Fe dan Ti mengalami peningkatan yang cukup signifikan, menunjukkan keberhasilan imobilisasi TiO_2 dan doping Fe^{3+} ke dalam struktur zeolit membentuk komposit. Analisis morfologi komposit Fe-TiO_2/zeolit MOR menunjukkan permukaan yang kasar. Permukaan kasar ini dapat mempengaruhi luas permukaannya. Fotokatalis Fe-TiO_2/zeolit MOR memiliki celah pita 3,08 eV sehingga dapat menyerap cahaya tampak dengan lebih efisien. Hasil studi aplikasi fotodegradasi metilen biru menggunakan fotokatalis Fe-TiO_2/zeolit MOR menunjukkan efektivitas degradasi yang lebih tinggi dibandingkan dengan penggunaan zeolit mordenit tanpa aktivasi, imobilisasi, dan doping. Dengan massa optimum sebesar 0,03 gram, waktu kontak selama 90 menit, dan pH 10 diperoleh persentase metilen biru yang terdegradasi mencapai 98,91%. Komposit Fe-TiO_2/zeolit MOR berpotensi untuk dimanfaatkan sebagai fotokatalis dalam reaksi fotodegradasi metilen biru.

Kata kunci: *imobilisasi, doping, fotokatalis, fotodegradasi, metilen biru*

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INTRODUCTION

The use of dyes has become an integral part of everyday life. Dyes are utilized in several sectors such as industry, textiles, paper, plastics, and education. In the textile, paper, and plastics industries, dyes are often used to add color to products, making them more appealing. Additionally, in education, dyes are used as materials in laboratory activities. These examples demonstrate the extensive application of dyes. It is estimated that approximately 800,000 tons of dyes are produced annually (Pizzicato *et al.*, 2023).

Most dyes have aromatic structures, large molecular sizes, and are difficult to degrade (Anwar & Mulyadi, 2015). Some dyes are carcinogenic, cytotoxic, and mutagenic (Ardila-Leal *et al.*, 2021). These dye wastes can reduce water quality in terms of color and odor and have the potential to enter the food chain, posing a danger to living organisms (Al-Tohamy *et al.*, 2022; Lellis *et al.*, 2019). Therefore, innovative waste management solutions that are environmentally friendly, cost-effective, and safe are required to protect the environment and public health.

One of the commonly used dyes is methylene blue. Methylene blue's IUPAC name is 3,7-bis(dimethylamino) phenothiazine chloride tetra methylthionine chloride. Methylene blue is a cationic dye that is toxic, carcinogenic, mutagenic, and difficult to decompose in water (Oladoye *et al.*, 2022). Thus, it requires treatment before being discharged into water bodies. Several methods are used to reduce the concentration of dye waste, including adsorption (Banerjee *et al.*, 2017; Ho, 2020), biosorption (Deniz, 2014; Stjepanović *et al.*, 2021), coagulation and flocculation (Jian & Nurhazwani, 2018), ozonation (Hu *et al.*, 2021), membrane filtration (Abdelhamid *et al.*, 2023; Fortunato *et al.*, 2021), liquid-liquid extraction (Orzolek & Kozlowski, 2021), and photocatalytic degradation (Altun *et al.*, 2021).

Photocatalytic degradation is an advanced oxidation reaction widely used to eliminate dyes by breaking them down into simpler compounds such as CO_2 and H_2O (Khan *et al.*, 2022). The advantage of the photocatalytic degradation method is that it can be performed at room temperature and pressure without generating waste (Agustina *et al.*, 2020). The photocatalytic degradation process involves a photocatalyst.

A photocatalyst is a material that can enhance the rate of a reaction when exposed to light. TiO_2 is a semiconductor frequently used as a photocatalyst due to its high photocatalytic activity and non-toxic nature. However, anatase phase TiO_2 has an energy band gap of 3.2 eV (Einert *et al.*, 2021). The large energy band gap reduces its ability to absorb visible light, thereby decreasing its efficiency in degrading dyes. To enhance its catalytic activity, TiO_2 can be immobilized on materials with a large surface area, such as zeolite. Utilizing zeolite as a support material for metal oxides has the potential to enhance its catalytic activity.

Additionally, the catalytic activity of TiO_2 can be further enhanced by doping with transition metals such as Fe, Mn, Cu, and Ni. Among these dopants, the ionic radius of Fe^{3+} is similar to that of Ti^{4+}, facilitating the doping process (Wojcieszak *et al.*, 2017). In previous studies, Fe-doped TiO_2 was immobilized on kaolinite. The band gap of the Fe-doped photocatalyst at a concentration of 0.25% decreased to 3.16 eV (Aritonang *et al.*, 2021). This reduction in the band gap increases the photocatalyst's ability to absorb visible light (Ismail *et al.*, 2021). In another study, Fe-TiO_2/zeolite H-A was synthesized with a band gap of 3.16 eV. However, the degradation of methylene blue achieved was only 89.58% (Cahyanti *et al.*, 2023). Based on these findings, research on the treatment of methylene blue dye waste using a photocatalyst made from mordenite (MOR) zeolite is important. This study focuses on the engineering of zeolite and the degradation mechanism of methylene blue dye using Fe-TiO_2/MOR zeolite as a photocatalyst. The objective of this research is to synthesize the Fe-TiO_2/MOR zeolite photocatalyst with a narrow band gap to absorb visible light more efficiently.

MATERIAL AND METHODS

Materials

The materials used in this research include mordenite zeolite (Sigma Aldrich), HCl 37% (Merck), ethanol (Merck), TiO_2 (Merck), $FeCl_3.6H_2O$ (Merck), glacial acetic acid (Merck), NaOH (Merck), deionized water, universal pH indicator, fine filter paper, methylene blue (Merck), and technical ethanol.

Instrumentation

The instrumentation used in this research include Spectronic 30 (Thermo Scientific Genesys 30 Visible Spectrophotometer), XRD (Rigaku MiniFlex 600), XRF (Rigaku NEX DE), UV-Vis DRS (Analytic Jena Specord 200 Plus), and SEM (FEI Inspect S50). The analysis using UV-Vis DRS and SEM was conducted at the Central Laboratory of Mineral and Advanced Materials, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang.

Procedure

Activation of mordenite zeolite

Mordenite zeolite was activated with HCl 6 M, then deionized water was added until a neutral pH was reached. After neutralization, the filtrate and residue were separated. The residue was dried at 120ºC, then calcined at 550ºC. The dried zeolite was referred to as active mordenite zeolite.

Synthesis of composite Fe-TiO_2/MOR zeolite

TiO_2 was weighed at 3% of the active mordenite zeolite weight, then 15 mL of ethanol was added and sonicated. Next, 30 mL of deionized water was added, and the active mordenite zeolite was gradually added while stirring. The solution was then neutralized by adding more deionized water, filtered, and the residue was dried at 120ºC. Subsequently, the residue was calcined at 550ºC. For the impregnation step, $FeCl_3.6H_2O$ was added with a calculated Fe^{3+} concentration of 3%, followed by the addition of 30 mL of deionized water, and stirred and heating at 70ºC. Afterward, the solution was again neutralized with deionized water, filtered, and the residue was dried at 120ºC, then calcined at 550ºC. This yielded Fe-TiO_2/MOR zeolite, which was then characterized using XRD, XRF, SEM, and UV-Vis DRS.

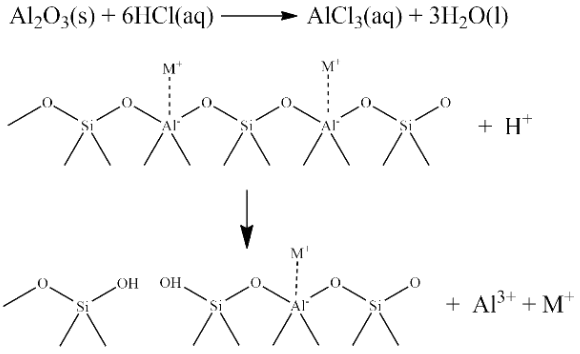
Photocatalysis Application Study

In this study, 5 mg of Fe-TiO_2/MOR zeolite photocatalyst was weighed and added to 25 mL of a 20 ppm methylene blue solution. The mixture was stirred and then irradiated UV light, followed by exposure to sunlight. After irradiation, the photocatalyst was separated from the mixture. The solution was then analyzed using a UV-Vis Spectrophotometer at the maximum wavelength of 664 nm for methylene blue to measure the percentage of degradation. The procedure was repeated with variations in contact time, photocatalyst mass, and pH to determine the optimal conditions for photocatalytic activity.

RESULT AND DISCUSSION

Synthesis of Composite Fe-TiO_2/MOR Zeolite

The synthesis of the composite begins with the activation process of mordenite zeolite. The activation is carried out by adding an HCl solution. Activation of the zeolite with the HCl solution causes the removal of extra-framework aluminium and increases its crystallinity (Kalvachev *et al.*, 2021). Thus, the activation alters the zeolite structure, enhancing its performance in absorbing methylene blue (Suhendar *et al.*, 2023). Subsequently, the zeolite is neutralized by adding deionized water and then heated to remove water molecules from the zeolite pores. After the activation stage, the active mordenite zeolite is used as the base material for composite synthesis. The following is the reaction that occurs during the activation of mordenite zeolite (Scheme 1).



Scheme 1. Activation mechanism of mordenite zeolite

After the activation process, TiO_2 is prepared by dissolving it in ethanol with the assistance of ultrasonic waves to ensure that the TiO_2 is evenly dispersed and forms a homogeneous mixture (Zhou *et al.*, 2024). The active mordenite zeolite is added to the TiO_2 and ethanol mixture, then stirred while being heated. Deionized water is added to the mixture until it reaches a neutral pH, followed by heating to remove the remaining ethanol and water. After heating, TiO_2/mordenite zeolite is obtained.

The TiO_2/mordenite zeolite is then mixed with a $FeCl_3$ solution and stirred while being heated, allowing Fe^{3+} to be evenly distributed on the surface and within the pores of the TiO_2/mordenite zeolite. Deionized water is added, followed by heating to remove water from the pores, resulting in the Fe-TiO_2/mordenite zeolite composite (Fe-TiO_2/MOR zeolite), which appears ivory yellow. Figure 1 shows the Fe-TiO_2/MOR zeolite composite.

Figure 1. Fe-TiO_2/MOR zeolite composite

X-Ray diffraction (XRD) analysis

The active zeolite mordenite sample, TiO_2, and the Fe-TiO_2/MOR zeolite composite were characterized using X-ray diffraction. The characterization was performed over a 2θ range of 10° to 90°. The diffraction measurement results are shown in Figure 2, which represents the diffraction patterns for each sample. The peaks observed indicate the crystal structure, which can be used to identify phases and detect structural changes in the samples.

The XRD analysis of the mordenite zeolite sample shows characteristic peaks at 2θ = 13.441°, 19.606°, 22.310°, 25.663°, 26.330°, 27.632°, and 30.883°. These peaks were then matched with reference data from JCPDS No. 6-239. The results indicate that diffraction peaks of the mordenite zeolite sample correspond to the standard diffraction pattern of mordenite zeolite. The mordenite zeolite, active mordenite zeolite, and Fe-TiO_2/MOR zeolite all exhibit crystalline phase. According to the obtained diffractogram, peaks appear at 2θ = 25.323°, 37.802°, and 53.915°. These peaks are characteristic of TiO_2 with an anatase phase (Foura *et al.*, 2017; Hamdan *et al.*, 2020). Before and after the immobilization and impregnation processes, there were no significant changes in the diffraction patterns. However, some peak shifts were observed. The shifts at 2θ = 27.663°, 30.930°, 37.802°, and 53.915° indicate that the immobilization of TiO_2 on the active zeolite and the impregnation of Fe^{3+} were successfully achieved.

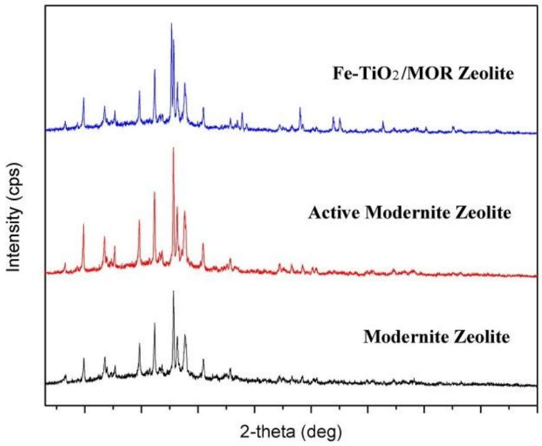


Figure 2. Diffraction patterns of mordenite zeolite, active mordenite zeolite, and Fe-TiO_2/MOR zeolite

X-Ray fluorescence (XRF) analysis

XRF analysis aims to determine the qualitative and quantitative composition of a sample. In this study, active MOR and Fe-TiO_2/MOR zeolite samples were characterized using XRF.

The primary components of active mordenite zeolite and the Fe-TiO_2/MOR zeolite composite are silicon (Si) and aluminum (Al) (Table 2). The dominant presence of Si and Al indicates that these samples are composed of an aluminosilicate framework (Sriatun *et al.*, 2020). The active zeolite serves as a support material for TiO_2 metal oxide. The porous structure of the active zeolite aids in the distribution of TiO_2 and Fe^{3+}. In the Fe-TiO_2/MOR zeolite sample, the percentages of Fe and Ti have increased significantly, indicating the successful immobilization of TiO_2 and doping of Fe^{3+} into the zeolite structure, forming a homogeneous Fe-TiO_2/MOR zeolite composite that is expected to have enhanced photocatalytic activity.

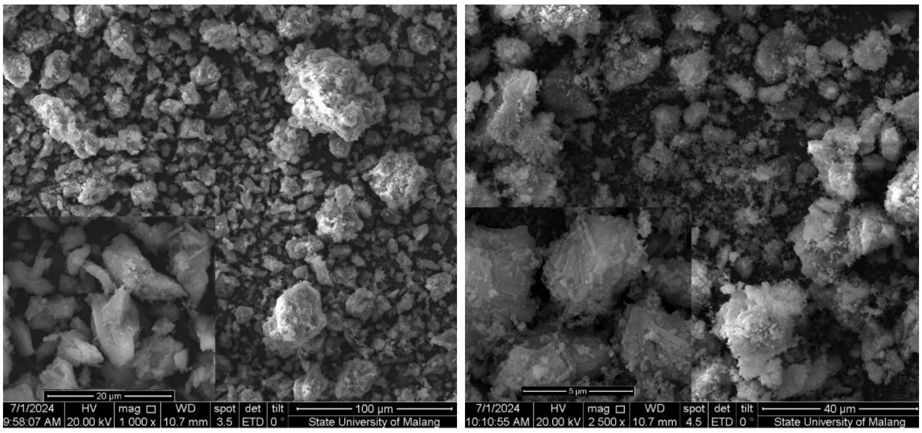
Table 2. Composition of the Samples

Composition (%)	MOR	Fe-TiO_2/MOR zeolite
Si	47.30	37.70
Al	7.96	6.68
Fe	0.681	2.860
Ti	0.214	8.710

Fe^{3+} (0.645 Å) and Ti^{4+} (0.605 Å) ions have ionic radii close to that of Al (0.535 Å), making it easier for Al to be substituted by Fe or Ti within the zeolite framework through an ion exchange mechanism (Rahm *et al.*, 2016). This process causes Al to be released from the zeolite framework, leading to decrease in its concentration. Additionally, Fe^{3+} and Ti^{4+} ions tend to interact with siloxane groups (Si-O-Si), which can weaken the bonds between Si atoms in the zeolite structure. When Fe^{3+} or Ti^{4+} binds to siloxane groups, Si becomes more prone to dissociation and subsequently forms $Si(OH)_4$ leading to a decrease in Si content. The simultaneous reduction of Si and Al results in a decreased Si/Al ratio.

Scanning electron microscope (SEM) analysis

SEM analysis aims to examine the surface morphology of the samples. The SEM analysis shows that both MOR zeolite and Fe-TiO_2/MOR zeolite have rough and porous surfaces. These pores represent the aluminosilicate framework. The rough surface of the and Fe-TiO_2/MOR zeolite is caused by the formation of agglomerates, which can reduce the surface area of the active zeolite. This is consistent with previous research indicating that immobilization and doping affect the morphology and surface area of the material (Li *et al.*, 2020).



(a) (b)

Figure 3. Surface morphology of (a) MOR zeolite and (b) Fe-TiO_2/MOR zeolite

Analysis of UV-Visible diffuse reflectance spectroscopy (UV-Vis DRS)

In this study, Fe-TiO_2/MOR zeolite with a band gap of 3.08 eV was obtained. The reduction in band gap energy occurred after the immobilization of TiO_2 and doping with Fe^{3+}. This reduction in band gap energy aligns with previous research, where it was found that doping Fe^{3+} into the TiO_2 structure led to a decrease in band gap energy (Gareso *et al.*, 2021). The band gap energy obtained in this study is lower compared to previous research, which reported a band gap energy of 3.16 eV for Fe-TiO_2/zeolite H-A (Cahyanti *et al.*, 2023). The band gap energy approaching 3 eV indicates that the immobilization of TiO_2 and doping with Fe^{3+} effectively reduce the band gap, thereby improving the composite's photocatalytic efficiency.

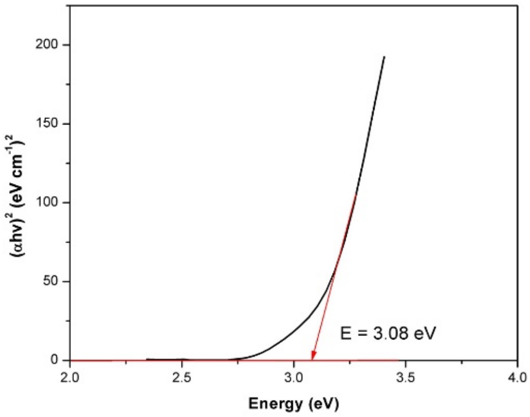
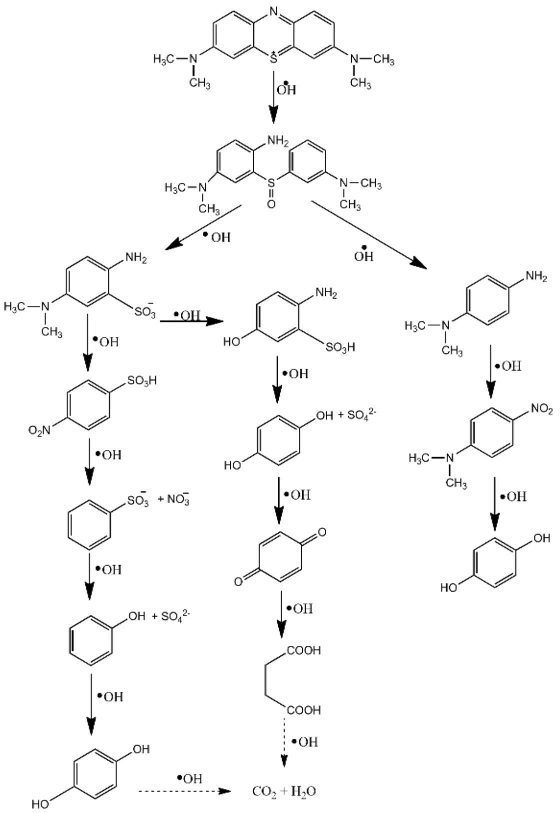


Figure 4. Tauc plot result of Fe-TiO_2/MOR zeolite

Photocatalysis Application Study

Reaction mechanism

Currently, photocatalytic degradation has become a popular technology for processing methylene blue due to its application of green chemistry principles. Photocatalytic degradation utilizes energy from UV light to generate hydroxyl radicals (•OH). These hydroxyl radicals then break down methylene blue into CO_2 and H_2O. The following is the proposed mechanism for the photocatalytic degradation of methylene blue based on previous research results using Gas Chromatography-Mass Spectrometry (GC-MS) (Scheme 2) (Wang *et al.*, 2018).



Scheme 2. Mechanism of the photocatalytic degradation of methylene blue

The effectiveness of photocatalysis is influenced by several factors, including the mass of the photocatalyst, contact time, light intensity, initial dye concentration, and pH. In this study, the effects of varying contact time, initial dye concentration, and pH were observed to determine the optimal conditions for the photocatalyst in degrading methylene blue.

Effect of photocatalyst

Under conditions without photocatalyst and light, the degradation percentage was minimal. Methylene blue showed an increase in degradation percentage when exposed to light. The concentration of methylene blue decreased as the contact time with the photocatalyst increased. The addition of the photocatalyst aims to accelerate the degradation reaction. The presence of sunlight allows the photocatalyst to generate more radicals, such as hydroxyl radicals (Santiago *et al.*, 2022). These radicals are highly reactive and can break down methylene blue molecules. As a result, the percentage of degraded methylene blue increased.

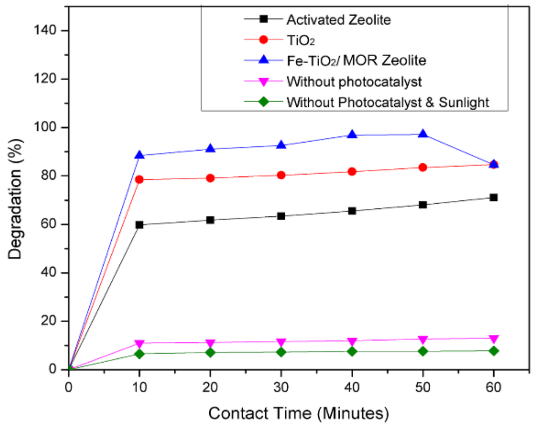


Figure 5. Effect of photocatalyst

Based on the obtained research data, it is evident that the addition of the Fe-TiO_2/MOR zeolite photocatalyst is effective in degrading methylene blue. The concentration of methylene blue after degradation with the Fe-TiO_2/MOR zeolite photocatalyst showed a significant reduction, indicating that the photocatalyst is capable of effectively degrading methylene blue.

Determination of optimum photocatalyst mass

The optimal mass of the photocatalyst was determined by adding photocatalyst in various amounts. Increasing the amount of photocatalyst increases the number of active sites and thus the number of radicals formed. An increase in radicals enhances the percentage of MB degradation. However, beyond the optimal mass, further addition of photocatalyst decreases the degradation percentage. This is due to the saturation of the photocatalyst surface (Awais *et al.*, 2022). The research indicated that the optimum photocatalyst mass is 0.03 grams. Therefore, in subsequent optimizations, 0.03 grams of Fe-TiO_2/MOR zeolite photocatalyst was used.

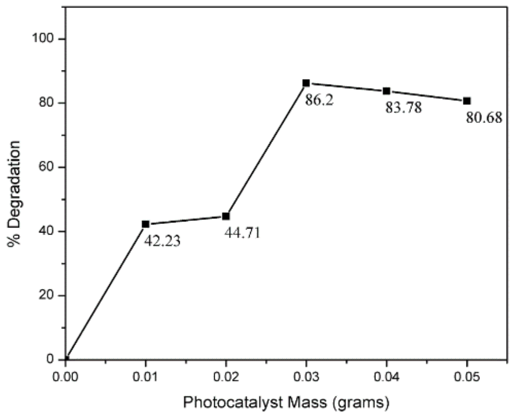


Figure 6. Determination of optimum photocatalyst mass

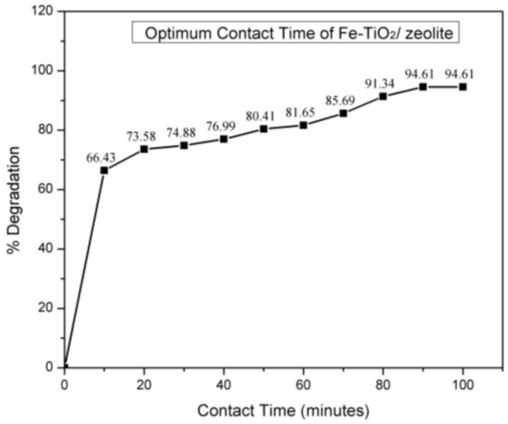


Figure 7. Determination of optimal contact time

Determination of optimal contact time

The variation in contact time is conducted to determine the duration of interaction between hydroxyl free radicals and methylene blue. Longer contact time allows the hydroxyl radicals to interact with methylene blue for a longer period, leading to an increased degradation percentage. On the other hand, shorter contact time may result in suboptimal interactions, which leads to a lower percentage of degraded dye (Groeneveld *et al.*, 2023). Based on previous research, it was found that the optimum contact time was reached at 90 minutes, with 94.61% of methylene blue being degraded (Figure 7).

Determination of optimum concentration

Variation in the initial concentration of methylene blue aims to determine its optimal concentration. By identifying this optimal concentration, it is possible to find the initial methylene blue concentration at which it can be degraded most effectively. As the concentration of methylene blue increases, the percentage of methylene blue degraded also rises. However, at very high concentrations, a decline is observed. This is because the concentration exceeds the capacity or ability of the photocatalyst to degrade methylene blue. In this study, the optimal concentration was found to be 20 ppm, with a methylene blue degradation percentage of 94.51%.

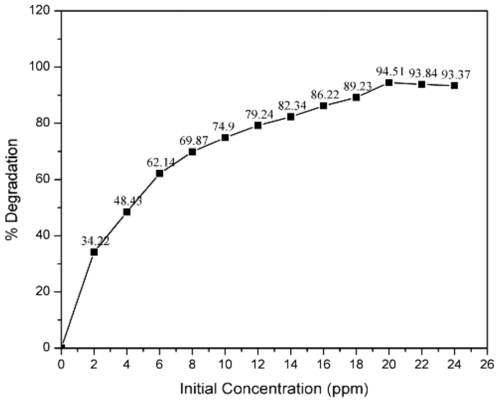


Figure 8. Determination of optimum concentration

Determination of optimal pH

The effect of pH varies depending on the type of dye. In this study, the highest methylene blue degradation percentage was observed at pH 10. In acidic solutions, there is competition between H^+ ions and the cationic methylene blue for interaction with the photocatalyst, resulting in fewer radicals being formed for the degradation process. Conversely, in basic solutions, there are more OH^- ions. These OH^- ions interact with holes to form hydroxyl radicals, which can decompose MB. Thus, the degradation percentage of methylene blue increases at basic pH levels, indicating that basic pH is the optimal condition for its degradation.

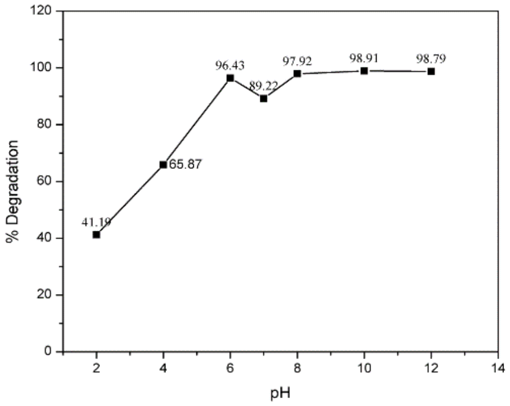


Figure 9. Determination of optimal pH

CONCLUSION

Mordenite zeolite can be utilized as a photocatalyst in the degradation of methylene blue dye. Photocatalytic degradation harnesses energy from UV light to generate hydroxyl free radicals (•OH). These hydroxyl radicals then break down methylene blue into CO_2 and H_2O. The study on the application of methylene blue photodegradation using Fe-TiO_2/MOR zeolite as a photocatalyst demonstrated higher degradation efficiency compared to using not activated, non-immobilized, and undoped mordenite zeolite. With an optimal mass of 0.03 grams, a contact time of 90 minutes, and a pH of 10, the percentage of degraded methylene blue reached 98.91%.

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