ENVIRONMENTALLY FRIENDLY BIFUNCTIONAL MATERIALS BASED ON ZnO/NATURAL ZEOLITE FOR METHYLENE BLUE DYE REMOVAL IN WATER

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Abstract

The treatment of dye wastewater, particularly from the batik industry, poses significant environmental challenges. This study explores the potential of ZnO-coated clinoptilolite natural zeolite as a dual-functional material for efficient and eco-friendly wastewater treatment through adsorption and photocatalysis. This study employed various solvents, i.e., aquadest and ethylene glycol and different treatments of heating and sintering to ensure the ZnO-coated natural zeolite. The ZnO/zeolite composite achieved a dye degradation efficiency of up to 98.68% under UV irradiation within 90 minutes. Characterization through SEM, FTIR, and XRD analyses confirmed the successful synthesis and structural integrity of the ZnO/zeolite composite. We also conducted an analysis of operational costs and energy consumption associated with the use of these bifunctional materials. The results indicate that the potential for utilizing these materials as a treatment method is promising, given their ease of use and low energy consumption, and warrants further investigation.

Keywords: *methylene blue, natural zeolite, photocatalysts, ZnO*

Introduction

Dye waste in Indonesia, originating from various industrial sectors, was particularly concerning in the case of the batik industry. According to the Central Statistics Agency in 2022, only about 77% of liquid batik waste is safely processed, leaving a significant portion unaddressed (Kozak *et al.*, 2021). The conventional waste treatment process had a negative impact on the quality of the environment which becomes ecosystem pollution, water and soil pollution and causes health impacts such as skin irritation, respiratory disorders, to the risk of poisoning and chronic diseases in the surrounding community (Masuku *et al.*, 2024). Meanwhile, although the adsorption method was often used to treat liquid waste, it showed limitations. Although the adsorption method was widely applied in liquid waste treatment, there were limitations in the absorption of waste to the adsorbent surface which required regeneration when it reaches its maximum capacity.

The adsorption method was widely used in liquid waste treatment has some significant drawbacks. One of the drawbacks was the limited capacity of the adsorbent, where the adsorbent reaches a saturation point after a certain number of waste molecules were absorbed on its surface. Regeneration and reuse of adsorbents was limited to three cycles, so the adsorbent must be regenerated or replaced, which adds to operational costs and potentially generates additional waste. In addition, adsorption only binds to pollutant molecules without destroying them, so the potential for contamination remains. Other methods such as aeration helps to oxidize organic substances and reduce odors, but are less effective at removing heavy metals and harmful chemicals (Boon *et al.*, 2018). Biofilters were also used as a method of aerobic wastewater treatment by utilizing aerobic microorganisms (Gayatri *et al.*, 2021). Meanwhile, membrane-based technology effectively separates pollutant molecules, but it tends to be expensive and often fouling, making maintenance complex and operational costs high (Wang *et al.*, 2024).

To overcome these limitations, the addition of degradation methods such as photocatalysis offers a more effective solution. Photocatalysis, such as the use of ZnO as a photocatalyst, not only absorbs but also destroys pollutant molecules, converting them into simpler and safer compounds, thereby reducing the risk of further contamination and the need for adsorbent regeneration (Utami *et al.*, 2023). Handling environmentally friendly catalysts was crucial for reducing environmental impacts while improving industrial efficiency. ZnO-coated zeolite acted as both an effective adsorbent for pollutants and a photocatalytic catalyst. Its large pore structure allowed ion exchange to capture harmful pollutants in water and air without toxic byproducts. Activated by UV light, this catalyst was energy-efficient. Photocatalysis technology, using ZnO, offers an eco-friendly alternative for interacting with organic compounds like dyes through chemical adsorption. (Gago and Ngapa, 2021).

Exposure to UV light, ZnO acts as a photocatalyst that produces hydroxyl radicals, resulting in the degradation of dye molecules into simpler and harmless forms. Various aspects that affect photocatalysis performance include the band *gap* and the recombination of electron-hole pairs in the photocatalyst. ZnO as a photocatalysis in degrading dyes by 98.68% with a time of 90 minutes was almost comparable to the research which explained that Zn-doped Zno is in optimal conditions of 99% to degrade dyes. The adsorption process serves a complementary purpose in enhancing photocatalytic performance. By initially adsorbing dye molecules onto the surface of the photocatalyst, the concentration of pollutants near active photocatalytic sites increases, facilitating efficient photodegradation. Furthermore, adsorption can pre-concentrate pollutants and reduce the impact of mass transfer limitations. This shows that the ZnO coating is efficient. These two aspects were influenced by the active surface area and pore size of semiconductor materials or photocatalysts (Mumtazah *et al.*, 2024). Zeolite had a large pore structure and ion exchange capability, effective in absorbing hazardous substances from wastewater, while ZnO as a photocatalyst were able to decompose complex organic compounds such as dyes into simpler and environmentally friendly compounds when exposed to UV light. This combination provided an efficient multifunctional solution to overcome the challenges of batik waste processing (Sodha *et al.*, 2022).

Increased purity levels could be achieved by the addition of ZnO (zinc oxide) as an effective strategy to optimize zeolite in several applications. The integration of ZnO into the structure of zeolite creates additional adsorption sites. It was particularly useful in adsorption applications, such as water or air purification of certain contaminants (Wang *et al.*, 2024). Modification of zeolite to overcome the problem of liquid waste from the batik industry. Solvents affected the dispersion of photocatalyst materials such as ZnO in solution. Characterization of natural zeolite materials uses UV-Vis spectrophotometry to measure photocatalytic efficiency in dye degradation (Utami *et al.*, 2023). FTIR to identify functional groups and chemical interactions in natural ZnO/zeolite bifunctional materials (Utami *et al.*, 2023). SEM-EDX to analyze the surface morphology and elemental composition, providing a visual and quantitative picture of the distribution of ZnO in zeolites (Gago and Ngapa, 2021).

In addition, the energy consumption ensured the energy that used in the synthesis or characterization process. Thus, the costs incurred for energy remain under control, making this method more cost-effective than other methods that are more energy-intensive or use expensive solvents (Melinda *et al.*, 2024). This efficiency in energy and solvents ensures that waste treatment technology is not only environmentally friendly but also economically beneficial (Agustina *et al.*, 2024a). Thus, the coating of ZnO on zeolite significantly improves the performance of adsorbents in handling pollutants, because in addition to zeolite ability to capture pollutants, ZnO can decompose harmful compounds through an efficient photocatalytic process. The technology is also energy-efficient because ZnO can be activated by UV light reducing external energy requirements (Norek, 2019). The ZnO coating process on the surface of the zeolite allows for more even distribution of the catalyst, increasing the active area for reaction and making the waste treatment more effective in the long run, making it a superior solution for environmentally friendly waste treatment.

Research Methods

Materials

The materials used are Natural Commercial Zeolite, ZnO with 100 nm size and 26 nm crystallite Merck, Aquadest, and Ethylene Glycol Merck (99%), and Methylene blue Merck 40 ppm as artificial dye waste. The tools used include Photodegradation Reactor, single beam *UV-Vis Spectrophotometer* UV1100N/752N, SEM test equipment HITACHI FLEXSEM 100.

Preparation of ZnO/Zeolite coating

The preparation of ZnO photocatalyst with aquadest solvent was carried out by taking 7 grams of ZnO solids dissolved in 100 mL of aquadest and adding 25 grams of natural zeolite to a 100 mL glass beaker. The next process was stirred with a closed magnetic stirrer at a temperature of 30°C for 60 minutes. After that, the oven was heated at 110°C for 60 minutes. Weighing was carried out until it produced a constant (weight) result. The same step was carried out with different solvents of ethylene glycol with a composition of 50 mL of ethylene glycol, natural zeolite 12.5 g and ZnO 3.5 gr. ZnO/Zeolite solids were then calcined in a furnace at a temperature of 450°C for 120 minutes (Mumtazah *et al.*, 2024)

Material characterization

Material characterization was carried out using various techniques to ensure the success of the ZnO/zeolite composite synthesis. The following are the types of characterization SEM-EDX (HITACHI FLEXSEM 100) used to analyze the surface morphology and distribution of ZnO particles on the zeolite. SEM results provide a visual depiction of the material distribution on a micrometer scale, as well as evaluate the homogeneity of the ZnO coating on the zeolite surface. XRD was used to determine the crystal structure and phase of the material in the ZnO/zeolite composite. The diffraction pattern was analyzed to identify the presence of ZnO in the wurtzite phase and the crystallinity of the zeolite after ZnO coating. XRD results help confirm changes in material structure due to thermal treatment during the synthesis process. UV-Vis Spectrophotometer (UV1100N/752N) used to measure the efficiency of photodegradation through changes in the absorbance value of the methyl blue solution at a maximum wavelength of 660 nm. This analysis helps determine the percentage of dye degradation after UV irradiation. FTIR used to identify relevant functional groups, such as the interaction between ZnO and zeolite, and to verify the presence of ZnO compounds in the zeolite structure.

Photodegradation under ultraviolet radiation against methylene blue

Methylene Blue as a working standard solution (40 ppm) was taken as much as 25 mL and natural ZnO/Zeolite as much as 0.15 grams was put in the glass beaker. The solution is put in a closed reactor in which there is a Ginga UV Lamp and processed with *a magnetic stirrer* for 90 minutes. The next step is a centrifugation process before a UV-Vis test is carried out (Alswata *et al.*, 2017)

The analysis carried out in this study is quantitative, namely through UV-Vis spectrophotometry testing with a wavelength range of 660 nm to identify the peak and intensity of UV absorption. UV-Vis helps determine the ability of materials to capture UV energy to produce efficient photodegradation. The process uses three UV lamps with a wavelength of 365 nm**,** which are selected to maximize the photocatalytic effect (Sanad *et al.*, 2021). The best results of dyestuff waste degradation were evaluated based on time efficiency, calcination and non-calcination methods, and ZnO coating on zeolites, which affected the degradation percentage and absorbance value (Acedo-Mendoza *et al.*, 2020).

Determining differences in pairs of elements uses the Tukey test to identify significant differences between certain pairs of elements or compounds after carrying out ANOVA analysis. This method is applied at the statistical analysis stage to determine groups that are truly significantly different, thereby providing a deeper understanding of the interactions between elements. This test was chosen for its ability to accurately compare means between groups, ensuring the validity of the results. Carried out after experimental data has been collected and analyzed, these tests reveal, for example, that element pairs such as O-Zn and Si-Al show significant differences, while Al-Zn does not. With these results, Tukey's test helps explain relevant statistical relationships in research.

The Methylene Blue Degradation % value can be calculated using the following Equation 1. C_0 is the initial concentration, and C_t is the final concentration after light irradiation (M *et al.*, 2021). The description of the sample to be tested is explained in Table 1. Sample Description to be used as a symbol for each sample.

$$\% \text{ Degradation} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\% \qquad (1)$$

Table 1. Sample description

Code	Description
ZZ-O	ZnO/Zeolite with H_2O as a solvent
ZZ-O3	ZnO/Zeolite with H_2O as solvent after the 3^{th} reuse
ZZ-E	ZnO/Zeolite with Ethylene glycol as solvent
ZZ-E3	ZnO/Zeolite with Ethylene glycol as solvent after the 3^{th} reuse

Code	Coating Treatment
S	Sintered at 450 °C for 2 h
H	Heated at 110 °C for 1 h

Results and Discussion

Characterization of chemical and physical properties of ZnO/natural Zeolite

The macroscopic observations of zinc oxide (ZnO) and natural zeolite in this research for the treatment of dye waste are depicted in Figure 1. ZnO was supplied by Merck and appears to be a fine and homogeneous white powder, while natural zeolite exhibits coarse and granular with non-uniform sizes. The well-coated natural zeolite by ZnO was shown in Figure 1c, while Figure 1d showed the ZnO/natural zeolite after applying for dye waste treatment. The recycled material undergoes a distinct color transformation, appearing blue, indicative of changes in its composition or surface chemistry due to repeated usage. This composite synergistically combines the properties of ZnO and zeolite to improve pollutant removal and decomposition performance.

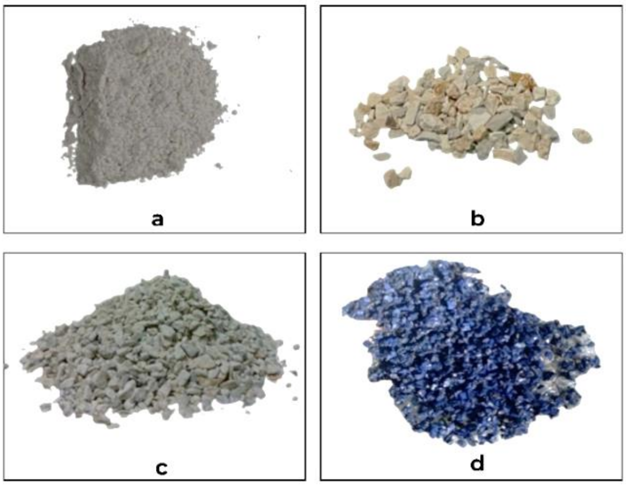

Figure 1. (a) ZnO *merck,* (b) Natural Zeolite, (c) ZnO/Zeolite O, (d) ZnO/Zeolite O3

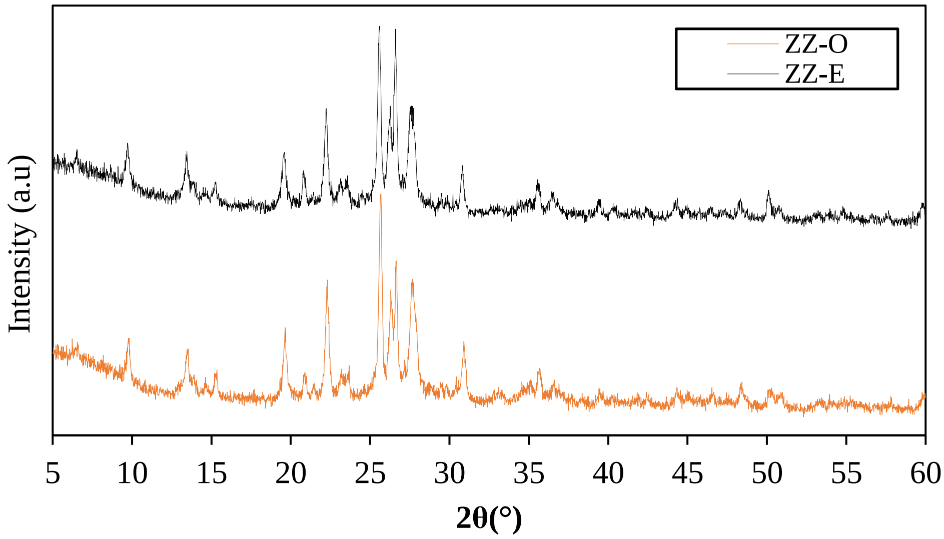

Figure 2. X-Ray Diffraction (XRD) patterns of ZZ-O (ZnO/Zeolite O) and ZZ-E (ZnO/Zeolite E)

Further characterization was performed using X-ray diffraction (XRD) to ensure the crystal structure and phase of ZnO/natural zeolite, which was prepared from different solvents and methods of attaching ZnO in the natural zeolite. The results showed that the calcination process can be seen in Figure 2. XRD data showed the presence of peaks at angles 2θ = 19.68, 22.30, 25.66, 26.59, 27.81, 30.92, and 35.55°. These peaks indicate the presence of a crystalline phase of ZnO, with some points of similarity at the 2θ value corresponding to the JCPDS data for ZnO (JCPDS 36-1451) was hexagonal-wurtzite (Liu *et al.*, 2019), specifically at the 2θ value range between 30° and 40° (Gayatri *et al.*, 2022). The XRD pattern revealed that the different solvents showed the same peak and phase of ZnO/Zeolite.

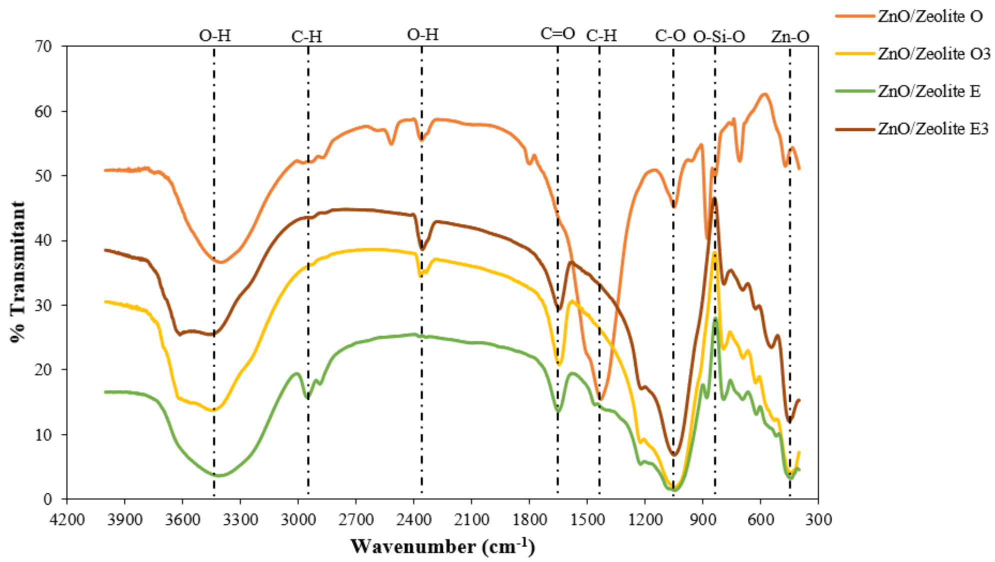

Figure 3. Fourier Transform Infrared (FTIR) Spectra of ZnO/Zeolite O, ZnO/Zeolite O3, ZnO/Zeolite E, ZnO/Zeolite E3

The functional group was identified using FTIR which showed the presence of ZnO (Zn-O bonds) at a wave number of 405.05 cm^{-1} in every different parameter condition as referred elsewhere (Yang *et al.*, 2021). Strong and dilated absorption at wave numbers of 3352.28 cm^{-1} was identified as O-H strain vibration of H_2O molecules trapped in the zeolite matrix due to their hygroscopic properties (Gayatri *et al.*, 2022). In addition, absorption at wave number 1687.71 cm^{-1} indicates C=O flex vibration of the H_2O molecule. Peak characteristic absorption of zeolite was seen at wave number of 877.61 cm^{-1}, which is identified as the O-Si-O strain vibration of zeolite minerals. The spectrum of Si-O peak shrinkage occurred in the interval of 501.49 cm^{-1} to 476.41 cm^{-1} which showed that ZnO was successfully carried out in Zeolite indicating the presence of a Zn-O-Si stretch vibration absorption spectrum in accordance with research (Agustina *et al.*, 2024b).

The use of distilled water and ethylene glycol solvents in the synthesis of ZnO/zeolite shows different effects on the material characteristics, especially when analyzed using FTIR. Aquadest as a polar solvent, allows a fairly good distribution of the ZnO precursor but tends to leave the dominant O-H group (3352 cm^{-1}) due to the hygroscopic nature of the zeolite. Meanwhile, ethylene glycol, with a higher viscosity, produces a more stable ZnO and zeolite interaction, as seen from the sharper intensity of the Zn-O peak (405 cm^{-1}). The process with 3 cycles increases the efficiency of ZnO attachment to zeolite compared to no cycle, resulting in clearer Zn-O vibration peaks and more even material distribution. Overall, the combination of ethylene glycol with 3x cycles gives the best results, with more controlled and stable material characteristics.

The SEM micrographs provide detailed morphology of the sample, allowing for more in-depth observation of the structure, shape, and size of the particles. ZnO/Zeolite E is shown in Figure 4(a). SEM analysis shows its main morphology consists of irregular layered structures of various sizes, resembling rough rock slabs. This rough surface reflects the brittle and amorphous nature of zeolite and shows a lack of crystallography regularity in the material. Zeolite appears with irregular particle shapes and varying sizes. This zeolite structure retains the pore characteristics visible from the rough surface and small cavities (de Dios *et al.*, 2023). ZnO particles appear as lighter, finer particles that adhere to the surface of zeolites. ZnO is seen adhering to the surface of zeolite, suggesting an interaction between ZnO particles and zeolite.

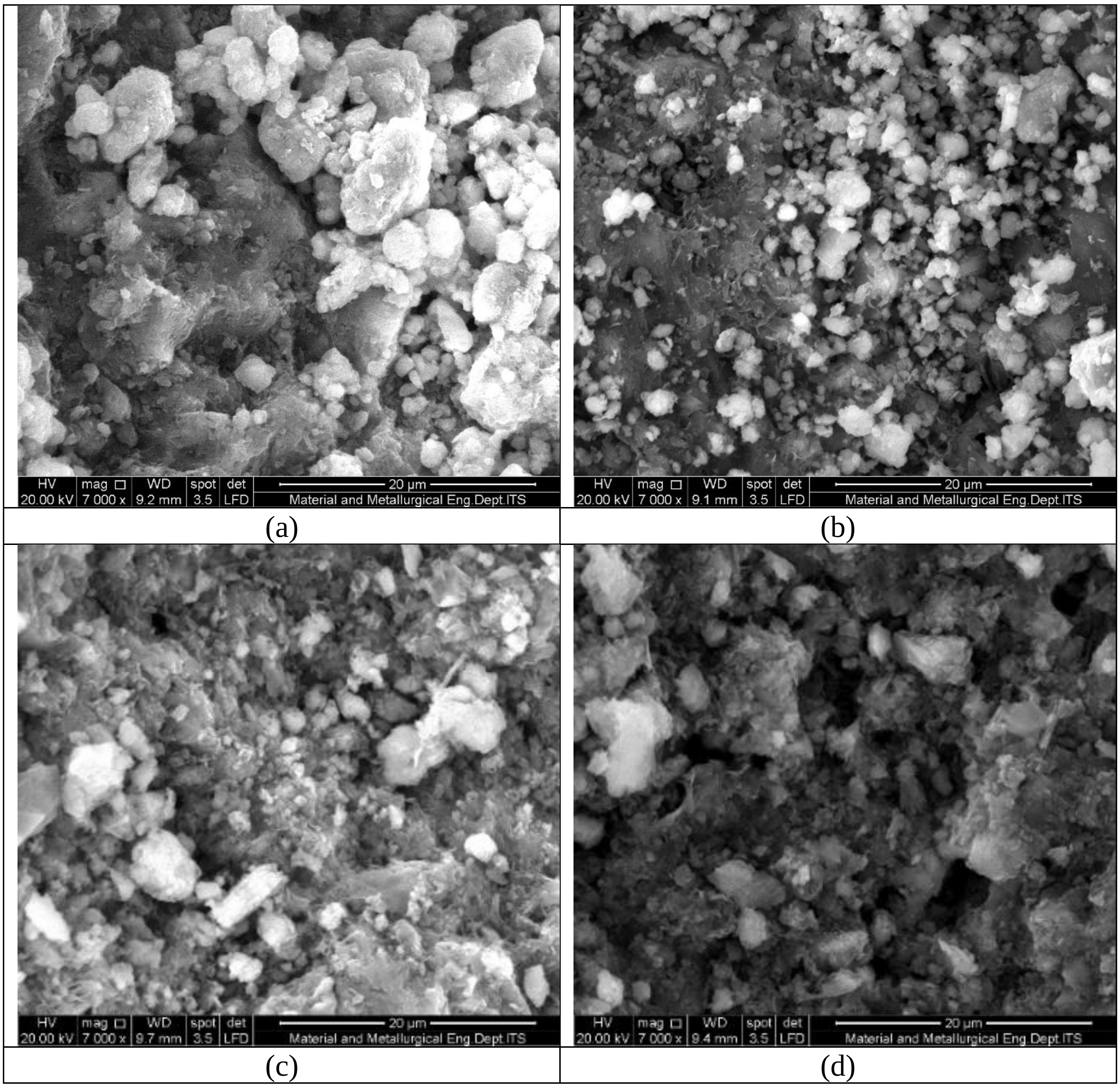

Figure 4. SEM-EDX results of (a) Zeolite ZnO-Ethylene Glycol, (b) Zeolite ZnO-H_2O, (c) H_2O Recycle 3×, (d) Ethylene Glycol Recycle 3×

The resulting Figure 4. (b) shows the morphology of the ZnO/Zeolite O material particles. The surface of the zeolite particles appears rough, with a structure that resembles a porous layer. There were brighter particles, which are ZnO particles. The ZnO particles formed generally appear in better distribution on the zeolite surface when employing aquadest as solvent, suggesting that the ZnO particles are located on the outer surface of the zeolite rather than within the pores of the material (Elfeky *et al.*, 2020).

From Figure 4. (c), it can be seen that the morphology of the ZnO/Zeolite O3 material has changed. The surface reveals particles adhered to the zeolite that are smaller compared to the previous observation. This suggests that during the recycling process, ZnO particles on the surface partially dissolved in the dye waste, accompanied by the disintegration of previous agglomerates due to stirring effects, leading to a reduction in particle size compared to the initial state (Foroughi *et al.*, 2024).

Figure 4. (d) shows the material morphology of ZnO/Zeolite E3. The size of zeolite particles appears smaller, while ZnO particles tend to form larger agglomerates. This is most likely the result of the recycling process, which causes the redistribution of ZnO to become less efficient. ZnO particle aggregation can result in a decrease in surface area, which directly affects the performance of materials in applications such as materials or adsorbents. If the recycling process is not optimal, the distribution of ZnO can be lower, and some of the ZnO may be lost in the washing process (Agustina *et al.*, 2024a).

In addition, to ensure the atom distribution of ZnO on natural zeolite, SEM-EDX characterization was employed. The result has been revealed in Table 2. It showed the concentration of different atoms (Zn, O, Al, and Si) distribution of 4 samples. In these samples, the concentration of oxygen (O) is highest across all groups. The materials prepared using aquadest as the solvent exhibited a higher percentage of Zn and lower levels of Al and Si. This indicates that the ZnO coating on natural zeolite was more substantial compared to the samples prepared with ethylene glycol (EG). This result is associated with the good dispersion of ZnO in water, enabling a greater amount of ZnO to adhere to the natural zeolite.

Table 2. Concentration of different atoms (Zn, O, Al, and Si) distribution of samples

Sample	**Atom Concentration (%)**			
	Zn	**O**	**Al**	**Si**
ZnO/Zeolite O	10.95	30.48	6.58	30.26
ZnO/Zeolite O3	4.42	35.67	7.94	40.34
ZnO/Zeolite E	4.23	32.32	8.03	39.59
ZnO/Zeolite E3	1.07	36.80	8.69	41.56

The Tukey test results show significant differences between some of the element or compound pairs tested. Pairs such as O-Zn, Al-O, Si-Zn, and Si-Al showed significant differences with a value of 1, which means that the interactions between the elements are statistically different (Table 3). In contrast, the Al-Zn and Si-O pairs showed no significant difference (value 0), indicating that the difference in values found between the two was not strong enough to be considered statistically significant. Thus, this Tukey test helped to identify truly distinct relationships between certain groups in this experiment (Partoazar *et al.*, 2019).

Table 3. Tukey test of concentration of different atoms (Zn, O, Al, and Si).

Element or Compound Pair	Q Value	Prob	Alpha	Sig
O Zn	15.68	4.84E-7	0.05	1
Al Zn	1.44	0.74	0.05	0
Al O	14.23	1.72E-6	0.05	1
Si Zn	17.93	1.19E-6	0.05	1
Si O	2.25	0.42	0.05	0
Si Al	16.49	2.23E-7	0.05	1

Figure 5 shows the box plot of the presence of Zn, O, Al, and Si on the surface. The peak intensity of Si appears to be the most dominant compared to the rest elements, which indicates a relatively higher concentration of silica (Greczynski and Hultman, 2020). Compare the elemental composition of Zn, O, Al, and Si in natural ZnO/zeolite materials before and after dye waste treatment. This image provides visual information regarding variations in the concentration of these elements, which can provide insight into changes in material composition after the activation process. The appearance of this box plot aims to illustrate significant differences in element content and to assess the uniformity of element distribution in the materials used for waste processing.

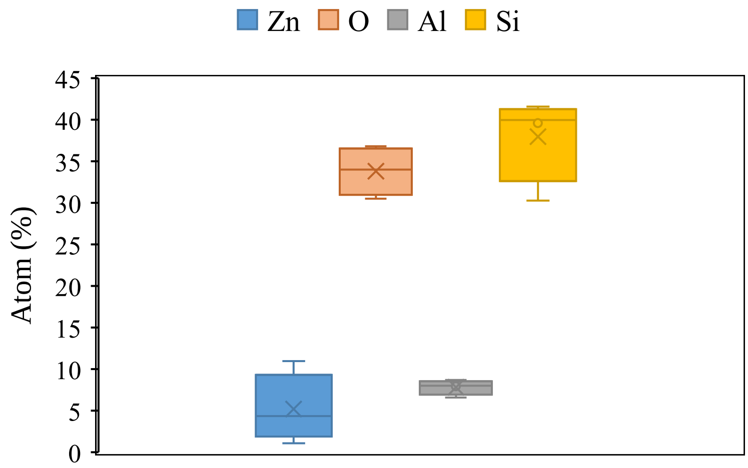

Figure 5. Box plot of the presence of Zn, O, Al and Si on ZnO/Natural Zeolite materials before and after dye waste treatment.

The Zn atom demonstrates a relatively low percentage. However, it shows a significant variation when compared to ZnO/natural zeolite prepared using different solvents and methods. (Krishna and Philip, 2022). Overall, all four samples showed a uniform elemental composition with a predominance of silica and oxygen, indicating that the samples may have originated from silica or zeolite-based materials (Nzereogu *et al.*, 2023).

The morphological changes after activation and the successful formation of ZnO/Zeolite materials indicate that the process of material synthesis and modification has been successfully carried out [15]. The increased regularity and fineness of the post-activation zeolite structure and the even distribution of ZnO particles demonstrate the potential of this material in applications such as heterogeneous materials or adsorbent materials with enhanced properties.

Performance of ZnO/Natural Zeolite for dye waste treatment

The performance of various preparation methods for ZnO/natural zeolite production is presented in Figure 6. The results indicate that the modification of ZnO on the natural zeolite surface enhanced methylene blue removal efficiency up to 98%. This highlights the role of ZnO as a degrader of organic pollutants, complementing the adsorptive properties of commercially utilized zeolite. Samples prepared using ethylene glycol (EG) as the solvent demonstrated slightly higher removal efficiency compared to those prepared with water. This aligns with the SEM results, which revealed that ZnO distribution was less concentrated on the surface when EG was used. Consequently, organic pollutants were more favorably adsorbed into the zeolite through adsorption processes for dye removal. Samples prepared through heating and sintering showed no significant differences in performance. However, these methods warrant consideration from an economic and energy consumption perspective for material preparation and performance.

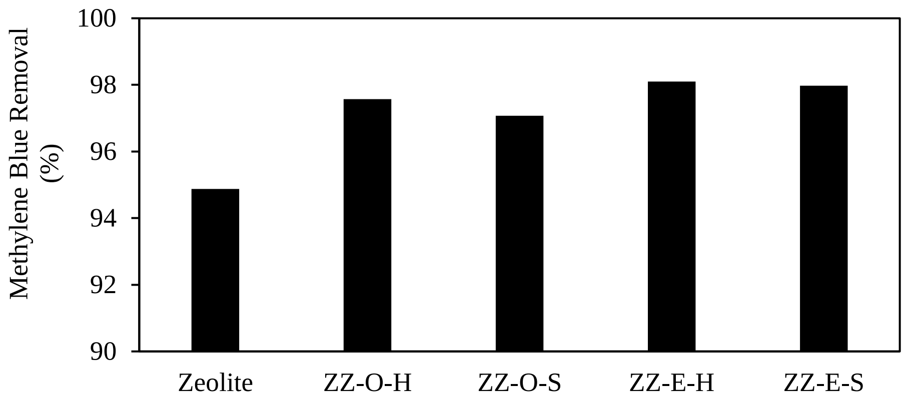

Figure 6. Percentage methylene blue removal using zeolite and modified zeolite with ZnO

Figure 7 visualizes the relationship between the time and percentage of degradation of methylene blue using an H_2O solvent. The kinetics performed on the graph data helps to show the pattern of increasing degradation effectiveness over time, reaching an optimum at 90 minutes and decreasing slightly thereafter. Showed the effect of time on the percentage of methylene blue removal. Over a time period from 10 to 120 minutes, the effectiveness of ZnO degradation against methylene blue increased with increasing irradiation time. Photocatalysis is an oxidation-reduction process triggered by light energy to degrade organic or inorganic compounds.

The mechanism in materials such as ZnO/natural zeolite with aquadest and ethylene glycol solvents consists of several main stages, including photocatalyst excitation, which occurs when ZnO is exposed to UV light or light with energy above its band gap (~3.37 eV), electrons (e^-) from the valence band are excited to the conduction band, producing holes (h^+) in the valence band. Holes (h^+) act as strong oxidants, while electrons (e^-) can reduce available species, such as molecular oxygen. In interaction with water and oxygen molecules, holes (h^+) react with water molecules or hydroxide ions (OH^-) to produce hydroxyl radicals (OH), while electrons (e^-) reduce oxygen (O_2) to superoxide anions (O_2^-). Both species are highly reactive oxidizing agents. Degradation of dye molecules, methylene blue molecules adsorbed on the ZnO/zeolite surface interact with free radicals (OH and O_2^-), breaking bonds in their molecular structure, resulting in simpler degradation products such as CO_2, H_2O, and inorganic ions.

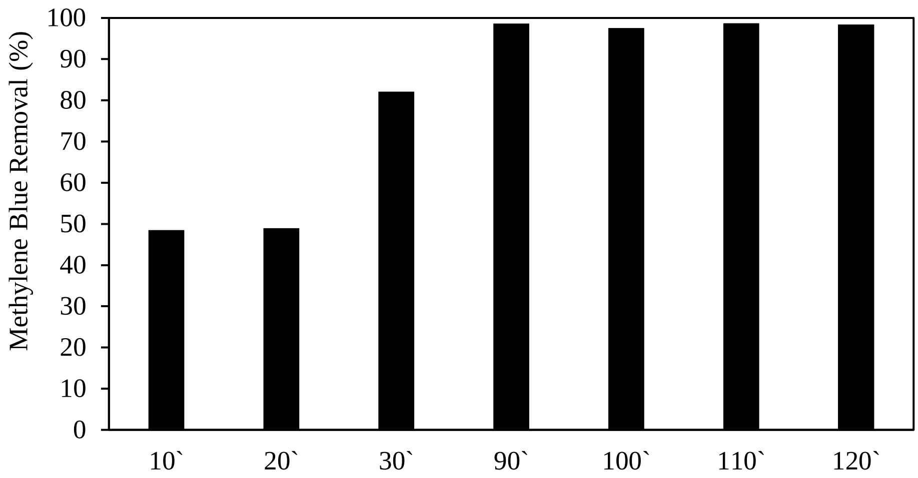

Figure 7. The effect of irradiation time on the methylene blue removal

The optimum irradiation occurred at a contact time of 90 minutes and obtained a degradation % of 98.68%. However, there was a decrease in degradation of 97.58% in the irradiation time of contact, reaching 90 minutes. This slight decrease might be caused by several factors, such as photocatalyst activity may decrease due to changes in the photocatalyst structure and a decrease in the number of hydroxyl radicals available due to a decrease in the concentration of methylene blue in solution (Nguyen *et al.,* 2022). Photocatalytic reactions occur through the interaction between ZnO and light (hν), which produce free radicals that play a role in the degradation of these dyes. The reactions are explained by Equation (2) to (9).

$$ZnO + h\nu \rightarrow ZnO\ (e^-_{cb} + h^+_{vb}) \quad (2)$$
$$O_{2ads} + e^- \rightarrow O^{\cdot -}_{2ads} \quad (3)$$
$$O^{\cdot -}_{2ads} + h^+ \rightarrow HO^{\cdot}_{2ads} \quad (4)$$
$$2HO^{\cdot}_{2ads} \rightarrow H_2O_{2ads} + O_2 \quad (5)$$
$$R_{ads} + h^+ \rightarrow R^{\cdot +}_{ads} \quad (6)$$
$$HO^-_{ads} + h^+ \rightarrow HO^{\cdot +}_{ads} \quad (7)$$
$$H_2O_{ads} + h^+ \rightarrow HO^{\cdot}_{ads} + H^+ \quad (8)$$
$$^{\cdot}OH + \text{Methylene Blue} \rightarrow \text{Degradation of dyes} \quad (9)$$

(Al-mamun *et al.*, 2023)

Estimation cost of ZnO/Natural Zeolite for methylene blue removal

Cost analysis was an important step in decision-making related to the selection of waste treatment methods, especially in using zeolite and ZnO (Table 4) (Satyam and Patra, 2024). The costs associated with adsorbents play a key role in the adsorption process, where many dye removal techniques generally use activated carbon at a fairly high price on the market. The use of activated carbon often becomes impractical from an economic point of view, resulting in the need for cheaper alternative materials, such as zeolite and ZnO (Osman *et al.*, 2023). This material has a comparable absorption capacity and is locally available. The costs associated with manufacturing zeolite and ZnO also need to be considered, including production, maintenance, raw materials, transportation, labor, and distribution costs (Sharma *et al.*, 2023). Taking into account all these cost aspects, the option of using zeolite and ZnO as adsorbents can be an efficient and environmentally friendly solution in liquid waste treatment.

The supporting tools and power specifications needed in the photodegradation process include UV Lamps and Hotplates with the following details of the needs (USD to IDR October 2024 exchange rate ➔ 1 USD = Rp 15,542.85). The cost of electricity per kWh in Indonesia is Rp 1,444.70/0.09 USD, with each operation requiring 19 Wh or 0.019 kWh, equivalent to Rp 27.44/0.0018 USD. For two daily operations, the total electricity cost reaches Rp 54.8986/0.0035 USD, so in one month, the total electricity cost becomes Rp 1,646.95/0.11 USD. The ingredients needed per day include 25 grams of zeolite for Rp 600/0.03 USD, 7 grams of ZnO for Rp 1,225/0.07 USD, and 100 mL aquadest for Rp 120, with a total cost of materials per operation of Rp 2,545/0.15 USD. In two daily operations, the total cost of the material is Rp 5,090/0.33 USD.

Table 4. Cost estimation of ZnO/Natural Zeolite for methylene blue removal

Material	Sum	Kwh	Price (IDR)	Price (USD)
Zeolite	0.75 kg		18,000	1.152
ZnO	0.21 kg		36,750	2.352
Aquadest	3 lt		3,600	0.2304
UV lamp		0.014	606.774	0.0388
Hotplate		0.005	216.705	0.0138
Total			59,173.479	3.787

The total manufacturing and operational costs for one operation in 30 days are Rp 59,173.479/3,78 USD. With these costs, the efficiency of using this tool can be assessed well if the results of the waste treatment produced are able to provide significant environmental benefits and are proportional to the operational costs incurred (Praveen *et al.*, 2021). In addition, this tool is able to effectively reduce waste and have a positive impact on the environment, as well as save other costs arising from inefficient waste treatment methods, so the use of this tool at this price can be considered efficient and profitable.

Conclusion

This study demonstrates the high potential of ZnO-coated natural zeolite as an efficient and eco-friendly solution for dye wastewater treatment. The ZnO/zeolite composite demonstrated an impressive dye degradation efficiency of up to 98.68%, with optimal performance achieved within 90 minutes of UV irradiation. Integrating ZnO into zeolite material plays an important role in increasing the effectiveness of photodegradation against organic pollutants. In this process, ZnO, as a photocatalyst, utilizes light energy (hν) to produce free radicals such as hydroxyl (OH), which are highly reactive. These radicals function to decompose complex organic compounds into simpler and safer products, such as water and carbon dioxide. Characterization using SEM, FTIR, and XRD confirmed the successful synthesis and compatibility of the ZnO/zeolite composite. However, the study was conducted under laboratory conditions, necessitating industrial-scale testing for practicality. The durability of material performance after multiple regenerations and the energy demands of UV photocatalysis also require further evaluation. Future research could focus on utilizing solar panels as an energy source, testing the material on other waste types, and exploring modifications to improve photocatalyst stability and efficiency.

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