

Synthesis and Characterization of ZnO-Zeolite Photocatalyst Nanocomposite for Heavy Metals Degradation

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ABSTRACT

Heavy metals are the major contributors to pollution due to their enduring presence and poisonous characteristics. Wastewater that contains heavy metals is classified as harmful and has the potential to contaminate the environment. Large-scale disposal of heavy metal discharged into the environment causes significant environmental harm. Commonly seen heavy metals in water deposits include non-biodegradable metals such as cadmium (Cd), copper (Cu), lead (Pb) and iron (Fe). To mitigate the adverse effects of environmental contamination, it is necessary to handle wastewater containing heavy metals properly and optimally. Photocatalysis is a technology that involves the breakdown of pollutants with the use of light. This study aims to synthesize and characterize the nanocomposite of ZnO-Zeolite photocatalyst on the degradation of Cd, Cu, Fe, and Pb heavy metals. The ZnO-Zeolite nanocomposites were characterized by using SEM-EDX, XRD, and BET methods. The degradation caused by exposure to ultraviolet (UV) light occurs within the time of between 60 to 120 minutes, with a pH range of 6–8. The removal of heavy metals proceeds within a time frame of one hour and two hours, resulting in an optimal percentage removal of metals that approaches 100%. The composite showed a surface area of 19.436 m²/g, a pore size of 17.227 Å, and a total pore volume of 0.112 cm³/g. The heavy metals Cu, Fe, and Pb exhibited the highest rates of degradation, reaching their maximum percentages after 60 minutes when exposed to ultraviolet radiation under ideal conditions at varying pH levels (pH 6–8). More precisely, the degradation percentage of Cu metal was 95.4% at pH 7, Fe metal achieved 96.1% at pH 6, while Pb metal obtained 95.5% at pH 8. The Cd metal removal percentage was found to be 98.9% under the conditions of a pH of 8 and an irradiation time of 120 minutes, indicating high effectiveness.

Keywords: ZnO-zeolite nanocomposite, photocatalytic, heavy metals

INTRODUCTION

Liquid wastewater is frequently generated by mining, industry, laboratories, and

home activities. Furthermore, the sector not only manufactures things on a vast scale, but also generates substantial volumes of hazardous waste. Industrial waste that contains heavy

metals and nitrates is classified as harmful and has the potential to contaminate the environment. Heavy metals are the major contributors to pollution due to their enduring presence and poisonous characteristics. Large-scale disposal of heavy metal discharged into the environment causes significant environmental harm (Nurhidayati et al., 2021).

Heavy metals, with a specific gravity exceeding 5 g/cm^3 , are the primary pollutants in the environment (Irianti et al., 2017). According to Kamarati et al. (2018), Commonly seen heavy metals in water deposits include non-biodegradable metals such as cadmium (Cd), copper (Cu), lead (Pb) and iron (Fe). Each metal has a detrimental influence on the well-being of living species, particularly humans. Both Cu and Cd metals possess hazardous and bioaccumulate characteristics. The solubility of Cu metal is high, allowing it to be readily absorbed into particles dissolved in water. Consequently, this metal has the potential to cause harm to the liver and kidneys, as well as induce anemia (Jundana et al., 2016). Cadmium metal pollution leads to a multitude of lung problems, bone fractures, and bone demineralization (Said, 2010). Long-term exposure to Pb metal may result in epilepsy, brain damage, and adverse effects on the neurological system (Nuraini et al., 2015). Fe metal, in the meanwhile, will induce inflammation of the eyes and skin (Winarmadani, 2019).

In order to mitigate the adverse effects caused by the presence of heavy metals with high levels in wastewater, further treatment must be conducted before its release into the environment. Photodegradation using photocatalyst is a technique used to treat heavy metal effluent. Photocatalysts were used to decompose constituents with the assistance of ultraviolet radiation (Sharfan et al., 2018). Photocatalysts are substances that enhance the rate of a reaction by utilizing photochemical reactions to convert light energy, specifically ultraviolet light. This process generates hydroxyl radicals, which effectively remove pollutants and transform harmful compounds in water into harmless substances like CO_2 and H_2O (Hidayatuloh et al., 2012).

Zinc oxide (ZnO) and titanium oxide (TiO) are commonly employed as photocatalyst materials. Nevertheless, when comparing the two, zinc Oxide represents supremacy due to its abundant availability, cost-effectiveness, and ability to absorb a broader range of light, which leads to

higher catalytic activity (Saravanan et al., 2013). Zinc oxide exhibits excellent chemical stability and is considered non-toxic (Kusdianto et al. 2019). Aprilia et al. (2020) reports that, Zinc oxide provides excellent electron mobility and features exceptional transparency. Zinc oxide possesses a band gap that spans within the range of 3.2–3.37 eV. This characteristic enables ZnO to act as a photocatalyst specifically in the ultraviolet light spectrum, where the wavelength is fewer than 387 nanometers ($\lambda < 387$ nanometers).

However, in order to enhance the adsorption capability of the photocatalyst, it is necessary to combine the photocatalyst with an adsorbent (Wismayanti et al., 2015). The merger of the photocatalyst material and the adsorbent will result in the formation of the nanocomposite. Prior research indicates that nanocomposites are an efficient method for reducing heavy metal concentrations. Nanocomposites can simultaneously carry out two processes: adsorption and photocatalytic elimination of contaminants. Zeolite is a highly utilized material as an adsorbent. Zeolite is a porous material that is often used as catalysts, adsorbents, and ion exchangers (Rahman et al., 2018). Zeolite is a mineral composed of porous aluminosilicate with a distinct crystal structure. The size of aluminosilicate pores ranges from 0.3 to 2 nanometers. The zeolite framework consists of interlinked tetrahedral units, namely SiO_4^{4-} and AlO_4^{5-} , linked together by oxygen atoms (Fitria and Surya, 2018; Sholeha, 2017). The disparity in charge between SiO_4^{4-} and AlO_4^{5-} enables the creation of a negatively charged framework that may effectively attract and bind cations. Zeolite can serve as a catalyst, waste treatment agent, textile color reducer, ion exchanger, and adsorbent.

Zeolite's extensive surface area can enhance the photocatalytic action. Furthermore, the zeolite exhibits a more homogeneous and uncontaminated distribution of pore sizes, resulting in an enhanced efficiency of the adsorption process. The objective of this study is to ascertain the extent of Heavy metal reduction in wastewater by identifying the optimal conditions for photocatalytic degradation. The efficacy of the ZnO-zeolite nanocomposite will be evaluated using synthetic wastewater including Cd, Cu, Fe, and Pb. The performance of the ZnO-Zeolite photocatalyst nanocomposite also will be evaluated under varying irradiation conditions, including ultraviolet light exposure and darkness.

MATERIALS AND METHODS

Materials

The materials involved included synthetic zeolite and other components such as $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (zinc acetate), $\text{Cd}(\text{NO}_3)_2$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$, were acquired from Merck. ethanol with a purity level of 96%, NaOH 0.4 M, distilled water, and HCl 2 M.

Heavy metals artificial wastewater preparation

The synthetic wastewater contained the following heavy metals: $\text{Cd}(\text{NO}_3)_2$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{Pb}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Every substance was dissolved in 1L of distilled water in a glass beaker (Agustina et al., 2022). The concentration of every single heavy metal was 20 milligrams per liter.

The synthesis of ZnO-zeolite nanocomposites

A sol-gel approach was employed to synthesize a nanocomposite of ZnO-Zeolite. The sol-gel approach involves a two-step procedure. The first stage involves the hydrolysis of metal alkoxide, followed by the condensation phase (Mahreni, 2010). The effectiveness of this technology in generating uniform nano-sized particles and regulating mass distribution has been demonstrated (Sucahya et al., 2016). According to a prior examination conducted by Gayatri et al. (2021), The synthetic zeolite is first crushed up with a grinder and then sieved until it reaches 400 mesh size. After that, 0.4 M HCl solution was added, and the zeolite was stirred for an hour with a stirrer. After rinsing the mixture with distilled water at that point the pH approached neutral, and then it was heated for two hours at 110 °C.

The Pre cursor $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ and synthetic zeolite are mixed in a ratio of 2:1. Later on, the mixture was combined by dissolved it in 96% ethanol. The mixture was heated up in a reflux flask for 2 hours, afterward the addition of 2 M NaOH and subsequent stirring for 1 hour. After the stirring process was finished, the solution was allowed to rest for 12 hours. In the next step, it was filtered and went through heating at a temperature of 60°C. The produced composite was pulverized using a mortar for additional characterization.

Heavy metals and ZnO-zeolite nanocomposite characterization

The wastewater samples will undergo XRD (*X-ray diffraction*) analysis to determine the concentration of heavy metals. XRD was used to quantify the levels of heavy metals in synthetic waste both before and after the degrading process. XRD is utilized to determine the chemical composition of the heavy metals contained in sample. The ZnO-zeolite nanocomposite will be characterized using SEM-EDX, XRD and BET method. SEM-EDX (*Scanning electron microscope-energy dispersive X-ray*), SEM is the method used to observe the morphology, structure, and crystal size of the samples (Tuas and Masduqi, 2019), while EDX is applied to acquire information regarding the composition contained in the nanocomposite. X-ray diffraction (XRD) tests are conducted to figure out and examine the crystal structure of a solid material by analyzing the unique peak patterns related to each material. The BET test (*Brunauer-Emmet-Teller*) is carried out to ascertain the pore size, surface area, and total pore volume.

Photocatalytic degradation activity test

The performance of ZnO-Zeolite nanocomposites in decomposing heavy metals such as Cd, Cu, Fe, and Pb will be evaluated using synthetic wastewater containing a concentration of 20 mg/L. The degradation process was conducted using a reactor that was fitted with Ultraviolet light exposure and placed around 20 cm away from the sample. The ZnO-Zeolite nanocomposite was measured at a weight of 100 mg. It was then mixed with 250 ml of synthetic waste in an Erlenmeyer flask that was equipped with a magnetic stirrer. Photocatalytic experiments were conducted, varying the pH values range from 6 to 8, and samples are collected at 60 minutes and the irradiation time will be extended to 120 minutes at optimum pH.

RESULTS AND DISCUSSION

Results of ZnO-zeolite nanocomposites characterization

This research aimed to prove the successful embedding of zinc oxide and zeolite for ZnO-zeolite nanocomposites produced. The ZnO-zeolite nanocomposite was characterized using

SEM-EDX, BET, and XRD methods. The characterization test was conducted not only on the ZnO-zeolite nanocomposite but also on the zeolite both before and after activation.

The SEM-EDX test results of zeolite in its original form, zeolite after undergoing activation, and ZnO-zeolite nanocomposites are presented in Figure 1 (a), (b), (c), and (d). SEM characterization delivers micrographs that display the morphology of the sample, which enables the observation of the structure, shape, and size of the particles. The SEM analysis of the inactivated zeolite samples reveals that their shape predominantly consists of uneven rock plates of varying sizes. The surface of the samples appears to be rough, exhibiting a brittle and amorphous nature (Yesica, 2016). Furthermore, the zeolite particles show a lack of uniformity in their size. Subsequently, the scanning electron microscopy (SEM) findings following activation indicate noticeable disparities that demonstrate an enhanced regularity and smoothness in the structure and shape of the zeolite. Additionally, numerous pore cavities of varying dimensions are visible.

While the nanocomposite was characterized through the process of attaching ZnO to the surface of the zeolite. It is clear that there are two components with distinct forms and opposing appearances. Zeolite is dark-colored, while ZnO is shining white. The ZnO composition appears to be higher compared to that of zeolite, mostly because the former nanocomposite material contains a greater quantity of Zinc Acetate precursor compared to the activated synthetic zeolite. The EDX spectrum of the ZnO-zeolite nanocomposite in Figure 2 gives information regarding the main elements involved in the nanocomposite, specifically Zn, C, O, Al, Si, and Na. The mapping results of the ZnO-zeolite nanocomposite indicate the presence of Zn, O, C, Si, and Al with weight percentages of 26.45%, 29.73%, 24.17%, 5.71%, and 1.59% respectively. The presence of Zn in the nanocomposite confirms a successful formation of zinc acetate precursor into the nanocomposite synthesis process that uses the sol-gel method.

By the Table 1, it can be inferred that the activated synthetic zeolite exhibited an concentrations elevation of Al and Si components. On the

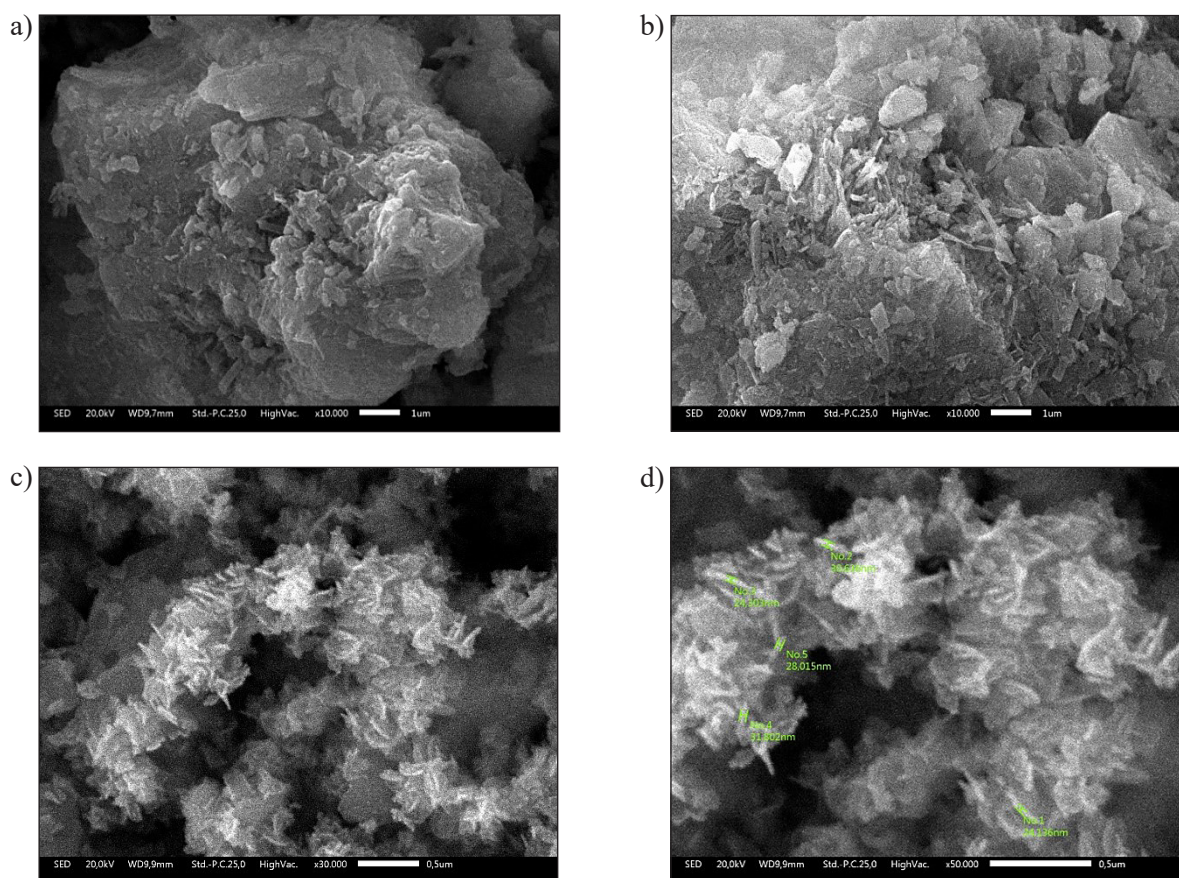


Figure 1. SEM result analysis of (a) zeolite before activation, (b) zeolite after activation, (c) ZnO-zeolite nanocomposite (magnifications $\times 30,000$), and (d) and ZnO-zeolite nanocomposite (magnifications $\times 50,000$)

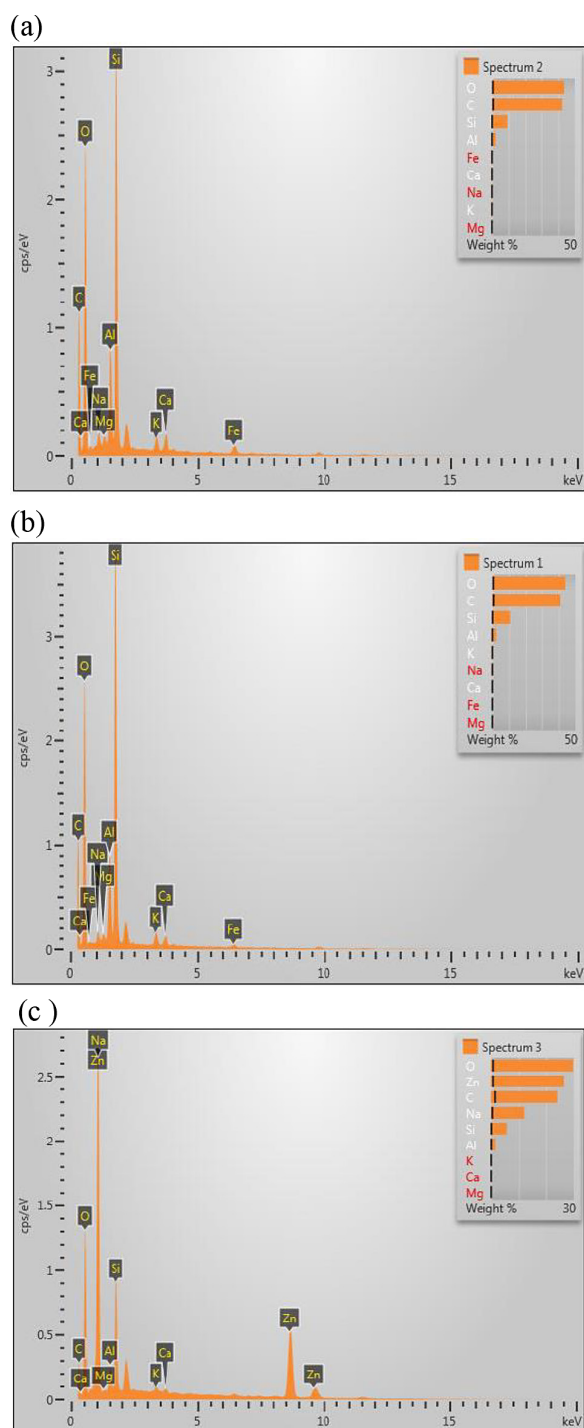


Figure 2. EDX result analysis of (a) zeolite before activation, (b) zeolite after activation, and (c) ZnO-zeolite nanocomposite (Ramadhini et al., 2023)

other hand, the Fe metal value decreased from 0.75% to 0.37% because of the immersion operation in HCl acid. Meanwhile, the reduction in Ca metal is likely a result of ion-induced pressure (Alfarisa et al., 2018).

Figure 3 shows the XRD results to analyze the structure and size of crystals in solid materials. XRD analysis is used to figure out the crystal

structure of a material by comparing the specific peaks observed in its diffraction pattern with data stored in a database ICSD pattern (Ref Journal of Applied Crystallography), reference code PDF 01-079-1910 for SiO_2 and ICSD collection code 034871. The XRD analysis of the zeolite before activation revealed peaks at 2 theta angles of 25.63° , 26.65° , 27.77° and 28.07° . After comparing it with the peak in the database, this peak signifies the existence of zeolite, specifically defined as Zeolite type A (Albite)(Na). The presence of peaks at 22-25 and 27-31 indicates that the zeolite is zeolite type A, which possesses a well-defined crystal structure (Gayatri et al., 2021). The zeolite after activation analysis gave the same results, zeolite classified as zeolite type A, known chemically as sodium aluminum silicate hydrate ($\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}\cdot 216\text{H}_2\text{O}$).

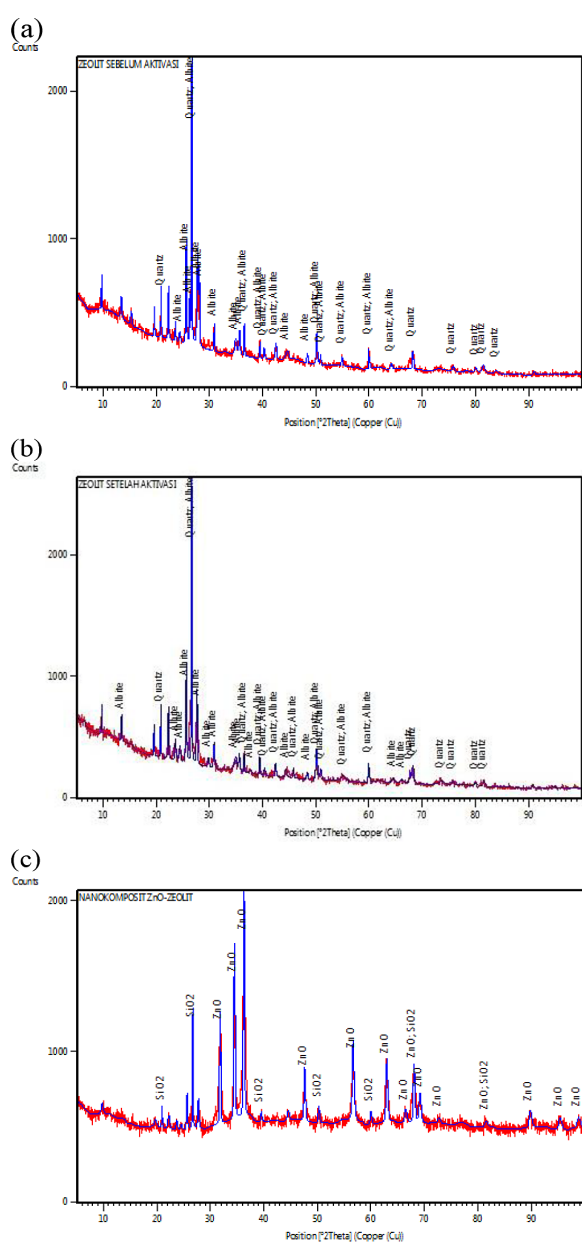
Regarding the XRD analysis, the results obtained for the ZnO-zeolite nanocomposites showed that the produced peaks matched exactly with the ZnO peak. These peaks were observed at angle values of 2θ 20.93° , 26.66° , 31.78° , 34.48° , 36.25° , 47.57° , and 68.02° . The observed peak indicates the existence of the components of the ZnO-zeolite nanocomposite, namely ZnO and SiO_2 representing zeolite. The BET test was used to determine the surface area, pore size, and total pore volume. Pore volume indicates the depth of pores in the sample. The fundamental principle of the BET method is the chemical process of gas absorption on the solid surface, which is examined under a constant temperature. The BET test results showed in Table 2 inferred that the ZnO-zeolite nanocomposites have a specific surface area of $19.436 \text{ m}^2/\text{g}$, a total pore volume of $0.112 \text{ cm}^3/\text{g}$, and a pore size of 17.227 \AA . Decreasing the size of the pores leads to a larger surface area for adsorption. The following larger surface area will result in a higher quantity of adsorbate molecules being absorbed. Consequently, the adsorption capacity will be elevated during the process of degradation of heavy metals.

Effect of ultraviolet irradiation in degradation of heavy metals

The photocatalytic degradation of heavy metals Cd, Cu, Fe, and Pb was carried out with the use of ZnO-Zeolite nanocomposites under ultraviolet light irradiation. The purpose of using nanocomposites is to investigate whether it can degrade heavy metal contaminants in wastewater.

Table 1. The result of EDX analysis

Component	Weight percentage (%)		
	Synthetic zeolite before activation	Synthetic zeolite after activation	ZnO-zeolite nanocomposite
C	42.34	41.00	24.17
O	43.55	43.90	29.73
Zn	-	-	26.45
Al	2.21	2.31	1.59
Si	9.23	10.73	5.71
Fe	0.75	0.37	-
Na	0.50	0.49	11.87
Ca	0.71	0.45	0.23
Mg	0.22	0.21	-
K	0.49	0.54	0.24

**Figure 3.** XRD result of (a) zeolite before activation, (b) zeolite after activation, and (c) ZnO-zeolite nanocomposite (Ramadhini et al., 2023)

Mahdavi et al., (2012) state that the percentage of heavy metal removal that occurs during the photocatalysis process is influenced by the pH of the solution involved. Increased acidity levels reduce the process of metal ion adsorption. The decomposition of heavy metals is carried out using light UV lamp, in the process the pH of the solution and the length of contact time become factors which influence reducing levels of heavy metal pollutants. Besides that, the use of ZnO-zeolite nanocomposites which function as adsorbents and photocatalysts also plays a role in the degradation of heavy metals. Gayatri (2021) stated when the ZnO-Zeolite nanocomposite is contacted with pollutants, it is possible that two processes occur sequentially, namely adsorption and photocatalytic. Adsorption pollutants into an adsorbent involves three main stages, namely first pollutants migrate from the solution to the adsorbent surface, then occurs binding of pollutants to the surface of the adsorbent and finally invasion of pollutants onto in an adsorbent framework.

Degradation of Fe metal begins with an absorption process that occurs in ZnO-Zeolite nanocomposite surface. The surface area of zeolite is quite large and enables the adsorption capacity of heavy metal pollutants so that it can reduce dissolved pollutants in waste. The adsorption process is deeply synergistic photocatalytic decomposition to reach optimum conditions for decomposing pollutants. A study by Inggrid et al. (2015) that the process of adsorption of heavy metal ions Cu begins with the absorption of Cu(II) ions on the photocatalyst surface, then Cu(II) ions that have been absorbed will come into contact with electrons present on the surface of the photocatalyst material so that an ion reduction reaction occurs heavy metal. The decrease in Cu(II) ion

Table 2. BET results analysis

Measurement subject	Zeolite before activation	Zeolite after activation	ZnO-zeolite nanocomposite
Specific surface area (m ² /g)	14.550	17.040	19.436
Pore volume total (cm ³ /g)	0.048	0.056	0.112
Pore size (Å)	15.460	15.380	17.230

concentration is caused by electrons and hydroxyl radicals obtained from photon energy from UV light rays. Agustina et al. (2022) also stated that there are two mechanisms for Cu removal, the processes that take place are adsorption and reduction processes.

Photocatalyst materials will reduce heavy metal ions in wastewater so that heavy metals are no longer dissolved in water, photocatalyst materials are able to mineralize them. The heavy metals contained make it easy to break down. Photocatalyst material activated exclusively by light

from a UV lamp (Ciptasari et al., 2022). During photocatalytic process, a combination of light and a catalyst triggers a chemical reaction. Electrons and holes (e⁻ and H⁺) formed in this reaction will then meet oxygen in the water to form anions. On the other hand, holes will oxidize the hydroxyl to produce a radical with more energy large, such as hydroxyl radicals. These hydroxyl radicals will break down contaminants organic into harmless green compounds that are environmentally friendly (Zawadzki et al., 2018). This statement is in accordance with a research review by Ong

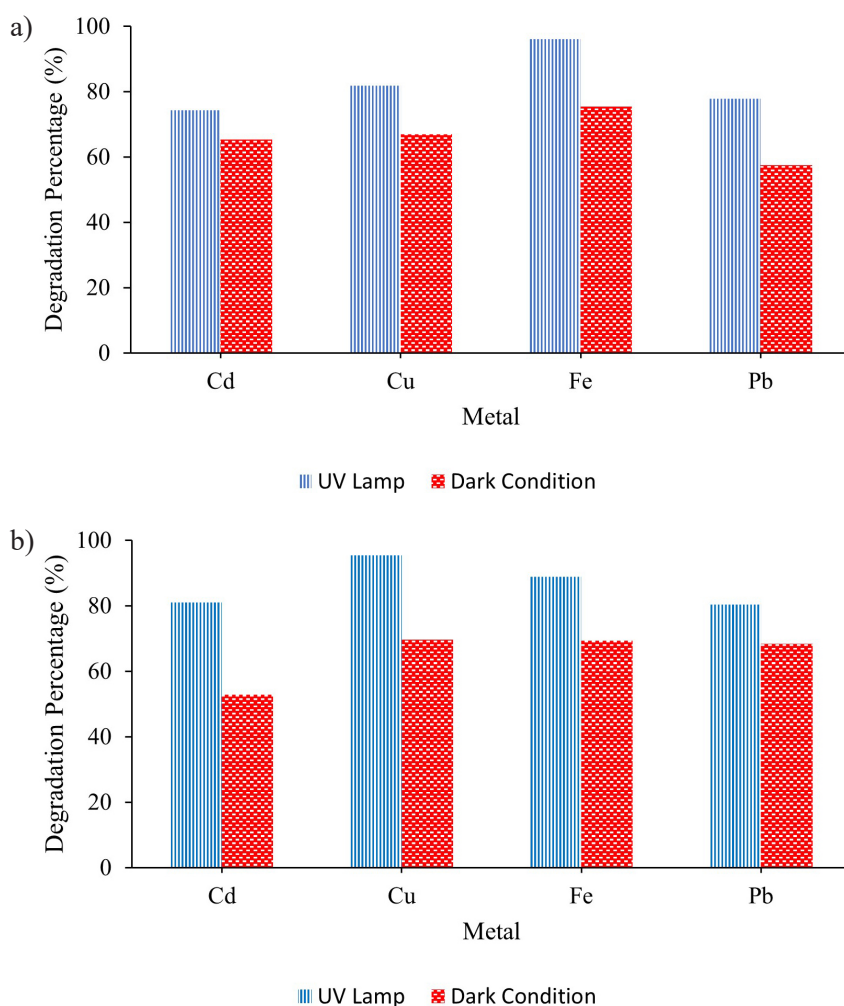


Figure 4. Effect of irradiation on heavy metal degradation using UV lamp and dark conditions for 60 minutes at different pH (a) pH 6, (b) pH 7

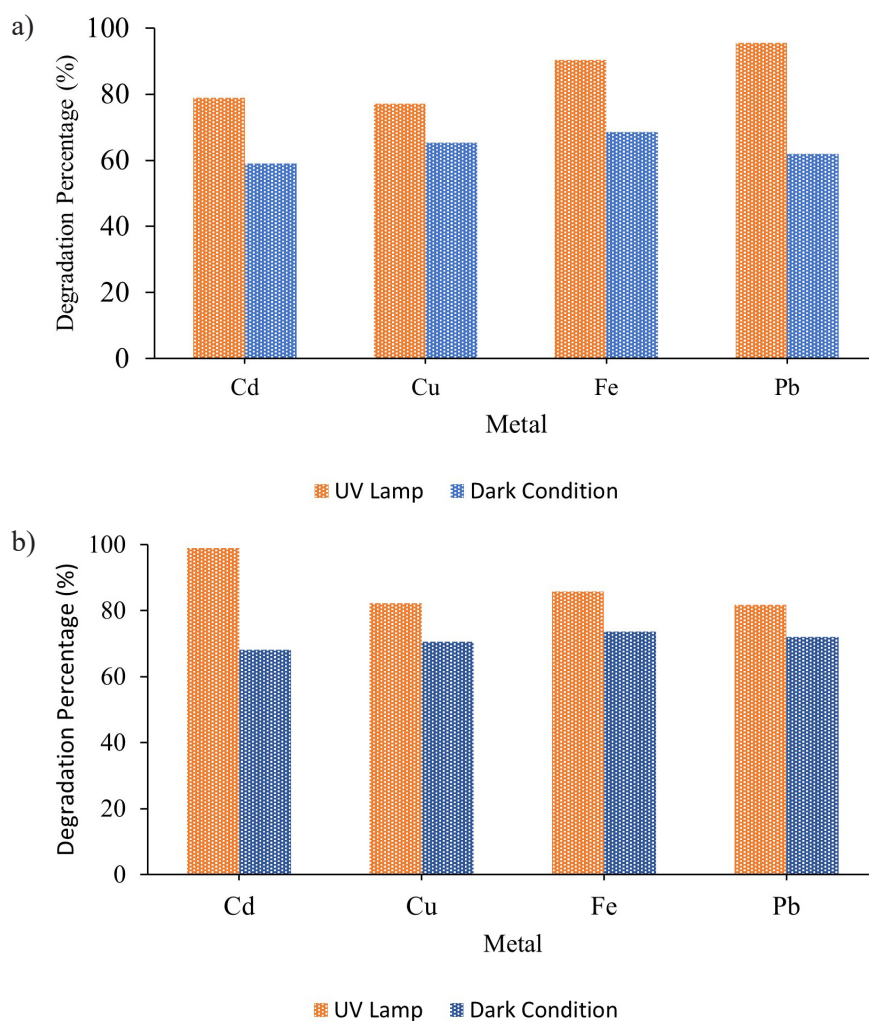


Figure 5. Effect of irradiation on heavy metal degradation using uv lamp and dark conditions at pH 8 for (a) 60 minutes, (b) 120 minutes

et al (2018) which states that when the photocatalyst material is induced by ultraviolet light, the electron-hole pairs will move towards the photocatalyst surface and become involved in reactions where H^+ ions react with water to produce hydroxyl radicals and electron ions react with oxygen to produce H_2O_2 and superoxide radicals. Hydroxyl radicals will attack pollutants adsorbed on the surface produce intermediate compounds. The intermediate compound is finally converted into harmless green compounds such as H_2O and mineral acids. The help of ultraviolet light can increase the degradation percentage heavy metal pollutants because they are capable of emitting UV irradiation from electrons which produces ultraviolet energy large enough to be able to describes pollutants that can harm humans (Lastriyanto et al., 2021).

Comparison of degradation values at optimum conditions using a UV lamp and without

a UV lamp at different pH (pH 6-8) can be seen in Figure 4 and 5. Heavy metals Cu, Fe, and Pb reported the highest degradation percentages after 60 minutes under optimal conditions using ultraviolet radiation. The primary chemical characteristic of the photocatalytic process is the generation of hydroxyl radicals, which act as oxidizers for organic contaminants (Zawadzki et al., 2018). Previous study by Prasetyaningrum et al. (2020) has shown that the use of UV irradiation treatment can significantly boost the reduction of heavy metal pollutants, such as copper (Cu), ion electroplating wastewater by around fifty percent. Specifically, Cd metal reached a degradation percentage of 74.3% at pH 6, 81.1% at pH 7, and 78.9% at pH 8. Cu metal reached 81.9 % degradation at pH 6, 95.4% at pH 7, and 77.2 at pH 8. Fe metal obtained 96.1% at pH 6, 88.1% at pH 7, and 90.4% at pH 8. Meanwhile, Pb metal obtained 77.80% at pH 6, 80.4% at pH 7, and

95.5% at pH 8. At a pH of 8 and an irradiation time of 120 minutes, the most effective Cd metal was determined, which led to a removal percentage of 98.9%, as presented in Figure 5. Overall, the degradation results in dark conditions without an ultraviolet lamp show the lower percentage. The degradation is not that high, this is due to the absence of photons able to activate the ZnO-zeolite nanocomposite so that there is no radical's hydroxyl is formed. Ultraviolet (UV) radiation, along with strong oxidants like H₂O₂ is extensively employed not only in photocatalysis but also in the elimination of heavy metal complexes (Aziz and Mustafa, 2023).

CONCLUSION

The sol-gel method had been used to successfully synthesize ZnO-zeolite nanocomposites. SEM-EDX, BET, and XRD characterizations showed that the ZnO and zeolite presence have been detected in the photocatalyst nanocomposite. The composite showed a surface area of 19.436 m²/g, a pore size of 17.227 Å, a total pore volume of 0.112 cm³/g. The degradation percentages of heavy metals Cu, Fe, and Pb were highest when using the ZnO-Zeolite photocatalyst nanocomposite under ultraviolet light after 60 minutes, as compared to the dark condition. Specifically, Cu metal reached a degradation percentage of 95.4% at pH 7, Fe metal obtained 96.1% at pH 6, and Pb metal obtained 95.5% at pH 8. At a pH of 8 and an irradiation time of 120 minutes, the most effective Cd metal removal percentage was 98.9%.

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