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Research Paper

Photocatalytic Degradation of Heavy Metals Cd, Cu, Fe and Pb Using ZnO-Zeolite Nanocomposite

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Abstract

Heavy metals are the main pollutant substances in the environment. Heavy metals are a type of metal with high density and are very dangerous to living organisms, especially humans. Living organisms can adsorb the bioaccumulative and sedimentation of heavy metals that settle in water. Some compounds which found in wastewater including Cadmium (Cd), Copper (Cu), Iron (Fe), and Lead (Pb). These heavy metals cannot naturally degrade, additional processing is required before it being released into the environment. To prevent environmental pollution impacts, wastewater containing heavy metals must be handled properly and optimally. One method that can be applied for wastewater treatment is degradation by photocatalysis, utilizing the assistance of light. This research is to investigate the effect of pH and irradiation time on the degradation of Cd (cadmium), Cu (Copper), Fe (Iron), and Pb (Lead) heavy metals. To enhance the photocatalytic activity, the synthesis of ZnO-Zeolite nanocomposites was conducted. The ZnO-Zeolite nanocomposites produced were analyzed by SEM-EDX and XRD. The utilization of ZnO-Zeolite nanocomposites is deemed effective in reducing heavy metal concentrations. The degradation with Ultraviolet (UV) light exposure runs within 15-120 minutes with pH variation between 4-8. The degradation of heavy metal runs at 60 minutes and 120 minutes showing an optimum percentage removal of metals approaching 100%. The optimum pH values for Cd, Cu, Fe, and Pb are pH 8, pH 7, pH 6, and pH 8, respectively. The sequential metal degradation percentages are 98.96%, 95.43%, 96.07%, and 95.53%, respectively.

Keywords

Photocatalytic, Heavy Metals, ZnO-Zeolite Nanocomposite

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1. INTRODUCTION

Wastewater is frequently produced as a byproduct of mining activities, industrial processes, and laboratory operations. In some cases, wastewater contains toxic heavy metals and is considered dangerous because of its toxicity which could pollute the environment. Heavy metals are the main pollutant substances in the environment. Heavy metal is a high-density and toxic metal that is very harmful to living things, especially humans because it can precipitate and turn into bioaccumulative that can be adsorbed by living organisms.

Rad and Anbia (2021) said that the massive discharge of wastewater into groundwater, lakes, and rivers causes serious risks to human life and ecosystems. Heavy metals commonly identified as Cadmium (Cd), Copper (Cu), Mercury, Iron (Fe), Lead (Pb) and Manganese (Mn) (Fu and Xi, 2020). Heavy metal pollutants cannot be degraded or destroyed naturally so it needs advanced treatment before being released to environment.

Lead (Pb) is toxic and detrimental to human health, contributing to adverse effects such as the shortened lifespan of red blood cells, epilepsy, and brain damage. Both Copper (Cu) and Cadmium (Cd) exhibit bioaccumulation and toxicity. The solubility of Cu varies depending on its compound, some Cu is easily adsorbed into particles that dissolve in water while other compounds are slightly soluble in water, especially $CuSO_4$. The limited solubility of Cu leads to its high resistance to adsorption by water-soluble particles (Egorova and Ananikov, 2016). Cu affected liver and kidney damage, anemia and intestinal irritation. Cadmium poisoning will cause kidney disease, lung cancer, bone fractures and bone softening (Azimi et al., 2017). Meanwhile, the presence of iron (Fe) in certain amounts is indeed needed by the human body, but in excessive amounts, it will cause toxic effects that trigger irritation to the eyes and skin and increase the risk of congestive heart failure (Fu and Xi, 2020). To prevent the effects of environmental pollution, optimal treatment is needed to mitigate the pollution of wastewater containing heavy metals. A possible method for addressing this concern regarding wastewater treatment is a photocatalytic degradation process for the reduction of heavy metal pollutants.

Photocatalytic is the process of activating chemical reactions by photocatalysts using light as its energy source. This reaction converts light energy, such as ultraviolet light, into chemical energy and forms hydroxyl radicals that will reduce contaminants and convert toxic compounds in water into harmless compounds, such as CO_2 and H_2O (Ong et al., 2018). This process is quite economical and effective in reducing the concentration of hard-decompose heavy metals and the amount of chemical oxygen (COD) required by wastewater.

Photocatalyst materials that are commonly used in the photocatalytic process are solid semiconductor materials such as ZnO, TiO_2, and CdS. ZnO is the most frequently used photocatalyst material because of its high effectiveness, low cost and high supply. Zinc oxide (ZnO) is commonly used as a photocatalyst due to its chemical stability and is classified as non-toxicity (Kusdianto et al., 2019). Roy and Chakraborty (2021) stated that ZnO is often used in green environmental treatment systems because it has a wide band gap energy area close to the ultraviolet spectrum and strong oxidation ability. ZnO has higher adsorption efficiency in the solar spectrum compared to TiO_2 photocatalyst materials (Ong et al., 2018).

However, in the photocatalytic process, photocatalyst shows suboptimal adsorption capacity. Therefore, to cover its deficiency, photocatalyst material is combined with adsorbents to enhance its photocatalytic activity. The combination of photocatalyst and adsorbent materials is to ensure optimal photocatalytic contact with contaminants (Saravanan et al., 2013). The combination of Zinc Oxide and adsorbent will form a nanocomposite.

According to earlier studies, the use of nanocomposites is considered effective for decreasing heavy metal levels due to its ability to carry out two processes simultaneously, namely adsorption and photocatalytic decomposition of pollutants. A substance that is widely used as an adsorbent is zeolite. Zeolite is a broad-pored material, commonly used as catalysts, adsorbents, and ion exchangers (Rahman et al., 2018). The photocatalytic process can be aided by the large surface area of zeolite. In addition, the zeolite pore size is also more homogeneous, evenly distributed and impurity-free which means that the adsorption process will be more effective.

This research aims to determine the reduction amount of heavy metals in wastewater by finding the optimum conditions for photocatalytic degradation. ZnO-Zeolite nanocomposite was tested on artificial wastewater that contains Cd, Cu, Fe, and Pb.

2. EXPERIMENTAL SECTION

The research was carried out in the analysis laboratory at the State Polytechnic of Sriwijaya. Photocatalytic degradation of heavy metal in artificial wastewater using nanocomposite ZnO-Zeolite. The ZnO-Zeolite nanocomposite was then characterized by using XRD and SEM-EDX. The degradation of heavy metal waste pollutants was observed in 15, 30, 60, 90 and 120 minutes with pH variation between 4,5,6,7 and 8. Samples were then tested using the XRF method.

2.1 Materials

The materials used consisted of synthetic zeolite, zinc acetate $Zn(CH_3COO)_2.2H_2O$, $Cd(NO_3)_2$, $CuSO_4.5H_2O$, $FeCl_3.6H_2O$, $Pb(NO_3)_2$ were obtained from Merck. HCl 2 M, NaOH 0.4 M, Ethanol 96%, and Aquadest.

2.2 Methods

2.2.1 Synthetic Wastewater

The synthetic wastewater contains the following heavy metals such as $Cd(NO_3)_2$, $CuSO_4.5H_2O$, $FeCl_3.6H_2O$, and Pb $(NO_3)_2.4H_2O$. Each compound was mixed in 1000 mL of distilled water into a glass beaker (Agustina et al., 2022). Each type of heavy metals concentration was at 20 mg/L.

2.2.2 The Synthesis of ZnO-Zeolite Nanocomposite

ZnO-Zeolite nanocomposite was produced by sol-gel methods. On the basis of a previous study by Gayatri et al. (2021), zinc oxide was combined with synthetic zeolite by mixing into ethanol and the solution then refluxed at 76°C for 2 hours. Sol-gel method consists of two-stage process, first appears metal alkoxide hydrolysis and then it will continue into the condensation phase. This method has proven its ability to produced homogeneous nano-sized particles and able to control mass ditribution (Hasnidawani et al., 2016).

2.2.3 Characterization of ZnO-Zeolite Nanocomposite

The ZnO-Zeolite nanocomposite was characterized using SEM EDX (Scanning Electron Microscope - Energy Dispersive X-ray) and XRD (X-ray diffraction) analysis. XRD is used to identify and analyze the phase of powder or solid inorganic materials samples consisting of polycrystalline and amorphous (Gayatri et al., 2021). The data is presented in a list of theta values, peak values, and lattice constants. From the data obtained, it can determine the identification of phase type, phase composition and crystal size. SEM-EDX analysis aims to determine surface morphology, structure and crystal size (Tuas and Masduqi, 2019).

2.2.4 Photocatalytic Degradation Activity Test

The effect of pH in photocatalytic degradation was investigated using ZnO-Zeolite nanocomposites at a dosage of 100 mg/L, as outlined by Mahdavi et al. (2014). This research involved pH variations ranging between 4 to 8 in artificial wastewater containing heavy metals Cd, Cu, Fe, and Pb. Adjustment of pH variations was made by adding 0.1 M HCl solution and 0.1 M NaOH solution until it reached the desired pH. The effect of reaction time was observed for 2 hours and samples were taken every 15, 30, 60, 90 and 120 minutes. The synthetic wastewater was tested under ultraviolet (UV) light irradiation 20 cm away from the sample. In order to examine the reaction mechanism, the samples were also tested under dark conditions without any light source, while maintaining consistent pH variations and reaction times. Subsequently, the samples then tested using XRF method to determine the heavy metal content contained in synthetic wastewater.

3. RESULTS AND DISCUSSION

3.1 Characterization of ZnO-Zeolite Nanocomposites

The Characterization of ZnO-Zeolite nanocomposites was to make sure that ZnO and zeolite were successfully embedded to form nanocomposite. This characterization also aimed to determine the crystal size and the specific area of the used nanocomposites during this research.

3.2 SEM-EDX (Scanning Electron Microscope- Energy Dispersive X-Ray)

Figure 1 presents the results of SEM morphological analysis of ZnO-Zeolite Nanocomposites. The nanocomposite was characterized by the attachment of ZnO to the zeolite surface. As can be seen in Figure 1, two components exhibit contrasting forms and colors. Zeolite is dark-colored and ZnO is dazzling white. The ZnO composition appears to be higher than that of zeolite, mostly because the former nanocomposite material contains a greater quantity of Zinc Acetate precursor compared to the activated synthetic zeolite. The nanocomposite particles have a more homogenous size and smoother, and more even distribution. It appears that the particles are arranged regularly.

Figure 2 shows the EDX spectrum of the ZnO-Zeolite nanocomposite that provides information regarding the elements in nanocomposite, which include Zn, C, O, Al, Si, and Na. The peak mapping results representing the elements show the content of Zn with a weight percentage of 26.45%, O: 29.73%, C: 24.17%, Si: 5.71% and Al: 1.59%.

3.3 XRD (X-Ray Diffraction)

X-ray Diffraction aims to study the structure and crystal size of solid materials. In determining crystal structure, XRD analysis compares specific peaks obtained by each material with diffraction data in the database. Based on the XRD result, after being compared to the database data, it shows that the ZnO-Zeolite nanocomposite peaks were identical to the ZnO peak with diffraction peaks at 2θ 20.93°, 26.66°, 31.78°, 34.48°, 36.25°, 47.57°, and 68.02°. These peaks

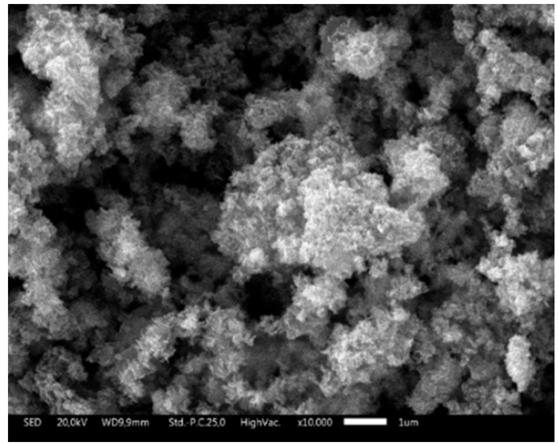

Figure 1. The Result of ZnO-Zeolite Nanocomposite by SEM Analysis (10,000 Times of Magnification)

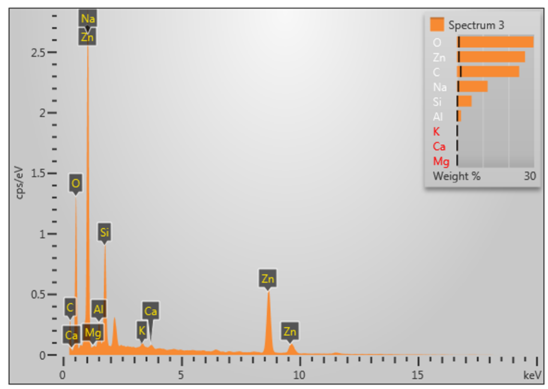

Figure 2. EDX Spectrum of ZnO-Zeolite Nanocomposite

indicate the components that make up the ZnO-Zeolite nanocomposite. It can be seen in Figure 3, that the degree of peak detects the presence of ZnO and the presence of Zeolite which is represented by SiO_2.

Through XRD analysis, the crystallite size can be determined by analyzing the main peak of the diffractogram using the Debye Scherrer approach, as expressed in the Equation (1).

$$D = \frac{k.\lambda}{Bcos\theta} \tag{1}$$

In Equation (1), D is defined for crystal size, K represents the crystal form factor with a value between (0.9-1) and λ represents the X-ray Wavelength value of 1.54056 Å. B is the FWHM value (Full width at half maximum), and θ denotes the diffraction angle. Both FWHM and θ values were obtained from XRD analysis.

Based on the calculation results in Table 1, it can be inferred that the average crystal size of ZnO-Zeolite nanocomposite is approximately 34.35 nanometers. This indicates that the nanocomposite crystal produced through the sol-

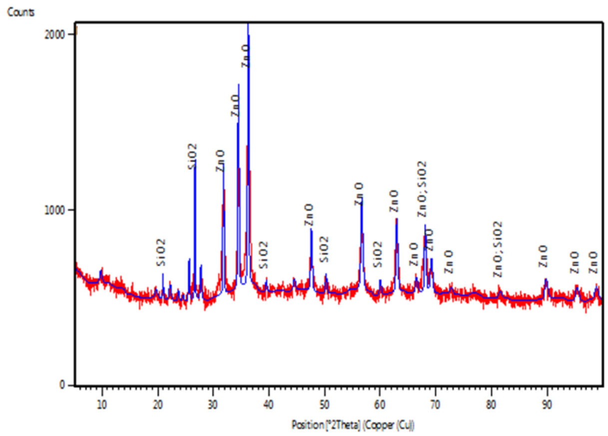

Figure 3. The Result of ZnO-Zeolite Nanocomposite XRD Analysis

gel preparation method has reached a nanoscale dimension. Therefore, it can concluded that the preparation technique was highly successful in forming nano-sized crystals of composites.

Table 1. The Average Crystal Size of ZnO-Zeolite Nanocomposite

Peak position 2θ	FWHM	Crystal size D (nanometers)
9.27	0.51	16.27
19.73	0.61	13.72
20.93	0.15	54.97
22.20	0.41	20.66
23.69	0.30	27.61
24.56	0.20	41.48
26.67	0.12	66.67
27.75	0.25	33.41
The average crystal size		34.25

3.4 Effect of Ph on Removal Percentage of Cd, Cu, Fe, and Pb in Photocatalytic Degradation

According to Mahdavi et al. (2014), pH influences the percentage of heavy metal removal during the ZnO photocatalysis process. Higher acidity conditions reduce the uptake of metal ion adsorption. The optimum percentage of each heavy metal can be seen in Figure 4 and Figure 5. As reported by Figure 5, the maximum reduction of Cd metal was up to 98.96% at pH 8. This outcome is similar to the results obtained by Heidari et al. (2013), in his research, the optimal condition for reducing Cd was also identified at pH range between 8-9. The percentage of Cd metal degradation could reach more than 80% at pH variations of 7-8 (Renu et al., 2017).

Meanwhile in Figure 4, the largest percentage of Cu was 95.43% at pH 7, similar to research by Agustina et al. (2022)

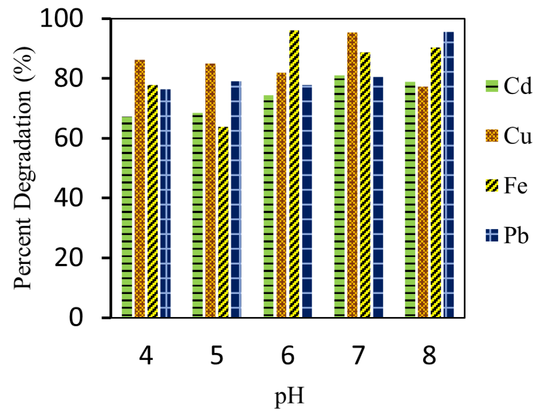

Figure 4. The Effect of pH Value with 60 Minutes Contact Time on Heavy Metal Degradation

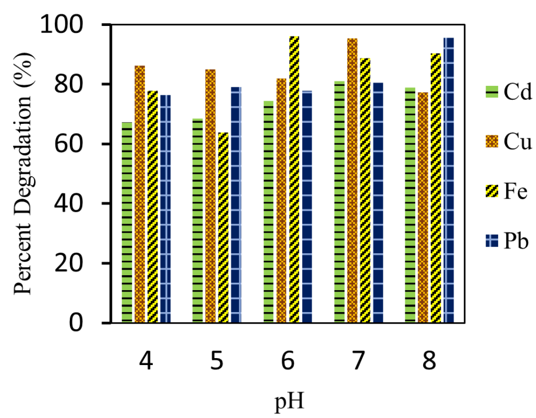

Figure 5. The Effect of pH Value with 120 Minutes Contact Time on Heavy Metal Degradation

which states that the optimum conditions for Cu metal are in the pH 7-8 range. This means that the degradation will be effective in alkaline conditions because the degradation of Cu metal in acidic conditions will have an impact on the low adsorption efficiency. Furthermore, the optimum condition for reducing Fe metal was found at pH 6, resulting in 96.07%, while for Pb metal, the optimum condition was at pH 8 with a percentage of 95.53%. For the optimum condition of Pb metal, several studies had different results, as reported by Heidari et al. (2013) Pb metal is optimum at pH 6, while Agustina et al. (2022) stated that pH 8 is the optimum condition for Pb metal degradation. This means that the pH range of 6-8 is very potential and possible to achieve the maximum percentage of degradation. The results show us that the optimum pH conditions for the degradation of heavy metals Cd, Cu, Fe and Pb were quite varied, namely in the range of pH 6-8.This is in accordance with the research report by Hegazi (2013) which states that the optimum conditions for heavy metal absorption are in

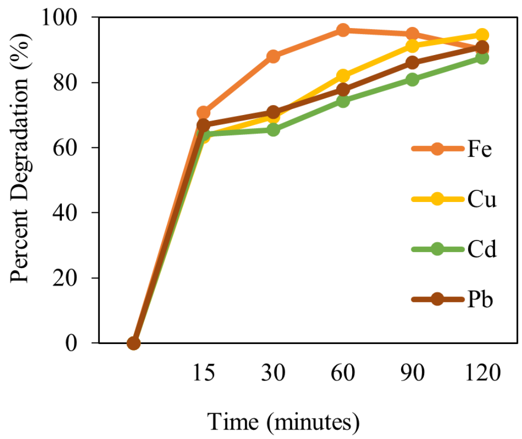

Figure 6. The Effect of Reaction Time on Heavy Metal Degradation pH 6

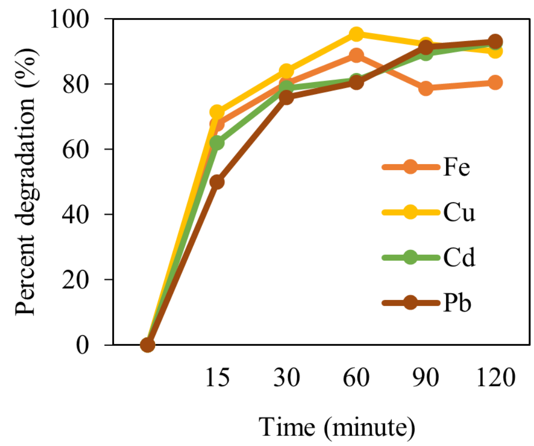

Figure 7. The Effect of Reaction Time on Heavy Metal Degradation pH 7

the range of pH 6-7. Elboughdiri (2020), contends that the most effective values for heavy metal removal efficiency are within the pH range of 5-7. The solution's acidic pH will affect ion exchange, with a higher pH value leading to elevate the efficiency of heavy metal degradation.

3.5 Effect of Irradiation Time and Nanocomposite ZnO-Zeolite Used on the Percent Removal of Cd, Cu, Fe, and Pb

Figure 6 and Figure 7 show that the percentage of degradation is quite fluctuating, in some conditions the maximum level of heavy metal reduction occurs at 60 minutes. After 60 minutes, the percentage of degradation tends to decrease. From the calculation results, the largest percentage of Cu, Fe and Pb metals was obtained at 60 minutes. The values were 95.43%, 96.07%, and 95.53%, respectively.

As for Cd metal as can be seen in Figure 8, the largest percentage of 98.96 was obtained at 120 minutes. In the initial 15 minutes, the average degradation of Cd, Cu, Fe and Pb metals ranged from 48%-70% with variations in solution pH. The achievement of almost 50% degradation percentage in the first 15 minutes shows that the ability of ZnO-Zeolite nanocomposite with irradiation under UV light in decomposing pollutants is quite effective. This means that as the contact time between the ZnO-Zeolite nanocomposite and heavy metal waste increases, the percentage of degradation will tend to increase. This is in line with the research conducted by Dhandole et al. (2020) which states that the percentage reduction in metal content will increase with the length of exposure time. Gayatri et al. (2021) believes that high photocatalytic activity will enhance degradation when pollutants are degraded with ZnO-Zeolite nanocomposite and ultraviolet light assistance. With a longer contact time, there will be more hydroxyl radical formation, which is an important component in the degradation of pollutants. As a result, the final concentration of pollutants will decrease.

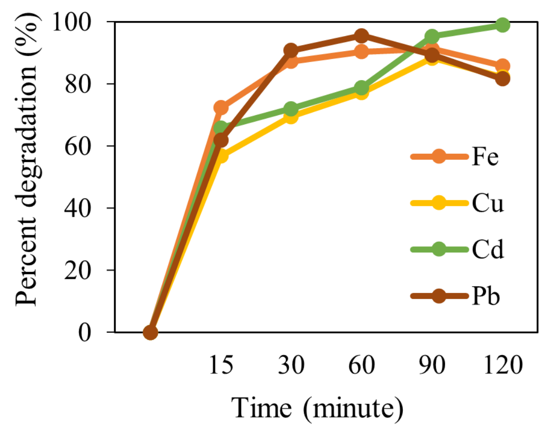

Figure 8. The Effect of Reaction Time on Heavy Metal Degradation at pH 8

Meanwhile, the degradation percentage tends to decrease after 60 minutes, indicating that the optimum ability of the ZnO-Zeolite nanocomposite has reached saturation conditions in absorbing heavy metal pollutants. All active sites on the adsorbent surface have worked optimally to adsorb the contaminants. As a result, the surface area of the adsorbent decreases and the adsorption efficiency also decreases (Mandal et al., 2021).

4. CONCLUSION

ZnO-Zeolite nanocomposites have been successfully synthesized through the sol-gel method, the composite has an average crystal size of 34.25 nanometer. Cu, Fe and Pb metals produced the highest percentage of degradation at 60 minutes with optimum conditions for Cu metal at pH 7 of 95.43%, Fe metal at pH 6 of 96.07% and Pb metal at pH 8 of 95.53%. Meanwhile, the optimum Cd metal was at pH 8 with an irradiation time of 120 minutes resulting in a removal percentage of 98.96%.

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