Reduction of Copper, Iron, and Lead Content in Laboratory Wastewater Using Zinc Oxide Photocatalyst under Solar Irradiation

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ABSTRACT

Heavy metal is a type of metal that has a high density and high toxicity when consumed by living things, especially humans. To prevent the impact of environmental pollution, optimal handling of wastewater containing heavy metals is required, including the wastewater from laboratories. This research aimed to study the effect of pH, catalyst dose, and irradiation time on the reduction of Copper (Cu), Iron (Fe), and Lead (Pb) heavy metals and their application to laboratory wastewater treatment. Among the Advanced Oxidation Processes (AOPs) methods, photocatalysis was chosen to reduce the level of Cu, Fe, and Pb heavy metals where zinc oxide (ZnO) is used as a photocatalyst and the sunlight as a light source. To determine the effect of pH, catalyst dose, and time on the reduction of heavy metal levels, firstly, this research used the synthetic wastewater containing Cu, Fe, or Pb heavy metals. On the basis of the experimental results, it is concluded that the pH value, catalyst dose, and time affect the photocatalytic process, decreasing the levels of Cu, Fe, and Pb metals. The optimum pH value obtained for Cu was at pH 7–8, for Fe it was at pH 6, and for Pb it was at pH 8; in turn, the metal removal percentages were 99.46, 99.91, and 99.70%, respectively. In the photocatalysis of synthetic wastewater, high removal percentage of more than 99% was achieved by using 0.1 g/L catalyst. The optimum decrease of metals occurred in the first 15 minutes of solar irradiation where the removal percentage was close to 100%. In this study, the application of ZnO photocatalyst under solar irradiation can reduce the heavy metals content in the laboratory wastewater by almost 100%, which meets the environmental quality standard for Cu, Fe, and Pb.

Keywords: AOPs, photocatalysis, heavy metals, sunlight, zinc oxide.

INTRODUCTION

The development of science cannot be separated from the role of the laboratory as a means to test new theories and hypotheses that have been put forward by scientists. Experimental and practical activities at Organic Chemistry Laboratory of the Integrated Laboratory of Universitas Sriwijaya are one of the sources of waste. Most of the activities carried out in the laboratory use the chemicals that are harmful to the environment. Although the volume is not as much as industrial waste, laboratory waste can reduce the water and environment quality if it is not treated properly before being discharged into water bodies and the environment.

Heavy metal is a type of metal that has a high density and has a high toxicity when consumed by living things, especially humans. Microorganisms cannot degrade the heavy metal waste, so the waste will be accumulated in the environment and cause pollution (Arita et al., 2022). In chronic poisoning, Cu can cause Wilson's disease, which is a degenerative process in the brain and cirrhosis of the liver. Excessive Fe levels can damage the intestines and cause death (Adhani and Husaini, 2017). Lead is a heavy metal within IVA group which is very toxic if it enters the human body.

The Pb poisoning can cause damage to the function of organs and systems of the human body, especially children.

The analysis of results of the Organic Chemistry Laboratory wastewater sample can be seen in Table 1. To prevent the impact of environmental pollution, optimal handling of wastewater in the laboratory is needed so that environmental pollution caused by the produced wastewater can be overcome. One method that can be used for wastewater treatment is by applying advanced oxidation processes (AOPs).

AOPs constitute a waste treatment technology involving radical hydroxyl groups that can break down chemicals in waste. This method is so popular due to its effectiveness in treating wastewater and its low operating cost. There are several types of AOP methods that are quite popular today, one of them is the photocatalysis method. Photocatalysis is a process of activation of chemical reactions by a catalyst that uses light as its energy source. Besides being economical, this method is quite effective in reducing the value of chemical oxygen demand (COD) and heavy metals that are difficult to decompose from wastewater (Farzadkia et al. 2014; Hosseini and Mohebbi 2020).

The commonly used photocatalysts are solid semiconductors, such as TiO_2, ZnO, CdS, ZnS, and others. Zinc oxide (ZnO) is one of the photocatalysts that is often used because of its high effectiveness, affordable price, and high supply in the market. In 2016, Indonesia imported around 7,456,128 kg of ZnO from all over the world. This makes ZnO solids very easy to obtain from within and outside the country. Due to its unique characteristics, ZnO has emerged as the leading candidate in green environmental management system, such as direct and wide band gap in the near-UV spectral region, strong oxidation ability (Roy and Chakraborty, 2020). ZnO has been shown that to exhibit higher absorption efficiency across a larger fraction of solar spectrum compared to TiO_2 (Ong et al., 2018). The photocatalysis process needs a light source to activate the catalyst. UV lamps, which require electricity supply for their use, were generally employed as the light source. Laboratory wastewater treatment in this study utilized sunlight as a light source. The use of sunlight in the photocatalytic process can replace the use of UV lamps to reduce electricity consumption. On the basis of the previous research, the use of solar irradiation in the photocatalysis process is considered effective for reducing the levels of heavy metals Cr (VI), Pb, Zn, and Cu (Shruthi et al. 2016; Sharma et al. 2020).

This research was conducted to obtain optimal photocatalytic conditions, especially to reduce the metal content in laboratory wastewater. For this reason, firstly, the ZnO photocatalyst was tested on synthetic wastewater containing Cu, Fe, or Pb.

MATERIALS AND METHODS

Materials

The materials used consisted of ZnO, $Pb(NO_3)_2.4H_2O$, $FeCl_3.6H_2O$, $CuSO_4.5H_2O$, HCl, NaOH, and Aquadest as solvents, were obtained from Merck. The laboratory wastewater sample was from Oganic Chemistry Laboratory of Universitas Sriwijaya.

Methods

Synthetic wastewater preparation

Synthetic wastewater was made by mixing each compound $Pb(NO_3)_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, or $CuSO_4 \cdot 5H_2O$ with 1000 mL distilled water into a separate glass beaker (Darmawan, 2017). The concentration of each synthetic waste is 20 mg/L for each type of heavy metal.

Photocatalyst characterization

Zinc oxide compounds were characterized by using x-ray diffraction (XRD) Rigaku Mini-Flex600 and scanning electron microscope

Table 1. Laboratory wastewater analysis results (before treatment)

Parameter	Unit	Environmental quality standard (Minister of Environment Regulation No. 5 of 2014)	Laboratory analysis results
Copper (Cu)	mg/L	2	44.68
Iron (Fe)	mg/L	5	119.91
Lead (Pb)	mg/L	0.1	0.97

(SEM). XRD is used for identification and phase analysis of a material, in the form of powder or solid (block) from inorganic samples, in the form of polycrystalline and amorphous. The data presented include a list of 2 theta values, peak value (intensity) and the amount of lattice constant. As for the phase analysis, it can be in the form of: identification of the type of phase, phase composition (percentage), crystallite size, orientation, and others. SEM is used to see the surface morphology, structure and crystal size.

Photocatalytic activity test

1. The samples for testing the effect of pH on wastewater using a ZnO catalyst dose of 0.5 g/L (Mahdavi et al., 2012) with variations in pH values between 4–8 in each type of synthetic wastewater containing heavy metals. The pH variation was adjusted by adding 0.1 M HCl and/or 0.1 M NaOH solution until the desired pH was obtained.

2. The test sample to study the effect of the catalyst dose used a variation of the concentration of each catalyst of 0.1; 0.2; 0.4; 0.5; and 0.6 g/L with synthetic wastewater containing Cu, Fe, and Pb in the amount of 20 ppm.

3. The ZnO samples were dispersed into laboratory effluent solutions with various concentrations for 30 minutes to achieve absorption and desorption equilibrium (Le et al., 2019).

4. After equilibrium, the solution was then irradiated under sunlight for 1 hour with a time span of 11.00–13.00 WIT (Shahmoradi et al., 2019).

5. The effect of time is observed for 1 hour of the process, the sample was taken every 15 minutes. Figure 1 illustrates the the experimental apparatus.

6. The best results with the most optimum conditions (pH, photocatalyst dose, and irradiation time) were tested on the original laboratory wastewater and then analyzed to obtain percent of removal.

RESULTS AND DISCUSSION

The research was conducted by optimizing the pH and dose of photocatalyst on synthetic wastewater first, which was then applied to laboratory wastewater. The pH value in the synthetic wastewater was between 4–8 by adding NaOH or HCl.

After obtaining the optimum pH value, the research continued to the optimization of photocatalyst dose in synthetic wastewater. The variation of the photocatalyst dose used was 0.1–0.6 g/L.

ZnO photocatalyst characterization

The characterization of the photocatalyst was performed with the aim of ensuring that the photocatalyst used was ZnO solid as well as seeing the structure and crystal size of the photocatalyst used when the research was carried out.

X-Ray diffraction

XRD analysis was carried out using the Rigaku MiniFlex600 XRD assay. The material analyzed is a white solid material in the form of powder. The results of the XRD analysis can be seen in Figure 2. It shows the results of XRD analysis readings. The red line in the figure shows the reading of the analyzed sample, while the blue line represents the peak of ZnO solid from the JCPDS database No.75–1526.

There are 11 peaks in the reading, with the three of highest peaks at 2-theta angle of 31,787; 34,469; 36,292 with respective intensities of 3250, 2248, 5718 counts per second (cps). If the reading results are compared with the peak data from the database, the peak XRD reading results can be concluded that the sample used is a solid of ZnO.
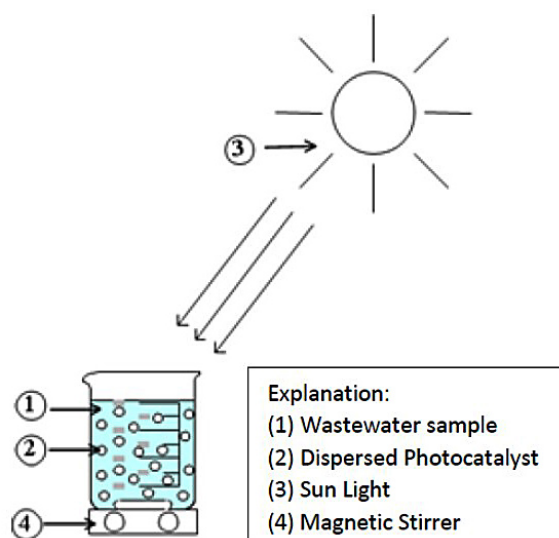

Figure 1. Scheme of experimental apparatus

Explanation:
(1) Wastewater sample
(2) Dispersed Photocatalyst
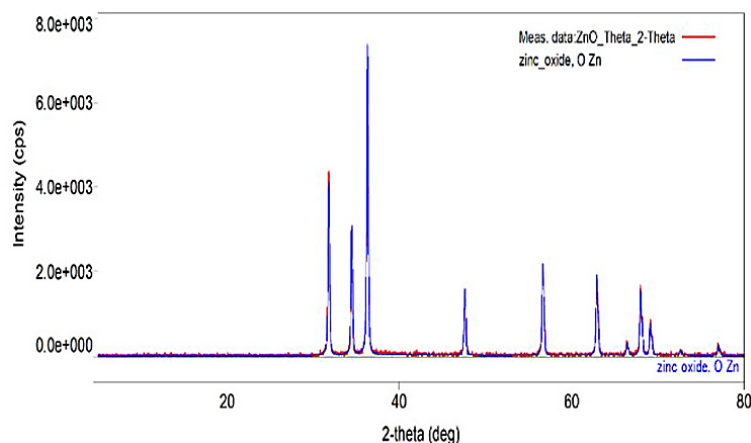(3) Sun Light
(4) Magnetic Stirrer

Figure 2. XRD sample result

Scanning electron microscope

Figure 3 shows that ZnO has a surface that tends to be homogeneous with a very porous morphology and small pore size on the solid surface. ZnO particles have particle sizes that tend to be the same as each other. From the results of the analysis, it can be concluded that the ZnO solids used have the smallest size scale in microns.

Effect of pH on removal percentage of Cu, Fe, and Pb metals in the photocatalysis process

According to (Mahdavi et al., 2012), the pH value affects the percentage of heavy metal removal in the ZnO photocatalyst process. Higher

acidity conditions are associated with lower metal ion adsorption. This may be due to the protonation of the functional group. The functional groups in metal oxides are generally enclosed by hydroxyl groups the shape of which varies at different pH. The effect of pH values was studied in the range of pH values of 4–8, a photocatalyst dose of 0.5 gram/L and irradiation time until 60 minutes.

The concentration of Pb has decreased since the 15th minute for both the pH and the catalyst dose variable. The Pb removal by photocatalytic method using ZnO catalyst was close to 100% for pH 7 and 8 after 15 minutes of irradiation. It can be seen in Figures 4–5. It can be concluded that the most optimal pH for the Pb photocatalysis
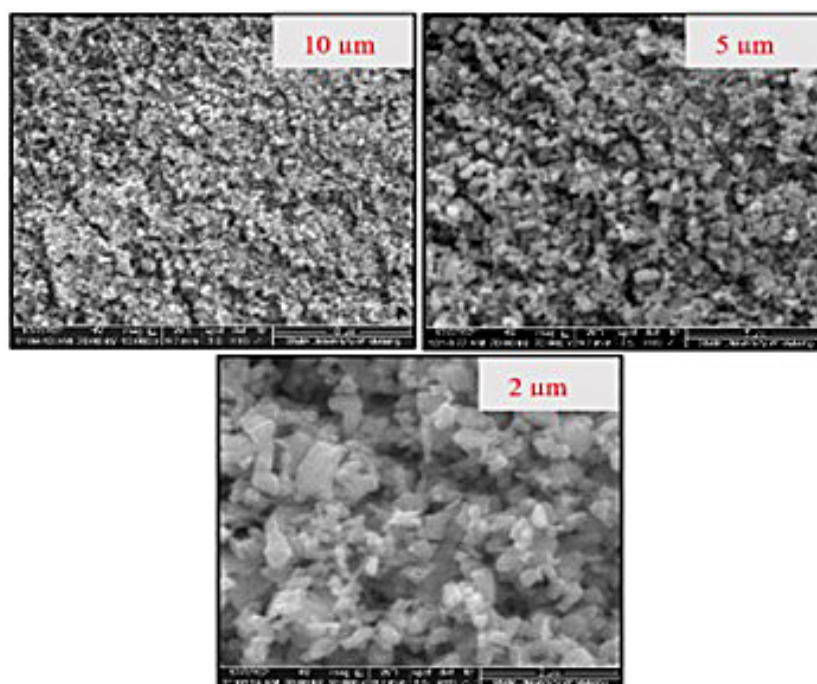

Figure 3. SEM analysis results of ZnO

process is pH 8 (99.69% of removal). The oxidation occurs in the Pb (II) ion. As long as a suitable optical excitation source is available, many electrons and holes can be generated continuously for the reduction or oxidation of metal ions. Thus, these metal/metal oxides can be present in the form of a thin layer on the surface of ZnO particles or as particles deposited on the surface of ZnO particles or in solution (Le et al., 2019).

The effect of pH on the percentage of Fe metal removal can be seen in Figures 4–5. It can be concluded that the most optimal pH for the photocatalytic process of Fe metal is at pH 6 (99.91%). Removal of Fe occurs due to adsorption on the surface of ZnO particles (Babarsad et al., 2019).

Figures 4–5 show the pH 7 and 8 variables, the percentage of Cu metal removal is close to 100%, while the increase in the percentage removal of other pH data tends to be very small. In Figure 4, it can be concluded that the optimal pH for photocatalysis of Cu metal is at pH 7–8 (99.70%) in the first 15 minutes of irradiation.

This is supported by a study conducted by (Le et al., 2019) which stated that the removal of Cu metal by the photocatalytic method using a ZnO catalyst was close to 100% at 15 minutes with UV light. Removal of Cu metal which is close to 100% is due to adsorption on the surface of ZnO particles. The mechanism of Cu removal by ZnO is a reduction-adsorption process. The thick CuO layer formed on the ZnO particles showed that Cu^{2+} ions were hydrolyzed and formed $Cu(H_2O)_6^{2+}$, then reacted with OH^- to form CuO.

Effect of photocatalyst dosage on removal percentage of Cu, Fe, and Pb metals in the photocatalytic process

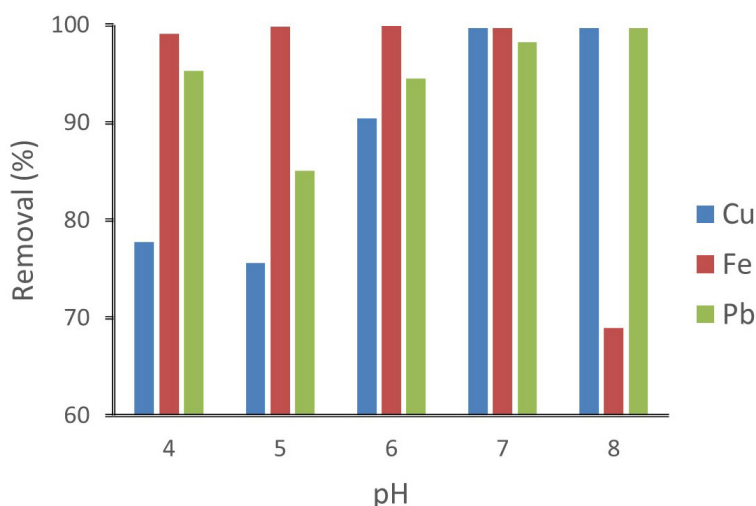The effect of photocatalyst dose was studied by varying the dose of photocatalyst in synthetic

Figure 4. The effect of pH on removal percentage of Cu, Fe, and Pb after 15 minutes of irradiation
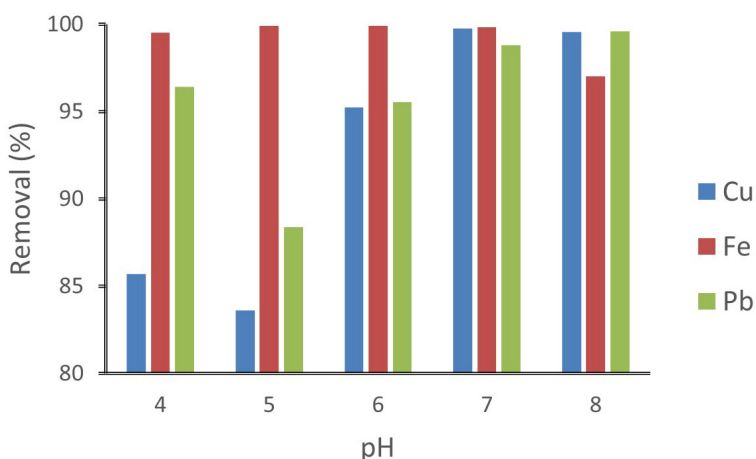

Figure 5. Effect of pH on removal percentage of Cu, Fe, and Pb after 30 minutes of irradiation
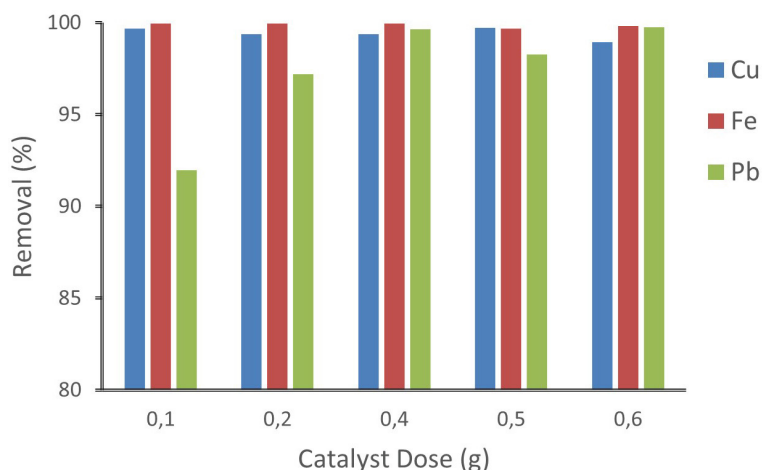
Figure 6. Effect of photocatalyst dose on removal percentage of Cu, Fe, and Pb after 15 minutes of irradiation

wastewater with a dose of 0.1–0.6 g. The pH value was set at 7 within 60 minutes under solar irradiation and the sample was taken every 15 minutes.

In the first 15 minutes, especially for Pb, it was seen in Figure 6 that the higher the catalyst dose, the greater the metal removal percentage. This is in accordance with a study conducted by (Shruthi et al., 2016) which stated that the higher the dose of ZnO catalyst allows the adsorption process and oxidation-reduction reactions to occur in wastewater to a greater degree. However, for Cu and Fe, with the use of 0.1 g of catalyst, the percentages of metal removal achieved were more than 99%.

Figure 7 shows that after 30 minutes of irradiation, all metals have reached removal percentages of more than 99%. A study conducted by (Sharma et al., 2020) who examined the effect of pH and CuO-ZnO dosage in removing the Pb and Cr levels from water, reported that the highest removal percentage obtained was 97.73% at pH 10 with the CuO-ZnO dose used of 1 g/L and the optimized initial metal content was between 10–60 mg/L. When compared to Sharma's research, it can be said that the percentage of Pb metal removal obtained in this study was greater (99.64%) with the use of less catalyst (0.1 g). This is probably due to the presence of CuO metal oxide which affects the appropriate pH conditions for metal absorption.

The removal percentage of Fe is close to 100% in all variations of the catalyst dose for the first 15 minutes until 60 minutes. Meanwhile, for Cu and Pb, there was no significant change in the percentage of removal after 30 minutes of irradiation under the sun. It can be concluded that, for economic reasons, the use of a catalyst dose of 0.1 g/L is sufficient to achieve a high percent of metals removal (more than 99%).
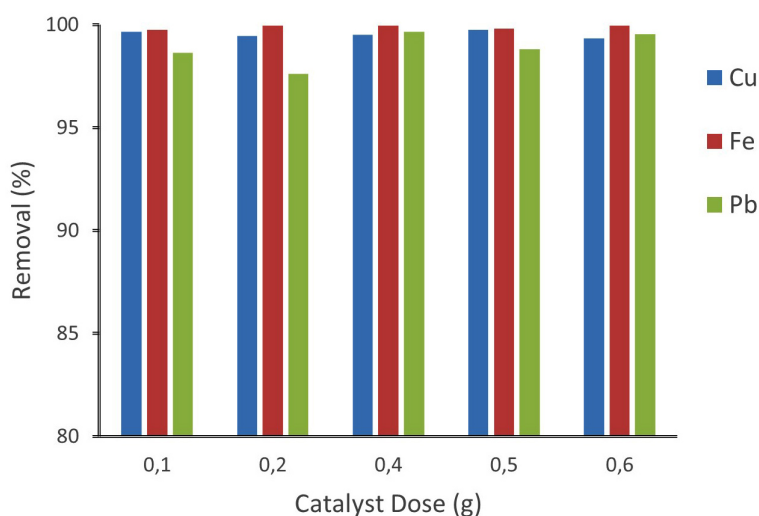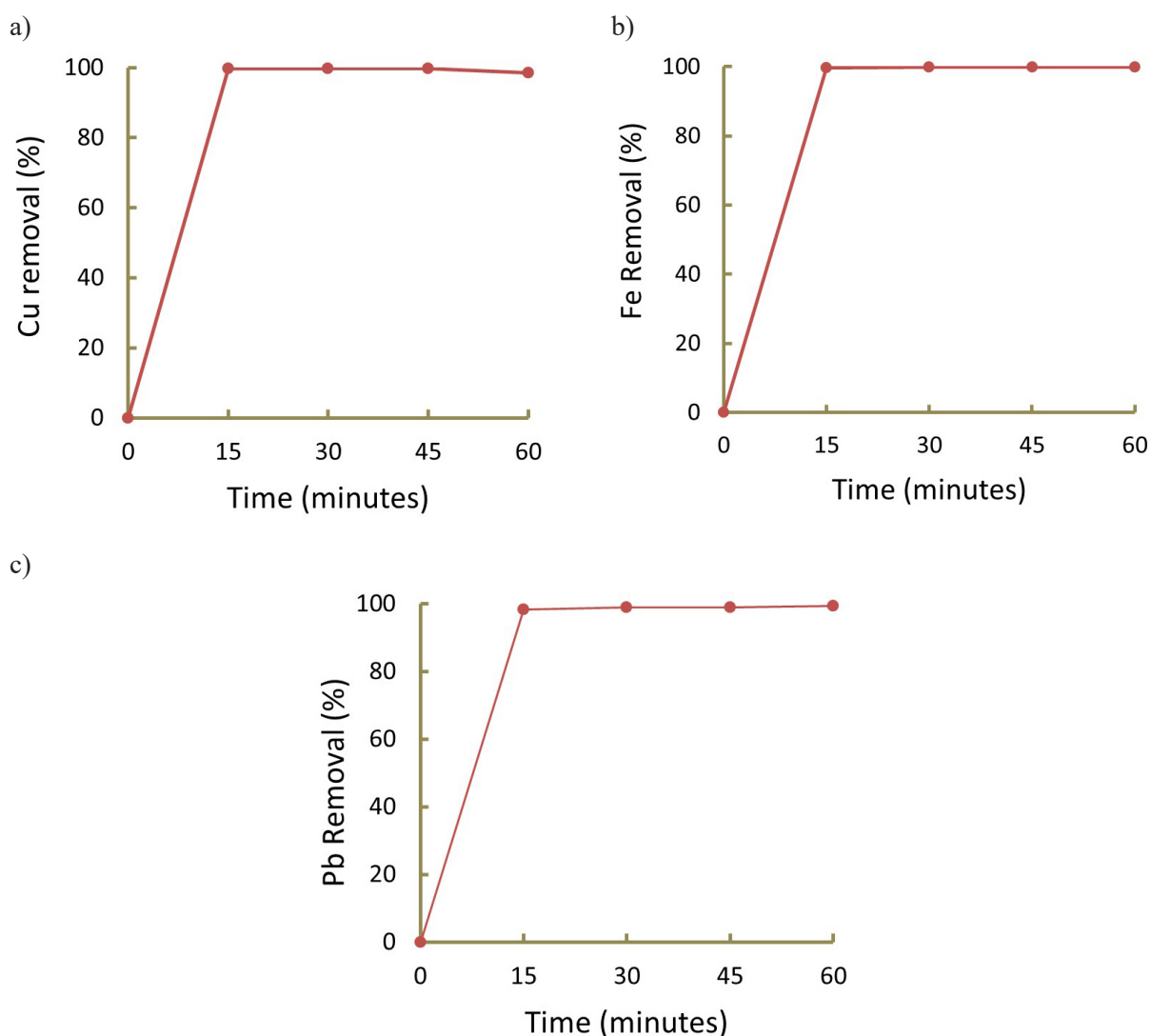

Figure 7. Effect of photocatalyst dose on removal percentage of Cu, Fe, and Pb after 30 minutes of irradiation

a)

b)

c)

Figure 8. Effect of time on removal percentage of (a) Cu metal, (b) Fe metal, and (c) Pb metal

Effect of irradiation time on removal percentage of Cu, Fe, and Pb in the photocatalysis process

The effect of time was studied by analyzing the content levels of each metal at 0, 15, 30, 45, and 60 minutes. The data presented is the result of photocatalysis with a pH value of 7 and a photocatalyst dose of 0.5 gram/L. The effect of time on the concentration of heavy metals can be seen in Figure 8.

On the basis of Figure 8, irradiation time greatly affects the removal percentage of each metal in the first 15 minutes. After 15 minutes, the treatment did not significantly affect the percentage of metal removal anymore. This is in line with what was confirmed by (Le et al., 2019) in their research on heavy metal removal using a photocatalytic process which explained that the percentage of Cu removal was close to 100% in

the first 15 minutes. However, in the study of Le et al., the percentage of Pb removal was only up to about 80%. This is possible because the initial levels of Pb metal and the light source in this study were different from those of previous researchers. In those previous studies, the initial metal content was 50 mg/L, and a light source used was a UV lamp.

This study also analyzed the levels of COD and TSS before and after photocatalysis treatment. This aims to determine whether the levels of COD and TSS in wastewater have met the environmental quality standards. From the results of the initial analysis, the COD levels in wastewater are very high at 24,600 mg/L and very far above the quality standard of 100 mg/L. In turn, the TSS level in the wastewater after the photocatalysis process is 12 mg/L which is below the quality standard of 200 mg/L. The result obtained is that the photocatalysis process can reduce the

COD levels in laboratory wastewater by 31.91% so that COD reaches 16,950 mg/L, but it does not meet the quality standards. It is recommended to continue the treatment for the pollutant organic content by other appropriate methods.

CONCLUSIONS

The pH value affects the decrease in heavy metal levels of Cu, Fe, and Pb. The optimum pH value for the removal percentage of each metal is: pH 7–8 for Cu (99.70%), pH 6 for Fe (99.91%), and pH 8 for Pb (99.69%).The catalyst dose affects the reduction of Cu, Fe, and Pb of heavy metal levels. The higher the catalyst dose, the higher the percentage of heavy metal removal tends to be. In the photocatalysis of synthetic wastewater, a high removal percentage of more than 99% was achieved by using 0.1 g/L catalyst. Irradiation time should affect the decrease of Cu, Fe, and Pb heavy metal levels. The optimum decrease occurred in the first 15 minutes of solar irradiation where the removal percentage was close to 100%. After 15 minutes, the decrease in metal content was no longer significant. The photocatalysis treatment by using ZnO photocatalyst under solar irradiation can reduce almost 100% the heavy metals content in the laboratory wastewater, which meets the environmental quality standard for Cu, Fe, and Pb.

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