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Recovery Ion Cu(II) Using Precipitation Method with NaOH for Methylene Blue Degradation

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Abstract. Copper (II) which is unbiodegradable is difficult to be decomposed by microbes, so it needs special handling, one of which is by precipitation method with NaOH as the precipitating agent. The purpose of this study was to obtain CuO material, characterize the precipitate using FTIR, XRD and DRS-UV as well as its photocatalytic activity with methylene blue. The research method was started by adding dropwise 0.1 M NaOH solution into 0.1 M $CuSO_4$ solution until a precipitate was formed. The precipitate was then dried at 100 °C and then calcined with variations in temperature of 400, 500, 600, and 700 °C for 24 h. The product was characterized using FTIR, XRD and DRS-UV. Then the product was examined for photocatalytic test to degrade methylene blue with time variation of 0, 30, 60, 90, 120 and 150 min. The results showed that the black CuO material was successfully synthesized at 600 and 700 °C was indicated by the presence of Cu(II)-O stretching vibrations. The product has monoclinic crystals and a copper oxide band-gap value of 1.53 eV. The photocatalytic activity test of the product on the degradation of methylene blue dye followed the second-order reaction kinetics and the rate constant values at 600 and 700 °C were 29.25 x 10^{-4} $M^{-1}s^{-1}$ and 30.99 x10^{-4} $M^{-1}s^{-1}$, respectively.

INTRODUCTION

The problem of heavy metal waste remains the focus of handling studies, because inorganic components are so harmful to the environment such as PCB waste containing metals , Cu, Fe, Al, Pb, Zn, Ni, Ag and Au [1] [2]. Copper which is unbiodegradable is difficult to be broken down by microbes, so it needs special handling. Whereas copper (II) can be made into more a useful compound, namely copper (II) oxide, one of which is as a photocatalytic compound [3] [4]. Photocatalytic is a reaction that involves the absorption of light by a catalyst. Photocatalytic utilizes semiconductors as catalysts that are activated by ultraviolet (UV) light to decompose organic compounds [3][4][5][6][7][8].

Various methods have been used to uptake Cu(II), one of which is the precipitation method. In this study the precipitation method was chosen because it requires low energy and temperature, as well as relatively low of 100, 200 and 300°C produces different characteristics. At a temperature of 100°C it produces a mixture of $Cu(OH)_2$ and Cu_2O crystals, while at a temperature of 200 and 300°C it produces CuO crystals [9].

Based on the various studies above, this research was carried out with the aim of synthesizing CuO using the precipitation method with the precipitating agent NaOH with 100°C heating and calcination variations of 400, 500, 600, and 700°C then the precipitate was characterized by XRD. The best synthesized product was tested for photocatalytic activity against the degradation of methylene blue dye.

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EXPERIMENTAL

Instruments and materials

Instruments: Analytical balance (Ken Als 220-4N), a set of glassware, 75 mL porcelain cup, filter paper, Hot Plate and Stirrer (cimarec SP131320-33Q), Oven, Furnace, FTIR (Frontier FT-IR 96681), UV-Vis Spectrophotometer (Genesys 105), DRS-UV/Vis (UV 1700 pharmaspec), XRD (Shimadzu 7000), Photocatalytic reactor.
Materials: Copper sulfate pentahydrate (Merck), Sodium Hydroxide (Merck), Methylene Blue (Merck), universal pH (Merck), distilled water

Procedure

The waste used in this research is artificial waste made from 50 mLof 0,1 M $CuSO_4$ solution and 85 mL of 0.1 M NaOH added dropwise into the solution. Then the mixture was stirred for 2 h. The precipitate formed was filtered and dried at 100 °C and then calcined at 400, 500, 600, and 700 °C for 24 h. The products were characterized using FTIR,. The best products were then characterized by XRD and DRS UV/Vis and tested for their activity to degrade methylene blue with time variations, 0, 30, 60, 90, 120 and 150 min.

RESULTS AND DISCUSSION

The process of copper precipitation from Cu(II) solution is as follows [9]:

$$CuSO_4.5H_2O(s) + H_2O(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + 6H_2O(aq) \quad (1)$$

$$Cu^{2+}(aq) + 2NaOH(aq) \longrightarrow Cu(OH)_2(s) + 2Na^{+}(aq) \quad (2)$$

The next stage is the calcination process. According to [10] the heating reaction of solid $Cu(OH)_2$ is:

$$Cu(OH)_2(s) \longrightarrow CuO(s) + H_2O(g) \quad (3)$$

Characterization

1. FTIR Analysis

The results of the FTIR analysis can be seen in fig. 1. Figure 1(a) is the result of the synthesis of copper oxide at 100°C heating (without calcination). The results of the FTIR analysis showed an absorption peak in the wave number region of 484 cm^{-1} indicating the stretching vibration of the Cu(II)-O metal bond [11]. At the absorption peak of 1137 cm^{-1}, it shows the bending vibration of Cu-O which still has a hydroxyl group (OH) on the surface [12].

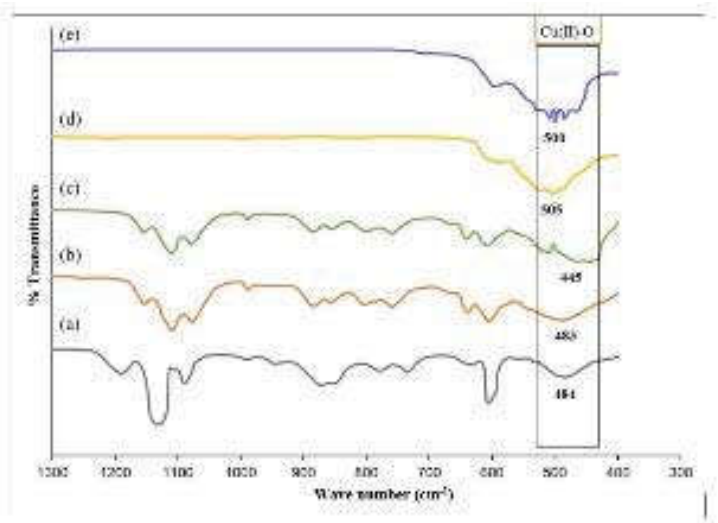

FIGURE 1. FTIR graph of CuO synthesis at (a) heating temperature of 100°C and calcination temperature (b) 400°C (c) 500°C (d) 600°C and (e) 700°C

Figures 1(b) and (c) are the results of the synthesis of copper oxide at calcination temperatures of 400 and 500°C. The presence of sharp peaks at wave numbers 500 and 445 cm^{-1} indicates the presence of Cu(II)-O stretching vibrations [11]. Figures 1(d) and (e) are the results of the synthesis of copper oxide at calcination temperatures of 600 and 700°C. The FTIR analysis results on the two samples only showed 1 sharp absorption peak, namely at wave numbers 505 and 500 cm^{-1} which indicated the presence of vibrations from the Cu(II)-O bond [11]. The absence of sharp peaks at other wave numbers confirm that at calcination temperatures of 600 and 700°C CuO has formed without any impurities $Cu(OH)_2$ and Cu_2O. Calcination temperature samples of 600°C and 700°C were then characterized using XRD to determine their crystal structure.

2. XRD Analysis

This characterization was carried out on three samples, namely samples before calcination (heating at 100 °C), samples calcined at temperatures of 600 and 700°C. Figure 2 is an XRD diffractogram for the three samples. Diffractogram identification was carried out by comparing 2Θ of the highest peak in the diffractogram of the three samples with the diffractogram peak of the database RRUFF ID R120076 for monoclinic crystal structure (cells a,b,c are 4.6697(8) Å ; 3.4121(8) Å and 5.128(1)Å with angles α, β and γ are 90° ; 99.46(5)° dan 90° respectively) . RRUFF ID R100193 for orthorhombic crystal structure ((cells a,b,c are 2.933(2)Å ; 10.545(5)Å and 5.228(5)Å with angles α, β and γ equal to 90°)

In fig. 2 (a) the diffraction peaks at 2Θ of 11.34, 16.50, 18.04 and 28.01° indicate that the sample has an orthorhombic crystal structure and the diffraction peaks at 2Θ of 35.63, 58, 04 and 61.75° indicate that the sample has a monoclinic crystal structure. From the description, it is confirmed that CuO from heating 100°C (before calcination) has a mixed crystal structure, namely monoclinic and orthorhombic.

In fig 2 (b) and (c) are copper oxide synthesized at calcination temperatures of 600 and 700°C all of the diffraction peaks correspond to the RRUFF ID R120076 database for monoclinic crystal structures. The relative intensity value of the diffraction peak of the calcined sample at 700°C is higher and sharper than the 600 calcined sample and the uncalcined sample, so that the crystallinity of the 700 sample is higher than the 600 calcined sample and the sample that has not been calcined. Samples at calcination temperatures of 600°C and 700°C were used for further analysis, namely the determination of the band-gap.

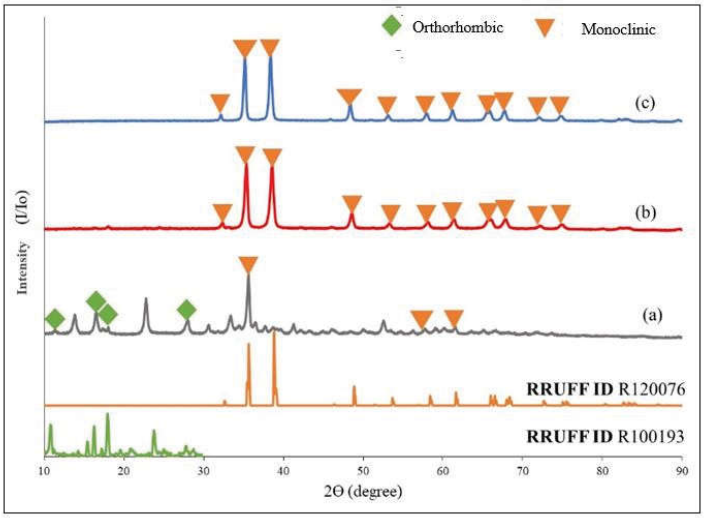

FIGURE 2. XRD diffractogram of synthesized CuO (a) with 100°C heating (b) 600°C calcination temperature and (c) 700°C calcination temperature along with databases RRUFF ID R100193 and RRUF ID R120076

3.Determination of Band-gap CuO value

The band-gap value of copper oxide can be determined by using the DRS-UV/Vis spectrophotometer. DRS-UV/Vis is based on the measurement of the intensity of UV-Vis light reflected (scattered) by the sample, the measurements are carried out at a wavelength of 200-800 nm. Figure 3 shows the relationship between Eg and $[F(R)h\upsilon]^{1/2}$ which is used to determine the band-gap value of the synthesized CuO compound.

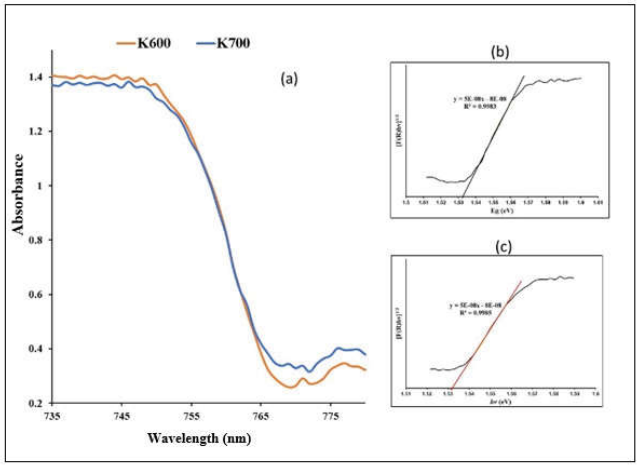

FIGURE 3. Graph of DRS-UV/Vis (a) absorbance vs. Wavelength and band-gap CuO calcination temperature of (b) 600°C and (c) 700°C.

Band-gap values of copper oxide compounds were obtained from the Kubelka-Munk calculation, namely graphing the relationship between hυ as the x-axis and $[F(R)h\upsilon]^{1/2}$ as the y-axis and extracting straight lines on the spectra of hv vs [F(R)hv]1/2 to intersect the energy axis (x axis). The band-gap value of copper oxide at calcination temperatures of 600 and 700°C is 1.53 eV. This value is in the CuO band-gap range, which is between 1.2-1.9 eV [13].

4. Photocatalytic Activity Test of CuO

The photocatalytic activity test of copper oxide was carried out in 5 ppm methylene blue (MB) solution as a dye model using 0.1 gram of synthesized CuO powder. Figure 4 shows the percentage degradation of MB dye by CuO synthesized at calcination temperatures of 600 and 700°C. The percentage of MB degradation is obtained by the following equation [3][12][14]:

$$\% \text{ Degradation} = \frac{C_0 - C}{C_0} \text{ x } 100\% \qquad (4)$$

Where C_o is the initial concentration of MB solution and C is the concentration after the degradation process. The percentage of MB degradation without light at CuO at calcination temperature of 600 and 700°C was 16.39 and 19.97%, respectively.

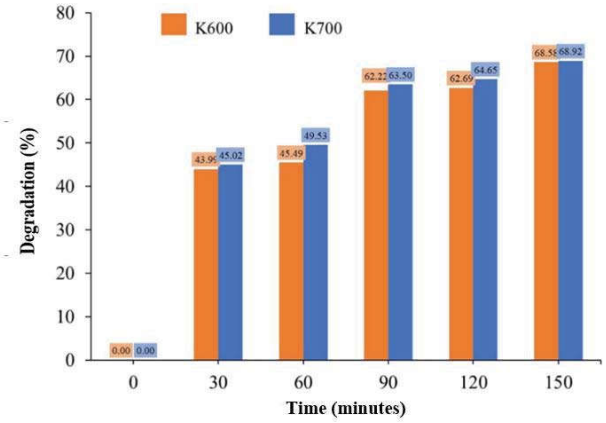

FIGURE 4. MB degradation percentage with time variation

At a calcination temperature of 600°C after the photocatalysis process with light successively with a time variation of 30, 60, 90, 120, and 150 min are 41.82; 43.50; 62.22; 62.74 and 69.32%. While at a temperature of 700°C the percentage of MB degradation using CuO after the photocatalysis process with light successively with variations in time of 30, 60, 90, 120, and 150 minutes are 42.99; 48.02; 63.64; 64.93 and 69.71%, respectively. From these data, it shows that there is an increase in the percentage of MB degradation with increasing photocatalysis time[15].

Photocatalytic activity of synthesized CuO against MB dye can be determined by calculating the rate of degradation through chemical kinetics. The degradation activity of MB dye follows the second-order reaction kinetics which is expressed by the formula [16]:

$$\frac{1}{C} = kt + \frac{1}{C_0} \qquad (5)$$

Where C_o is the initial concentration (ppm), C is the concentration at time t (ppm), k is the reaction rate constant and t is time (min). Comparison of the correlation coefficient (R^2) on the graph of the first-order and second-order reaction rates on MB degradation by CuO at temperatures of 600 and 700°C. The graph of the second-order reaction in the photocatalytic process for MB degradation can be seen in fig. 5.

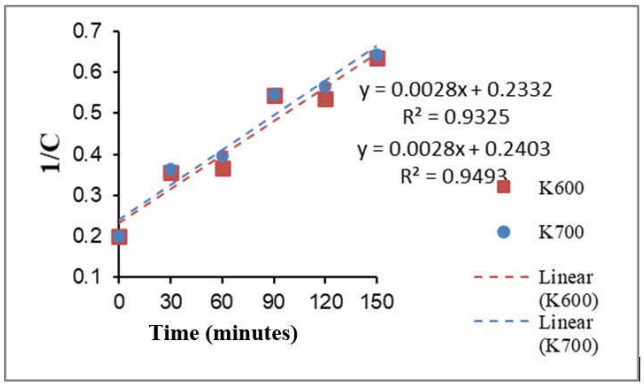

FIGURE 5. Graph correlation between 1/C vs t for MB degradation

The value constant for the degradation rate of MB by product at calcination temperatures of 600 and 700°C for MB degradation was 29.25 x 10^{-4} $M^{-1}s^{-1}$ and 30.99 x 10^{-4} $M^{-1}s^{-1}$, respectively. Based on the value of these constants, the higher the value of the reaction rate constant obtained, the greater the photocatalytic activity, so that the best MB solution degradation rate is using CuO at a calcination temperature of 700°C.

CONCLUSION

The results of the synthesis using the precipitation method at calcination temperatures of 600 and 700°C produced black CuO crystals. At calcination temperatures of 600 and 700°C the results of characterization using FTIR, XRD, and DRS-UV/Vis showed as follows the presence of stretching vibrations of Cu(II)-O, the product has a monoclinic crystal system and a band-gap value of 1.53 eV. The results of the photocatalytic activity test of the product at calcination temperatures of 600 and 700°C for MB dye degradation followed second-order reaction kinetics and the rate constant values were 29.25 x 10-4 $M^{-1}s^{-1}$ and 30.99 x 10-4 $M^{-1}s^{-1}$.

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