

Modification of Activated Carbon from Coconut Shell Charcoal with Copper (CuCl_2/AC , $\text{Cu}(\text{OH})_2/\text{AC}$, CuO/AC) for Adsorption of Paracetamol Contaminant

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ABSTRACT

This study provides information about the physicochemical properties and performance of activated carbon combined with copper to remove paracetamol from waste models. The activated carbon (AC) comes from coconut shell charcoal. CuCl_2 was used as the copper source which then combined with activated carbon (AC). The AC was obtained by activating the coconut shell charcoal using KOH and 500 °C calcination for 10 minutes. Carbon functionalization were done using H_2SO_4 6M as an oxidizer and temperature of 80 °C for 3 hours. The impregnation of activated carbon with CuCl_2 produces CuCl_2/AC , then the CuCl_2/AC was reacted with NaOH 5M to form precipitation of $\text{Cu}(\text{OH})_2/\text{AC}$. CuO/AC composite was finally produced by calcining the $\text{Cu}(\text{OH})_2/\text{AC}$ to 950 °C for 5 minute. The composite was characterized by FTIR, SEM-EDX, XRF and X-ray diffraction. The adsorption of paracetamol with CuO/AC composite gave the best results with 95.56% efficiency.

Keywords: CuCl_2/AC composite, $\text{Cu}(\text{OH})_2/\text{AC}$, CuO/AC , adsorption.

INTRODUCTION

Pharmaceutical industry is one of source of the increasing pharmaceutical waste concentration in aquatic ecosystems. Pollution made from the pharmaceutical waste causes metabolic disorders in organisms in the ecosystem, such as accumulation in body tissues, damage to the reproductive system, inhibition of cell growth, changes in organism's behaviour and decrease in water quality [1].

The pharmaceutical industry produces liquid waste from the production process, the cleaning of equipment, and laboratory activities. The liquid waste is toxic and contains several dissolved organic and inorganic compounds [2]. One of the organic wastes produced from the pharmaceutical industry is paracetamol waste. Paracetamol, Figure 1, is a compound known to reduce fever and pain. However, in high concentration (4000 mg/L for adults), it can have a negative impact on health and may cause death [3].

Various ways can be used to overcome water pollution by paracetamol waste, namely by means of oxidation, ozonation, perozone, and photocatalysis [3]. The adsorption method can also be applied. The adsorption method has the potential as one of the effective methods because it is more affordable than some other methods, efficient, and easy to apply [4]. Adsorption is the process by which atoms, ions or molecules from substances such as gases,

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liquids or dissolved solids or adsorbates are concentrated in the porous surface of an adsorbent [5]. Examples of materials that can be used as adsorbents are alumina, zeolite, activated carbon, biomass, polymer and silica gel [6]. Adsorbents from activated carbon have been widely used and developed, because they are non-toxic, abundant, economical and biodegradable. Activated carbon is effective in tackling polluted water because it has a porous structure, has a large surface area and has plenty of functional groups. This makes activated carbon able to distribute pollutants on the surface with a large capacity so that the reactants can enter and bind to the adsorbate [4].

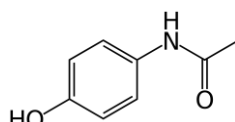


Figure 1. Structure of paracetamol [3]

Development is mostly done to improve the performance of activated carbon as an adsorbent. Research conducted by Dutta et al. [7] showed that the adsorption of acetaminophen or paracetamol was carried out with activated carbon from tea waste with an adsorption capacity of 99.42 mg/g at pH 3 [7]. Biochar, from activated patchouli biomass with CoCl_2 and modified with CrCl_3 , ZnCl_2 , Cr_2O_3 , and ZnO , for paracetamol adsorption showed that the adsorption of paracetamol by $\text{Cr}_2\text{O}_3/\text{Biochar}$ composites was 3.5 times higher than by $\text{CrCl}_3/\text{Biochar}$, and $\text{ZnO}/\text{Biochar}$ has adsorption capacity that 3 times higher than that of $\text{ZnCl}_2/\text{Biochar}$ [8]. Meanwhile CuO/AC obtained from the oxidation with peroxide gives phenol adsorption percentage up to 98% [9].

In this research, copper salts were used. Cu(II) have a positive charge so they have an affinity for polar organic compounds such as paracetamol. Anions that are bound to Cu(II) (oxides, hydroxides, chlorides) will give different ionic bond strengths due to different ion size and charge. In addition, different types of anions will also attract different dipoles from paracetamol polar group. Both of these factors are expected to affect the affinity of the adsorbent in the adsorption of paracetamol. Therefore, this study aims to examine the effect of these anion types on the adsorbent surface functional groups and study the adsorption of paracetamol by this adsorbent.

EXPERIMENTAL

Chemicals and Instrumentations

Chemicals were obtained from Merck (except paracetamol) and used without further purification, namely KOH (4 M), HCl 37% (1 M), H_2SO_4 96% (6 M), CuCl_2 (0,2 M), NaOH (5 M), and paracetamol (Pharmacy). Coconut shell charcoal as source of activated carbon was obtained from local market.

Instrumentations used in this work are Fourier-Transform Infrared Spectroscopy (8400S-FTIR), Scanning Electron Microscopy-Energy Dispersive X-Ray (Hitachi S-4200), UV-Vis spectrophotometer (Shimadzu-1601A), X-ray Powder Diffraction (PANalytical Type X'Pert PRO), and Furnace (6000-Branstead Thermolyne).

Preparation of CuCl_2/AC , $\text{Cu(OH)}_2/\text{AC}$ and CuO/AC Composites

A 1 kg of coconut shell charcoal was pounded to get fine powder with particle size of 30-60 mesh. A 10 g of the fine powder was taken and mixed with 100 mL KOH 4 M. The mixture then shaken for 2 hours at 175 rpm at room temperature. Next, the mixture was decanted and

the precipitate was dried (105°C), and followed by calcination to 500°C (maintained for 10 minutes at 500°C). The solid then washed several times with 1 M HCl and water in sequence and finally dried (105°C, 6 hours). This activation procedure is based on previous study [11].

Activated carbon was oxidized with 6 M H₂SO₄ solution with a ratio of 1:10 (g/mL). The oxidation reaction temperature was set at 80°C for 3 hours. The oxidized activated carbon then washed with water and dried at 70°C for 24 hours.

The following procedure refers to Hongo et al. [10] by replacing sulfate salt with chloride salt and also refers to Meilia et al. [11] by replacing impregnation of Zn-Fe-LDH and ZnFe₂O₄ with CuCl₂, Cu(OH)₂, and CuO. Oxidized activated carbon (0.5 gram) was mixed with a solution of CuCl₂ (0.20 M; 50 mL) and then shaken for 1 hour at 175 rpm. Next, the precipitate was isolated and dried at 70°C for 24 hours. The product then divided into 2 parts, in which one of them was coded as CuCl₂/AC.

For the other part, CuCl₂/AC was added drop by drop with NaOH 5 M solution while stirring to pH 7 and heated at 80°C for 3 hours in a closed vial. The mixture was then filtered, washed with distilled water, and dried at 70°C for 24 hours to produce Cu(OH)₂/AC composite. The product was also divided into 2 parts. One part was characterized as Cu(OH)₂/AC, and the other part was calcined to 950°C for 5 minutes, in which CuO/AC composite was produced.

Adsorption Test of Paracetamol

The CuCl₂/AC, Cu(OH)₂/AC, and CuO/AC composites are all used for the adsorption test using batch method. Each composite (0.1 g) was mixed with 25 ml of paracetamol 100 mg/L then the solution was shaken at 200 rpm for 24 hours at room temperature. Next, the solution was filtered off and the concentration of paracetamol after adsorption was analyzed by UV-Vis spectrophotometry. The absorbance data was used to determine the concentration of paracetamol after adsorption using the standard curve equation. Data on paracetamol concentration before and after adsorption were used to determine the adsorption percentage. This adsorption test was repeated 3 times for each composite.

Data analysis

The adsorption percentage is calculated based on equation 1.

$$\text{Adsorption percentage (\%)} = \left[\frac{C_o - C_s}{C_o} \right] \times 100\% \quad (1)$$

Where C_o is paracetamol concentration before adsorption (ppm) and C_s = paracetamol concentration after adsorption (ppm). Furthermore, the amount of adsorbed paracetamol (q_e) is also calculated, based on equation 2.

$$\text{Adsorbed paracetamol} = \left[\frac{(C_o - C_s) \times V}{W} \right] \text{ mg/g} \quad (2)$$

Where C_o is paracetamol concentration before adsorption (in ppm). C_s is paracetamol concentration before adsorption (in ppm). V is a total volume of paracetamol solution (in L), and W is adsorbent mass (in g).

RESULT AND DISCUSSION

This work studies CuCl₂/AC, Cu(OH)₂/AC and CuO/AC composites for paracetamol adsorption. The composites were prepared in several stages from CuCl₂/AC to Cu(OH)₂/AC to

CuO/AC, respectively. The impregnation of different types of copper(II), namely chloride, hydroxide, and oxide, into activated carbon and its effect toward paracetamol adsorption is discussed.

FTIR Characterization

FTIR analyses was conducted to identify possible functional groups which might be involved in the paracetamol adsorption and to determine possible differences of the composite based on frequency shift. All three infrared spectra of the composites (Figure 1) were compared each other and the interpretation of the bands is presented in Table 1.

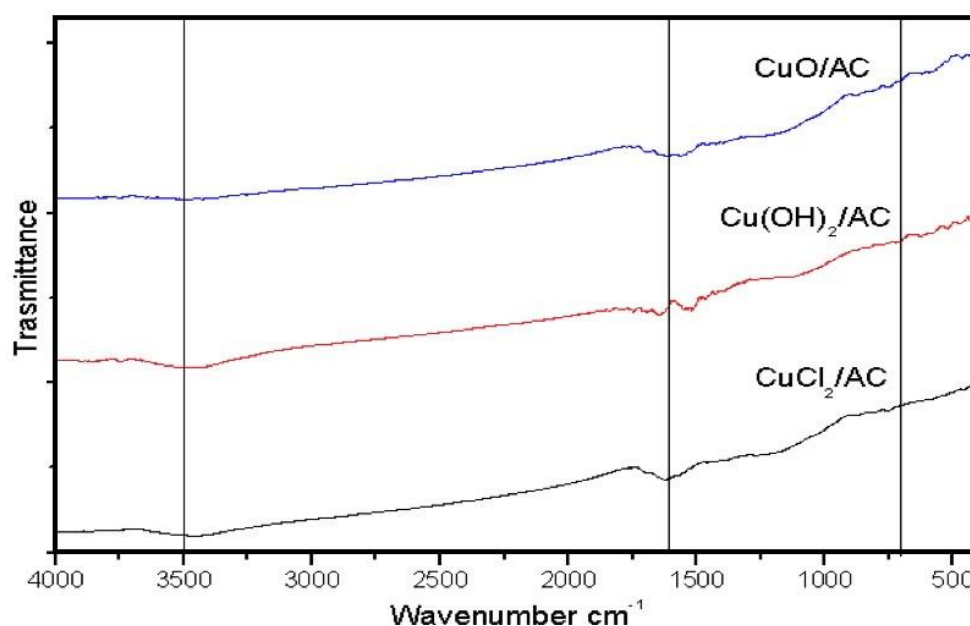


Figure 1. The infrared spectra of CuCl₂/AC, Cu(OH)₂/AC, and CuO/AC composites

Table 1. Interpretation of infrared spectra of the composites

CuCl ₂ /AC (cm ⁻¹)	Cu(OH) ₂ /AC (cm ⁻¹)	CuO/AC (cm ⁻¹)	References	Assignments
3458.89	3451.18	-	3750–3000 [12]	$\nu(\text{O-H})$
1620.98	1647.86	1617.00	1675–1500 [13]	$\nu(\text{C=O})$
1404.84	1464.63 1516.71	1563.00	1500–1400 [13]	$\nu(\text{C=C})$
1267.91	1132.90	1238.98	1200–1000 [14]	$\nu(\text{C-O})$ <i>in-plane</i>
903.39	-	-	900–800 [11]	$\nu(\text{C-Cl})$
754.88	629.51	752.95 876.38	900–400 [12,14]	$\nu(\text{Cu-O})$

In all composites, peaks that correspond to $\nu(\text{C=O})$, $\nu(\text{C=C})$, and $\delta(\text{C-O})$ in-plane from the activated carbon are observed. An absence of broad peak around 3400 cm⁻¹ in CuO/AC, which initially observed in CuCl₂/AC and Cu(OH)₂/AC, suggest that all the water and hydroxyl groups are fully converted into the oxide group due to high temperature calcination process.

The washing process during Cu(OH)₂/AC preparation is also completed as indicated from the absence of peak around 900 – 800 cm⁻¹ in both Cu(OH)₂/AC and CuO/AC.

Powder XRD Characterization

XRD analyses was done to identify the crystal structure that formed in the CuO/AC composite. The powder pattern of CuO/AC composite (2θ = 10–90) obtained from this work is shown in Figure 2, whereas the power XRD data is presented in Table 2. The powder XRD data of CuO/AC has characteristic peaks for CuO (*Tenorite*) crystals, compared to JCPDS No. 41-254, which is close to 35.9°, 39.0° and 43°. This indicates that the impregnated activated carbon after the calcination treatment was in the form of CuO.

Tabel 2. Powder XRD data of CuO/AC composite

2θ Angle (°)	Height (cts)	FWHM (°)	d-spacing (Å)	Relative Intensity (%)
36.3132	25.88	0.4723	2.47400	41.63
43.2418	62.17	0.2362	2.09230	100.00
50.3200	11.91	1.1520	1.81184	19.16

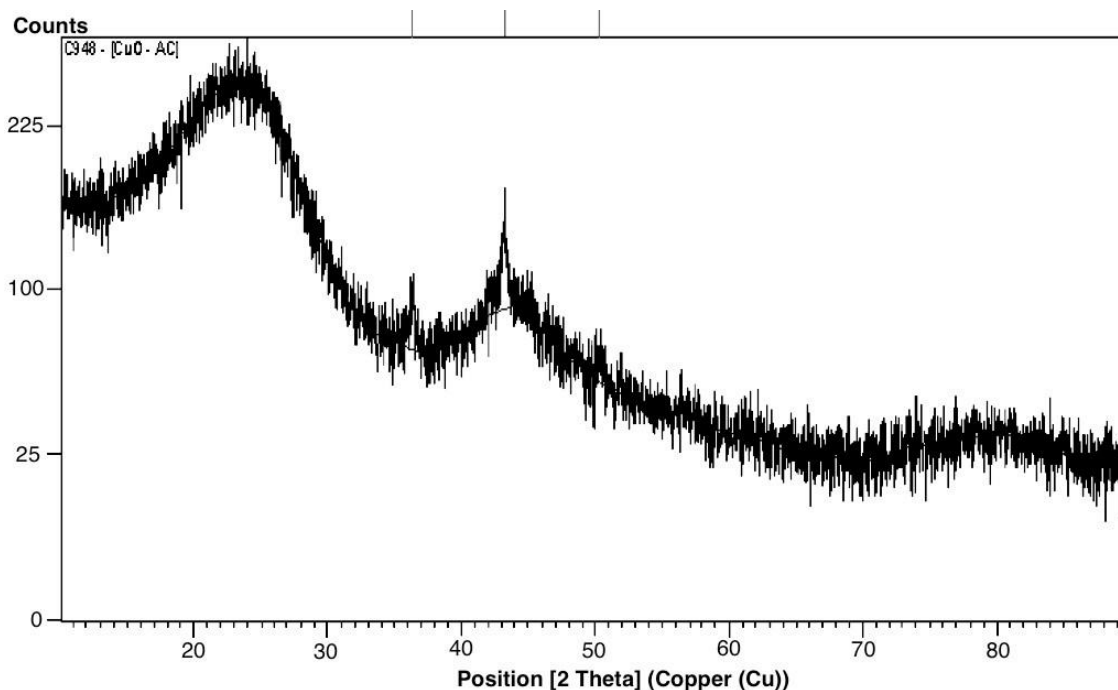


Figure 2. Powder XRD pattern of CuO/AC composite

SEM-EDX Characterisation

SEM analyses was conducted to study the morphology of composite's surface, whereas EDX analyses was done to determine the composition of copper in the composite. The SEM image, given in Figure 3, shows that the activated carbon surface has some holes and some smaller white solid particles which indicates the presence of CuO. EDX data, shown in Figure 4, reveals

that the CuO/AC composite contains $13.25 \pm 1.31\%$ of Cu, $12.24 \pm 3.34\%$ of O, and $74.53 \pm 4.65\%$ of C atoms.

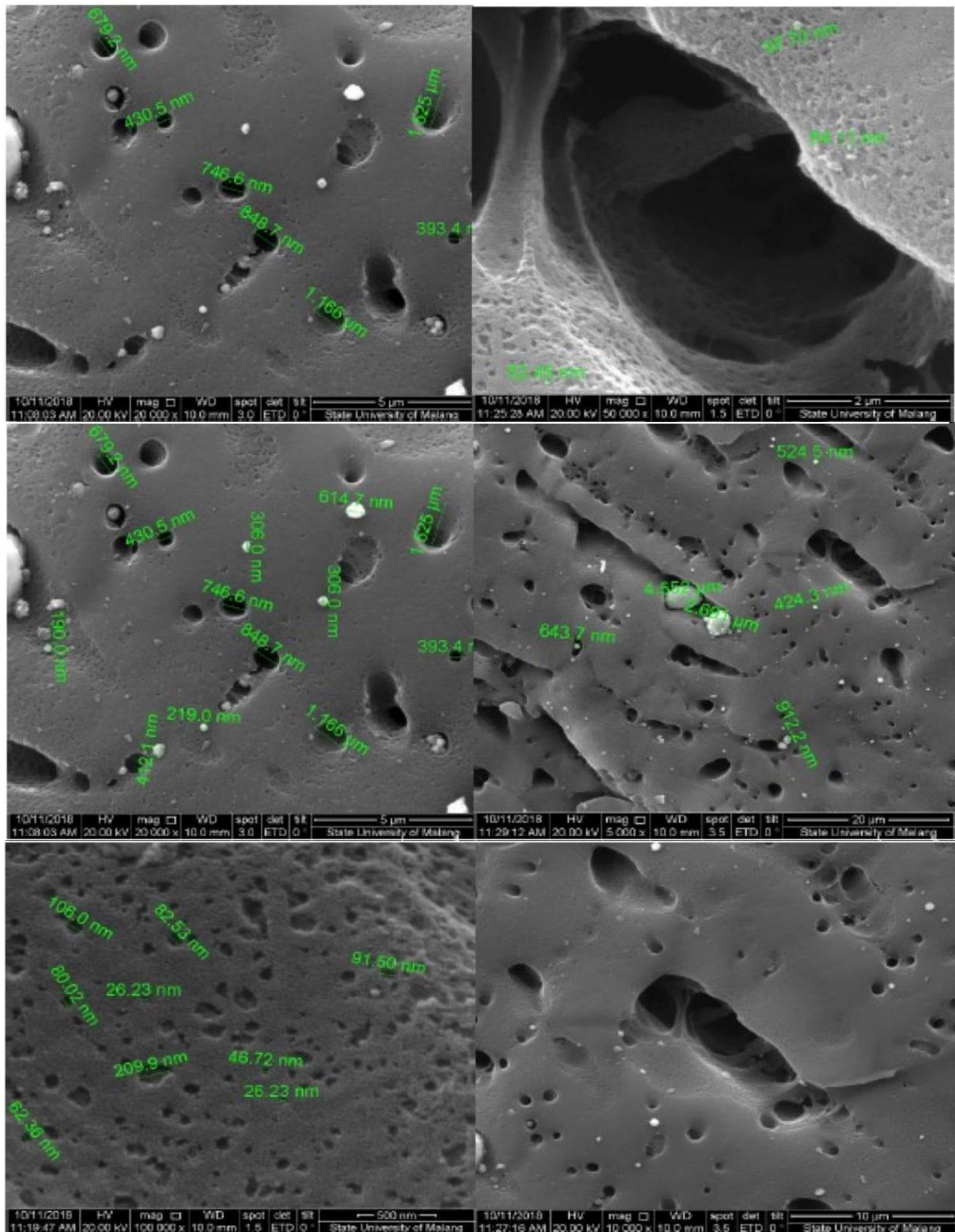


Figure 3. SEM images of CuO/AC composite in different expansion

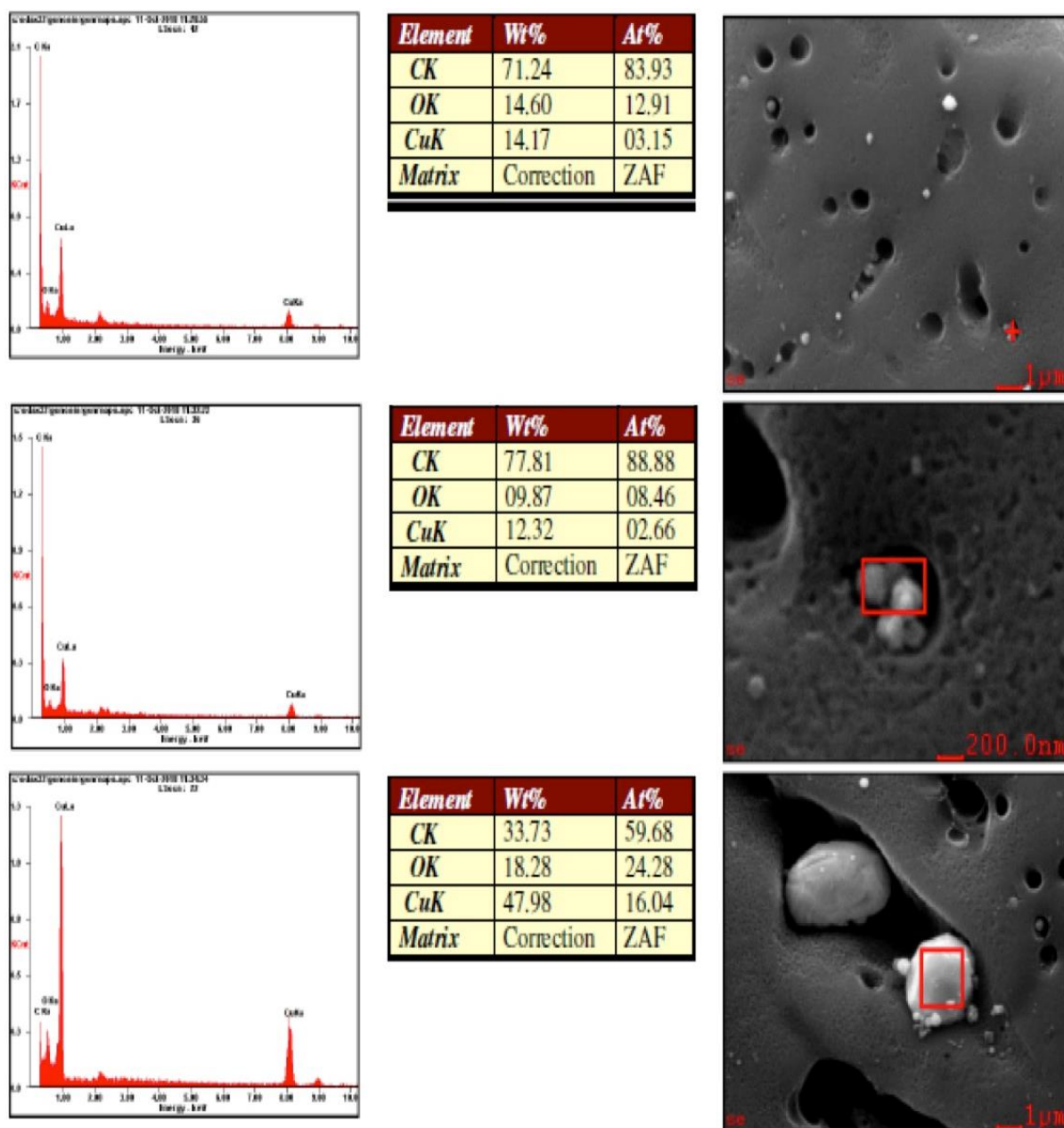


Figure 4. Energy dispersive X-ray (EDX) data of CuO/AC

Adsorption Test

The adsorption tests for paracetamol were conducted to all composites and the data is presented in Figure 5. The amount of adsorbed paracetamol (q_e) and adsorption percentage are increasing from composite CuCl_2/AC to $\text{Cu}(\text{OH})_2/\text{AC}$ and CuO/AC , successively, in which the significant incline was observed between $\text{Cu}(\text{OH})_2/\text{AC}$ and CuO/AC . The hydroxide group of $\text{Cu}(\text{OH})_2$ increases the number of polar sites in the composite which then increases the hydrogen bond between $\text{Cu}(\text{OH})_2$ and the polar groups in paracetamol. Paracetamol has functional group of $\text{C}=\text{O}$, $-\text{OH}$, and $-\text{NHR}$ (Figure 1), and these groups are likely form hydrogen bonding with the $-\text{COOH}$ group from the activated carbon [8].

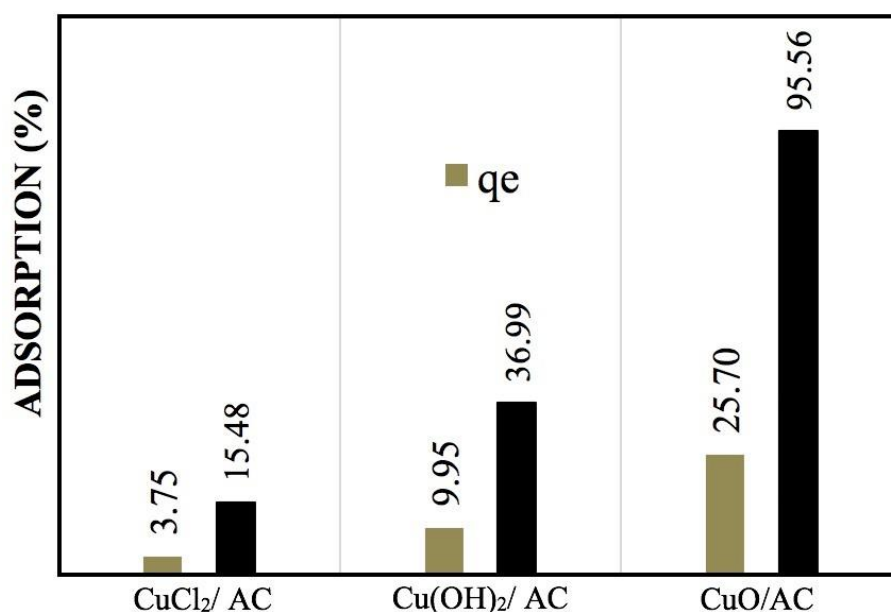


Figure 5. The amount of adsorbed paracetamol (q_e) and adsorption percentage of CuCl₂/AC, Cu(OH)₂/AC, and CuO/AC composites.

Adsorption percentage using CuO/AC composite was higher than Cu(OH)₂/AC composite because the oxide of CuO has an ionic dipole attraction force with paracetamol's polar groups. Furthermore, calcination during CuO/AC composite preparation can cause dehydration, dehydroxylation, and evaporation of Cl⁻ as chlorine gas, thus the activated carbon pores become wider. In addition, the size of CuO is much smaller than the size of Cu(OH)₂. Combination of these factors led to more available pores on the composite's surface that can be occupied by paracetamol molecules. The adsorption test showed an increase in the adsorption percentage in the order of CuCl₂/AC < Cu(OH)₂/AC << CuO/AC, in which the adsorption value of CuO/AC was 3 times higher than that of Cu(OH)₂/AC and 6 times higher than that of CuCl₂/AC.

CONCLUSION

Composites of CuCl₂/AC, Cu(OH)₂/AC, and CuO/AC were synthesized successively in three stages by co-precipitation using CuCl₂ and activated charcoal (AC) from coconut shell charcoal, which was activated by KOH and functionalized with H₂SO₄. The adsorption percentages of CuO/AC was three times higher than that of Cu(OH)₂/AC and six times higher than that of CuCl₂/AC with the highest values obtained by the CuO/AC composite (25.70 mg/g or 95.56%).

CONFLICT OF INTEREST

Authors declare no conflict of interests.

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