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Synthesis and Characterization of Copper Nanoparticles using Different Concentration of Rice Straw

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ABSTRACT

New copper nanoparticles (CuNPs) have been synthesized via chemical reduction method in the presence of rice straw as supports and seaweed as a stabilizer. Characterizations of the CuNPs were carried out using UV-visible spectroscopy (UV-vis), Fourier Transform Infrared (FT-IR), Field Emission Scanning Electron Microscopy (FESEM), and Energy Dispersive X-ray (EDX). The UV-vis adsorption spectra confirm the formation of CuNPs through the peaks of the surface plasmon resonance (SPR) bands around 500 to 600 nm. Morphological characterization showed the formation of a spherical structure of the CuNPs. Similarly, EDX spectra showed that the nanoparticles produced are copper based. The size of nanoparticles formed by this method was controlled easily by using different concentration of rice straw.

Keywords: Chemical Reduction, Copper Nanoparticle, Rice Straw; Seaweed

INTRODUCTION

Studies on metal nanoparticles are increasing significantly for the past few years due to their interesting properties and applications that cut across different areas of science and technology. Their applications in the field of nanotechnology is highly dependent on the preferred sizes and shapes, hence, it is crucial to have controlled preparation of these metal nanoparticles (Shameli *et al.,* 2012) . Among all the metallic nanoparticles nowadays, silver and gold metals nanoparticles are very popular among many researchers (Wani *et al.,* 2011). However, in recent time, copper nanoparticles have attracted so much attention among many scientists. This is because copper is relatively cheaper than gold and silver but at the same time have almost the same features as the noble metals (Maity *et al.,* 2013). Even though copper tends to oxidize during the nanoparticle's preparation steps, it is still considered as a better alternative for gold and silver in the areas of thermal conducting as well as micro-electronics. In addition, its unique novel optical, catalytic, mechanical, electrical, magnetic and heat conduction properties have also captured a lot of attentions. Copper nanoparticles can be synthesized by many different methods including polyol process, metal vapour synthesis, laser ablation, micro-emulsion techniques and thermal reduction (Gedanken, 2004). Other than that, microwave irradiation, liquid phase reducing sol–gel and electrochemistry are also other ways of synthesizing copper nanoparticles (Zain *et al.,* 2014). All these different methods have their own advantages and disadvantages. After all, chemical reduction method has been proven to be the easiest and the most effective among all the other techniques (Tan and Cheong, 2013). Musa *et al.,* (2016), reported the synthesis of copper nanoparticles stabilizer using nanocrystalline cellulose as stabilizer by chemical reduction methods. By using this method, the size and shape of the nanoparticles can easily be controlled. As a result, the method is hereby employed in the course of this study.

Rice straw (RS) is one of the residues obtained from rice cultivation procedure that is left on the field after harvest and it is apparently costly to gather/pack. Rice straw is often considered as a waste product and is always disposed by burning on the field. For every 4 tons of rice grain, 6 tons of rice straw is obtained (Khandanlou *et al.,* 2015). This results in production of about 550 million tons of rice straw in Asia each year (Khandanlou *et al.,* 2015). Rice straw is considered as one of the famous cellulose-based natural fibers, mainly consists of cellulose and hemicellulose, and is used for nanocomposites as the reinforcing filler due to its lingo-cellulosic characteristic (Khandanlou *et al.*, 2015).As a result, it is considered as one of the most abundant renewable natural polymers on the universe that has proved as one of the suitable supports for metal nanoparticles (Zhou *et al.*, 2013).

The focus of this research is to synthesize copper nanoparticles by chemical reduction using rice straw as a support. Seaweed was used as the stabilizing agent while ascorbic acid and sodium hydroxide were used as an antioxidant and pH controller respectively. Hydrazine on the other hand was added as a reducing agent. The effect of concentration of the rice straw on the characterization of copper nanoparticles produced was also examined. In this study, characterizations of copper nanoparticles were carried out using UV-visible spectroscopy, Fourier Transform Infrared (FT-IR), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray (EDX).

MATERIALS AND METHODS

Materials

All reagents in this work were of analytical grades and used as received. Rice straw was obtained from a local farm (Bukit Tinggi, Kedah, Malaysia). $CuSO_4.5H_2O$ (99%) was used as copper ions precursor and was provided by Bendosen Laboratory Chemicals. Ascorbic acid (90%) was provided by Hamburg Chemicals, while sodium hydroxide (99%) and hydrazine hydrate (35% hydrazine) were supplied by MERCK (Germany). Raw seaweed was purchased from Sabah, Malaysia. All solutions were prepared using distilled water. Glass wares utilized in the experiment were washed with distilled water and air dried before use.

Methods

Preparation of Rice Straw Powder

The rice straw obtained was washed under running water and then distilled water. It was then dried in an oven at 60 ˚C. After that, the dried rice straw was ground by a grinding machine and was sieved. Finally, the product was stored until further processing.

Preparation of seaweed powder

First, as previously described by Khanehzaei *et al.*, (2014). The seaweed was washed under running water to remove salt, dirt and foreign impurities. It was then soaked overnight (24 hr.) in distilled water to remove the yellowish colour of the seaweed. After that, the seaweed was rinsed and dried in the oven at 60 ˚C. The dried seaweed was chopped into small pieces before being blended using a hammer mill with a 3mmdiameter filter. Finally, the product was stored until further processing.

Synthesis of Copper nanoparticles

For synthesis of copper nanoparticles (CuNPs), as previously described by Musa *et al.*, (2016). Different concentrations of rice straw powder (0.5, 1.0, 1.5, 2.0 and 2.5 w/v %) were dissolved each in 50mL of distilled water and then added 10mL 0.05M of $CuSO_4{\cdot}5H_2O$ was added with continuous stirring for 30 minutes. This was followed by the addition of 30mL of 0.5% of seaweed with further stirring for 20 minutes. Then, 10mL of distilled water was added to make it a total of 100mL solution. 5mL of 0.02M ascorbic acid was then added with constant stirring for about 5 minutes and followed by the addition of 10mL of 0.5M NaOH solution for another 20 minutes under constant stirring. Finally, 2.5mL of 35% hydrazine was added for reduction of copper ions with constant stirring for about 20 minutes.

Characterization Methods

In this study, a UV-Visible spectrophotometer [UV 1650 PC-Shimazu B (Shimazu Osaka, Japan)] was used in detection of SPR bands of nanoparticles obtained from the synthesis. About 70 μL of the sample was poured into quartz cuvette. The spectra were run in the range of 300 to 1000 nm. Field Emission Scanning Electron Microscopy (FESEM) was used to observe the morphology of the samples using Jeol JSM-7600F Field Emission Scanning Microscope JEOL, (Eching b. Munchen, Germany) instrument. The samples were mounted on an aluminum stub using carbon tape and then sputtered with gold under vacuum at 20 mA for 30 min using a sputter coater Baltec SCD005 Sputter-coater (Bal-tec. Canonsburg, Penn-sylvaniassss, USA). The FTIR spectra of the samples were obtained at ambient temperature using the KBr disc method. The disk containing 1 mg of the sample was recorded with the wave number range of 200 to 4000 cm^{-1}

RESULTS AND DISCUSSION

The results indicate that the RS/CuNPs could be obtained by chemical reduction of $CuSO_4.5H_2O$ salt using hydrazine, rice straw, and NaOH solution as reducing agent, biotemplate support, and pH moderator respectively. A light blue colour solution was formed when the rice straw was added to the Cu^{2+} ions solution. Since copper tends to oxidize very quickly, ascorbic acid was added at this stage to prevent further oxidation. No colour change was observed after this addition. However, a light green colour was observed when NaOH was added to moderate the pH.When hydrazine was added, the solution immediately changed to brownish red which indicates that the copper ions are being reduced to copper.

RS/CuNPs was prepared/synthesized as shown by equations 1 to 3:

$$Cu^{2+} + RS \longrightarrow \left[RS/Cu\right]^{2+} \quad (1)$$

$$\left[(RS/Cu)\right]^{2+} + 2OH^- \longrightarrow \left[RS/Cu\,(OH)_2\right]^{2+} + 2e^- \quad (2)$$

$$\left[RS/Cu(OH)_2\right]^{2+} + N_2H_2 + 2e^- \longrightarrow \left[RS/CuNPs\right]^{2+} + N_2 + 2H_20 + H_2 \quad (3)$$

Characterization of Rice Straw/Copper Nanoparticles

UV-visible Spectroscopy

The formation and size of CuNPs can be determined by using the UV-vis spectroscopy. According to previous studies, the spherical CuNPs contribute to surface plasmon resonance (SPR) absorption bands around 500-600nm (Usman *et al.*, 2012). Figure 1 shows the spectra of the CuNPs produced by using different concentration of rice straw. As shown in figure 1below, the absorbance peak increases as the concentration of the RS increases i.e. from 0.5% to 2.5%. This indicates that the concentration of CuNPs produced increases as the concentration of the rice straw used increases. Furthermore, the gradual increase of rice straw used resulted in a blue shift in the SPR band position from 597nm to 586nm. This confirms the generation of smaller CuNPs as the amount of rice straw used increases.

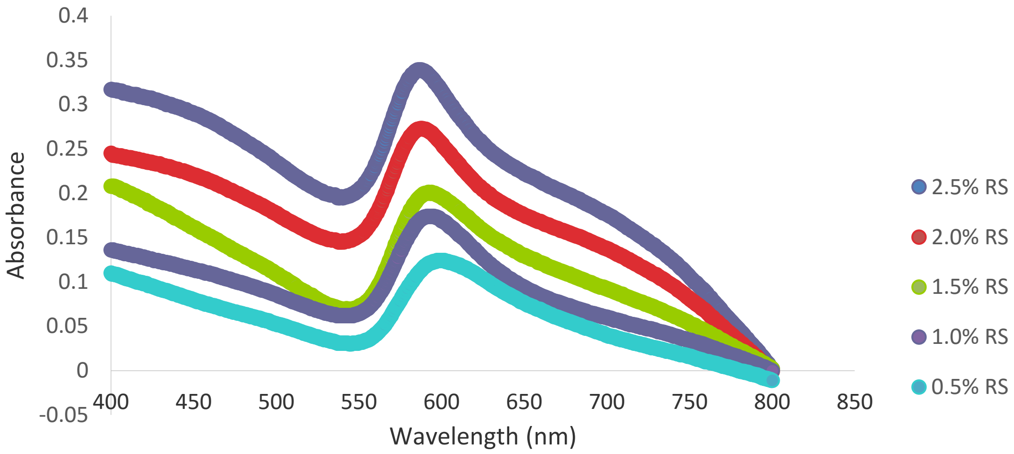

Fig.1. UV-visible adsorption spectra of RS/CuNPs with different amounts of rice straw.

Field Emission Scanning Electron Microscopy

The surface morphology and structure of RS/CuNPs in different amount of rice straw were further investigated by field emission scanning electron microscopy. From the result of the analysis it is obvious that the morphology of the RS/CuNPs is spherical in shape as shown in figure 2. However, the nanoparticles produced have various sizes and distribution patterns depending on the concentration of the rice straw. The FESEM images for the RS/CuNPs synthesized are shown in Figure 2. The agglomeration is observed to be varied according to the amount of rice straw used. The agglomeration is at its highest for the sample with 0.5% RS (Fig. 2a) but a better distribution is observed at 2.5 % RS (Fig. 2e). This means that as the amount of rice straw increases, there are more available surface for the nanoparticles to get attached resulting into less agglomeration, and hence, providing a better distribution. This also leads to a higher surface area to volume ratio nanoparticles, a property that makes it highly effective NPs. Besides that, the micrographs showed smaller nanoparticles in the 2.5% RS sample, the results of which correlate with the UV-vis analysis where it shows the strongest SPR peak at lower wavelengths.

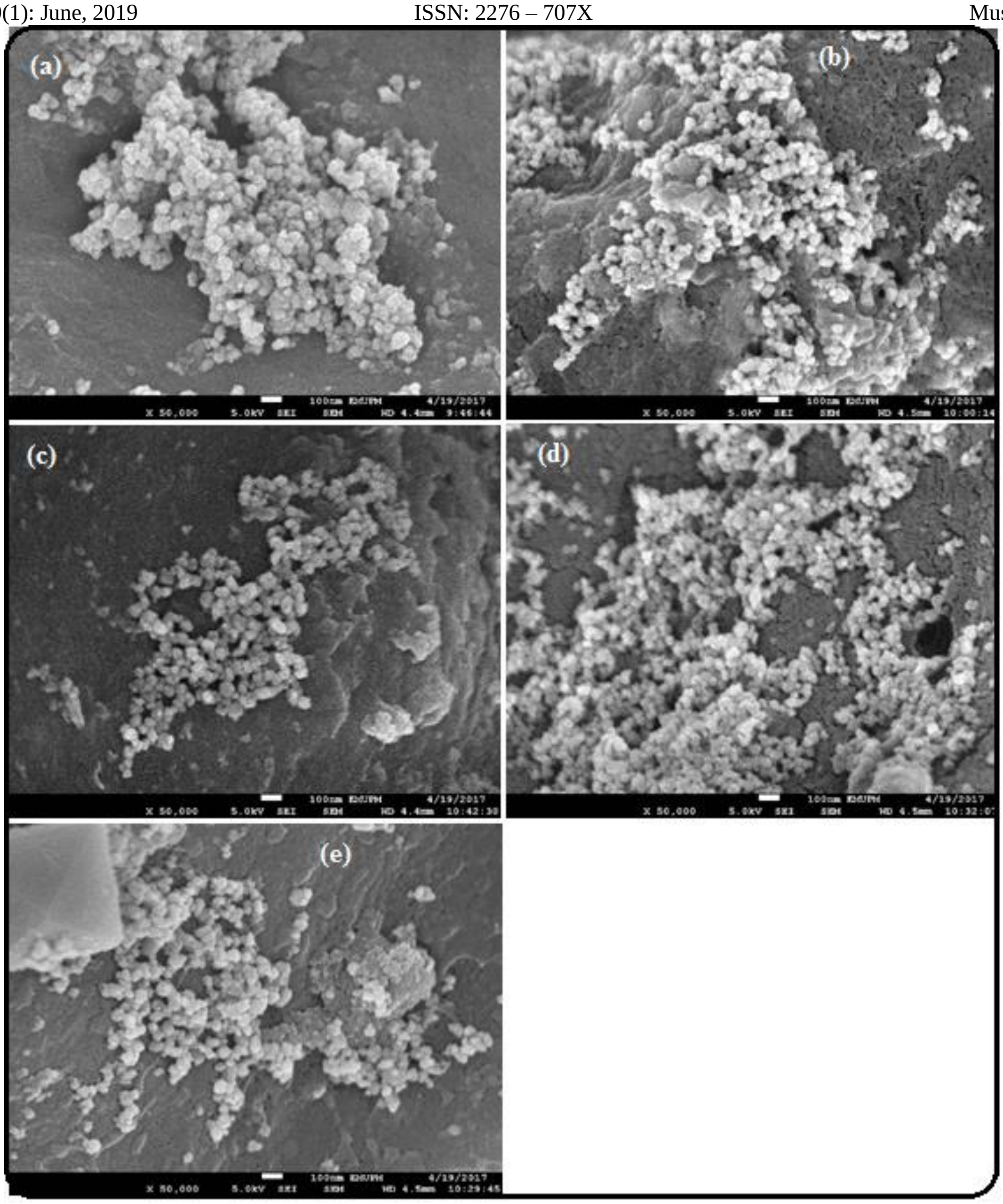

Fig. 2: FESEM micrographs of CuNPs with various concentrations of rice straw (a) 0.5% (b) 1.0 % (c) 1.5 % (d) 2.0 % and (e) 2.5 %.

Energy Dispersive X-ray Spectroscopy

EDX was used to determine the elemental composition of the samples. Fig. 3 shows the EDX spectra of CuNPs supported on rice straw. We can clearly see from the spectra that the nanoparticles produced are copper based. The C, O, S, Si and Ca signals arise from the rice straw and seaweed (stabilizer). The Silica peak as seen in the figures is due to the ash content of raw rice straw. However, the presence of Aluminum peak might be due to the contaminant left on the coated grid of FESEM from the previous analysis. As the concentration of rice straw increases from 0.5% to 2.5%, the height of the peak of Cu also increases. This shows that the energy of copper in the sample is increasing along with the concentration. In addition, the Copper to Carbon ratio increases from 0.076to 0.226 as shown in Table 1 below. This result proves that the formation of CuNPs increases as the amount of rice straw increases. This is consistent with the UV-vis result.

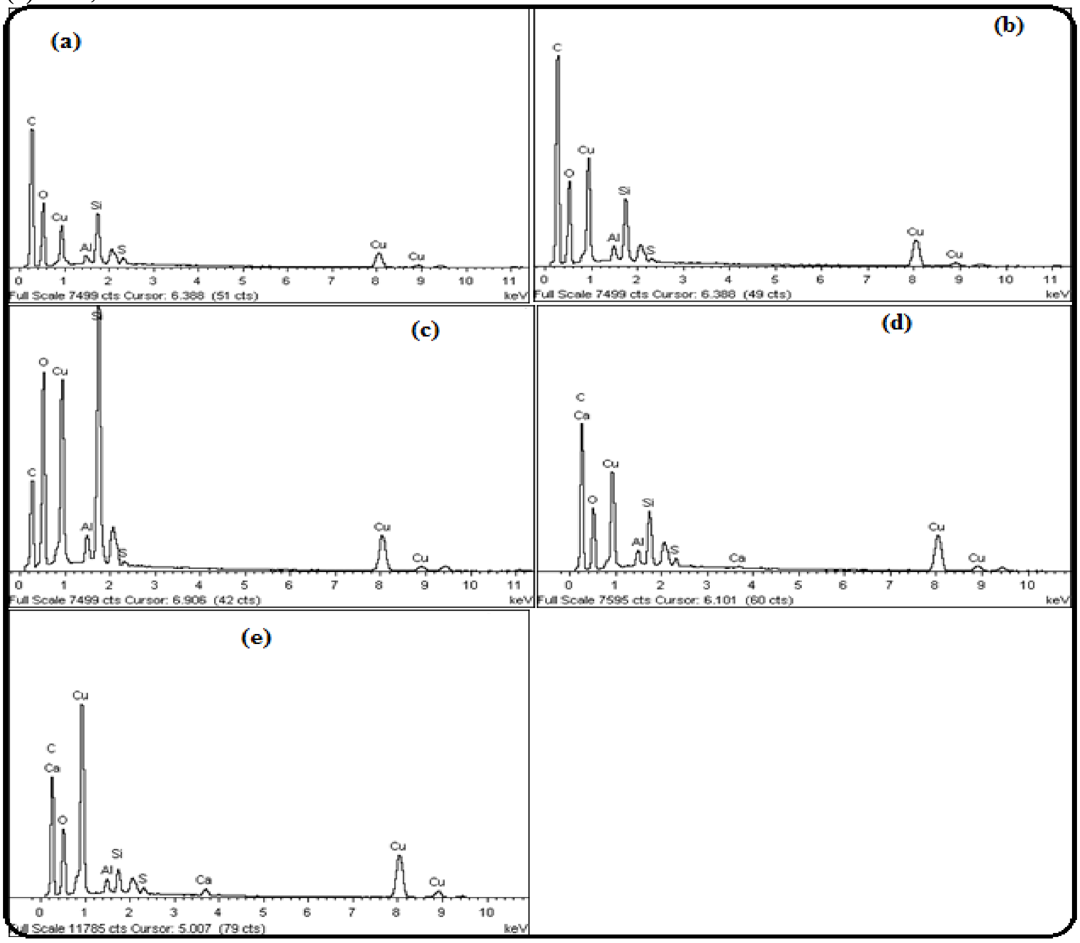

Fig. 3: EDX spectroscopy for CuNPs at various concentrations of rice straw (RS) (a) 0.5%, (b) 1.0%, (c) 1.5%, (d) 2.0% and (e) 2.5%.

Table 1. Elemental chemical analysis for RS/CuNPs at different concentrations of RS (a) 0.5 (b) 1.0 (c) 1.5 (d) 2.0 (e) 2.5Mass fraction %

Element	**Mass fraction %**				
	(a)	**(b)**	**(c)**	**(d)**	**(e)**
C	60.52	61.62	12.82	14.90	14.05
O	32.40	30.50	6.95	5.24	4.68
Al	0.30	0.40	0.75	0.60	0.55
Si	1.87	1.58	6.57	1.07	1.07
S	0.28	0.08	0.13	0.23	0.23
Cu	4.63	5.82	6.87	11.31	12.68
Cu/C	0.076	0.094	0.175	0.191	0.226

Fourier Transform Infra-Red Spectroscopy

Fig. 4 shows the spectra for the synthesized CuNPs with different amount of rice straw. According to Table 3, the representative's peaks that can be observed are situated around 3294–3317 cm^{-1} which represent the broad and strong O-H stretching, at 2854 – 2927 cm^{-1} for the C-H stretches, 1630–1639 cm^{-1} for C=C stretching, and the wavelength 1033 cm^{-1} represents the C-O stretching of cellulose. All these peaks shown for rice straw match that of the cellulose. This implies that the rice straw exhibits typical characteristics of cellulose (Chowdhury *et al.*, 2013). Direct comparison of FTIR of Tables 2 and 3 reveals that Table 2 (FTIR for RS only) shows a peak value of 1514 cm^{-1} for the C=C stretching of lignin found in the rice straw but interestingly this peak disappears in Table 3 which is the combination of RS and CuNPs. This might be because of the breaking of C=C bond to form a new bond with the CuNPs. In general, as the amount of RS increases, almost all the peak's intensity decreases as shown in Fig. 4. Also, the intensity of the peak at 1033cm^{-1} shows a slight decrease as the concentration of rice straw increases from 0.5% to 2.5% (Fig. 4). This indicates the coordination of rice straw with the copper nanoparticles.

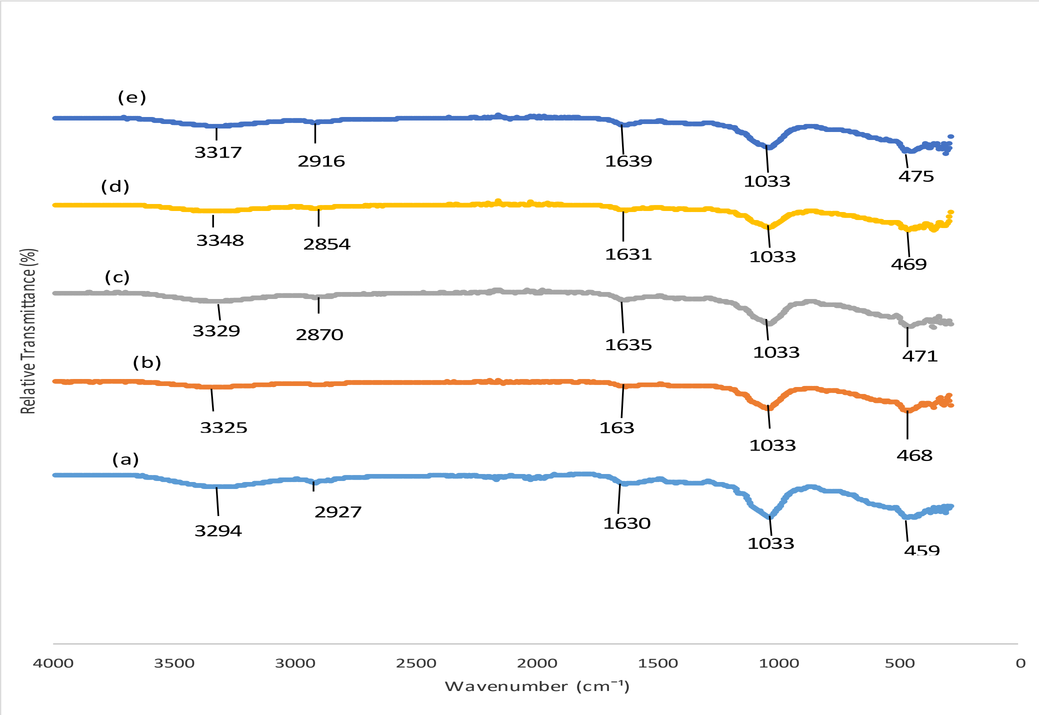

Fig.4. FTIR spectra for CuNPs with different amount of rice straw (a) 0.5%, (b) 1.0%, (c) 1.5%, (d) 2.0% and (e) 2.5%

Table 2. FTIR peak for Rice straw (Xiao *et al.*, 2014)

Functional group	**Absorption (cm^{-1})**
O–H stretching vibration	3404
C–H stretches	2909, 2852
C=C/C=O stretching	1640
C=C stretching of Lignin	1514
Alcohol C-O of cellulose	1054
Si–O–Si	471

Table 3. FTIR peak for RS/CuNPs

Functional group	**Absorption (cm^{-1})**
O–H stretching vibration	3294–3317
C–H stretches	2854–2927
C=C stretching	1630–1639
Alcohol C-O of cellulose	1033
Si–O–Si	459–475

CONCLUSION

In this study, new copper nanoparticles (CuNPs) supported by unmodified rice straw has been successfully prepared/synthesized via chemical reduction method. The formation of CuNPs with different concentration of rice straw was determined by UV-vis spectroscopy and EDX.

The UV-vis analysis shows the surface plasmon resonance (SPR) absorption bands around 500‒600nm, which indicates the presence of CuNPs. Whereas the EDX spectroscopy clearly shows that the nanoparticles produced is copper. Besides that, UV-vis analysis also confirms the generation of smaller CuNPs when the amount of rice straw used was increased. This was further proved by FESEM micrographs that show the decrease in the CuNPs size as the rice straw used was increased. Other than the nanoparticles size, FESEM also revealed that the distribution and agglomeration of nanoparticles depend on the concentration of the rice straw. The higher the amount of rice straw lead to less agglomeration and better distribution. As for the FTIR results, it showed that there is an interaction between the rice straw and the CuNPs. The disappearance of the C=C stretching of lignin from rice straws indicates that there is a new bond formed with the copper nanoparticles which further confirms the synthesis of CuNPs. Furthermore, the use of different concentration of rice straw in the synthesis of CuNPs has allowed us to be able to control the size of the nanoparticles.

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