



COMPARISON OF ADSORBING ON DISSOLVED COPPER METAL BY NATURAL AND ACTIVATED CARBON FROM RAMBUTAN (*Nephelium Sp.*) RODS

Bode Haryanto, Krissandarta Tarigan and Vikram Alexander

Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Padang Bulan, Medan, Indonesia
E-Mail: bode.haryanto@usu.ac.id

ABSTRACT

There are two adsorbents used in this research. The first one is natural carbon from rambutan rods and the other is the carbon rambutan rods that were synthesized and used nitric acid as a modifying agent. The performance of the modified carbon rambutan rods (MCRR) and natural carbon rambutan rods (NCRR) was characterized by SEM-EDX, FTIR, and AAS. Cu (II) adsorption from aqueous solutions with MCRR and NCRR was studied at varying adsorbent doses, initial Cu (II) concentration, and stirring speed. The batch equilibrium data fitted well to the Langmuir isotherm. The maximum adsorption capacity of MCRR and NCRR for Cu (II) was 5.504 mg/g (100/200 mesh, 70 ppm, 150 rpm) and 3.347 mg/g (100/200 mesh, 70 ppm, 150 rpm). MCRR was relatively large compared to NCRR as reported. Kinetic data were best fitted with the pseudo-second-order kinetic model. The intra-particle diffusion model was applied to investigate the adsorption mechanisms. The obtained thermodynamic parameters showed that Cu (II) adsorption onto the adsorbent was a chemical interaction process. These results showed that the carbon from modified rambutan rods could be considered as a potential adsorbent for the removal of Cu (II) ions from aqueous solutions than NCRR.

Keywords: rambutan, adsorption, kinetic, copper, isotherm.

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INTRODUCTION

Pollution from heavy metals is a big issue in developing countries. Heavy metal waste discharged into water bodies is a serious pollution problem affecting water quality. Increased concentrations of heavy metals in water bodies can cause health hazards because they cannot be decomposed and are toxic [1]. Copper is one of the metals that was first extracted and utilized by humans and has contributed greatly to civilization. Despite the extensive benefits and applications of copper, inevitably, copper waste as one of the dominant heavy metals cannot be avoided. The concentration of copper waste in water must not exceed 1.0 mg / L and the output of copper waste from the source must not exceed 0.1 mg / L; ecosystems in water bodies need copper concentrations of not more than 0.01 mg / L which in addition will cause fish death - fish in a body of water. As an essential element in the human body, copper is needed in the formation of red blood cells. However, excessive concentration can also damage the kidneys and liver, causing swelling of body tissues, depression, and necrosis [2]. So according to the World Health Organization (WHO), it is recommended that the concentration of copper in drinking water should not exceed 1.5 mg/L [3].

Adsorption is a popular method used in water treatment applications around the world. The liquid-solid adsorption system is based on the ability of certain solids to adsorb certain substances from the solution to the surface of the solids. This principle can be used in cleaning pollutants in the form of metal ions and organic substances in wastewater. Studies have been conducted in the last decade to obtain inexpensive and high-capacity adsorbents for metal ion cleaning, one of which is

activated carbon [4]. Adsorption proved economical and efficient in removing heavy metals such as copper [5-9], zinc [10], cadmium, lead, chromium, and nickel from contaminated waters [11].

The purpose of this study was to compare between adsorption ability of the natural carbon rambutan rods and modified carbon rambutan rods using Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX), Fourier-transform infrared spectroscopy (FTIR) and Atomic Absorption Spectrophotometer (AAS) analysis. This research is useful as information regarding the modified carbon rambutan rods' carbon due to waste from metal ions.

MATERIALS AND METHODS

The materials used in this study are rambutan tree charcoal as an adsorbent from the charcoal factory in Tuntung Village, Deli Serdang Regency. Copper (II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) as a source of copper (Cu^{2+}), hydrochloric acid (HCl), sodium hydroxide (NaOH) as a regulator of pH, and water (H_2O) as a solvent. Figure-1 shows the steps used in this research. While the main analysis tools used in this study are Atomic Absorption Spectroscopy (AAS), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX), and Fourier-transform infrared spectroscopy (FTIR) as seen in Figure-2. The research was conducted at the Chemical Engineering Operations Laboratory, the Microbiology Engineering Laboratory, and the Chemical Analysis Laboratory of the Chemical Engineering Department, the Faculty of Engineering and the Research Laboratory, Faculty of Pharmacy, Universitas Sumatera Utara, Medan, Indonesia.

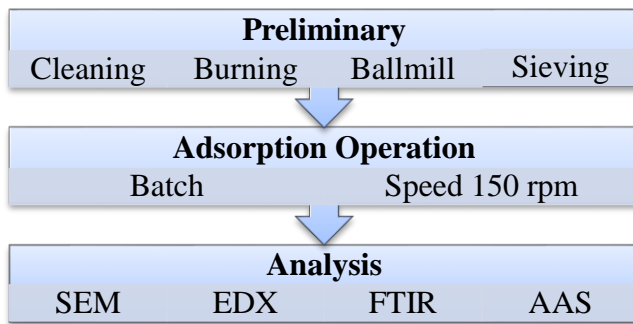


Figure-1. Steps on natural carbon study.

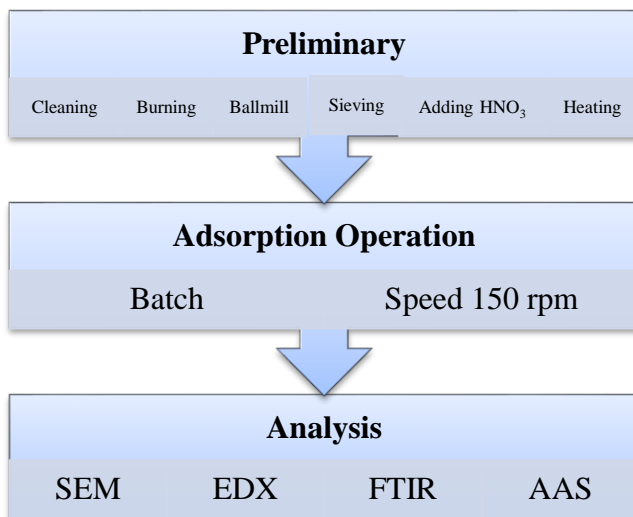


Figure-2. Steps on activated carbon study.

The adsorption kinetics was measured by measuring the metal adsorption capacity of Cu^{2+} against the increased operating time. At the metal ion concentration of Cu^{2+} 70 ppm, the size of the adsorbent was 100 mesh with a stirring speed of 150 rpm. A solution of Cu^{2+} 70 ppm was taken as much as 100 mL from a 2.5 L bottle and then put into Erlenmeyer, after that the rambutan rods carbon adsorbent was added as much as 10 grams and then stirred using a shaker at 150 rpm at room temperature. After that, the sample was taken as much as 2 mL at an interval of 10 minutes to 2 hours. The ion concentration of Cu^{2+} in the solution after adsorption was analyzed by AAS, the q_t value is the capacity of adsorbs at a certain time (t) and the R% percent capacity adsorbed by the adsorbent is calculated by equations 1 and 2 [6,11].

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$R\% = \frac{(C_0 - C_e) \cdot 100\%}{C_0} \quad (2)$$

Measurements from the effect of the size of the adsorbent on the rambutan rods' carbon adsorption ability were measured by the sizes of 50, 70, and 100 mesh. Adsorption capacity value with stirring speed 150 rpm and

solution concentration of Cu^{2+} 70 ppm with a duration of 2 hours and 24 hours. The procedure for analyzing adsorption capacity is carried out by the same process and formula. Measurements of the effect of adsorption capacity with variations in metal ion concentration were measured at 30, 50, and 70 ppm. Stirring speed of 150 rpm and size of 100 mesh rambutan rods carbon adsorbent [12]. Stages of analysis follow the same procedure.

RESULTS AND DISCUSSIONS

Characteristics of Modified Carbon Rambutan Rods (MCRR)

Physical Form

The physical form of the charcoal rod rambutan can be seen in Figure-3. Figure-3 A is the physical form of charcoal rod rambutan natural charcoal. The physical form of charcoal is dark black with homogeny particle size. After using nitric acid as the activated charcoal rambutan is roughly on the surface, it may impact the presence of the copper ions on the surface (Figure-3B) [5]. The physical images of natural charcoal particles were relatively changed compared to the activated form of charcoal rod rambutan. Charcoal activated with nitric acid color changes, although not significantly.

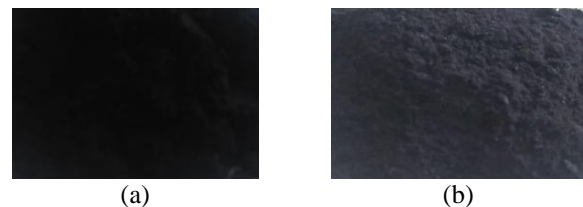
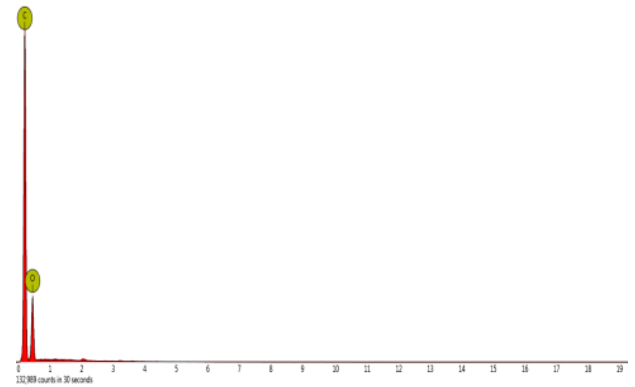
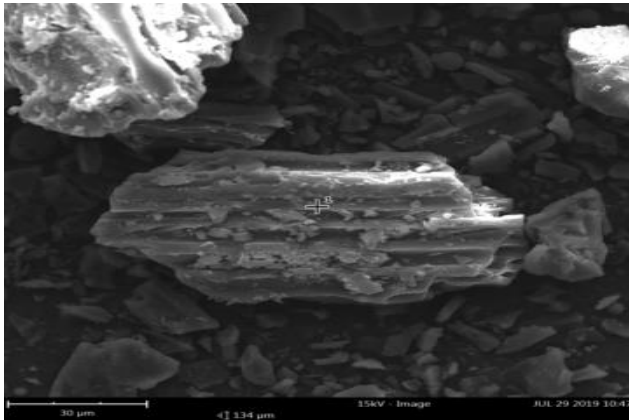


Figure-3. (A) Natural carbon and (B) modified carbon of rambutan rods.

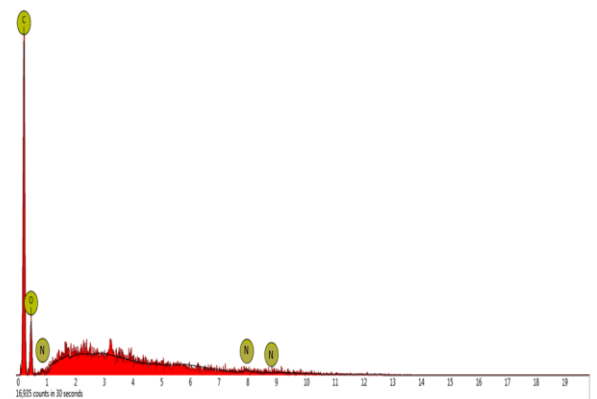
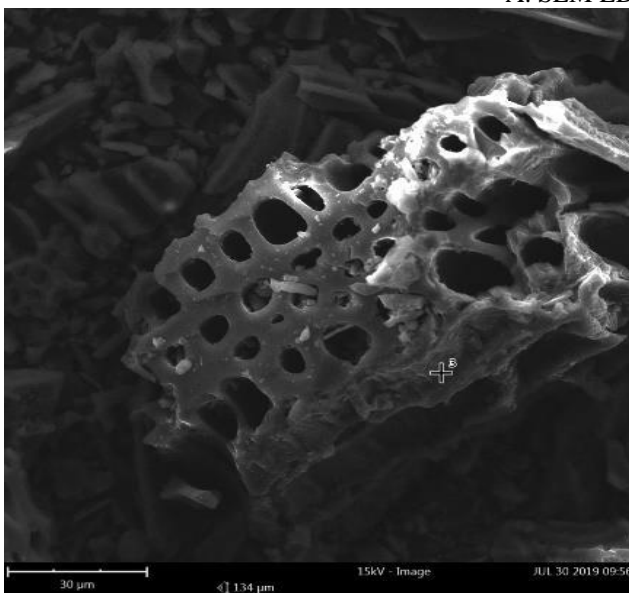
Scanning Electron Microscope-Energy Dispersive X-Ray Analysis

Figure-4 shows that there is a change in the pore structure where there is a larger porous channel so that the active side of the surface is greater for binding. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) analysis on the rambutan rod was carried out at 500x magnification SEM results reveal that there is a change in negative charged surface characteristics which can be seen in Figures-4 A and Figure-4 B so that it can increase the adsorption of Cu (II) metal.

Based on Figure-4 also it can be seen that there is more of the impurity composition in the mixed and bonded charcoal rambutan rod. Whereas in Figure-4 B it looks less and there is even a missing composition in Figure-4 (a). In Figure-4 (b) there is an N atom which indicates the acid used as an activator for the surface of the rambutan stem. So it can be concluded that after the modification of nitric acid, it causes the surface of the rambutan rod to become negative which is able to attract metal cations. In addition, the loss and reduction of the impurity composition cannot be immediately removed by washing using water [10].



A. SEM EDX natural carbon



B. SEM EDX modified carbon

Figure-4. SEM EDX of natural and modified carbon before adsorbing.

From Figure-5, the results of the SEM analysis of carbon after adsorption tend to show more significant changes than the EDX results after adsorption. In the results of SEM analysis there was a change in the

structure where there was a larger porous channel so that the active side of the surface was greater for bonding which can be seen in Figures 5 a and 5 b so that it can increase the adsorption of Cu (II) metal ion.

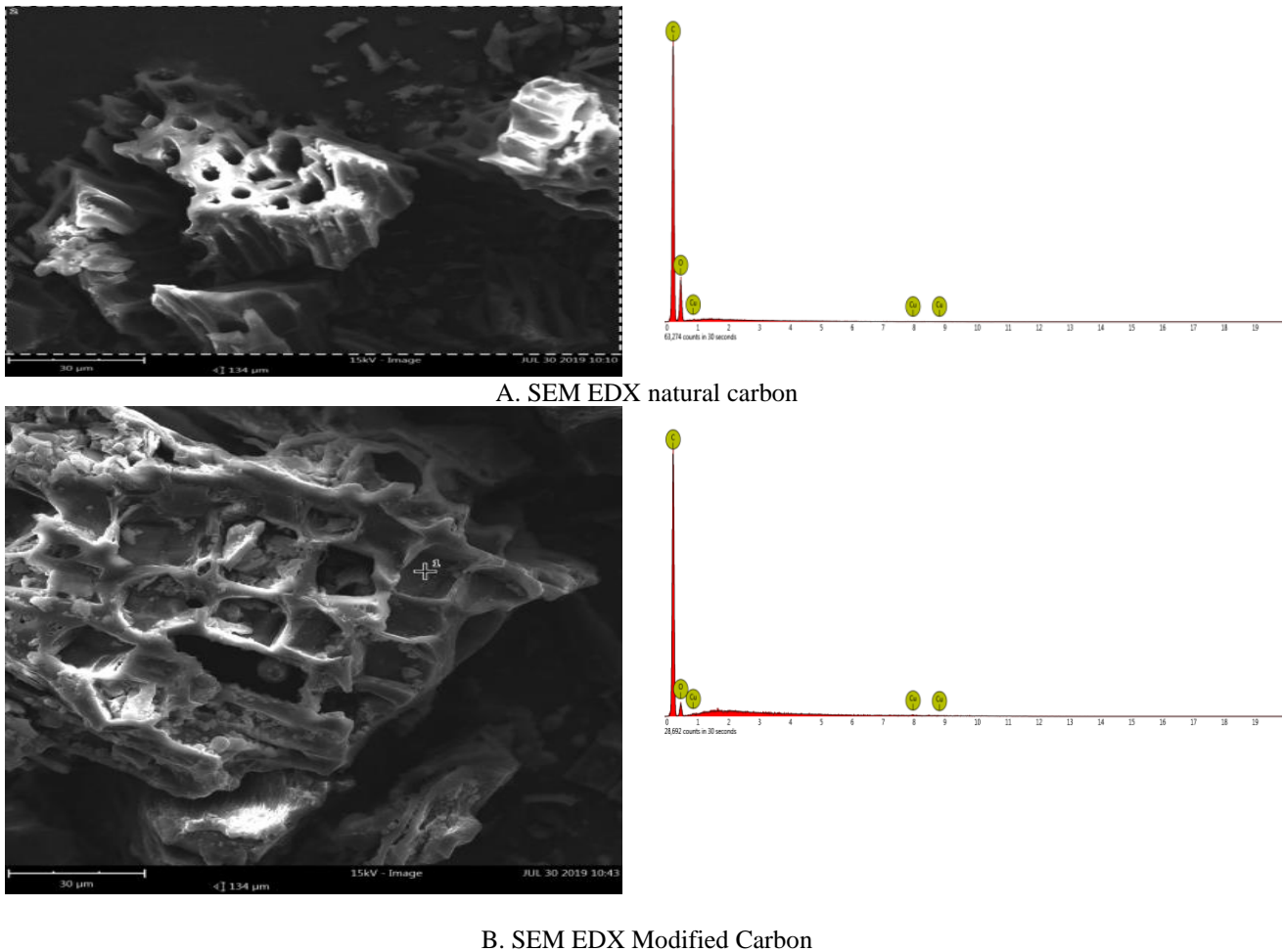


Figure-5. SEM EDX of natural and modified carbon after adsorbing operation.

Fourier-Transform Infrared Spectroscopy Analysis

Figure-6 shows the functional groups of Fourier-transform infrared spectroscopy (FTIR) results before and after the modification of nitric acid. The adsorption peaks of the rambutan stem before the modification of nitric acid and after the modification of nitric acid were 3223.7559 cm^{-1} and 3262.70 cm^{-1} , respectively. According to Lambert (1987), the adsorption peak at $3500\text{-}3200\text{ cm}^{-1}$ indicates the presence of an O-H (Hydroxyl) group [13]. The presence of a hydroxyl group indicates that there are

strong hydrogen bonds such as carbonyl, alcohol, and phenol. However, there was a decrease in the adsorption of 1216.3569 cm^{-1} and 558.1396 cm^{-1} to 1199.85 cm^{-1} and 528.6672 cm^{-1} . Retno Harti, *et al* (2014) stated that the more functional groups that are adsorbed, the more the intensity of the %transmission will decrease [14]. This decrease means that the modification process results in an additional functional group. This is why the acid modification process plays an important role in the metal adsorption process carried out in this study.

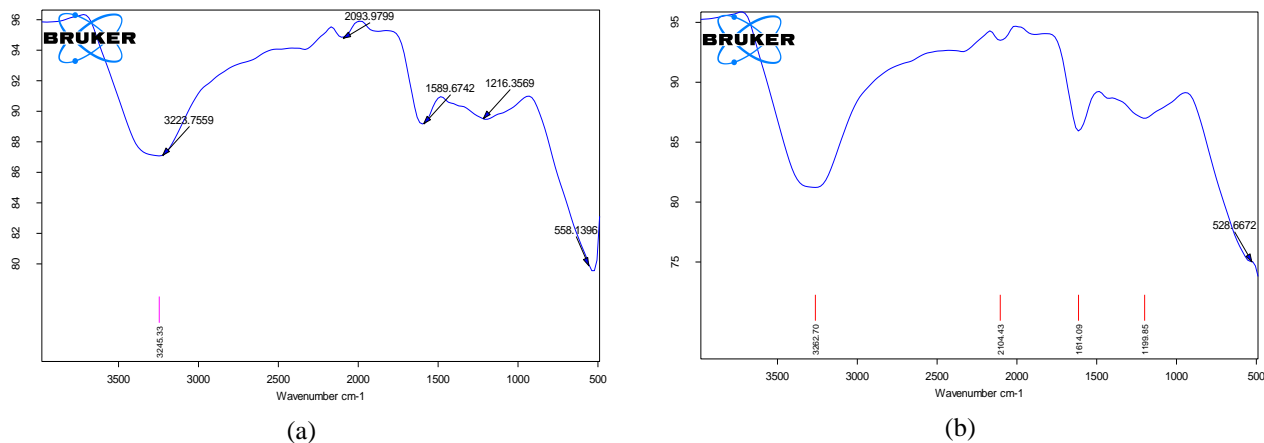


Figure-6. FTIR analysis of natural and modified carbon.

Effect of Contact Time and Initial Concentration on Cu (II) Adsorption

Contact time is the length of time required for the adsorbent (Carbon rambutan rod) to optimally adsorb adsorbate (Cu (II)) in the adsorption process to determine its kinetics. The effect of contact time on the removal of Cu (II) on modified carbon rambutan rods (MCRR) and Natural Carbon Rambutan Rods (NCRR) is shown in Figure-7. Figure-7 shows that the metal removal percentage increases with increasing contact time and will be constant at a certain time. The increase in adsorbed Cu (II) concentration reached its optimum point at 120 minutes with the adsorption rate (q_{ads}) of Cu (II) of 5,504 mg / g (MCRR) and 3,345 mg / g (NCRR). In the first 5 minutes, the adsorption rate (q_{ads}) of Cu (II) was 2.59 mg / g (MCRR) and 2.188 (NCRR). The uptake of Cu^{2+} ions increased until 90 minutes with the adsorption capacity (q_{ads}) of Cu^{2+} of 4.89 mg / g (MCRR) and 2.85 mg / g (NCRR). After the interaction lasted for 90 minutes, the adsorption of Cu (II) was almost constant. This indicates that equilibrium has been reached. In this situation, the adsorption capacity on the surface of rambutan wood charcoal has been saturated and an equilibrium has been reached between the concentration of Cu (II) in the carbon rambutan rod adsorbent so that the adsorption at the contact time of 120 minutes to 240 minutes becomes constant or almost the same.

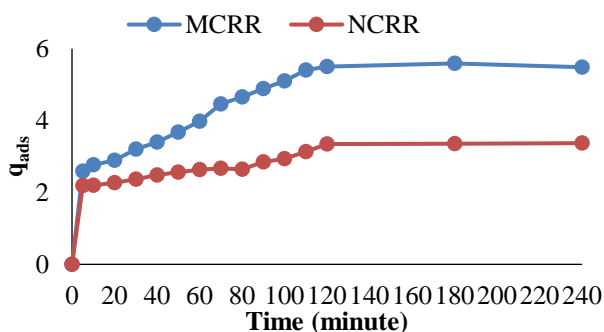


Figure-7. Effect of time and initial concentration on Cu (II) adsorption (conditions: adsorbent dose = 70 mg/L; particle size = 100 mesh; stirring rate = 150 rpm).

Adsorption Kinetics

To investigate the adsorption of Cu (II) on the modified carbon rambutan rods (MCRR) and Natural Carbon Rambutan Rods (NCRR), different kinetic models were used to describe the rate of adsorbate uptake on the adsorbent. In this study, the pseudo-first-order, pseudo-second-order kinetic models were applied to study the kinetics of the adsorption process and find the best-fitted model for the experimental data.

Pseudo-First-Order Kinetic Model

In many cases, the pseudo-first-order kinetic model does not fit well to the whole range of the contact time and is generally applicable at the initial stage of the adsorption process. The adsorption rate constant based on the adsorption capacity was determined from the pseudo-first-order kinetic model given by Lagergren as equation 3.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

where q_e and q_t are the amounts of adsorbate adsorbed (mg/g) at equilibrium and at any time, t (min), respectively, and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}).

The plot of $\log(q_e - q_t)$ versus t gave a straight line for the pseudo-first-order adsorption kinetics to obtain the rate parameters. The values of R^2 obtained from the plots for adsorption of Cu (II) on the MCRR and NCRR were presented in Table-1. The value of R^2 was relatively small. This indicated that the adsorption of Cu (II) onto MCRR and NCRR did not follow the pseudo-first-order kinetics.

Pseudo-Second-Order Kinetic Model

The pseudo-second-order model is based on the assumption that the rate-limiting factor may be chemisorption involving valence forces through sharing of electrons between the amino group and metal ions. The pseudo-second-order model predicted the behavior over the whole range of adsorption expressed as equation 4.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$



where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min). The values of q_e and k_2 were calculated from the linear plot of t/q_t versus t with a slope of $1/q_e$ and intercept $1/k_2q_e^2$ (graph shown in Figure-8).

From Table 1, it can be concluded that the adsorption process that took place in this study involved a dominant chemical interaction (chemisorption) compared to the physical interaction. Evidenced by the R^2 value of the pseudo order two modeling is closer to 1. According to Thambavani, *et al.* (2014), the second-order equation is based on the assumption that the possible rate determination step is chemical adsorption between adsorbent and adsorbate [15].

Table-1. Kinetic parameters for the adsorption of Cu (II) ions onto MCS at different initial concentrations.

Type Adsorbent	Pseudo-first-order	Pseudo-second-order
	R^2	R^2
MCRR	0.6437	0.9849
NCRR	0.5012	0.9887

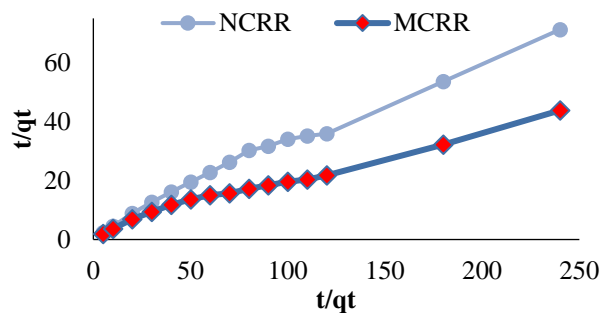


Figure-8. Pseudo-second-order model for adsorption of Cu (II) on MCRR and NCRR.

Intraparticle Diffusion Study

The adsorption mechanism of adsorbate onto adsorbent may be assumed to involve one or more steps, e.g. film or external diffusion, intra-particle diffusion or pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step. Generally, in a batch reactor intra-particle diffusion is often rate-limiting. Weber and Morris proposed an empirically found functional relationship that if intra-particle diffusion is the rate-controlling factor, uptake varies with the square root of time. To elucidate the diffusion mechanism, the kinetic results were analyzed by the intra-particle diffusion model expressed as equation 5 [16].

$$q_t = k_{id}\sqrt{t} + C \quad (5)$$

where the k_{id} is the intra-particle diffusion rate constant (mg/(g min^{1/2})) and C is the intercept (mg/g). Figure-9 represents the plot of q_t versus $t^{1/2}$ for intraparticle transport at different initial Cu (II) concentrations. If the

Weber–Morris plot of q_t versus $t^{1/2}$ is linear and passes through the origin, then the adsorption process is controlled only by intra-particle diffusion. However, the data exhibited multi-linear plots, indicating that two or more steps influenced the sorption process. The first, sharper portion was attributed to film diffusion. The second linear portion was the gradual adsorption stage where intra-particle diffusion is the rate limiting. The third portion was attributed to the final equilibrium stage where intraparticle diffusion started to slow down due to extremely low adsorbate concentrations in the solution. Referring to Figure-9, none of the linear lines passed through the origin. This indicated that intraparticle diffusion was not the only rate-limiting step in the sorption process.

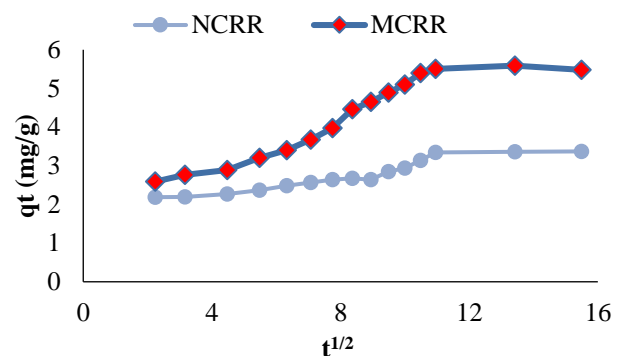


Figure-9. Intraparticle diffusion plot for adsorption of Cu (II) on MCRR and NCRR.

Adsorption Isotherms

Adsorption isotherms describe how adsorbate interacts with adsorbents, and therefore are critical in optimizing the use of adsorbents. To optimize the design of an adsorption system, it is essential to establish the most appropriate correlation for the equilibrium curve. Several isotherm equations are available for analyzing experimental data and two important isotherms were selected in this study, namely the Langmuir and Freundlich. These isotherms relate the Cu (II) uptake per unit weight of modified carbon rambutan rods (MCRR) and Natural Carbon Rambutan Rods (NCRR), q_e , to the equilibrium Cu (II) concentration in the solution, C_e (shown in Figures 10 and 11). Determination of the Cu metal ion adsorption isotherm can be seen in Figure-10 for the Langmuir isotherm and Figure-11 for the Freundlich isotherm. The MCRR adsorbent test on the Langmuir adsorption equation and also the Freundlich adsorption equation is proven by a good linearization graph and has a determination coefficient value of $R^2 \geq 0.9$, while the NCRR adsorbent test only the Freundlich equation has a determination coefficient value $R^2 \geq 0.9$. This assumes that the maximum ion exchange is better at MCRR than NCRR.

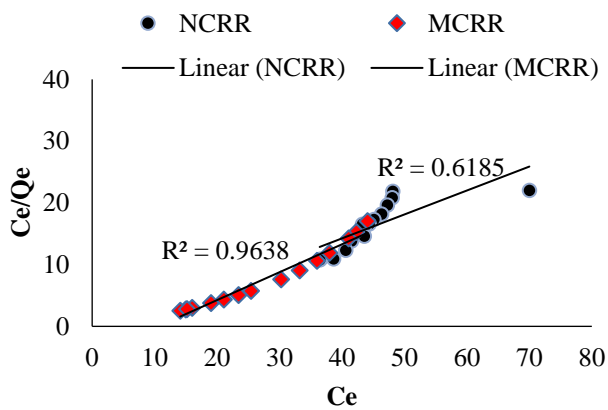


Figure-10. Langmuir adsorption isotherm curve on MCRR and NCCR.

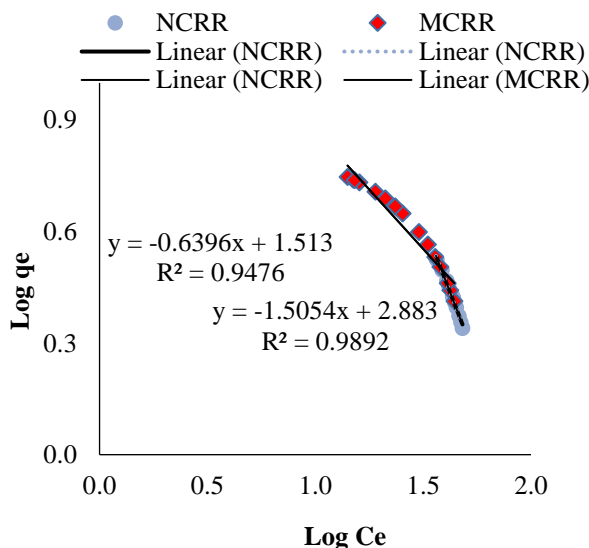


Figure-11. Freundlich adsorption isotherm curve on MCRR and NCCR.

CONCLUSIONS

Modified Carbon Rambutan Rods (MCRR) successfully increased the physical properties of activated carbon involving surface area, pore size distribution, and pore volume. The result also supports that nitric acid has successfully removed some contaminants attached to the surface-activated carbon. The pore on the surface activated carbon was seen with cavities. MCRR was identified to be an effective adsorbent than NCCR for removing Cu (II) from aqueous solution. Cu (II) uptake increased with the increase of Cu (II) initial concentration, contact time, and solution temperature. Equilibrium data were best described by the Langmuir isotherm model, with a maximum adsorption capacity of 5.504 mg/g, which was relatively large compared to some data reported in the literature. Kinetic data were adequately fitted by the pseudo-second-order kinetic model and though intra-particle diffusion was not the only rate-controlling step, it still played a significant role in the adsorption mechanism.

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