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Adsorption of Cu(II) by biosorbents from Arenga pinnata Merr fruit shell waste modified using ultrasound

A. Muslim[1*], P. N. Alam[1], Abubakar[1], Saifullah[1], F. M. Djuned[1], B. R. Ardiani[1], F. Rahmatika[1], T. Hadibarata[2]

[1]*Department of Chemical Engineering, Faculty of Engineering, Syiah Kuala University, Banda Aceh, Indonesia*.
[2]*L Department of Environmental Engineering, Curtin University, Sarawak, Malaysia*.

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abrar.muslim@unsyiah.ac.id;
Phone: +626517552222;
Fax: +626517552222

Abstract

This study reported the adsorption of Cu(II) ions from aqueous phase onto biosorbent prepared using Arenga pinnata Merr fruit shells waste modified using NaOH with ultrasound assistance. The biosorbents adsorption capacity were investigated over independent variables of contact time, NaOH concentration, initial Cu(II) ions concentration in aqueous phase and adsorption temperature. The adsorption experiments were conducted in batch mode at constant pH of 4.5. The biosorbents functional groups and morphology were characterized by FTIR and SEM techniques, respectively. The maximum adsorption capacity of ultrasound assistance-based modified biosorbent was 50.97 mg/g which was higher than without ultrasound assistance (24.25 mg/g). The Cu(II) ions adsorption on the biosorbent should have best fit for Freundlich model. It followed the pseudo second order of adsorption kinetic model with adsorption capacity and rate constants being 50.01 mg/g and 4.44 g/mg.min, respectively at 27°C, and the constants decreased to 43.11 mg/g and 0.03 g/mg.min, respectively at 47°C. Physical adsorption should control dominantly Cu(II) ions adsorption on the biosorbents. Based on data obtained in this study, it can be concluded that the Arenga pinnata Merr Fruit Shell are a promising biosorbent.

1. Introduction

Heavy metal ions might enter to environment from the waste water of industrial practices such as mine operation, extraction of metal, refining of petroleum [1], food and agricultural processing [2], and even university laboratories [3]. Among the heavy metal ions, Cu(II) ions is one of the toxic ones and might be presented in the waste water of mine operation, chemical processing and electroplating [4, 5]. It can cause tissues and organs dysfunctions in the human body [6, 7]. Among other methods for heavy metal removal, adsorption is known as the most effective and simplest method to apply in reducing water pollutant [8] and in reducing heavy metal ions in contaminated water bodies [9, 10].

Low cost biosorbents from lignocellulosic waste have been used for heavy metal ions adsorption. Brazilian tea and nut shells [11], coffee bean and husks [12], water melon peel [13], guava seeds [14], sugarcane bagasse [15, 16], Erytherina variegate orientalis leaf [17], Imperata cylindrical leaf powder [18], Castor leaf [19], bamboo leaf [20], paper mulberry leaf [21], saw dust and neem barks [22], cocoa husk [23], Moringa oleifera bark [24], grape fruit peel [25], pecan nut shell [26] and walnut shell [27] had been proposed for low cost biosorbent materials.

Arenga pinnata Merr fruit shell waste is a promoting material for biosorbent because its amount has inclined due to increasing Arenga pinnata Merr plantation across Asia for foods and beverages, biofibres, timber commodities, biopolymers, biocomposites and bio-ethanol. [28]. Arenga pinnata Merr biosorbent (APMB) was used by modifying using nitric acid for adsorption of Cr(III), Cr(VI), Cd(II) and Zn(II) ions from aqueous phase. However, the APMB adsorption capacity was still very low which were 0.28, 0.52, 0.43 and 0.58 mg/g, respectively [29]. A study for Cu(II) ions adsorption using the APMB had not been done, and it needs more modification method to increase its capacity.

The previous study highlighted some activating chemicals, adsorption conditions and methods to prepare adsorbent [30]. Microwave radiation was used for modification of adsorbent [31-32]. Ultrasound was applied during adsorption of 4-dodecylbenzene sulfonate by corn cob activated carbon [33] and adsorption of copper by activated water melon waste [13]. Ultrasound assistance using 1 MHz using an ultrasonic probe in preparation activated carbon from pithecellobium jiringa (jengkol) shells increased its Cu(II) adsorption capacity [34].

Therefore, the current study proposed the APMB by modifying the raw material of Arenga pinnata Merr fruit shell waste using NaOH with ultrasound assistance. The biosorbents functional groups and morphology were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM), respectively. The effect of contact time, initial Cu(II) ions concentration, ultrasound assistance and NaOH concentration in modification on adsorption capacity were investigated. The adsorption isotherm and kinetic parameters were determined at the optimum condition.

2. Material and Methods

2.1. Preparation and characterization biosorbents

Arenga pinnata Merr fruit shell waste was collected from an Arenga pinnata Merr fruit processing industry in the village of Pucok, Pidie District, Aceh Province. To prepare the APMB, 1 kg of the fruit shell waste was rinsed thoroughly using tap water. It was dried in an oven drier (Memmert, NN-ST342M, Western Germany) at 120 ^{o}C for 4 h to remove water. Then, it was cut, milled and sieved to get the powder size of 100-120 mesh. The powder of 25 g was chemically activated using 200 ml NaOH solution at 0.3 M (97% NaOH, Merck) in 250-mL beaker glass for 6 h with stirring speed of 150-rpm (IKA, type C-MAG HS 7) at room temperature of 27 ^{o}C (± 1 ^{o}C). After activation, it was washed using distilled water and filtered using vacuum filter, and it was repeated until the waste water reaching neutral pH of 7. The biosorbent was dried in an oven drier at 120 ^{o}C until the weight being constant. This 1st biosorbent was labelled as the APMB0.3.

The APMB0.3 preparation procedure was repeated by adding ultrasound assistance. The APMB0.3 chemical activation was carried out in an ultrasonic bath (Bransonic 8510, 40 kHz, USA). The 2nd biosorbent produced was labelled as the APMBU0.3. The APMBU0.3 preparation procedure was also repeated with different concentration of NaOH which was 0.5 M and 0.7 M to produce the 3rd and 4rd biosorbents, and labelled as the APMBU0.5 and APMBU0.7, respectively. The biosorbents were stored separately in sealed bottles for adsorption experiment. The biosorbents morphology were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM), respectively.

2.2. Experiments of Cu(II) ions adsorption

The experiments of Cu(II) ions adsorption were carried out in batch mode. The system of biosorbent-solution consisted of 1 g of the biosorbent and 100 mL of Cu(II) ions solution. It was stirred at 75-rpm, 1 atm and pH 4.5 [34, 35]. The predetermined concentration of Cu(II) ions in aqueous phase, the same procedure in previous study was taken into account to prepare the 500 mg/L of 1000-mL stock Cu(II) ions solution using $CuSO_4.5H_2O$ (99% pure, Aldrich) [36]. It was analysed using Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA-6300, Japan) to determine the concentration of Cu(II) ions in aqueous phase.

The Cu(II) ions adsorption capacity of the biosorbent was investigated over independent variables of the contact time (0–120 min), the type of biosorbents (APMB0.3, APMBU0.3, APMBU0.5 and APMBU0.7) NaOH activator concentration (0.3–0.7 M), Cu(II) ions concentration, C_0 (11.042–510.920 mg/L based on the AAS reading), and adsorption temperature (30–47 °C). The optimum condition with the highest Cu(II) ions adsorption capacity on the biosorbent was obtained.

3. Results and discussion

3.1. Functional groups of biosorbents

Figure 1 shows the biosorbents FTIR transmission spectra of 650 to 4000 cm^{-1} with the functional groups as highlighted in previous studies [34, 35]. As shown in Figure 1, a wide band with a peak at approximately 3280.16 cm^{-1} is assigned to O–H stretch of alcohols and phenols at 3200-3650 cm^{-1} of wavenumber. A band with 2 peaks at 2925.12 and 2861.75 cm^{-1} refers to C–H stretch of alkanes and aldehydes, respectively at 2895-2970 cm^{-1}. A band with a peak at 1667.12 cm^{-1} is attributed to ketones and aldehydes (C=O stretch) at 1665-1760 cm^{-1}. A band with a peak at 1309.08 cm^{-1} is for aromatic amines (C–N stretch) at 1200-1350 cm^{-1}. A strong band with a peaks at 1008.53 cm^{-1} is attributed to carboxylic acids, ethers and ester at 1000-1300 cm^{-1} (C–O stretch). A band with 2 peaks at 890.72 and 780.15 cm^{-1} refers to alkenes (=C–H bend) at 690-900 cm^{-1}.

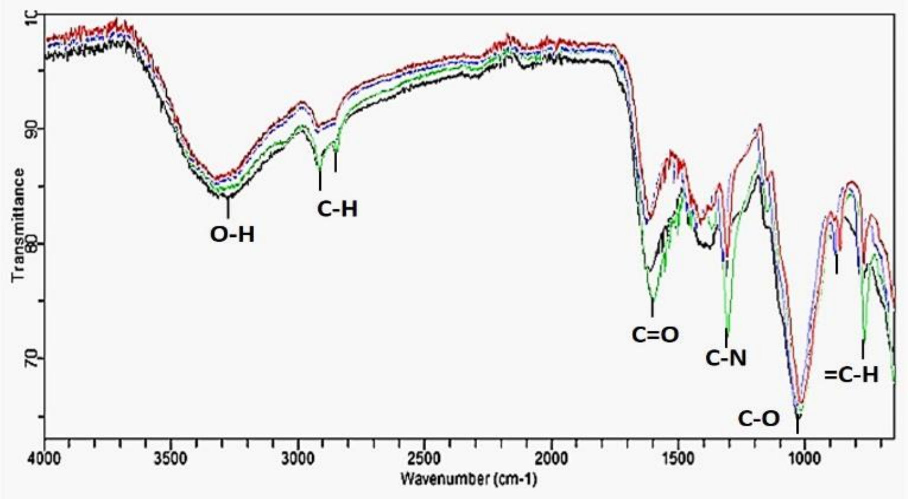
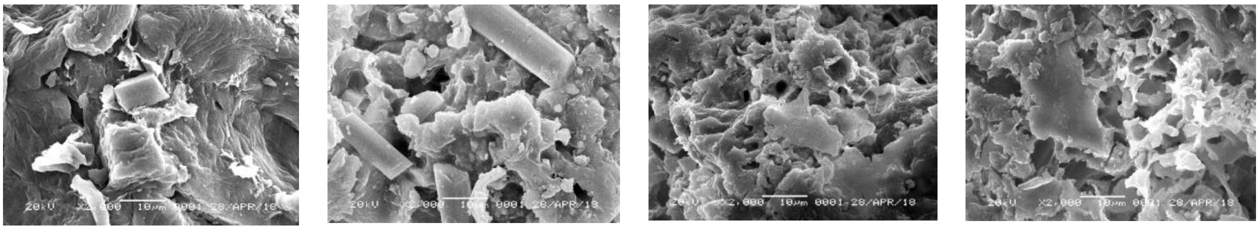


Figure 1: FTIR transmission spectra of the APMB0.3 (black), APMBU0.3 (green), APMBU0.5 (blue) and APMBU0.7 (red)

Overall, all the samples have volatile matter such as alcohols, phenols, alkanes, aldehyde, ketones, aromatic amines, carboxylic acids, ethers and ester. As shown by the FTIR spectra in Figure 1, ultrasound assistance in the chemical modification of biosorbent lifted up few functional groups transmittance except ketones, aldehydes, carboxylic acids, ethers and ester in the APMB0.3. The effect of ultrasound assistance can be seen clearly when increasing the NaOH concentration in modification where the functional groups transmittance of APMBU0.5 and APMBU0.7 increased. It means that more volatile matters being released would produce more potential pores and adsorption surface area leading to higher capacity of the biosorbent. Because the change in transmittance of functional groups peaks were insignificant, physical adsorption of Cu(II) ions on the biosorbent would be dominant rather than chemical adsorption [34].

3.2. Surface morphology of biosorbents

As can be seen in Figure 2, ultrasound assistance changed surface morphology of biosorbent where more pores was formed in the APMBU0.3 compared to APMB0.3. There were also more pores being formed when increasing the NaOH concentration from 0.3 M to 0.5 and 0.7 M in chemical modification. More volatile matters would be released from biosorbent due to ultrasound cleaning and breaking the stretching of chemical functional group. This result was supported by the FITR result. Because of more pores on biosorbent with ultrasound assistance as shown in Figure 2, there would be larger surface area being formed when applying ultrasound wave and increasing activator concentration. Therefore, the adsorption of Cu(II) ions on ultrasound assistance-based modified biosorbent should be higher than the one without ultrasound assistance. More NaOH concentration result in higher capacity of biosorbent in adsorbing Cu(II) ions from aqueous phase even in it would be insignificant based on the FTIR result expectation.

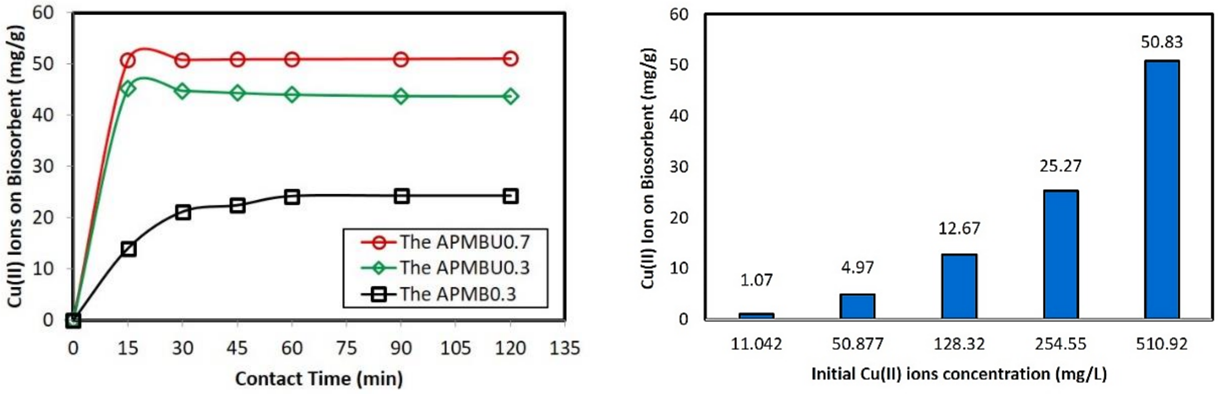


(a) (b) (c) (d)

Figure 2: The SEM micrographs of the APMB0.3 (a), APMBU0.3 (b), APMBU0.5 (c) and APMBU0.7 (d)

3.3. Effect of contact time on adsorption capacity

As clearly shown in Figure 3(a), Cu(II) ions adsorption capacity of the APMB0.3 increased moderately in the first 45-min of contact time to reach approximately 22.38 mg/g at 45 min. The adsorption capacity were 24.17 and 24.25 at 60 and 120 min, respectively. Meanwhile, it increased sharply in the first 15 min for the APMBU0.3 and APMB0.7 which was 45.25 and 50.70 mg/g, respectively at 120 min. It did not change too much from 15 to 120 min, and it was 47.72 and 50.97 m/g at 120 min. It showed that Cu(II) ions from aqueous phase were no longer to be adsorbed on the biosorbent for the rest of contact time, and it was exponential trend over contact time [34, 37, 38]. Therefore, 60-min contact time was fairly as taken into account as an equilibrium time for isotherm adsorption experiments.



(a) (b)

Figure 3: Effect of contact time (a) and initial Cu(II) ions concentration (b) on adsorption capacity. Experiment: 100 mL Cu(II) ions in aqueous phase with C_0 at 510.92 mg/L with 1 g of biosorbent (a) and C_0 at 11.42-510.92 mg/L with 1 g the APMBU0.5 (b), 75-rpm magnetic stirring, pH 4.5, 1 atm and 27 °C.

3.4. Effect of initial Cu(II) ions concentration on adsorption capacity

Effect of initial Cu(II) ions concentration on the adsorption capacity of the APMBU0.5 is shown in Figure 3(b). It is clear that the biosorbent adsorption capacity consciously increased from 1.07 to 50.83 mg/g for the C_0 increase from 11.04 to 510.92 mg/L, respectively. The same trends were also shown in the previous studies [34, 39]. The adsorption capacity should increase until all active sites on the adsorbent being occupied by adsorbate. Further investigation was done at the temperature of 47 ^oC, and the same trend was occurred whereas the biosorbent adsorption capacity was 0.96, 1.18, 3.04, 12.99 and 32.28 mg/g for the initial Cu(II) ions concentration being 11.04, 50.88, 128.32, 254.55 and 510.92 mg/L, respectively.

3.5. Effect of ultrasound assistance and NaOH concentration on adsorption capacity

Effect of ultrasound assistance in chemical modification on Cu(II) ions adsorption capacity of biosorbent is shown in Figure 4. It was clearly that at the same NaOH concentration, ultrasound assistance lifted up adsorption capacity by 80.32% from 24.5 to 43.72 mg/g at 120 min (Figure 4), and it was by 82.24% from 24.17 to 44.04 mg/g at the equilibrium time, respectively (Figure 3(a)). Ultrasound assistance increased the adsorption capacity because ultrasound waves would increase mass-transfer of NaOH dehydrating agent to clean the surface and pores of biosorbent. As the result, there more volatile matters being released from biosorbent, as expected in the FTIR previous discussion. Ultrasound assistance also accelerated Cu(II) adsorption on biosorbent where an steady state adsorption capacity of the APMBU0.3 and APMBU0.7 reached faster (15 min) compared to the APMB0.3 (60 min). Meanwhile, the effect of increasing NaOH concentration on adsorption capacity was insignificant under ultrasound assistance whereas it was only 16.25% and 16.59% increase for the NaOH concentration increase from 0.3 to 0.5 M and from 0.3 to 0.7 M, respectively. It can be included that a maximum adsorption capacity for the experiment condition was found to be 50.97 using the APMBU0.7.

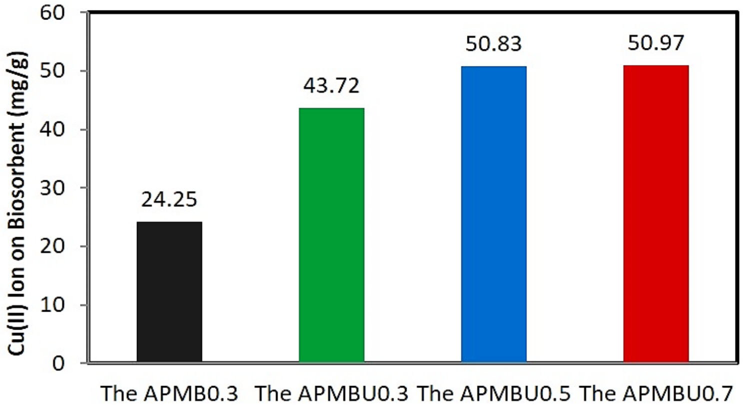


Figure 4: Effect of ultrasound assistance and NaOH concentration on adsorption capacity. Experiment: 100 mL Cu(II) ions in aqueous phase with C_0 at 510.92 mg/L with 1 g of biosorbent, 75-rpm magnetic stirring, pH 4.5, 1 atm and 27 ^oC.

3.6. Adsorption isotherm

The linearized Langmuir model (Equation 1) and Freundlich model (Equation 2) were used for adsorption isotherm [34, 39].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \qquad (1)$$

where C_e (mg/L) is equilibrium Cu(II) ions concentration in aqueous phase, q_e (mg/g) denotes as the equilibrium adsorption capacity, q_m (mg/g) is the adsorption capacity based on Langmuir model, and K_L (L/mg) is the Langmuir porous volume constant.

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{2}$$

where K_F (L/mg) is the Freundlich model-based adsorption capacity, and $1/n$ denotes as the adsorption intensity. The K_L, q_m K_F and $1/n$ values are calculated using the slope and intercept of related equation.

As highlighted by the R^2 values in Figure 5, adsorption isotherm based on Freundlich model fitted vey well compared to the Langmuir's one. There should be a cooperative adsorption taking place in the system because the R2 of Freundlich and Langmuir models were close to 1. However, because the R^2 of Freundlich model was higher than the R^2 of Langmuir model, physical adsorption might control dominantly the Cu(II) ions adsorption in a cooperative adsorption [34].

The K_F and $1/n$ value at 27 °C was approximately 3.04 L/mg and 3.02, respectively, and it was 5.02 L/mg and 0.67, respectively at 47 °C. The K_F value increased by increasing the temperature, and the $1/n$ value decreased by increasing the temperature. This trend was also in the previous study whereas the adsoprtion capacity decreased with the increase in temperature for physical adsorption [35].

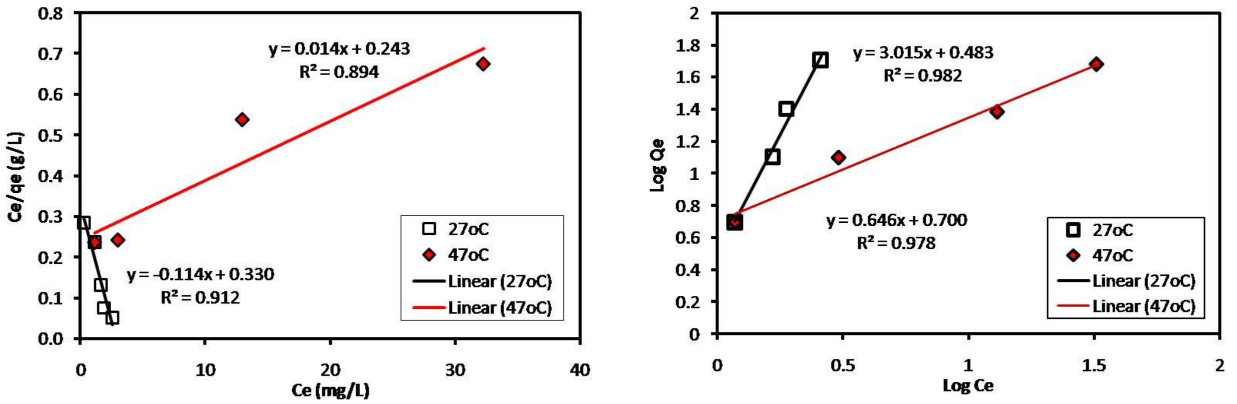
3.6. Adsorption kinetic

The linearized Lagergren pseudo first order kinetic model (LFOK) (Equation 3) [34, 39, 40] and and Ho pseudo second order kinetic model (HSOK) (Equation 4) [41, 42, 43] were taken into account for adsorption kinetic.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_L t}{2.303}\right) \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_H {q_e}^2} + \frac{t}{q_e} \tag{4}$$

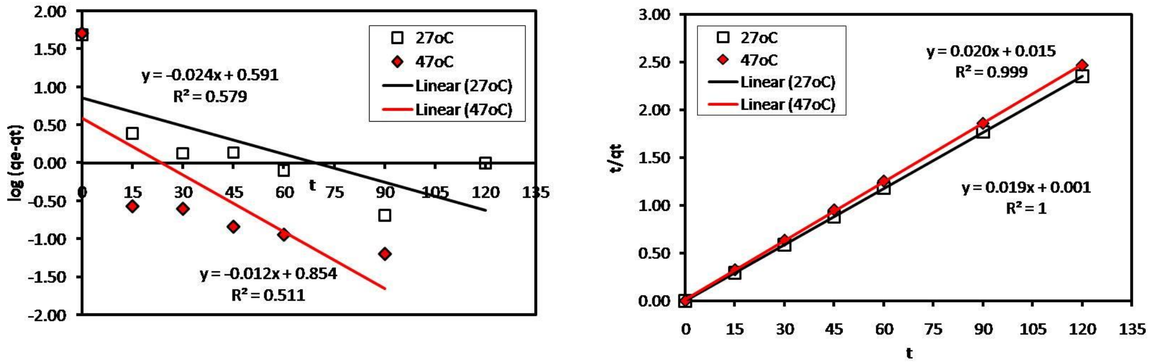
where q_t (mg/g) denotes as the Cu(II) ions adsorption capacity at certain contact time. The k_L (/min) is the (LFOK rate constant, and k_H (g/mg.min) is the HSOK rate constant. The k_L, k_H and q_e values are calculated using the slope and intercept of related equation.



(a) (b)

Figure 5: Plots of linearized Langmuir model (a) and Freundlich model (b). Experiment: 100 mL Cu(II) ions in aqueous phase with C_0 at 11.42–510.92 mg/L with 1 g of the APMBU0.7, 75-rpm magnetic stirring, pH 4.5, 1 atm, 27 and 47 °C.

As can be seen in Figure 6, the HSOK fitted much better and favourable. The HSOK equilibrium adsorption capacity at 27 and 47°C were 50.01 and 43.11 mg/g, respectively. Meanwhile, the HSOK rate constant was 4.44 and 0.03 g/mg.min at 27 and 47°C, respectively. Based on Le Chatelier's principle, adsorption capacity increase when temperature being increase for chemical adsorption because it increase chemical interaction between adsorbate and active site on adsorbent. However, we found a contradictory trend where adsorption capacity was decreasing when temperature being increasing. Therefore, there should be physical adsorption of Cu(II) onto biosorbent being taking place dominantly in the cooperative adsorption [34, 35]. Table 1 shows a comparison of maximum adsorption capacity for Cu(II) using different biosorbents which are non-activated carbon reported in the previous studies and present study.



(a) (b)

Figure 6: Plots of linearized Lagergren (a) and Ho model (b). Experiment: 100 mL Cu(II) ions in aqueous phase with C_0 at 510.92 mg/L with 1 g of the APMBU0.7, 75-rpm magnetic stirring, pH 4.5, 1 atm, 27 and 47 °C.

Table1: a comparison of maximum adsorption capacity for Cu(II) using different biosorbents.

Lignocellulosic materials	**Preparation Method**	**Adsorption**		**$q_{maximum}$ (mg/g)**	**Ref.**
		T (°C)	**pH**		
Wheat bran	D, G	60	5	51.5	[44]
Tree fern	D, G	40	NA	11.7	[45]
Cellulose pulp waste	G	22	<6	4.98	[46]
Ceratophyllum demersum	G. HCl	25	5-6	10.37	[47]
Crab carapace	D, G	20	5	79.4	[48]
Banana peel	D, G	room	6-6.5	20.37	[49]
Palm oil fruit shell	D, G	20	5	60.0	[50]
Wheat straw	C, D, H_2SO_4, NaOH	40	7	12.40	[51]
Pine Cone Powder	D, G, NaOH	18	5	26.32	[52]
Barley straw	D, G	30	7	31.71	[53]
Newspaper pulp	D, G, $NaHCO_3$	30	5.5	30.00	[54]
Tobacco dust	D	25	5.5	36.00	[55]
Sugar beet pulp	D, G	25	4	28.50	[56]
Saltbush leaves	D, G, HCl	25	5	68.00	[57]
Arenga pinnata Merr Fruit Shell	D, G, NaOH, U	27	5	50.01	PS

Note: C = cut; D = dried; G = grounded; U = ultrasound

I was noted that biosorbents from Arenga pinnata Merr fruit shell waste modified using ultrasound better adsorption capacity in comparison to other 11 biosorbents listed. However, it was a bit lower compared to the biosorbents prepared from wheat bran, crab carapace, palm oil fruit shell and saltbush leaves.

Conclusion

The adsorption of Cu(II) ions onto biosorbent prepared from Arenga pinnata Merr fruit shells waste was investigated in batch mode. The effect of ultrasound, contact time, NaOH concentration for modification, initial Cu(II) ions concentration and adsorption temperature were investigated. The FTIR and SEM were used to characterize the biosorbent functional groups and morphology, respectively. Freundlich model of adsorption isotherm and the pseudo second order of adsorption kinetic model were reliable for the Cu(II) ions adsorption on the biosorbent. The adsorption capacity and rate constant based on adsorption kinetic was approximately 50.01 mg/g and 4.44 g/mg.min, respectively at 27^{o}C, and it declined to 43.11 mg/g and 0.03 g/mg.min, respectively at 47^{o}C. The ultrasound assistance-based modified Arenga pinnata Merr fruit shell waste biosorbent would a promising adsorbent to be applied for adsorption heavy metal in the future. The sorption of Cu (II) show that the Arenga pinnata Merr Fruit Shell are suitable for adsorption of Cu(II) ions from water and wastewater.

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