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Biosorption of CU(II) Ions by *Leucaena Leucocephala* Leave from Aqueous Solution

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Abstract. As a preliminary study, this project aims to remove the copper (Cu II) from aqueous solutions using *Leucaena leucocephala* leaves. Effect of free cell and immobilized form of biosorbent on adsorption capacity were evaluated in this study. Kinetic models of pseudo-first order, second order and equilibrium isotherms of Langmuir and Freundlich were used to predict the efficiency of Cu^{2+} absorption by *Leucaena leucocephala* leaves adsorption system. The functional groups involved during the adsorption were identified using Fourier Transform Infrared (FTIR) whereby the *Leucaena leucocephala* leaves has the large amount of hydroxyl functional groups at the wavelength of 3411.66 cm^{-1}. Atomic Absorption Spectroscopy (AAS) were used to measure the metal concentration before and after the adsorption process. The maximum percentage removal of the Cu^{2+} was achieved by immobilized form of *Leucaena leucocephala* leaves as biosorbent in aqueous solutions with a 72.3% of removal. Adsorption kinetics of pseudo-second order was well fitted with the adsorption data with the R^2 of 0.9622. In addition, the results reveal that Langmuir isotherm was the best model to explain the adsorption of Cu^{2+} using immobilized *Leucaena leucocephala* leaves with the R^2 of 0.9974. This result showed that *Leucaena leucocephala* leaves as an effective and potential biosorbent for the adsorption of Cu^{2+} from the wastewater.

1. Introduction

Heavy metal is a natural element with a high atomic weight with five times greater density than water [1]. Due to their toxic characteristic in nature, heavy metals were getting attentions to many environmental chemists. Heavy metals usually exist in a bit amount in natural water but usually most of them are toxic even in low concentrations [2]. There are several types of heavy metals which are extremely toxic even in low concentrations like copper, lead, arsenic, cadmium, nickel, mercury, chromium, cobalt, zinc and selenium. For this study, copper ion (Cu^{2+}) which mostly found in industrial water streams such as mining, electroplating, non-ferrous metal industry, electrical, production of steel, the printing and photographic industries, metal working and finishing processes. This metal was chosen because of its common bad impacts that can caused like catastrophic if this kind of metal problem not been resolved [3]. Nonetheless, Cu^{2+} only will gives a health complication through the persistent contact with a human [4].

To overcome the release of Cu^{2+} into the environment, several treatments that can be consider to treat the heavy metal, which are chemical precipitation, membrane process, electro-dialysis and coagulation [5]. However, for low concentration of Cu^{2+}, these treatments are not so effective and produce the others

pollutants by the finish of treatment procedure [6]. Another potential treatment that can used for Cu^{2+} removal is biosorption, a simple and cost-effective method. Currently, biosorption has developed as a possible and promising solution with the aim of heavy metal removal with a several benefits like simple operation, no extra nutrient requirement, small amounts of sludge generation, low operating cost, very competence, recyclable and absence of the chemical oxygen demand (COD), or else main boundaries for most of the predictable methods [7].

The *Leucaena leucocephala,* which is belong to family *Fabacae* is easily available plant in Malaysia. In this study, biosorbent from L*eucaena leucocephala* leaves, which it is a low cost of biosorbent was used to remove the Cu^{2+}. It's unique characteristic with various types of functional groups that capable in binding the metal ion make it this new biosorbent as a competent biosorbent for copper ions removal.

2. Methodology

2.1. Sample preparation
Stock copper (Cu II) solutions (1000 mg/L) was prepared by dissolving 3.93 g of $CuSO_4.5H_2O$ in 1000 mL distilled water. The concentration of Cu^{2+} was prepared between 20 and 100 mg/L by diluting the copper stock solution by dissolving in distilled water.

The sample of *Leucaena leucocephala* were collected from nearby Tasik Melati, Perlis, Malaysia. The leaves were kept in an oven overnight at 80 °C [8]. The dried leaves were ground to powder form and sieved to obtain average particle size of 180 – 300 μm.

2.2. Characterization of Leucaena leucocephala biosorbent
Leucaena leucocephala leaves was analyzed using FTIR (Perkin-Elmer) to determine the functional group of *Leucaena leucocephala* leaves.

2.3. Preparation free and immobilized biosorbent of Leucaena leucocephala
The sodium alginate 3% (w/v) were prepared by dissolving 3 g of sodium alginate in 100 mL of distilled water. Then, the sodium alginate solution was mixed with the leaves powder and the mixture were dropped into 2% calcium chloride ($CaCl_2$) solution at 3500 rpm for 10 minutes by using syringe. Next, the alginate beads were washed by using distilled water to remove the $CaCl_2$ solution. The beads then were dried using filter paper.

For free biosorbent, 0.1g of the *Leucaena leucocephala* leaves powder were with 50 mL of aqueous solutions that contained of Cu^{2+}. The samples were shake in incubator shaker for about 90 min at 120 rpm. For immobilized biosorbent, 20 mL alginate solutions were mixed with the mixture of 0.1g leaves powder and 10 mL of distilled water. Then, by using syringe, the mixed of alginates solutions were slowly dropped into the calcium chloride, $CaCl_2$ solutions. The beads were left in $CaCl_2$ solutions for one hour. After one hour, the beads were washed by using distilled water and were dried by using filter paper.

2.4 Adsorption Study
The free and immobilized biosorbents were mixed with the 50 mL of Cu^{2+} aqueous solutions and shake for about 90 min at 120 rpm. Experiment were run in triplicate and average data were calculated. The samples were analysed using Atomic Absorption Spectroscopy (AAS) (Shimadzu AA-7000) for metal concentration and the amounts of Cu^{2+} absorbed (Q_e) and the percentage removal (R%) were calculated by the following equation (1) and equation (2):
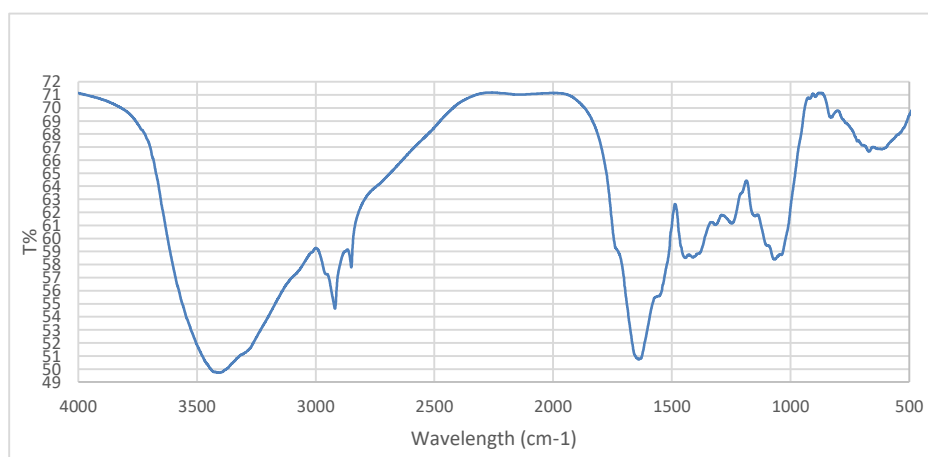
$$Q_e = \frac{(Ci - Ce)V}{m} \tag{1}$$

$$R\ \% = \frac{Ci - Ce}{Ci} \times 100 \qquad (2)$$

3. Results and Discussion

3.1. Characterization of the biosorbent

The functional group of the sample which is *Leucaena leucocephala* leaves were identified through the peak of the spectrum. Figure 1 shows the graph plotted T% versus wavelength (cm^{-1}) of *Leucaena leucocephala* leaves.

**Figure 1.** FTIR result for *Leucaena leucocephala* leaves.

From the Figure 1, the strong and broad peak that observed at 3411.66 cm^{-1} which in range of 3500 to 3200 cm^{-1} indicated to the O-H stretching vibration that has the presence of functional group alcohol and phenol. The characteristic of medium C-H stretching vibration that has the presence of alkenes group shown at 2919 cm^{-1} in the range of 3000 to 2850 cm^{-1} of the wavelength.

Another peak was observed at 2852.3 cm^{-1} is the O-H stretching vibration that has the presence of functional group carboxylic acid in the range of 3300 to 2500 cm^{-1} wavelength. The strong peak C=C stretching vibration which is the presence of alkene represented at the peak 1641.1 cm^{-1} in the range of 1648 to 1638 cm^{-1} wavelength [9].

The strong C-O stretching vibration, which are the presence of alcohols, carboxylic acids, esters and ethers are shown at peak 1247.4 cm^{-1} in the range of 1320 to 1000 cm^{-1} wavelength. Then, at the peak of 1067.2 cm^{-1}, it is shown that the medium C-H stretching vibration, that has the presence of aliphatic amines group in the range of 1250 to 1020 cm^{-1} wavelength.

3.2. Comparison between free and immobilized biosorbent

For the comparison between the free and immobilized biosorbent of *Leucaena leucocephala* leaves, the study was done at the optimum parameter that obtained from the previous study using the optimum pH of 5 [10], optimum temperature of 30°C and the optimum time of 90 min [8]. Figure 2 shows the comparison between free cell and immobilized biosorbent for the adsorption process of Cu^{2+} using *Leucaena leucocephala* leaves.
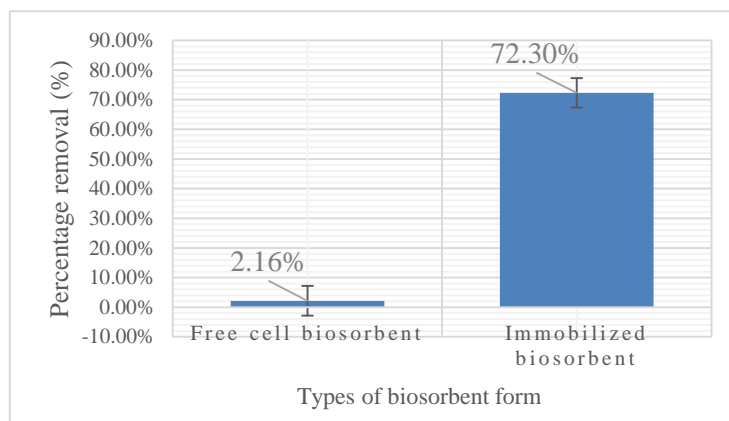
Figure 2. Comparison between free and immobilized biosorbent for the adsorption process of Cu^{2+} using *Leucaena leucocephala* leaves.

From Figure 2, it can be observed that the initial concentration of Cu^{2+} in aqueous solution was 9.4351 mg/L. After 90 min of adsorption process by using *Leucaena leucocephala* leaves as biosorbent, the concentration of Cu^{2+} in solution was drop to 2.6137 mg/L which is 72.3% of removal when the immobilized types of biosorbent was used. This result is slightly different when the free cell of *Leucaena leucocephala* leaves were used as biosorbent for the adsorption of Cu^{2+}. Only 2.16% of removal occur with the final Cu^{2+} concentration of 9.2314 mg/L.

Based on the previous study of adsorption of Pb (II) ions on sulphuric acid treated *Leucaena leucocephala* leaf powder [9], the highest percentage removal of Pb (II) ions was 99.53% by using 0.10g of treated *Leucaena leucocephala* leaves biosorbent. However, the removal of Cu^{2+}, the *Leucaena leucocephala* leaves biosorbent that has been used in this study were much lower due to the untreated leaves used which has limit the amount of Cu^{2+} to be adsorbed and also the types of metal adsorbed. In addition, it is known that treated biosorbent can absorb more heavy metal due to the break of the rigid structure of the lignocellulosic material [11].

However, there are no previous study about the immobilized form of *Leucaena leucocephala* leaves used as biosorbent and this is as a new approach for the removal of the Cu^{2+} from the aqueous solutions. It was proved that immobilized *Leucaena leucocephala* leaves biosorbent can be an effective biosorbent to remove the Cu^{2+}. The percentage removal of Cu^{2+} for immobilized biosorbent is 72.3%. Based on previous study by Abdel Hameed [12], it was reported that immobilized beads were more effective than the free cells. The maximum percentage of lead removal by immobilized beads of *Chlorella vulgaris* is 92%. The mainly caused of the removal of lead was by the alginate beads matrix with the minor contribution by *Chlorella vulgaris*. Immobilization tends to increase the accumulation of metal by biomass [13]. Immobilized cells more effective than free cells for metal removal by biomass due to increase in the cell wall permeability [14]. It can be assumed that the removal of Cu^{2+} also due to the immobilized beads with the slight contribution of *Leucaena leucocephala* leaves.

3.3. Kinetic study and adsorption isotherm of Cu^{2+}

3.3.1. *Biosorption capacity.* Figure 3 shows the adsorption capacity of immobilized *Leucaena leucocephala* leaves as biosorbent for the adsorption of Cu^{2+} where the Q_e was increased when the concentration of Cu^{2+} available in solution was decreased. This result shows that the adsorption process was effective using *Leucaena leucocephala* leaves as biosorbent. The biosorption capacity for this study was increase from 0 mg/g at 0 minutes to maximum biosorption capacity which was 1.0895 mg/g at 100 minutes. The contact time that were used in this study were 0 minute to 100 minute because the biosorption is predicted to be stopped at 90 minutes (based on previous study) but based on the results showed in Figure 3, it was contradicted. This trend may be due to the different types of heavy metals

used. The previous study used Pb(II) ions where equilibrium at 90 minute with the Q_e value was 83.15 mg/g by using treated *Leucaena leucocephala* leaves [8] but in this study the heavy metal that has been used was Cu^{2+} with the Q_e value at 90 minute was 1.0439 mg/g. It also may due to the types of biosorbent used where in this study was a new approach which is immobilized *Leucaena leucocephala* leaves was used as biosorbent. It can be concluded that the equilibrium time for the concentration of Cu^{2+} absorb by using immobilized *Leucaena leucocephala* leaves biosorbent were more than 100 minutes.
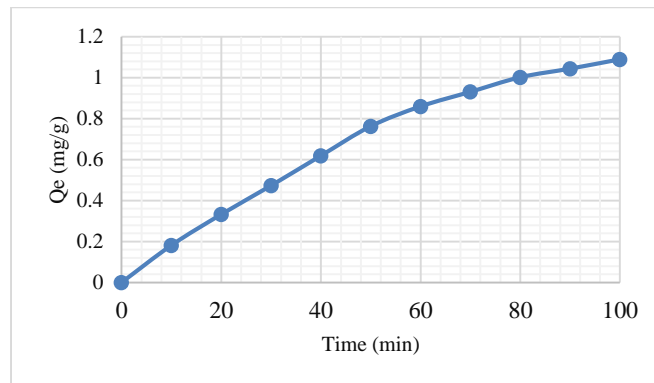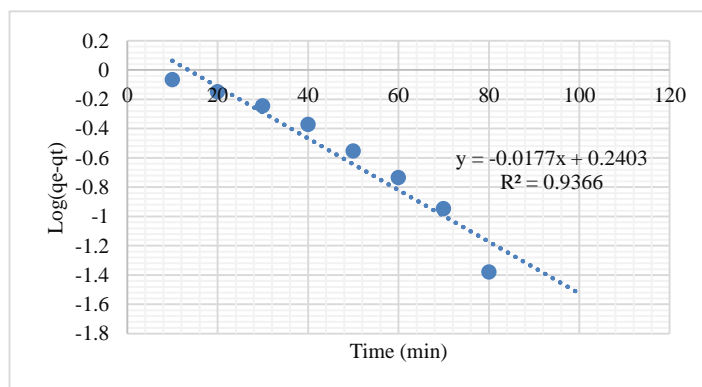

Figure 3. Adsorption capacity of immobilized *Leucaena leucocephala* leaves as biosorbent for the adsorption of Cu^{2+}.

3.3.2. *Pseudo-first order model.* The linear relationship of the plots indicates the validity of the equation. The pseudo-first order model calculated by using the following equation (3) [15]:

$$\log(Q_e - Q_t) = logQ_e - \frac{K_1}{2.303}t \tag{3}$$

Based on the Figure 4, it was observed that correlation coefficient, R^2 of the pseudo-first order reaction is 0.9391. The calculated Q_e values from first order reaction is 1.7390 mg/g while the experimental Q_e is 1.0439 mg/g. The calculated Q_e values does not close to experimental Q_e values. Experimental Q_e was obtained from the value in adsorption at equilibrium while the calculated Q_e is the predicted value by using the equation of kinetic model [16]. When the calculated Q_e values does not closed to experimental Q_e values, it shows that it does not fit to this kinetic model.


Figure 4. Plot for Pseudo-First Order Kinetic Model for the adsorption of Cu(II) ion using *Leucaena leucocephala* leaves as biosorbent.

3.3.3. *Pseudo-second order model.* The plot of t/qt versus t based on Figure 5 shows a linear relationship that calculated by using the following equation (4) [17]:

$$\frac{t}{Q_t} = \frac{1}{h} + \frac{1}{Q_e}t$$

(4)

The value for Q_e and K_2 can be determined from the slope and the intercept of the plot. It found that the value for K_2 is 0.00316 g/mg.min and the calculated Q_e value is 2.5246 mg/g. It shows that calculated Q_e values also does not close to experimental Q_e value but for the correlation coefficient R^2 of pseudo-second order was higher than pseudo-first order which is 0.9622. For the calculated Q_e value, it should be close to experimental Q_e value in order to show the good agreement of the model. In this case, the error might be happened due to the biosorption of Cu^{2+} since it is predicted to be stopped at 90 minutes [10], but in this study, the biosorption still increases more than 90 minutes. It also may due to the different types of biosorbent used, based on previous the type of biosorbent used is the *Leucaena leucocephala* (Subabul) seed pods for the removal of the Cu^{2+} in aqueous solutions. Table 1 shows the summarized of parameters values for pseudo-first order and pseudo-second order.
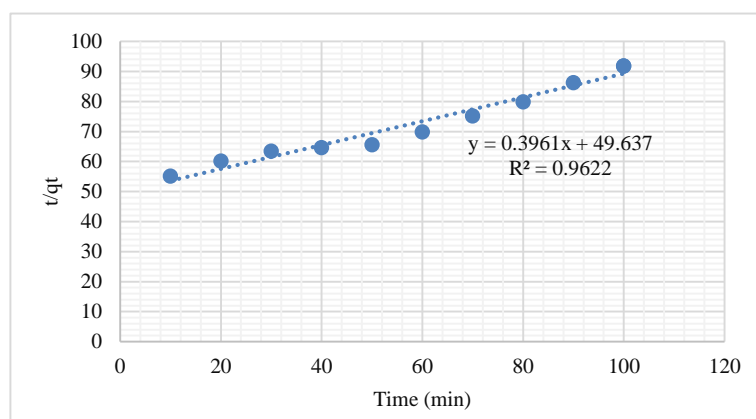
Figure 5. Plot of Pseudo Second Order Model for adsorption of Cu^{2+} by *Leucaena leucocephala* leaves in aqueous solution.

**Table 1.** Summarized values for pseudo-first and pseudo-second order.

Parameter	Pseudo-first order	Pseudo-second order
K_1 (min^{-1}) & K_2 (g/mg min)	0.04099	0.00316
$Q_{e,exp}$ (mg/g)	1.0439	1.0439
$Q_{e,cal}$ (mg/g)	1.7673	2.5246
R^2	0.9391	0.9622

3.3.4. *Freundlich isotherm.* The Freundlich isotherm calculated by using the following equation (5) [19]:

$$\log(Q_e) = \log K_f + \frac{1}{n}\log C_e$$

(5)

Figure 6 shows the linear plot of loq Q_e versus log C_e that indicates the adsorption of Cu^{2+} using *Leucaena leucocephala* leaves with the correlation coefficients R^2 for the Freundlich isotherm was

found to be 0.9266. The values for adsorption coefficient K_f and $1/n$ can be obtained from the graph plotted. Based on the graph loq Q_e versus log C_e, the value of $1/n$ is -8.9266 and the value of K_f is 342294562.3 L/g. Based on the previous study by Patil et al [10] for the removal of Cu^{2+} by *Leucaena leucocephala* (Subabul) seed pods in aqueous solution, the linearity of Freundlich plot suggested the formation of homogenous monolayer of Cu(II) on the outer surface of the adsorbent, the adsorption coefficient K_f of Cu^{2+} by *Leucaena leucecephala* (Subabul) seed pods was found to be 4.562 L/g and the value for $1/n$ is 0.01057. It showed that there are too much gap between K_f value from previous study and current study. It may have some errors while conducted the experiment since the K_f value is very high and it might due to the adsorption of Cu^{2+} by *Leucaena leucocephala* leaves does not fit to the Langmuir isotherm model. Table 2 shows the data summarization for Freundlich isotherm equation.
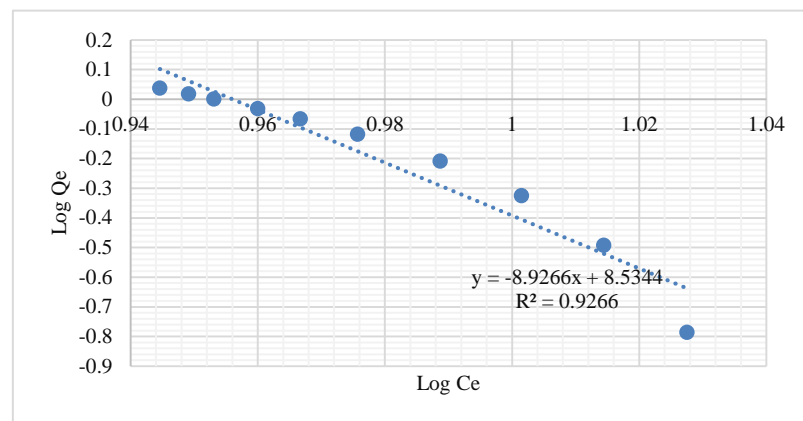
Figure 6. Plot of Freundlich isotherm model for adsorption of Cu^{2+} by *Leucaena leucocephala* leaves in aqueous solution.

Table 2. Summarized values for Freundlich isotherm

| Parameter	Freundlich isotherm
K_F (L/g)	342294562.3
$1/n$	-8.9266
R^2	0.9266

3.3.5. *Langmuir isotherm*. Based on the previous study by Mohammadi *et al* [19], the modified Langmuir isotherm equations has been proposed in order to get the best fit of adsorption isotherm. The reasons why the modified Langmuir isotherm equations has been proposed are due to the direct application of Langmuir isotherm frequently leads to the poor data fitting. In this study, the modified Langmuir isotherm equation also used in order to get best fit of adsorption isotherm. The purpose of the modified Langmuir isotherm equation is because direct application of the Langmuir isotherm equation leads to the poor data fitting. Table 3 shows the linear and non-linear isotherms equation for modified Langmuir isotherm.

Table 3. Linear and non-linear isotherms equations for modified Langmuir isotherm [19].

Isotherm	Non-linear equation	Linear equation	Plot
Langmuir-1		$\dfrac{C_e}{Q_e} = \dfrac{1}{(Q_{max})(b)} + \dfrac{C_e}{Q_{max}}$	C_e/Q_e vs. C_e
Langmuir-2	$q = \dfrac{q_{max}bC_e}{1 + bC_e}$	$\dfrac{1}{Q_e} = \dfrac{1}{(Q_{max})(b)}\left(\dfrac{1}{C_e}\right) + \dfrac{1}{Q_{max}}$	$1/Q_e$ vs. $1/C_e$
Langmuir-3		$Q_e = Q_{max} - \left(\dfrac{1}{b}\right)\left(\dfrac{Q_e}{C_e}\right)$	Q_e vs. Q_e/C_e
Langmuir-4		$\dfrac{Q_e}{C_e} = (b)(Q_{max}) - (b)(Q_e)$	Q_e/C_e vs. Q_e

Modified Langmuir coefficients for four linearized modified Langmuir equations were obtained by plotting the graphs between C_e/Q_e versus C_e for Langmuir-1, $1/Q_e$ versus $1/C_e$ for Langmuir-2, Q_e versus Q_e/C_e for Langmuir-3 and Q_e/C_e versus Q_e for Langmuir-4. The values of Q_{max} and b were determined from slopes and intercepts of the Langmuir plot for all four modified equations. Figure 7 (a), (b), (c) and (d) shows graphs plot for all four modified Langmuir isotherms equations for the adsorption of Cu^{2+} by *Leucaena leucocephala* leaves as biosorbent.

(a)

(b)

(c)

(d)
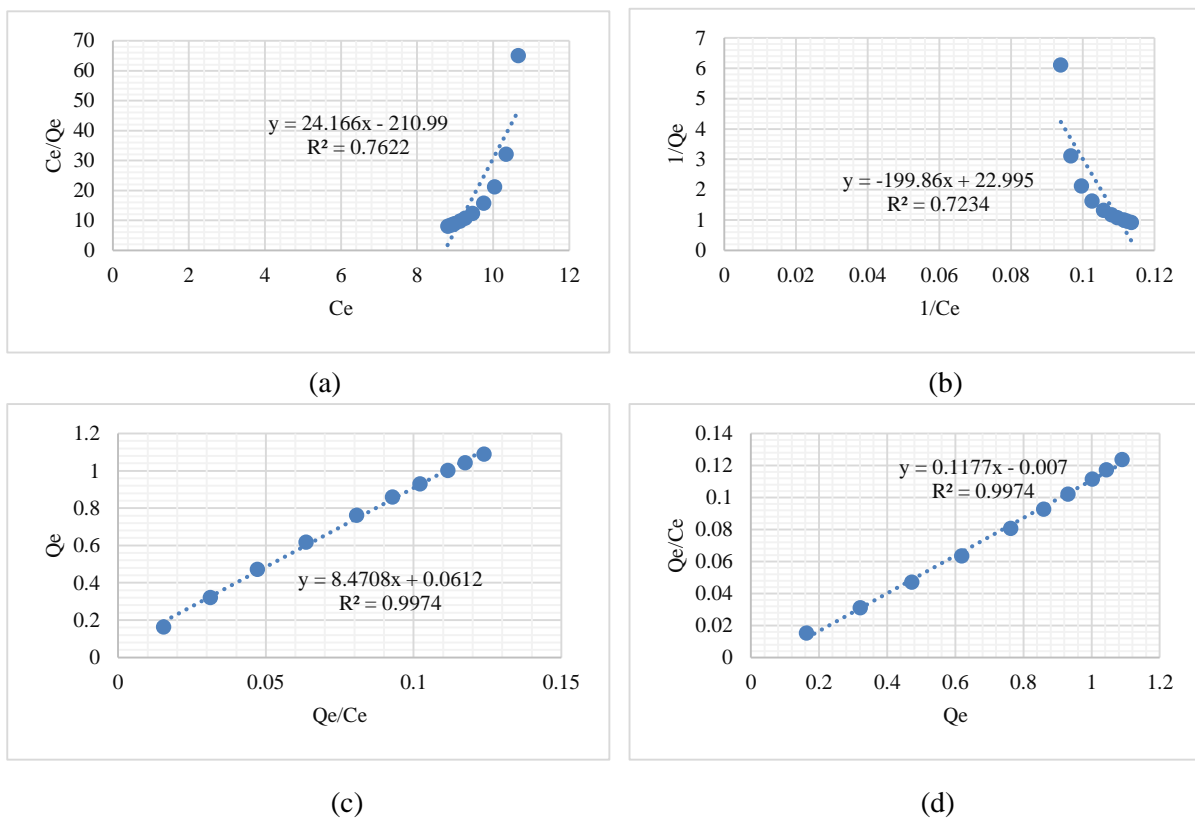
Figure 7. Plot of Langmuir isotherm for adsorption of Cu^{2+} by *Leucaena leucocephala* leaves in aqueous solution; (a) Langmuir-1; (b) Langmuir-2; (c) Langmuir-3; and (d) Langmuir-4.

The values of Q_{max}, b and correlation coefficients R^2 for all four modified Langmuir isotherm equations were presented in Table 4. The low values of b for Cu^{2+} in this case was suggestive of greater affinity of adsorbent for Cu^{2+}. A good metal adsorbent in general should have high Q_{max} and low value of b which is Langmuir constant [20].

Table 4: Summarization values for modified Langmuir isotherm.

Langmuir isotherms	b (mg/L)	Q_{max} (mg/g)	R^2
Langmuir-1	-0.1145	0.04138	0.7622
Langmuir-2	-0.1152	0.04349	0.7234
Langmuir-3	-0.1181	0.0612	0.9974
Langmuir-4	-0.007	0.05947	0.9974

From the result, the modified Langmuir isotherm equations that has low value of b is Langmuir isotherm equation 4, which is -0.007 mg/L. For Q_{max} value, the modified Langmuir isotherm that has high value of Q_{max} value is Langmuir isotherm equation 3, which is 0.0612 mg/g. For overall result, the modified Langmuir isotherm equations that has been chosen is Langmuir isotherm equation 4 which is the value of b is -0.007 mg/L and Q_{max} value is 0.05947 mg/g. Even though Langmuir isotherm equation 3 has the highest value of Q_{max}, but the low value of b was needed due to when the value of b is low it has a great affinity of adsorbent for Cu^{2+}.

It has been proved that biosorption of Cu^{2+} using *Leucaena leucocephala* leaves follows the Langmuir isotherm model. The reason why biosorption of Cu^{2+} fit with the Langmuir isotherm because it is a monolayer based sorption and it assumes that all the binding sites on the sorbent are free sites and ready to accept the sorbent from the solutions [21]. For some reason, all the values of b for all four modified Langmuir isotherm equations are negative. The negative Langmuir constant were caused by using the low concentration of heavy metal, which is Cu^{2+}. If the capacity is low, then it will have negative intercept due to the experimental deviations.

4. Conclusion

Immobilized form of *Leucaena leucocephala* leaves as biosorbent was the most effective form of biosorbent for the adsorption of Cu^{2+} from aqueous solution compare to free cell biosorbent with the 72.3% of Cu^{2+} removal. It is proved that immobilized form of *Leucaena leucocephala* leaves as biosorbent is more effective than free cell biosorbent. For the kinetic study of Cu (II) ions adsorptions, the biosorption of Cu^{2+} using *Leucaena leucocephala* leaves as biosorbent is followed the pseudo-second order model with the correlation coefficient R^2 is 0.9622 while for the pseudo-first order only 0.9391. For the adsorption isotherm model, the biosorption of Cu^{2+} using *Leucaena leucocephala* leaves as biosorbent is followed the Langmuir isotherm model. In this study, modified Langmuir isotherm equations has been used in order to get the best fit of the adsorption isotherm. Among 4 modified Langmuir isotherm equation tested, Langmuir isotherm equation 4 is the best fit of the adsorption isotherm due to the low value of b. The characterization of *Leucaena leucocephala* leaves has the presence of large amount of hydroxyl functional groups at the peak 3411.66 cm^{-1}, ethers and other functional groups that could provide an active site for the adsorption of Cu^{2+} [9].

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Acknowledgement