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Oil palm Root as Biosorbent for Heavy Metals: Biosorption, Desorption and Isothermal Studies

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Abstract: The study was carried out was to investigate the ability of oil palm root as biosorbent for different heavy metals in aqueous solution under different conditions. The effect of physico-chemical parameters, namely pH and metal ion concentration on the removal efficiency were investigated. Behaviour of mixed metal ion biosorption and desorption using oil palm root were studied. Investigation and comparison were made for the metal-binding capacity and the performance of biosorbent in the function of aforesaid paraments, through isotherm models, namely Langmuir, Freundlich and Dubinin-Radushkevich models. The results show that the equilibrium data of Cu and Pb fit well to all isotherm models except that of Zn metal ion. The removal efficiency of metal ions is strongly affected by pH and metal ion concentration. The biosorption capacity increases sharply from pH 6.0 to 7.0 while the pH < 3.0 inhibits the biosorption of metal ions. The maximum biosorption is 31.11 mg/g at pH 7.0. The uptake capacity, q_e of Cu and Pb increases from 50 mg/L to 200 mg/L, while the uptake capacity of Zn increases from 50 mg/L to 150 mg/L. The results of this study imply that oil palm root is a suitable biomass to remove Cu, Zn and Pb metal ion from aqueous solution.
Keywords: Oil palm root, biosorbent, heavy metals, biosorption, desorption, isotherms.

Introduction

Rapid industrial activities have caused many environmental problems due to the release of toxic and hazardous chemicals especially heavy metals in the industrial effluents [1,2]. Heavy metals are non-biodegradable and tend to bio magnify and accumulate in our food chain [3,4] Therefore, a proper treatment is essential to alleviate the impact of heavy metals to the environment and public health [5]. Biosorption can be an alternative for the conventional wastewater treatment methods such as ion exchange, chemical precipitation and membrane filtration, due to its effectiveness, simplicity and economically viable sound [6-9]. Biosorption is a rapid physico-chemical process which involves the binding of metals on the biological materials [10] One of the biosorption approaches is using oil palm biomass as biosorbent. Based on previous studies, oil palm biomass such as trunks, fronds, empty fruit bunches (EFB), leaves and shells were used as effective biosorbents to remove heavy metals [1,11]. However, to date, there is no report on oil palm root used in removing heavy metals from aqueous solution. Thus, this research was carried out to investigate of the feasibility of oil palm root biomass as a biosorbent. In this study, oil palm root biosorbent was used to remove heavy metals Copper (Cu^{2+}), Zinc (Zn^{2+}) and Lead (Pb^{2+}) using oil palm root biosorbent from aqueous solution under different pH and metal ion concentrations. The performance of oil palm root as biosorbent for heavy metal was evaluated, particularly in single and multiple metals systems. Desorption and isotherm studies were also carried out to give insight of the oil palm root biosorbent system.

Material and methods

$CuSO_4.5H_2O$, $Zn(NO_3)_2$, $PbCl_2$, HNO_3 and NaOH of analytical grade were purchased from Merck. Oil palm root was obtained from rural palm estate at Jeli, Kelantan, Malaysia. Figure 1 shows the oil palm root before and after washing and drying.

(a) (b)

Figure 1. Oil Palm root before (a) and after (b) washing.

Preparation of biosorbent and metal ion aqueous solution

Oil palm root obtained was washed thoroughly using tap water and deionized water before drying in oven at 100 ºC. The oil palm root was grounded into powder prior to treat with 0.3 M HNO_3. The oil palm root powder was then sieved into the size of 150 μm. Standard solutions for Cu, Pb and Zn were prepared through a series of dilution from stock solutions. The solution was diluted with 1% HNO_3 solution.

Biosorption Studies

The batch biosorption experiments were carried out for single metal ion system and mixed metal ions system. The regeneration of biosorbent was investigated through desorption process. The concentration of metal ion in aqueous solution was analyzed using atomic absorption spectrophotometer. The biosorption capacity and the rate metal uptake were calculated using isotherm models.

Atomic Absorption Spectrometry (AAS)

Atomic Absorption Spectrometer (Perkin Erlmer, USA) was used to carry out atomic absorption studies. The analysis was performed at wavelengths 324.754 nm, 213.856, 226.502 nm for Cu, Zn, and Pb, respectively.

Metal Uptake Capacity

The removal of metal ion from aqueous solution using oil palm biosorbent was calculated by equation 1.

$$\text{Removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (1)$$

The metal uptake capacity was assessed using isotherm models. The data obtained was fitted into isotherm models to determine the fitness of the model. The metal ion uptake was obtained by equation 2.

$$\text{Equilibrium adsorption capacity (mg/L)}, q_e = \frac{(C_o - C_e)}{m} \times V \qquad (2)$$

Where, C_o and C_e represent the initial and final metal ion concentration, respectively. V is the volume of aqueous solution (L), and m is the dry weight of biosorbent in g.

Biosorption Isotherm Models

Langmuir Isotherm Model

Langmuir accounts for the maximum amount, q_m of metal ions required to form single layer biosorption. High q_m and steep initial isotherm slope represents a desirable high affinity, which explains the good performance of biosorbent in general. The affinity between metal ions and biosorbent (sorbate-sorbent) was calculated using R_L, depending on the value of Langmuir constant (K_L). K_L is related to sorption energy as given equation 3.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (3)$$

Freundlich Isotherm Model

Freundlich's isotherm model determines the heterogeneity of biomass. K_F and n in Freundlich is related to adsorption capacity and intensity of biosorbent, respectively. Low value of K_F indicates less adsorption of metal ions, whereas when value of (1/n) is unequal to unity (1), the biosorption is decreased with increasing of metal ion concentrations as yielded from equation 4.

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (4)$$

Dubinin Radushkevich (D-R) Isotherm Model

This isotherm was used to determine the physical and chemical parameters of biosorption dependent on temperature. The theoretical maximum capacity, Q_D and Dubinin constant, B_D is calculated from intercept and slope of plot of ln (q_e) versus ln (1+1/C_e).

Analysis and Interpretation

The data collected from the experiments was analyzed using Microsoft-Excel 2007 and SPSS software. Regression analysis was employed for reliability and statistical validation between theoretical data of isotherm model and experimental data.

Results and Discussion

The feasibility of oil palm root biomass as biosorbent in removing three metal ions namely copper (Cu), zinc (Zn) and lead (Pb) was investigated The effect of pH and initial metal ion concentration were examined to determine the biosorption efficiency. A single and mixed metal system as well as desorption studies were also carried out.

Effect of Ph

pH is the most important parameter, which affects various factors in biosorption process such as functional group of biomass (biosorbent), degree of ionization of metal solution (biosorbate), and solubility of metal ions [12]. The competition abilities of hydrogen ions with metal ions to unite with the active sites of biosorbent are occurred in biosorption process [13]. The effect of pH on biosorption of metal ions was studied in the pH range from 2.0 to 7.0, while keeping the concentration of metal ion 250 mg/L. The removal efficiency and uptake capacity of Cu, Zn and Pb ions as a function of pH is shown in Figure 2 and Table 1. It is noted that the metal ions removal efficiency increases with the increasing of pH although there is a fluctuation of removal efficiency between pH 3.0 to 6.0 for Cu and Pb. The fluctuation of results could be attributed to irregular measurements of pH. The maximum adsorption is detected at pH 7.0. The removal efficiency is relatively lower at pH 2.0 because the overall surface charges become positive as H^+ occupies the active sites of biosorbent and thus metal ions compete for binding in the active sites of biosorbent. The active sites become more negatively charged and the functional group become deprotonated as the pH increases. Hence, more active sites are available for metal ions [5].

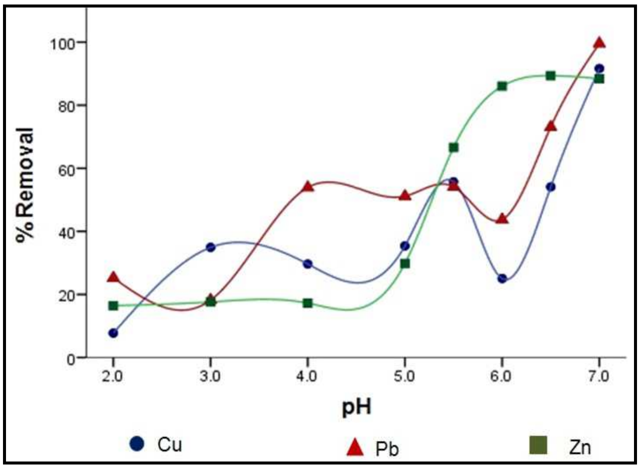

Figure 2. Effect of pH on metal ions removal efficiency.

Table 1. Metal uptake capacity, q_e and % removal for pH of Cu, Zn and Pb

Metal Ions pH	Cu		Zn		Pb	
	q_e	% Removal	q_e	% Removal	q_e	% Removal
2	2.43	7.76	7.89	25.24	5.14	16.44
3	10.91	34.92	5.69	18.20	5.50	17.60
4	9.26	29.64	16.85	53.92	5.39	17.24
5	11.06	35.40	15.99	51.16	9.33	29.84
5.5	17.41	55.72	16.91	54.12	20.82	66.61
6	7.83	25.04	13.66	43.72	26.89	86.04
6.5	16.91	54.12	22.84	73.09	27.94	89.39
7	28.64	91.64	31.11	99.55	27.62	88.39

Effect of initial metal ion concentration

The previous studies revealed that the uptake capacity of biosorbent increase with the increasing of metal ion concentration [8-10, 14-16] .The effect of initial metal ion concentration was studied at different metal ion concentrations ranging from 50 mg/L to 250 mg/L. Figure 3 depicts the metal ions removal efficiency against the initial concentration of metal ions. It is noted that there is a similar trend shown for Cu and Pb, in which the removal efficiency decreases gradually from 50 mg/L to 150 mg/L, but increases slowly after 150 mg/L and decreases again after 200 mg/L. However for the adsorption of metal ion Zn, there is an increase of removal efficiency from 50 mg/L to 150 mg/L. The metal uptake drops sharply after 150 mg/L. The decrease in removal efficiency may be caused by the saturation of adsorption sites [10] . Figure 4 shows the comparison of uptake capacity (mg/g), q_e for each metal ion; Cu, Zn and Pb. The selectivity order for metal ions towards oil palm root biosorbent is Pb>Cu>Zn, which is in agreement with the study of Ashraf *et. al.* 2011 for biosorption of Pb, Cu, Zn and Ni using mango biomass. [10].

Competitive biosorption: Mixed metal system

Competitive biosorption of Cu, Zn and Pb by the oil palm root biosorbent was conducted with three different metal ion concentrations, 50 mg/L, 100 mg/L and 250 mg/L. In the experiments, a 50 mL of mixed metal ion solution was treated with a 0.4 mg of oil palm root biosorbent at room temperature, 25^{o}C. Table 2 exhibits the adsorption of three-metal system that compared with single metal system. In general, the percentage removal and uptake capacity of metal ion are influenced by the presence of other metal ions. According to the results, majority of metal ions show drastic increase in the percentage adsorption and uptake capacity, q, of three-metal system when compared to single metal system. For Pb in metal concentration of 50 mg/L the decline in percentage removal is very small and unnoticeable. In summary, the presence of other ions significantly affects the biosorption of metal ions.

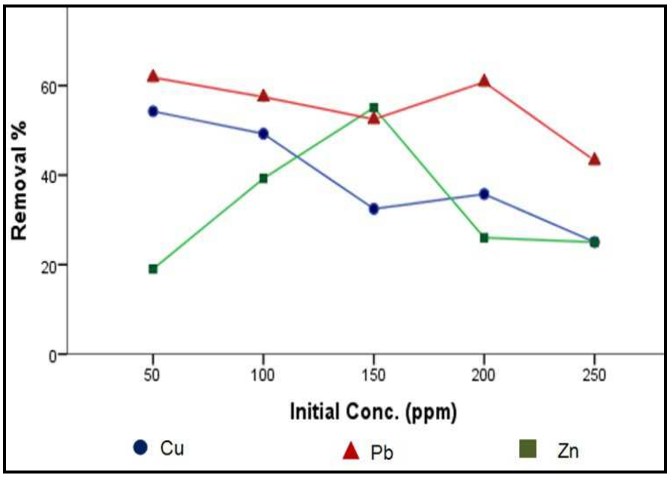

Figure 3. Effect of concentration on adsorption of metal ion.

Desorption study

Desorption study was conducted to determine the regeneration and reusability of biosorbent for the evaluation of the efficiency and feasibility of metal removal process. Desorption of metal ions that bound on the biomass was conducted by allowing the metal bound-biosorbent immersed in two different eluents, HCl and HNO_3 for 15 minutes. The eluents performed as desorbing solution, in which the eluents separates metal ions that have bound on biosorbent during biosorption process into eluents solution. The desorption efficiency is shown in Figure 5. The desorption of Pb and Cu from oil palm root biosorbent is higher than Zn. Higher recovery of Pb and Cu could be due to the lower affinity between Pb and Cu with biosorbent. Zn has lower recovery due to the higher affinity of Zn towards biosorbent compared to Pb and Cu. As the desorption efficiency of HNO_3 is higher than that of HCl, it can be concluded that HNO_3 is a relatively more effective eluents for recovering metal ions from oil palm root biosorbent. The result also shows that oil palm root biosorbent can be utilized in multiple-sorption-desorption cycles as the metal ions can be recovered from the biosorbent.

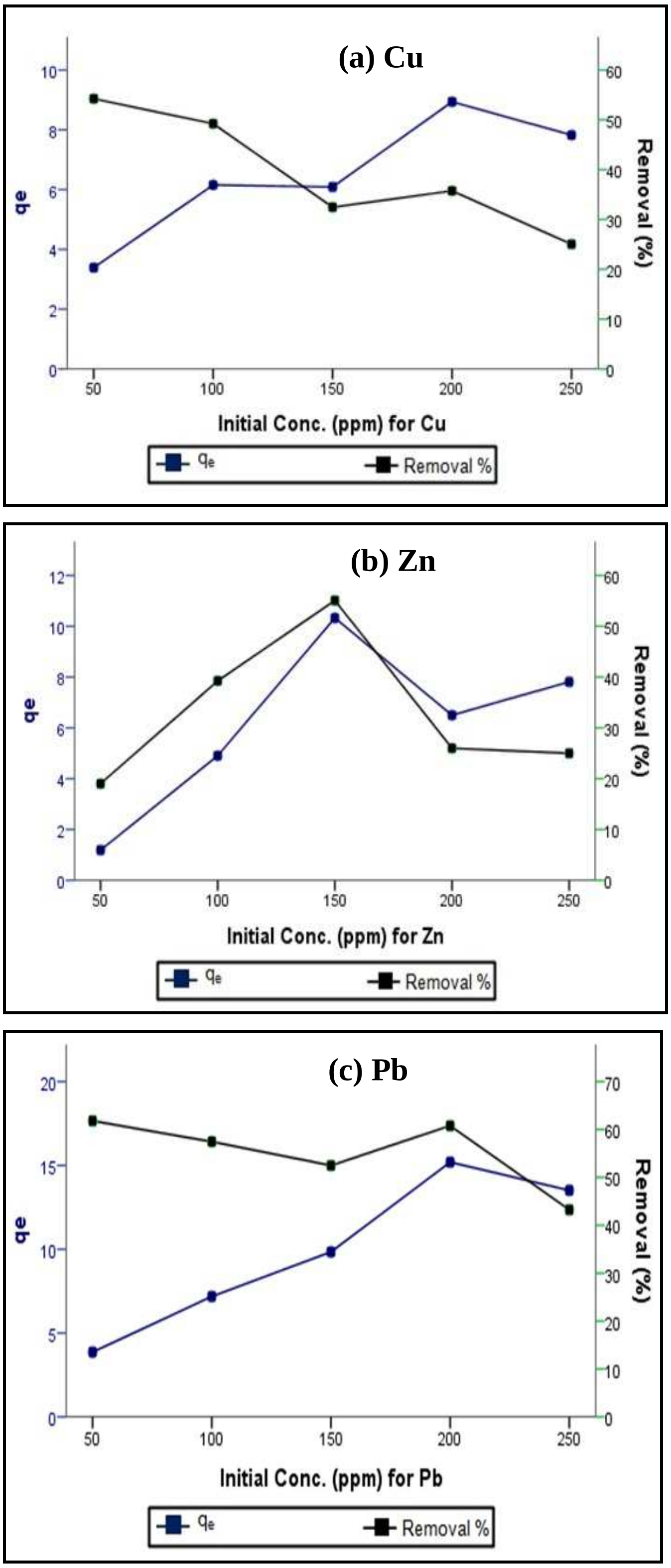

Figure 4. Metal uptake capacity and percentage removal as a function of metal ion concentration by oil palm root biomass as biosorbent: (a) Cu, (b) Zn, (c) Pb.

Table 2. Competitive biosorption of Cu, Zn and Pb.

Metal ion	Metal ion conc. (ppm)	Single metal system		Three-metal system	
		q	% Removal	q	% Removal
Cu	50	3.39	54.24	5.64	90.304
	100	6.15	49.23	10.84	86.75
	150	6.09	32.47	17.81	95.01
Zn	50	1.19	19.02	5.05	80.76
	100	4.91	39.25	10.08	80.66
	150	10.33	55.07	15.22	81.15
Pb	50	3.86	61.8	3.86	61.76
	100	7.18	57.46	9.23	73.87
	150	9.84	52.49	15.10	80.55

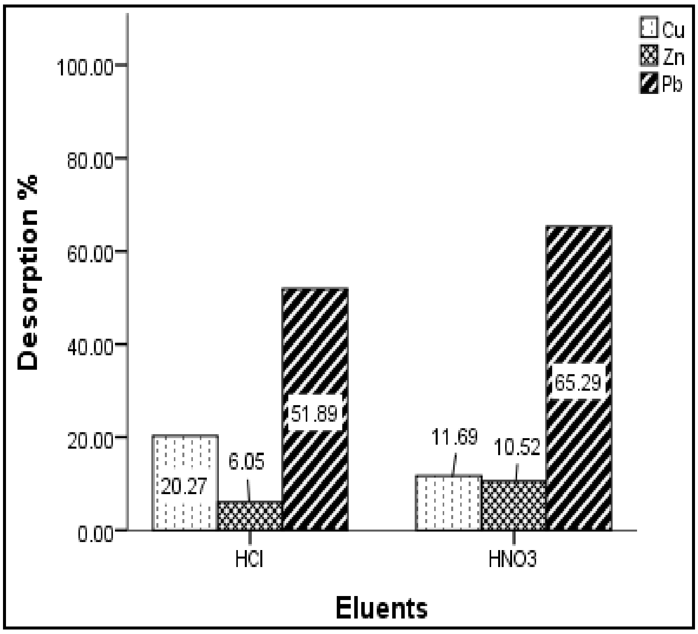

Figure 5. Desorption efficiency of metal ions for HCl and HNO_3.

Biosorption isotherm

The biosorption isotherm models such as Langmuir, Freundlich, and Dubinin-Radushkevich models were employed to evaluate the biosorption equilibrium between metal ion solution and oil palm root biosorbent. Langmuir and Freundlich isotherms were used to examine the biosorption performance in metal ions uptake and determine the mechanism of monolayer and multilayer adsorption, respectively. The physical and chemical of biosorption are determined by Dubinin-Radushkevich. The data obtained from the biosorption experiment were used for the linear fits of the isotherm models. The constants of the isotherm models obtained from the linear fits are tabulated in the Table 3, including the linear regression coefficients, R^2. The constants from isotherm models are used to generate the nonlinear fits of the isotherm models. These nonlinear fits are used to evaluate the behaviour of biosorption isotherm model with the experimental value.

Langmuir isotherm model

The linear plots of Langmuir isotherm model obtained for different metal ions are given Figure 6. The maximum amount of metal ion required to form monolayer, q_m and Langmuir constant, K_L are estimated by plotting graph of C_e/q_e against C_e. The results obtained shows that the Langmuir isotherm model is fit for the biosorption of Cu and Zn using linear regression, with R^2 of 0.924 and 0.774, respectively. Table 3 demonstrates the Langmuir isotherm parameter for each metal ion. The separation factor, R_L and surface coverage, θ are both the essential parameter in Langmuir isotherm model. Separation factor (SF) is the equilibrium parameter that specifies the nature of adsorption and the shape of isotherm. SF can be defined by the following relationship.

$$\text{Separation factor, } R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

The SF values are calculated from the equations and graph of SF against initial concentration. **Figure 7** shows the graph of separation factor. Favourable isotherm can be obtained when the SF value falls between 0 and 1. [10]. Table 5 shows the SF values, R_L for each metal ion. The data indicates that the oil palm root biosorbent is a relatively effective adsorbent at lower metal concentrations.

To assess the adsorption behaviour of metal ions on biosorbent, surface coverage (SF), which is the Langmuir type equation, is used. The equation of surface coverage is:

$$\text{Surface coverage, } \theta = \frac{K_L C_0}{1 + K_L C_0} \quad (6)$$

The graph of SC against metal ion concentration was plotted to study the surface portion of biosorbent that are covered by metal ion. The data is presented in Figure 8 and Table 5.

Based on the data presented, the surface coverage indicates that the increasing of metal ion concentration leads to the increase of surface coverage of oil palm root biosorbent until the surface is almost covered with monomolecular layer. The highest surface coverage value for metal ions is copper, followed by lead and zinc. Therefore, it can be concluded that oil palm root biosorbent is the most effective in uptaking Cu at all initial concentrations.

Table 3. Coefficients of isotherm models

Isotherm parameters	Oil palm root biomass		
	Copper (II)	Zinc (II)	Lead (II)
Langmuir			
q_{max} (mg/g)	9.71	41.67	23.26
K_L	2.63 x10^{-2}	1.37 x10^{-3}	1.16 x10^{-2}
R^2	0.924	0.020	0.774
Freundlich			
q_{max} (mg/g)	8.82	9.75	16.45
1/n	0.406	0.850	0.684
K_F	1.054	0.114	0.555
R^2	0.826	0.417	0.874
Dubinin-Radushkevich			
q_{max} (mg/g)	8.05	9.90	13.78
Q_D (molg^{-1})	9.09	15.47	17.00
B_D (kJmol^{-1})	4.65 x 10^{-3}	1.71 x 10^{-2}	6.10 x 10^{-3}
E (kJmol^{-1})	9.64 x 10^{-2}	1.85 x 10^{-1}	1.11 x 10^{-1}
R^2	0.890	0.595	0.903

Freundlich isotherm model

Freundlich isotherm model was employed to estimate the adsorption capacity and intensity of oil palm root biosorbent. Freundlich isotherm is not limited to monolayer formation and reversible adsorption, and it can be illustrated through this isotherm. Graph log Q_e against log C_e was plotted to attain the straight line with slope 1/n and intercept log K_F. Figure 9 shows the linear graphs of Freundlich isotherm with their linear regression coefficients, R^2. The graph reveals that the experimental data obtained in this study are well fitted into Freundlich isotherm models, except for Zn, which has the lowest value of linear regression, R^2.

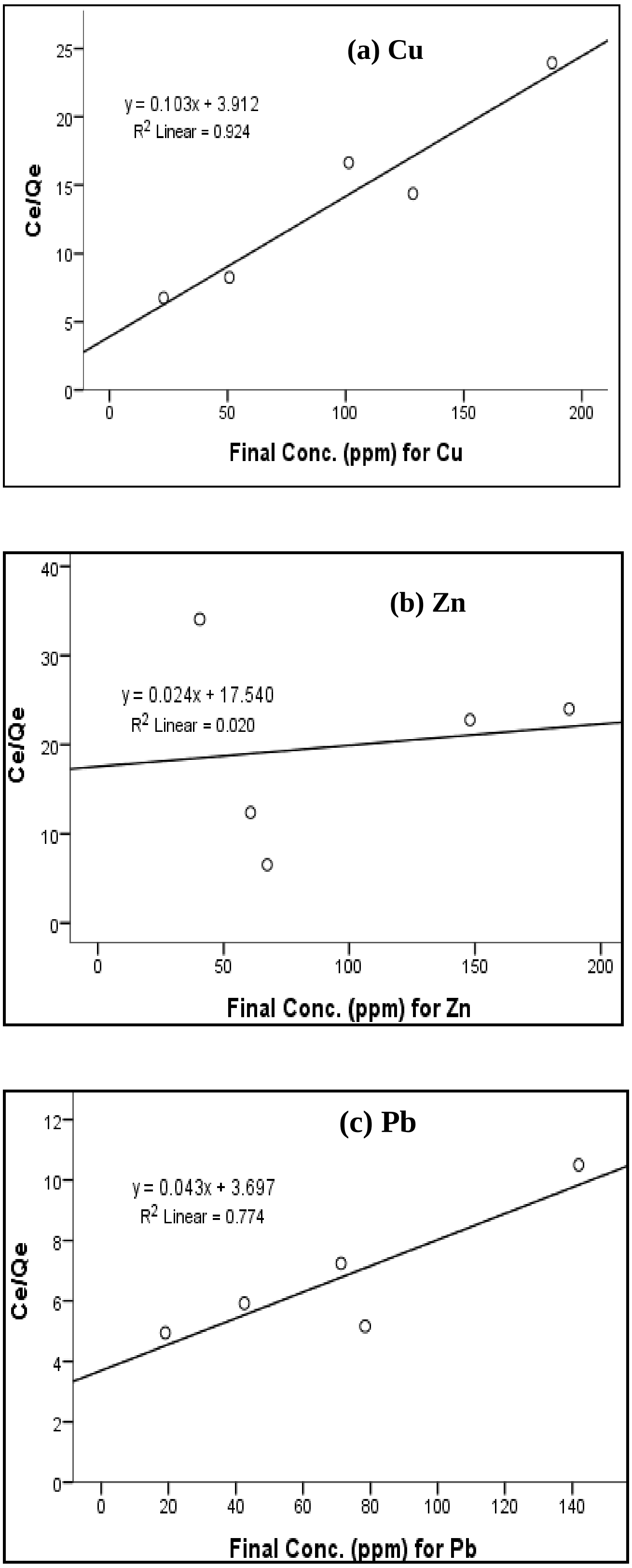

Figure 6. Langmuir isotherms model for (a) Cu, (b) Zn and (c) Pb.

Table 4. Separation factor of copper, zinc, lead

C_O (mg/L)	Separation factor (SF), R_L		
	Cu	Zn	Pb
50	0.431965	0.935891	0.632911
100	0.275482	0.879507	0.462963
150	0.202224	0.829531	0.364964
200	0.159744	0.784929	0.301205
250	0.132013	0.744879	0.25641

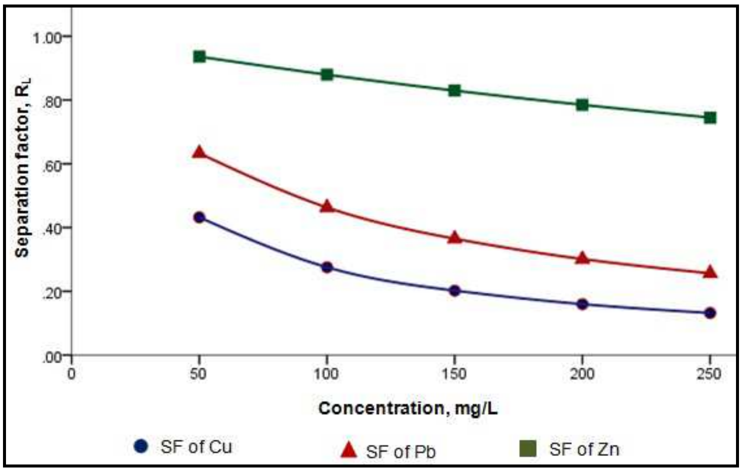

Figure 7. Separation factor (SF) for biosorption on Cu, Pb and Zn

Table 5. Surface coverage of Cu, Zn and Pb

C_O (mg/L)	Surface Coverage (SC), θ		
	Cu	Zn	Pb
50	0.568035	0.064109	0.367089
100	0.724518	0.120493	0.537037
150	0.797776	0.170469	0.635036
200	0.840256	0.215071	0.698795
250	0.867987	0.255121	0.74359

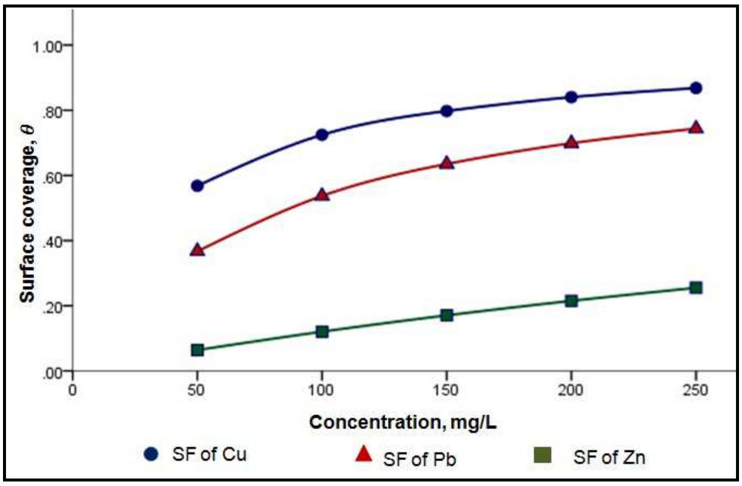

Figure 8. Surface coverage θ against metal ion concentration

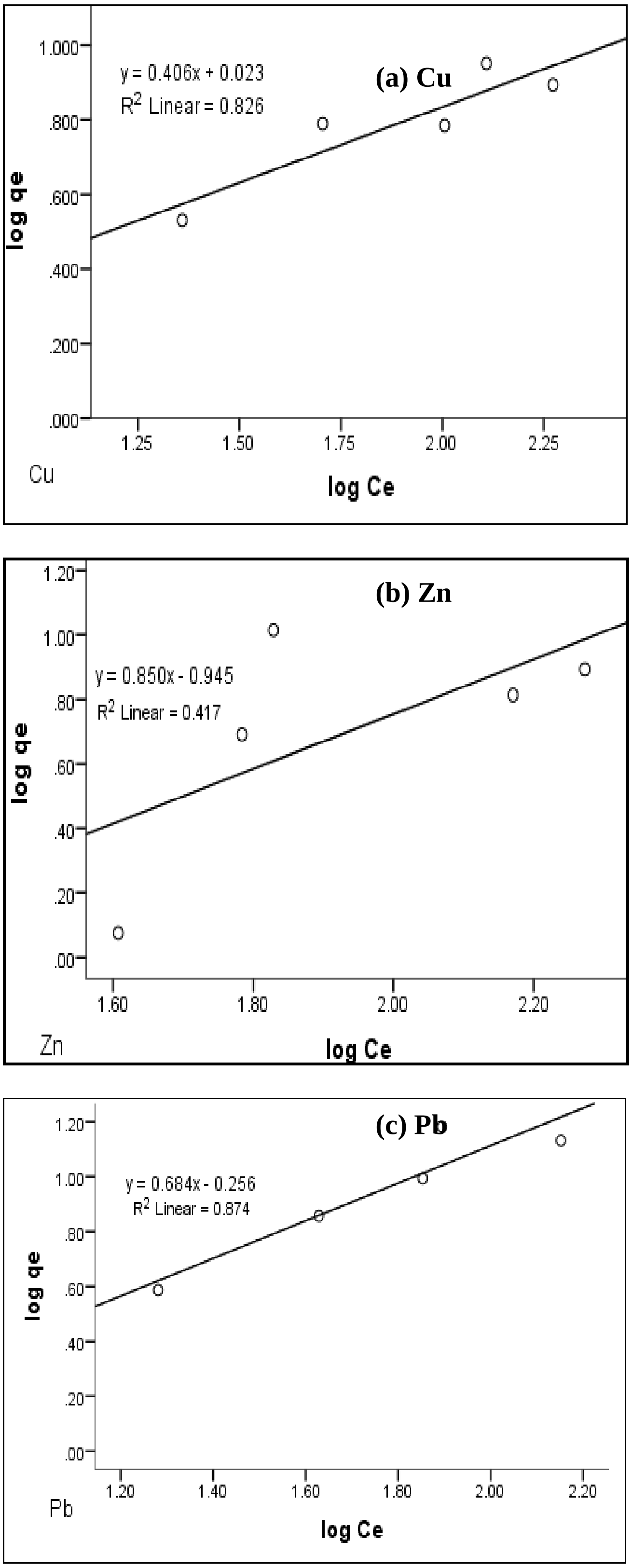

Figure 9. Freundlich isotherms for (a) Cu, (b) Zn, and (c) Pb

Dubinin–Radushkevich isotherm model

Dubinin-Radushkevich (D-R) isotherm provides information on the physical and chemical of biosorption which is dependent on temperature [17]. The theoretical value of maximum capacity, Q_D and D-R constant, B_D was obtained from the intercept and slopes of linear fits, ln q_e versus ln $(1 + \frac{1}{C_e})$. The result obtained from **Figure 10** depicts the Dubinin-Radushkevich is able to fit the biosorption data of Cu and Zn with the linear regression coefficient, R^2 of 0.890 and 0.903, respectively. The maximum E values determined for the D-R isotherm is 0.096, 0.185 and 0.111 for Cu, Zn and Pb, respectively. The low value of mean adsorption energy, E in Dubinin-Radushkevich model specifies that attraction forces are Van Der Waal instead chemical bonding [18]. Hence, the results gained from this experiment denote that the adsorption has low potential barrier and physical adsorption (physico-sorption) is the sorption process that involves in oil palm root biosorbent. **Table 6 shows** the value of mean adsorption energy, E and the linear regression coefficient, R^2 for each metal.

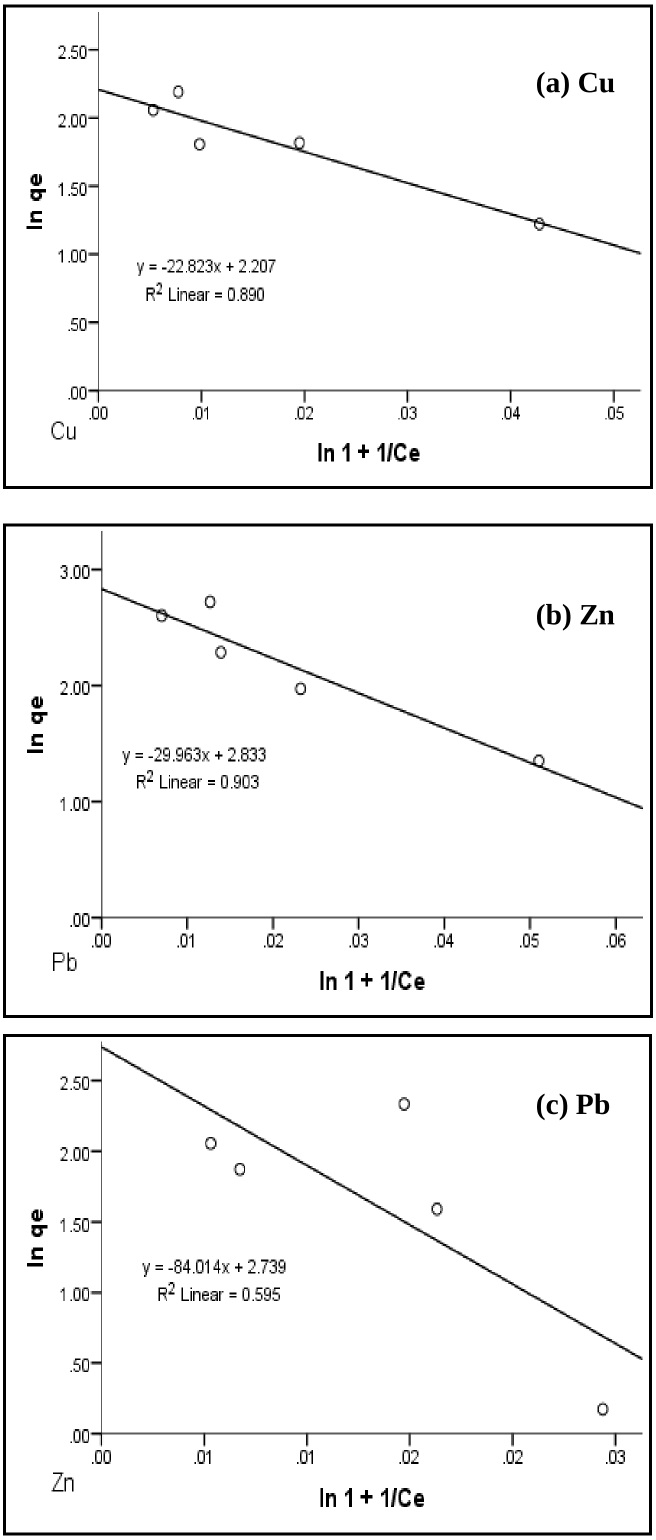

Figure 10. Dubinin-Radushkevich (D-R) for (a) Cu, (b) Zn and (c) Pb.

Nonlinear fit isotherm model

From the linear fit of isotherms model, it is observed that the biosorption of metal ions, namely Cu and Pb obeys the Langmuir, Freundlich and Dubinin-Radushkevich isotherm as it shows high linear regression coefficients, R^2. These results can also be validated by nonlinear fits isotherm model. According to the data obtained from biosorption of Cu and Pb by oil palm root biosorbent the Langmuir isotherm correlates very well with the experimental values. Figure 11 shows the nonlinear fits of isotherm models given with the experimental values. Table 4 summarizes the coefficients value of three different isotherm models for Cu, Zn and Pb, including the coefficients of determination (R^2).

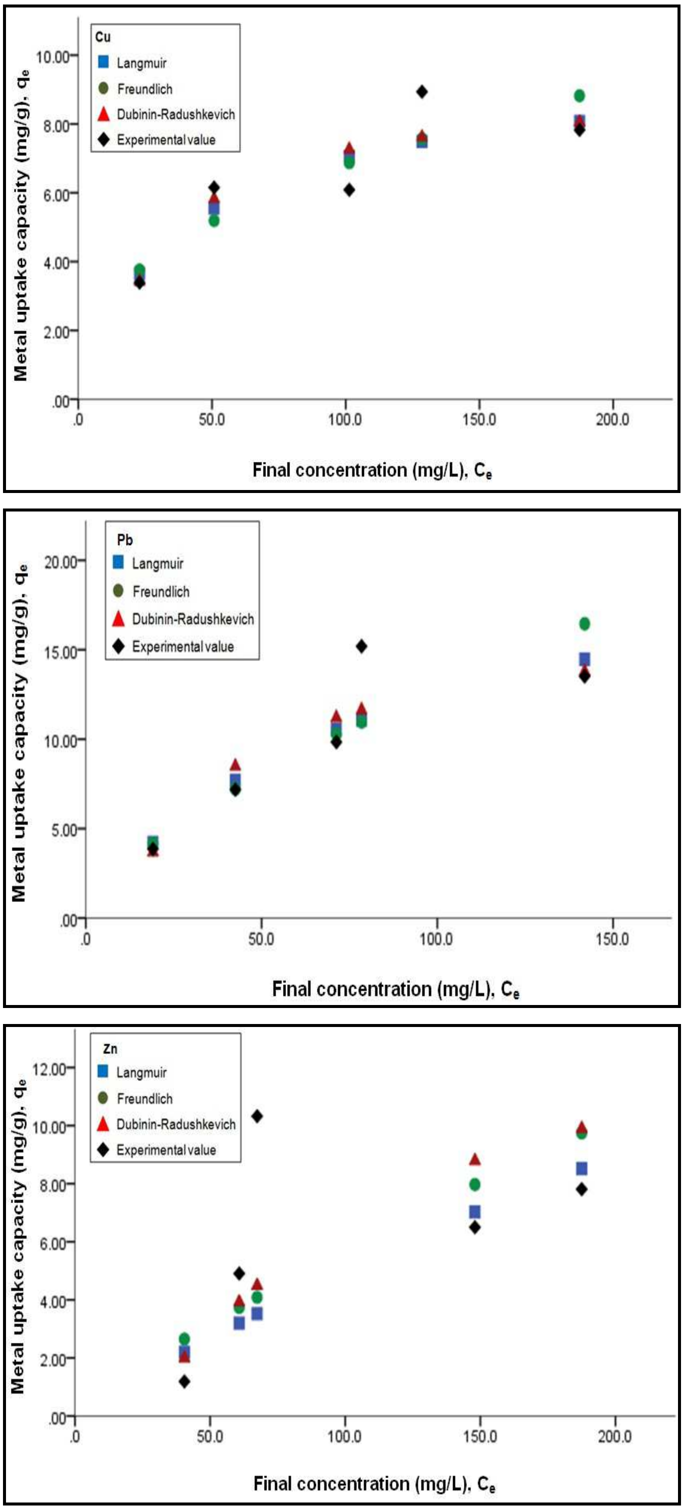

Figure 11. Isotherms model and experimental value of (a) Cu, (b) Zn and (c) Pb.

Table 6. Coefficient value, E and R^2 of metal ions

Value of coefficient derived from D-R isotherm model	Metal ion		
	Cu	Zn	Pb
E	9.64×10^{-2}	1.85×10^{-1}	1.11×10^{-1}
R^2	0.890	0.595	0.903

Conclusions

It has been shown that oil palm root biosorbent can be utilized for the biosorption of Cu, Zn and Pb metal ions. Increasing metal ion concentration leads to the increase of metal uptake capacity of oil palm root biosorbent. The biosorption favours the neutral condition as the maximum metal uptake capacity occurs at pH 7.0. The maximum removal efficiency for Cu and Pb are reported at metal concentration of 200 mg/L, whereas 150 mg/L is reported for Pb. Increasing of pH leads to the increase of removal efficiency of metal ions. The performance of biosorbents increases as the metal uptake in the mixed metal systems show higher metal uptake capacity, q_e compared to that of single metal system. The desorption studies showed that HNO_3 is a relatively better eluents in recovering metal ions from oil palm root biosorbent. In conclusion, oil palm root biomass has great potential to become eco-friendly biosorbent, in which can be utilized commercially for the removal of selected toxic metal ions from aqueous solution.

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