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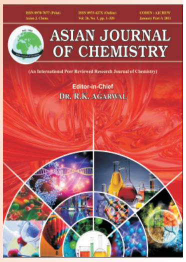

Isotherm and Kinetic Modeling of Pb(II) and Cu(II) Uptake by *Annona muricata L.* Seeds

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Isotherm and kinetic modeling of Pb(II) and Cu(II) uptake by *Annona muricata L.* seeds has been investigated. Batch adsorption studies were conducted to examine their optimum condition. For the biosorption of Pb(II), the optimum pH solution, contact time and stirring speed were 3, 45 min and 150 rpm, respectively. Those values for Cu(II) ions were 4, 60 min and 100 rpm, respectively. Data obtained from these studies fitted well with pseudo second-order and Freundlich isotherm model. The maximum capacity for Pb(II) and Cu(II) ions were 5.585 and 4.1685 mg/g, respectively. The biosorption capacity decreased as the dosage of biomass increased. FTIR spectra analysis might revealed that carboxyl and hydroxyl groups were dominant in the process of metal ions uptake. Biosorption of binary solution did not influence the adsorption capacity of the leading ion (its optimum condition was used in binary solution) onto *Annona muricata L.* seed.

Keywords: Isotherm and kinetic modeling, *Annona muricata L.* seeds, Toxic metals, FTIR.

INTRODUCTION

Heavy metal including lead and cupper are major pollutants in aquatic ecosystem caused by rapid industrial and technologies activities and its consequences and posses a serious environmental problem. Conventional methods used to remove toxic heavy metals from aquatic environment include reverse osmosis, electro-dialysis, ultra-filtration, ion-exchange, chemical precipitation and phyto-remediation[1].

Recently, research focused on biosorption technology, which utilizes the ability of agricultural byproduct or biological materials for the removal of toxic metal ions from wastewater. The method based on metal binding capacities of various functional groups present in biological materials[2-6]. The major advantages of biosorption over conventional treatment methods were low cost, high efficiency, no additional nutrient requirement, regenerated of biosorbent and possibility of metal recovery. The mechanism of biosorption was complex, mainly ion exchange, chelation and adsorption by physical forces[3]. In this study, the biosorption of Pb(II) and Cu(II) by *Annona muricata L.* seeds from single and binary mixtures were investigated.

The objective of this study was to find a biosorbent with high stability, low in price, high metal uptake and easy to be regenerated. This paper presents the conception and optimization of the biosorption process according to the following steps such as biosorbent characterization, optimization of biosorption process, determination of the biosorption kinetics and isotherm modeling. For this purpose we would determine the optimum biosorption conditions as a function of pH, contact time, stirring speed, initial metal ion concentration and amount of biosorbent dose in the biosorption of Pb(II) and Cu(II) by *Annona muricata L.* seeds.

EXPERIMENTAL

In present works, the biosorption experiments were conducted by using stock standard solution (1000 mg/L) of $Pb(NO_3)_2$ and $Cu(NO_3)_2$ in 0.5 M HNO_3. These solutions were purchased from Merck (Germany). Working standard solutions were prepared just before used by the appropriate dilution of the stock solutions.

Seeds preparation and characterization: *Annona muricata L.* seeds were used as a biosorbent for sorption of Pb(II) and Cu(II) from an aqueous solution. The chemical composition of *Annona muricata L.* seeds was reported by Andrade *et al.*[6]. *Annona muricata L.* fruit (Fig. 1a) were collected from flea market of Padang city. Then black brown and hard seeds of *Annona muricata L.* (Fig. 1b) were washed with deionized water, air-dried for 3 days and ground using crusher (Fritsch, Germany). Then the powder was dried in an oven (Memmert, Germany) at 60 °C for 40 h and finally ground using mortal grinding (Fritsch, Germany). The working powder (Fig. 1c) was activated by soaking 20 g biomass in excess of 80 mL HNO_3 0.01 M for 2 h, followed by washing thoroughly with deionized water and then air-dried. The resulting pale brown powder can be stored for a long time.

Fig. 1. (a) *Annona muricata L.*; (b) *Annona muricata L.* seeds; (c) dry powder of *Annona muricata L.* seeds

The dry powder was treated with 25 mL Pb(II) or Cu(II) 10 mg/L, shaked for 1.5 h with 100 rpm and then was filtered. The filtrate (colorless, has no smell and pH about 6) was treated with AAS (VARIAN SPECTRAA240) to determine the total amount of Pb(II) or Cu(II) left in the solution at 217 and 324.8 nm, respectively. There were several parameters to be treated to get the optimal adsorption of heavy metal ions with biomass.

The amount of adsorbed metal ions per gram of the biomass (biosorption capacity, Q) was obtained using the following eqn. (1):

$$Q = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o and C_e were initial and equilibrium metal ions concentration in solutions (mg/L), respectively; V was volume of the solution (L); m was the amount of biomass (g).

RESULTS AND DISCUSSION

FTIR characterization was carried out to analysis the major functional group which exists in the biomass.The broad and intense peak at 3435.56 cm^{-1} (ranging from 3600 to 3200 cm^{-1}, Fig. 2a) was assigned to the stretching of O-H groups due to inter- and intra-molecular hydrogen bonding of polymeric compound, such as alcohols, occasionally phenols and carboxylic acids. The 1744.30 cm^{-1} peak was a carboxyl stretch in ester, while the 1647.87 cm^{-1} was a carboxyl stretch in amide. The peak at 1055.84 cm^{-1} could be connected to the existence of stretching vibration C-O of alcohol groups and carboxylic acids[5,7]. Thus, *Annona muricata L.* seeds showed an abundance of carboxyl and hydroxyl groups. These groups present in the biomass may coordinate with heavy metal ions in deprotonated forms. Fig. 2b showed the intensity attenuation of the peaks in the region of 3600 to 3200 and 1100 to 900 cm^{-1}. These were indicated a decrease of the free hydroxyl group on the biomass. Meanwhile, for the peaks 1744.0 and 1647.87 cm^{-1} was suggested the involvement of the carboxyl groups. These changed may revealed that carboxyl and hydroxyl groups were dominant in the process of metal ions uptake.

Effect of pH solution: The pH of solution had a significant impact on the removal of heavy metals, since it determined the surface charge of the adsorbent (has carboxylate, phosphate and amino group) and its degree of ionization. Fig. 3 showed the maximum biosorption of Pb(II) occurred at pH 3. The amount of adsorbed heavy metal ions of that pH was found to be 0.3995 mg/g for prepared biomass. There was a decrease in biosorption capacity (Q) with an increase pH from 3 to 7. The uptake of Cu(II) increased from 0.1985 mg/g to 0.4249 mg/g when the pH increased from 2 to 4 and then decreased to 0.4113 mg/g at pH = 5. When pH was further increased up to 5 until 7 for Pb(II) and Cu(II) respectively, the percentage

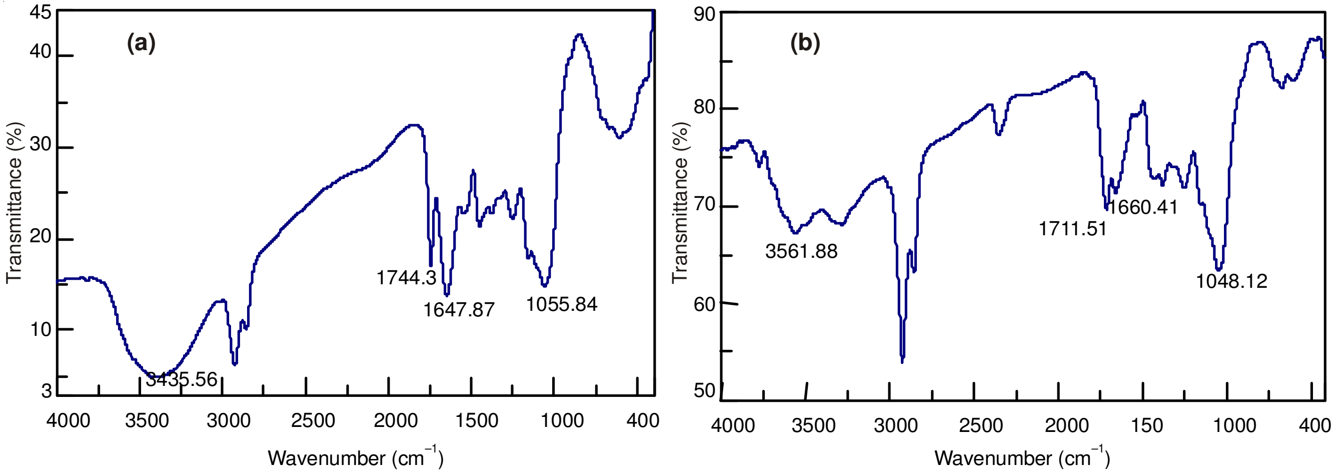

Fig. 2. FTIR of (a) untreated *Annona muricata L.* seeds and (b) treated seeds with HNO_3 0.01 M after intereacting with metal ion

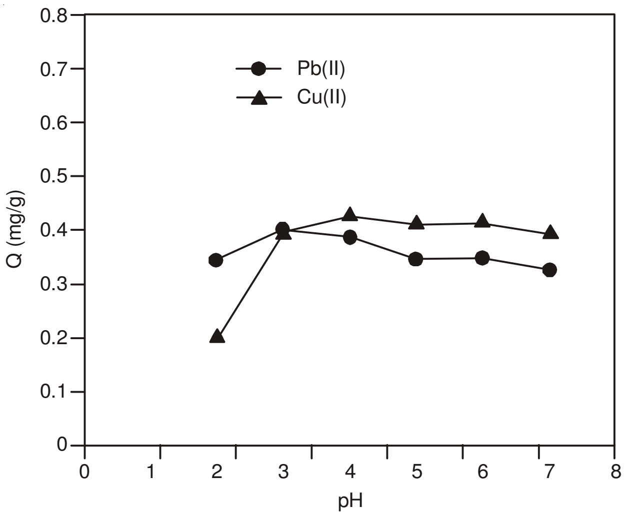

Fig. 3. Effect of pH on Pb(II) and Cu(II) biosorption by *Annona muricata L.* seed; 25 mL metal solution; concentration = 10 mg/L; mass of biosorbent = 0.5 g; contact time = 90 min; stirring speed = 100 rpm

adsorption was decreased. This was due to reason that divalent cations might react with OH^- ion to give some precipitation and thereby decreased the free metal ions available in the solution. Heavy metal cations seemed to be mostly unsorbed at low pH values (pH = 1- 2). Increased acid concentration, metal ions in solution entered into competition with H^+ for the sorption sites.

Oyedepo[8] investigated the biosorption of lead (II) ions on *Calotropisprocera* (Ait.) also got the optimal pH for biosorption as 4. On the other hand Homagai *et al.*[9] who studied adsorption kinetics of Pb(II), Cd(II), Zn(II) and Fe(III) onto saponified apple waste found the optimum pH for Pb(II) uptake as 3.5. Suhaimi *et al.*[10] used treated corn leaves for Pb(II) adsorption showed that maximum pH for Pb(II) uptake as 3. Gupta *et al.*[11] used bassage, fly ash, a sugar industry waste material for the removal of Pb(II), the optimum pH of Pb(II) was 3. However, Argun *et al.*[12] who investigated heavy metal adsorption by modified oak sawdust found the optimum pH for Cu(II) uptake as 4.0. Slaiman *et al.*[13] used bamboo for biosorption of heavy metals ions and showed the maximum pH for Cu(II) uptake as 4.5.

Effect of contact time: The biosorption capacity of metal ions was evaluated as a function of contact time. The initial concentration of metals was 10 mg/L. The metal uptake was rapid for both ions at the beginning of the biosorption process and gradually decreased as time progressed to attain equilibrium after 45 and 60 min for Pb(II) and Cu(II), respectively (Fig. 4). The metal uptake capacity of biomass at 10 mg/L metal solution was different for two metals. The highest metal uptake obtained for Pb(II) and Cu(II) were 0.4630 mg/g and 0.4104 mg/g, respectively of dried biomass.

Gupta *et al.*[11] found that the optimum contact time of Pb(II) was within 1 h. Moreover, Marandi *et al.*[14] used *Phanerochaete chrysosporium* for biosorption Pb(II), the maximum contact time was after 60 min. However, Nuhoglu and Oguzwho studied removal of Cu(II) from aqueous solutions by biosorption on the cone biomass of *Thujaorientalis* got the optimal contact time for Cu(II) was reached within 60 min[15].

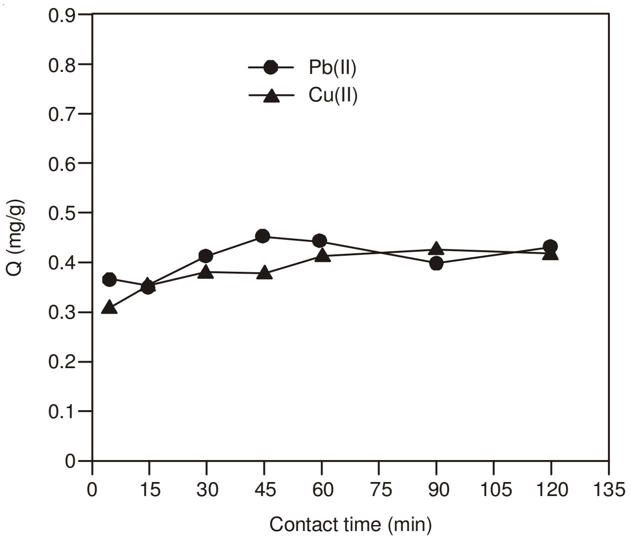

Fig. 4. Effect of contact time on Pb(II) and Cu(II) biosorption by *Annona muricata L.* seed; 25 mL metal solution; concentration = 10 mg/L; pH of Pb(II) = 3 and Cu(II) = 4; mass of biosorbent = 0.5 g; stirring speed = 100 rpm

Adsorption kinetics: In order to test the experimental data of these works, kinetic models have to be used. The kinetics studied of Pb(II) and Cu(II) adsorption were carried out by batch adsorption that formerly were used to determine optimum condition of contact time.

For pseudo first-order rate, samples were taken at preset time intervals up to 30 and to 45 min for Pb(II) and Cu(II), respectively. The pseudo first-order rate:

$$\frac{dQ}{dt} = k_1(Q_e - Q_t) \tag{2}$$

In this case the kinetic order was one with respect to the number of available sites for the exchange reaction. The linear first-order rate expression was generally expressed as:

$$-\ln(Q_e - Q_t) = k_1 \cdot t - \ln Q_e \tag{3}$$

For pseudo second-order rate, samples were taken until 120 min for Pb(II) and Cu(II), respectively. The pseudo second-order rate:

$$\frac{dQ}{dt} = k_2(Q_e - Q_t)^2 \tag{4}$$

It was assumed that the kinetic order was two with respect to the number of available sites for the exchange reaction. The linear form of pseudo second-order can be written:

$$\frac{t}{Q_t} = \frac{1}{k_2 \cdot Q_e^2} + \frac{t}{Q_e} \tag{5}$$

where Q_e and Q_t were the amount of Pb(II) and Cu(II) ions adsorbed at equilibrium and at time t (mg/g), k_1 was the pseudo first-order rate constant (min^{-1}) and k_2 was the pseudo second-order rate constant (g/mg min). The pseudo first- and second-order kinetic models consider that the rate of occupation of adsorption site to be proportional to the number of unoccupied sites and the concentration of adsorbate, while the rate of desorption to be proportional of the occupied sites. If the initial adsorbate concentration was high it produced the pseudo first-order reaction [eqns. (2) and (3)][11-4].

As can be seen from Figs. 5 and 6, the pseudo second-order kinetic models were more suitable than first-order for modeling the adsorption of Pb(II) and Cu(II) by *Annona muricata L.* seeds. We started with low initial metal ions concentration (R of first-order less than second-order for both Pb(II) and Cu(II) ions). The rate constant (k_1) of Pb(II) and Cu(II) were 0.0329 and 0.0276 min^{-1} (Fig. 5). However, the rate constant (k_2) of Pb(II) and Cu(II) were 1.8290 and 0.5924 g min mg^{-1} (Fig. 6). Those were in agreement with the contact time of Pb(II) < Cu(II).

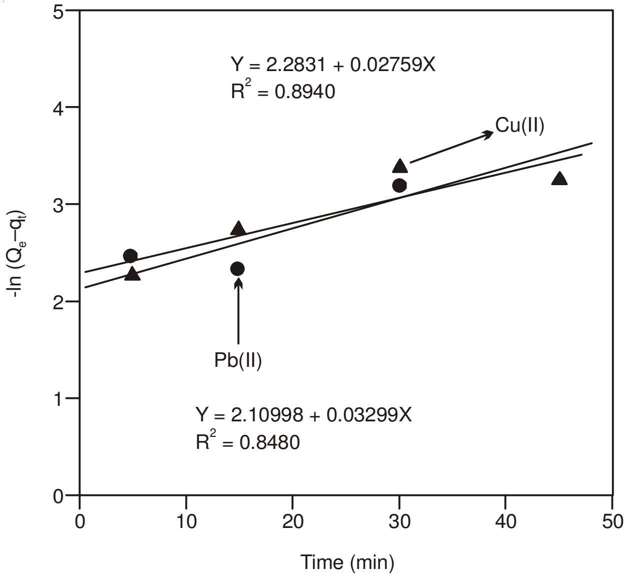

Fig. 5. Pseudo-first order kinetic model for Pb(II) and Cu(II)

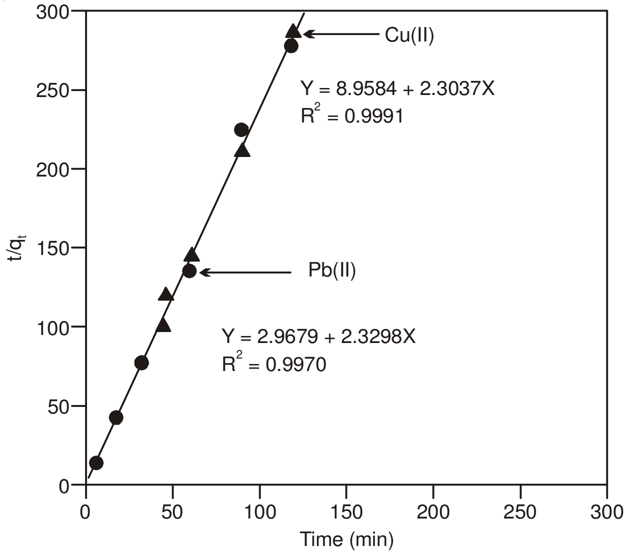

Fig. 6. Pseudo-second order kinetic model for Pb(II) and Cu(II)

Raju *et al.*[16] used *Carica papaya* leaf powder for biosorption of Pb(II) did find that the pseudo second-order model kinetic was better compared to the pseudo first-order. Ljupkovic *et al.*[17] investigated the removal Cu(II) ions from water by *Lagenaria vulgaris* shell, also found the kinetic data more good fitted by pseudo second-order than pseudo-first order.

Effect of stirring speed: Biosorption studies were carried out in a shaker at pH = 3 and pH = 4 for Pb(II) and Cu(II), respectively. The stirring speed varied from 30 to 250 rpm. Fig. 7, illustrated the influence of the stirring speed on the biosorption, showed that an optimum value was obtained at 150 and 100 rpm for removal of Pb(II) and Cu(II), respectively. A thin liquid film surrounding the biomass particles offered resistance to the mass to absorb the ion by diffusion. When the stirring speed was high, complex between metal ion and biomass was ruptured.

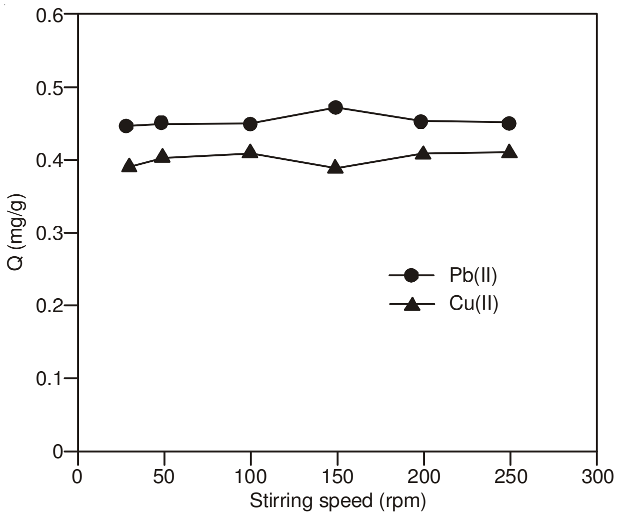

Fig. 7. Effect of stirring speed on Pb(II) and Cu(II) biosorption by *Annona muricata L.* seed; 25 mL metal solution; concentration = 10 mg/L; pH of Pb(II) = 3 and of Cu(II) = 4; mass of biosorbent = 0.5 g; contact time = 45 min for Pb(II), 60 min for Cu(II)

Ekmekyapar *et al.*[18] studied *Cladonia rangiformis Hoffm* for biosorption of Pb(II), did find the optimum stirring speed was 150 rpm. According to Marandi *et al.*[14] used *Phanerochaete chrysosporium*, the maximum stirring speed was150 rpm. However, Xinjiao[19] investigated the biosorption of Cu(II) from aqueous solutions by pretreated *Cladosporium sp.* got the optimal of stirring speed for Cu(II) was 100 rpm.

Effect of initial metal ion concentration: Fig. 8 showed the heavy metal ion biosorption capacities of *Annona muricata L.* seed as a function of the initial concentration of Pb(II) and Cu(II) ion within the aqueous solution. The amount of metal ions adsorbed per unit mass of seeds increased with an increased in initial metal ion concentrations and then decreased. This increased could be due to the increased in electrostatic interactions (related to covalent interactions).

Adsorption isotherm: An adsorption isotherm describes the relationship between the amount of adsorbate taken by the adsorbent and the adsorbate concentration remaining in solution. This isotherm was derived from equilibrium constant of the interaction of adsorbate with adsorbent. In the present study, the equilibrium data for Pb(II) and Cu(II) adsorption on *Annona muricata L.* seed were evaluated by the Langmuir and Freundlich models.

The Langmuir isotherm was based on assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, the energy of adsorption constant and there was no transmigration of adsorbate in the plane of the surface. The Langmuir model was described by the following eqn. (6):

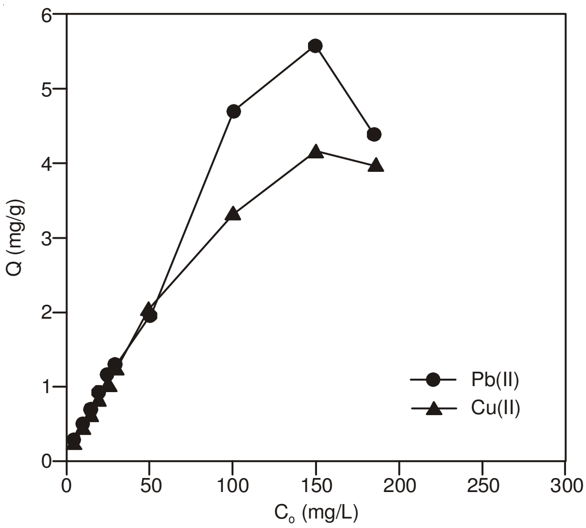

Fig. 8. Effect of initial metal ion concentration on Pb(II) and Cu(II) biosorption by *Annona muricata L.* seed; 25 mL metal solution; pH of Pb(II) = 3 and of Cu(II) = 4; mass of biosorbent = 0.5 g; contact time = 45 min for Pb(II), 60 min for Cu(II); stirring speed = 150 rpm for Pb(II), 100 rpm for Cu(II)

$$Q_e = \frac{K_L \cdot Q_m \cdot C_e}{1 + K_L \cdot C_e} \tag{6}$$

A linear expression for the Langmuir isotherm could be written as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m \cdot K_L} + \frac{C_e}{Q_m} \tag{7}$$

where Q_m was the maximum metal uptake corresponding to the saturation capacity (mg/g), K_L was energy of adsorption (L/mg), Q_e was the amount of metal adsorbed on the biomass (mg/g) and C_e was equilibrium metal concentration in solution (mg/L). In contrast, the Freundlich isotherm could be used for non-ideal adsorption that involves heterogeneous. The general Freundlich eqn. (8) was given as:

$$Q_e = K_f \cdot C_e^{1/n} \tag{8}$$

The linear form of this model was:

$$\ln Q_e = \ln K_f + \left(\frac{1}{n}\right) \cdot \ln C_e \tag{9}$$

where *n* was adsorption affinity and K_f was Freundlich constant (as a measure of the degree or strength of adsorption). As the Freundlich isotherm equation was exponential, it could only be reasonable applied in the low to intermediate concentration ranges. Langmuir and Freundlich models could be applied at a constant pH[1].

Based on the slope of linear functions from Fig. 9, the theoretical values of Q_m for Pb(II) and Cu(II) ions were 6.8306 and 5.5463 mg/g, respectively. However, those experimental values were 5.585 and 4.1685 mg/g, respectively (Fig. 10).

In these experiment, according to the higher values of correlation coefficient, Freundlich was better fit than Langmuir model either for Pb(II) or for Cu(II). Raju *et al.* who studied biosorption of Pb(II) ions using *Anacardiumoccidentale* and *Carica papaya* leaves powder found the Freundlich fit better than Langmuir model[20].

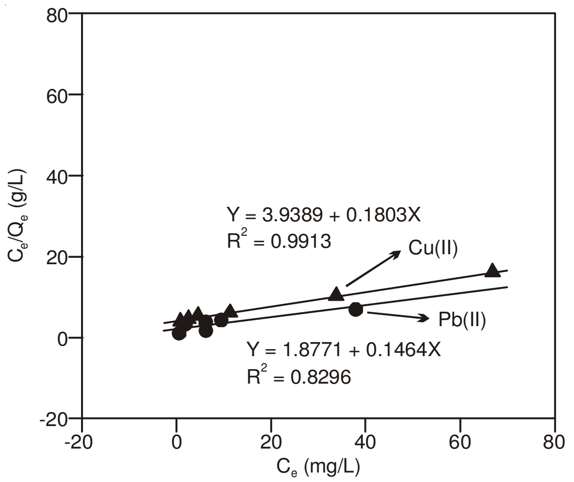

Fig. 9. Linearized Langmuir equation for Pb(II) and Cu(II)

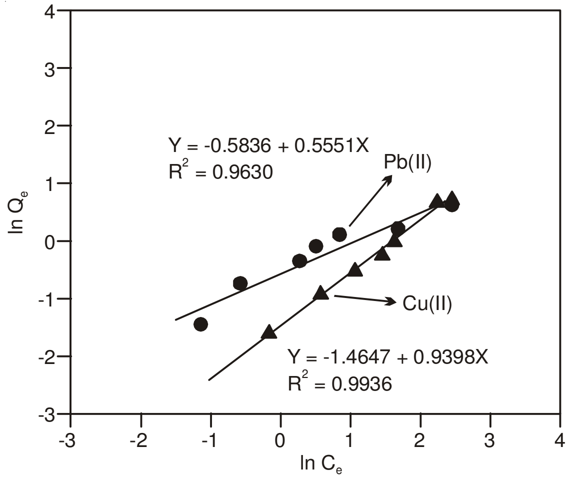

Fig. 10. Linearized Freundlich equation for Pb(II) and Cu(II)

Effect of biomass dosage: Fig. 11 showed the heavy metal ion biosorption capacities of *Annona muricata L.* seed as a function of the biomass dosage of Pb(II) and Cu(II) ion within the aqueous solution. The biosorption capacity (Q) decreased as the dosage of biomass increased.

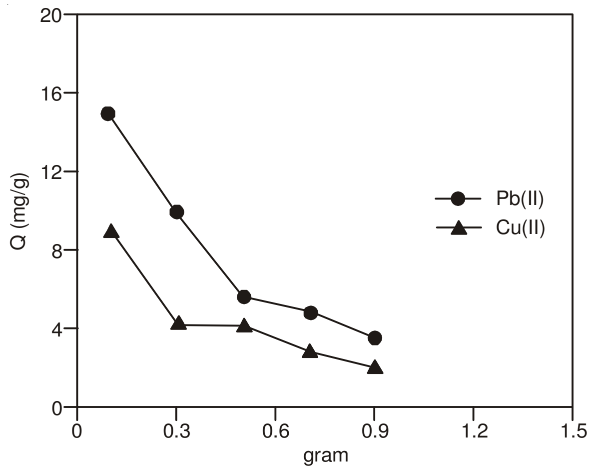

Fig. 11. Effect of biomass dosage on Pb(II) and Cu(II) biosorption by *Annona muricata L.* seed; 25 mL metal solution; concentration = 150 mg/L; pH of Pb(II) = 3 and of Cu(II) = 4; contact time = 45 min for Pb(II), 60 min for Cu(II); stirring speed = 150 rpm for Pb(II), 100 rpm for Cu(II)

Biosorption in mixed-metals system: The biosorption of Pb(II) ions from its binary metal solutions with Cu(II) was showed in Fig. 12. It was defined that Pb(II) as a leading ion, when its optimal conditions were used in the mix solution. In the single-ion situation, the maximum uptake of Pb(II) ions was found to be 1.1335 mg/g (Fig. 8). This value was 1.1075, 1.135 and 1.0625 mg/g when the initial concentration of Cu(II) in the binary solutions was 10, 20 and 25 mg/L, respectively. This showed that even though Cu(II) in solution was absorbed by *Annona muricata L.* seed, it did not influence the adsorption capacity of the leading ion.

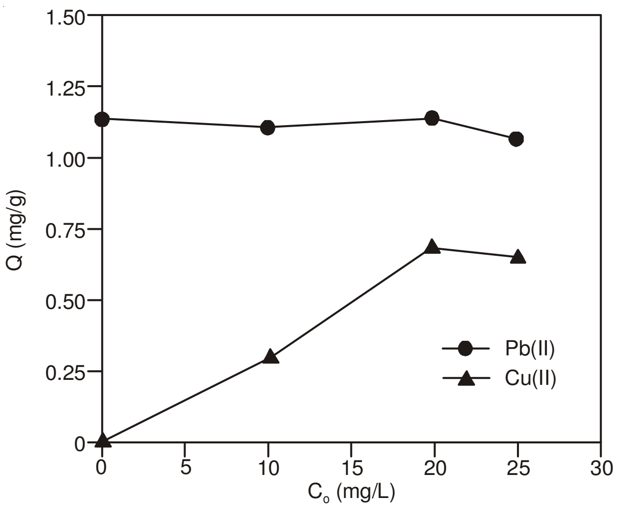

Fig. 12. Adsorption isotherm for Pb(II) in the presence of Cu(II) by *Annona muricata L.* seed; 25 mL binary metal solution; pH = 3; mass of biosorbent = 0.5 g; contact time = 45 min; stirring speed = 150 rpm; initial Pb(II) concentration = 25 mg/L, Cu(II) = 0, 10, 20, 25 mg/L

The biosorption of Cu(II) ions from binary metal solutions, with Pb(II), was showed in Fig. 13. Adsorption capacity of Cu(II) in single metal system was reported previously to be 1.0042 mg/g, while it were reduced to 1.0387, 0.9742, 1.0135 and 0.997 mg/g when the initial concentration of Pb(II) ions was 10, 15, 20 and 25 mg/L, respectively. Although Pb(II) ion solutions were not competitive for interacting with the seed. Homagai *et al*. in adsorption kinetics of single and binary was absorbed by seeds, the capacity adsorption of the leading ion was almost remain constant. In other words those mix solutions of Cd(II) and Zn(II) ions on to saponified apple waste, found that adsorption capacity of Cd(II) remain constant in the presence of Zn(II) in the solution[9].

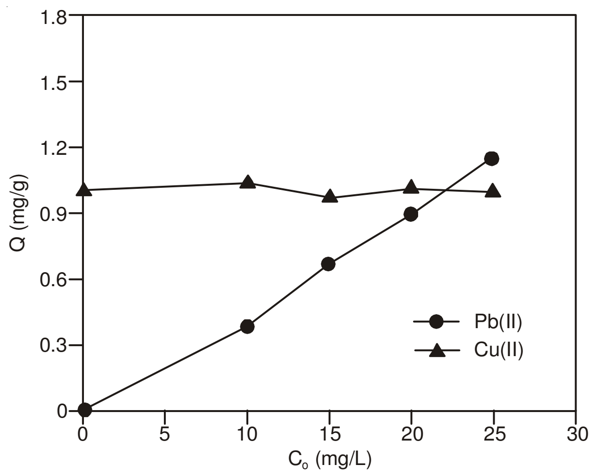

Fig. 13. Adsorption isotherm for Cu(II) in the presence of Pb(II) by *Annona muricata L.* seed; 25 mL binary metal solution; pH = 4; mass of biosorbent = 0.5 g; contact time = 60 min; stirring speed = 100 rpm; initial Cu(II) concentration = 25 mg/L, Pb(II) = 0, 10, 15, 20, 25 mg/L

Compared with other biomaterial as shown in Table-1, the sorption capacities for Pb(II) and Cu(II) (seem to be fairly the same). Its mean that the present biosorbent could be a biomaterial alternative for the sorption of toxic metals.

TABLE 1
COMPARISON OF SORPTION
CAPACITIES OF THE BIOSORBENTS

No.	Sorbents	Sorption capacities (mg/g)		References
		Pb(II)	Cu(II)	
1.	Hazelnut shells	1.78	-	21
2.	Rice husk	4.00	-	22
3.	Cocoa shells	6.23	-	23
4.	Saw dust	-	3.22	24
5.	Tea waste		8.64	25
6.	*Annona muricata* L. seeds	5.59	4.17	Present study

Conclusion

FTIR spectra of *Annona muricata L.* seed revealed the presence of O-H, C-H and C-O streching in the adsorbent. These groups were responsible in the process of metal ions uptake since there was some intensity attenuation of those peaks. Results of these studies indicated that the capacity biosorption of Pb(II) and Cu(II) ions by *Annona muricata L.* seed were affected by pH solution, contact time, stirring speed, initial metal ion concentration and biomass dosage. The optimum pH for adsorption of Pb(II) and Cu(II) ions were found to be at pH 3 and 4, respectively. The uptake of Pb(II) and Cu(II) ions increased with increasing contact time and equilibrium were attained in 45 and 60 min of contact, respectively. The influence of the stirring speed on the biosorption showed that an optimum value was obtained at 150 and 100 rpm for removal of Pb(II) and Cu(II), respectively. The biosorption capacity decreased as the dosage of biomass increased.

The kinetic data obtained from this study fitted well with pseudo second-order model, with the rate constant (k_2) of Pb(II) and Cu(II) were 1.8290 and 0.5924 g min mg^{-1}, respectively. Those were in agreement with the contact time of Pb(II) < Cu(II). The equilibrium data fitted well to the Freundlich isotherm. However, Langmuir isotherm may be used to predict the theoretical values of Q_m for Pb(II) and Cu(II) ions, those were 6.8306 and 5.5463 mg/g, respectively. The experimental values of Q_m for Pb(II) and Cu(II) ions were 5.585 and 4.1685 mg/g, respectively. The biosorption of binary solution showed that adsorption capacity of the leading ion onto *Annona muricata L.* seed relatively did not influenced by another ion. *Annona muricata L.* seeds can be considered as an alternative biomass for removal of Pb(II) and Cu(II) ions, respectively since it has high stability, relatively high in biosorption capacity, low cost and abundant.

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