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# Biosorption of lead(II) and copper(II) from aqueous solution by *Nypa frutican* husk

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**ABSTRACT**

*Absorption of Pb(II) and Cu(II) ions by Nypa fruticans husk biomass using Batch method has been studied. It was found for the absorption of both metal ions, where is the optimum pH and contact time respectively as 4 and 5 minutes for Pb(II) ions and as 5 and 30 minutes for Cu(II) ions. Stirring speed to a both metal ions biosorption process is fixed at 150 rpm. The optimum absorption capacity for Pb(II) and Cu(II) ions were obtained respectively as 20.825 mg/g and 7.572 mg/g. In fact the adsorption capacity decreases with increasing biosorbent mass. The equilibrium adsorption isotherm models of Langmuir and Freundlich were executed based on the experimental datas. The equilibrium adsorption isotherm model of Langmuir give a better result than the Freundlich due to its high correlation in $R^2$ coefficient. Nypa fruticans husk biomass was characterized by SEM and FTIR methods. Where is the FTIR spectra analysis explains that the carboxyl and hydroxyl amine groups play an important role in the absorption of the metal ions. Biosorption in binary solution does not affect the absorption capacity of the target ion (optimum conditions used in the binary solution) by Nypa fruticans husk.*

**Keywords**: *Nypa fruticans*, biosorption, Heavy Metals, FTIR, SEM.

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## INTRODUCTION

Aquatic environmental contamination by heavy metals is becoming dilemma due to the ecotoxicological effects and bioaccumulation in flora and fauna that cause potential chronic health hazards to human beings and adverse impacts to the ecosystem. Hazardous heavy metals such as mercury, lead, zinc, cadmium, copper, chromium, nickel, etc, make their way into water bodies via wastewater from leather industries, pulp and peppermills, metal plating industries, refineries, steel work foundries, pigment manufacturing, textile and photographic and cosmetics industry [1].

Lead is also considered among the most toxic heavy metals due to its bioaccumulation potential, inhibition of plant and microbial growth by influencing the pH of the substrate and inactivating the cell enzymes. Lead accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anemia, kidney disease, nervous disorders and sickness even death [2]. While copper is a widely use material, there are many actual or potential sources of copper pollution. Copper is essential to life and health but, like all heavy metals, is potentially toxic as well. For example, continued inhalation of copper-containing spray is linked with an increase in lung cancer among exposed workers [3].

Conventional methods for metal removal include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. These conventional methods for metal removal of heavy metals from wastewaters, however, are often cost prohibitive having inadequate efficiencies at low metal concentrations, particularly in the range of 1-100 mg/L. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physic-chemical pathways of uptake. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional nutrient requirement, regeneration of biosorbent and the possibility of metal recovery [4].

Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to some extent to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution [5].

*Nypa fruticans* husk is one of the abundant lignocelluloses waste materials, in terms of chemical composition, the straw predominantly contains cellulose (36.5 %), hemicelluloses (21.8 %) and lignin (28.8 %) [6]. The lignin is promptly available to interact with cations, by firstly exchanging with protons and subsequently by chelating with the metallic ion [7].

The removal of heavy metal ions using low-cost abundantly available adsorbents: agricultural wastes such as *Garcinia mangostana* L. shell [8], Maize stover [9] *Annona muricata* L. seeds [10], *Nypa fruticans* Merr shell [11], Rice straw [5]. Nypa husk has several characteristics to predict group of functional groups on their surface that makes nypa has the potential to sequester metal ions having been no previous reports using nypa shoots as biosorbent [11,12].

Based on the above description, in this research study about the use of nypa fiber in the absorption of Lead and Copper ions. Therefore do approach involving the influence of variations in the metal ion solution pH, contact time, stirring speed, biosorbent weight and concentration of metal ions.

## EXPERIMENTAL SECTION

**Biomass Preparation**

Waste Nipah palm (*Nypa fruticans*) is taken in Tarusan, Painan, West Sumatera, Indonesia (Figure **1**a). Husk palm (Nypa fruticans) that will be examined from an old palm fruit, nipah husk is cleaned from skin and shells then dried under the sunlight (Figure **1**b). Once dried palm fiber polished by tools Crusher and sieved with a size of 180 µm. Husk palm with the size soaked in a solution of 0.01 M HNO3 for 2 hours while stirring occasionally. Results marinade filtered and then washed with distilled water and dried aired and can be used to determine the optimum conditions for absorption of Pb(II) and Cu(II) ions (Figure **1**c).

**Chemicals and apparatus**

Pb(NO3)2 and Cu(NO3)2 working standard solution was prepared from 1000 mg/L These solutions were purchased from Merck (Germany). Working standard solutions were prepared just before used by the appropriate dilution of the stock solutions. HNO3 65 %, NaOH p.a and Distillation water. The apparatus used were siever size 180 µm , an analytical balance (Kern&Sohn GmbH), a sheker (Edmund Buhler 7400 Tubingen), a pH meter (Lovibond Senso Direct), Grinder (Christy Hunt), FTIR (Unican Maattson Mod 7000 using KBr pellets), and atomic absorption spectrometer (AAS : Varian Spektra AA 240 Spectrometer), Scanning Electron Microscope (SEM SU 3500).

**Batch biosorption studies**

The dry powder was treated with 25 mL Pb(II) or Cu(II) 20 mg/L, stirred for 1.5 h with 100 rpm and then was filtered. The filtrate (brown, has no smell and pH about 6) was treated with AAS (VARIAN SPECTRA A240) 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 equation (1):

$$Q = \frac{C_o - C_e}{m} \, x \, V$$

where Co and Ce 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

### Fourier transform infra red analysis

This analysis aimed to investigate the changes in the vibration frequency of functional groups contained in the *Nypa fruticans* husk powder. The functional group acts as a binding site of metal ions to be absorbed, the spectrum area 4000-400 $cm^{-1}$. In Figure **2**. Can be explained that the presence of a stretch of amino (-NH) and hydroxyl (-OH) on the wave number 3412.72 $cm^{-1}$ (Figure **2**b), after absorption by the Pb(II) ion of the peak is shifted to 3422.55 $cm^{-1}$ and Cu(II) at 3421.19 $cm^{-1}$. In the wave number 2918.86 $cm^{-1}$ is a CH vibration (Figure **2**b), then the strain shifted to 2921.42 $cm^{-1}$ (Figure **2**d). Strain CO contained in the wave number 1034.73 $cm^{-1}$ then the strain shifts the wave number 1035.67 $cm^{-1}$ after the absorption of Pb(II), whereas after absorption spectra of Cu(II) strain of the stood at 1054.05 $cm^{-1}$. Of *Nypa fruticans* husk powder FTIR spectra showed that the carboxyl group, hydroxyl and amine dominant involved in the uptake of Pb(II) and Cu(II) ions.

**Table 1. Comparison of ion absorption capacity of Pb (II) and Cu (II) by various biomaterials**

| Sorbents | Sorption capacities (mg/g) | | Reference |
|---|---|---|---|
| | Pb(II) | Cu(II) | |
| *Cladonia rangiformis* | 26.204 | - | [2] |
| Rice straw | - | 74.7 | [5] |
| *Nypa frutican* W shoot | 15.59 | 21.85 | [12] |
| *Phanerochaete chrysosporium* | 87 | - | [14] |
| *Eriobotrya japonica leaves* | 34.6 | 33.33 | [19] |
| *Nypa frutican* husk | 20.83 | 7.57 | This study |

**Figure 1. (a) *Nypa fruticans*.; (b) *Nypa fruticans* husk; (c) dry powder of *Nypa fruticans* husk**

### Scanning Electron Microscope

Scanning Electron Microscope used to see *Nypa fruticans* husk powder surface topography before and after absorption. Figure **3**a is a picture of *Nypa fruticans* husk powder surface before activation, the picture is not so visible pores *Nypa fruticans* husk powder and once activated (Figure **3**b), the pores of the *Nypa fruticans* husk powder in sight and punch. Figure **3**c and **3**d are *Nypa fruticans* husk powder surface image which has absorbed the Pb(II) and Cu(II) ions. Figure 3c look around the pore surface covered with *Nypa fruticans* fiber for Pb(II) ions, while Figure **3**d, not all the pores of the surface of the *Nypa fruticans* husk powder filled by Cu(II) ions.

### Effect of pH

Effect of pH is an important parameter in the absorption of the metal ions. Here pH varied metal ions 2-7, in Figure **4** can be seen more clearly the effect of pH on the absorption capacity of the metal ion. From the picture above it can be seen that the absorption capacity of the Pb(II) ions with increasing pH from pH 2 to pH 5, increasing the absorption capacity of the metal ions occurs not significant, and at pH 6 to pH 7 absorption capacity decreased, but the decrease was also not significant. Based on the calculation of the pH optimum absorption capacity for Pb(II) ions is at pH 4, whereas for Cu(II) ions is at a pH of 5. The absorption of Pb(II) ions is at pH 3-5, while the Cu(II) metal ions is at pH 3-6. With increasing pH, the active side biosorbent be able to bind negatively charged and positive metal ions in solution. Metal ions absorption decreases when the pH is reduced because of competition between protons and metal ions to the active side of the same on the biosorbent [13]. At high pH, metal ions will precipitate because of highest concentration of $OH^-$ ions in solution [2].

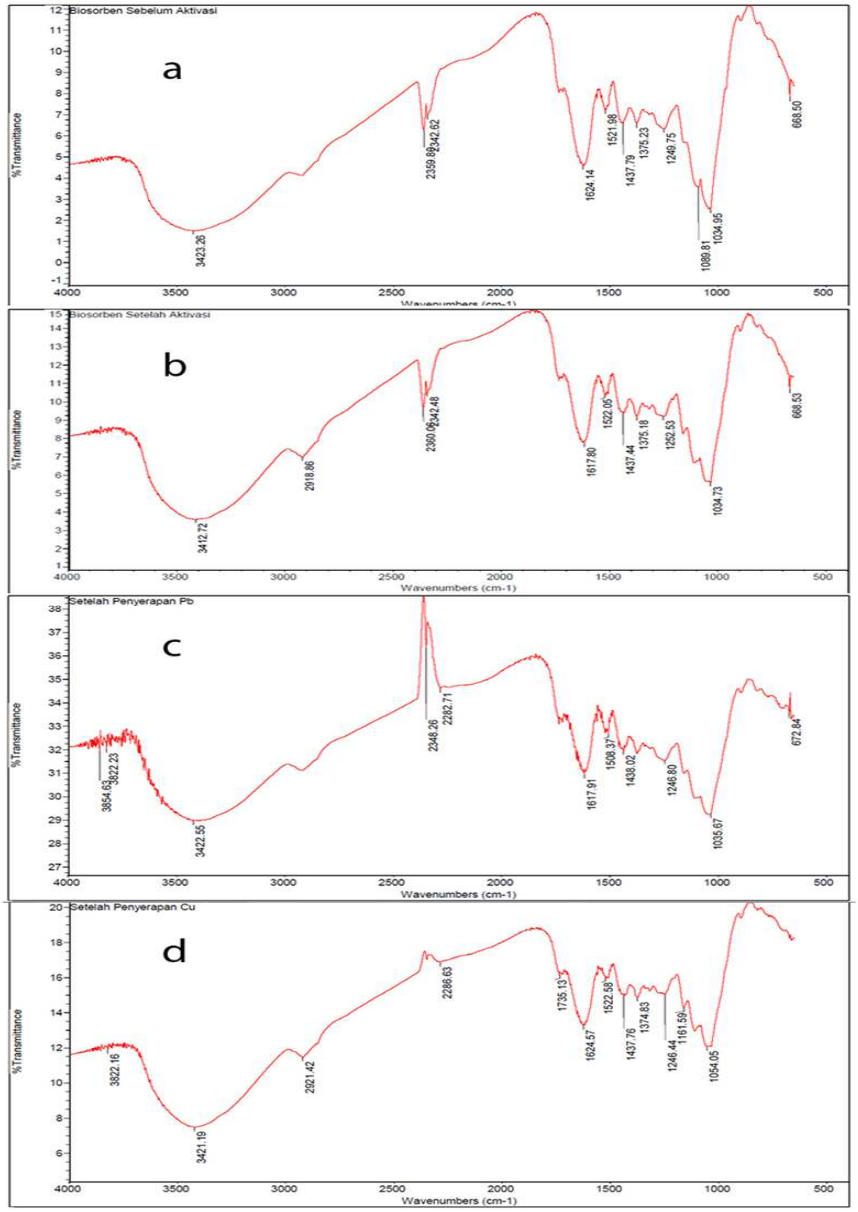


**Figure 2. FT-IR of *Nypa fruticans* husk before (a) and after (b) activation, (c) after Pb(II) ions uptake and (d) after Cu(II) ions uptake**

### Effect of Contact Time

Figure **5** shows the effect of contact time with the metal ions biosorben *Nypa fruticans* fruit husk powder. Contact time studied with variation of 5-75 minutes to see how long it takes to achieve optimum absorption. From the picture above it can be seen that the absorption capacity of the metal ions increased slightly at the contact time of 5 to 30 minutes, and the absorption capacity decreased slightly at the contact time 45-75 minutes. The optimum contact time uptake of Pb(II) ions is at 5 minutes with the absorption capacity of 1.9918 mg/L, although the contact time of 15 minutes gives the absorption capacity of 1.9924 mg / L but did not show a significant difference. While the uptake of Cu(II) ions is at 30 minutes with absorptive capacity is smaller than the ion absorption capacity of Pb(II) is equal to 1.9753 mg / L. This is because the Pb(II) ion has a radius larger than the Cu(II) ions, which is 1.20 Å and 0.69 Å, so that the Pb(II) ions more quickly binds to the biosorbent active sites. Contact time required to reach equilibrium is very short, these results indicate that the adsorption mechanism is more dominant chemical interactions. Similar results were also obtained by the absorption of Pb(II) and Cu(II) ions using *Nypa fruticans* shoots [12].

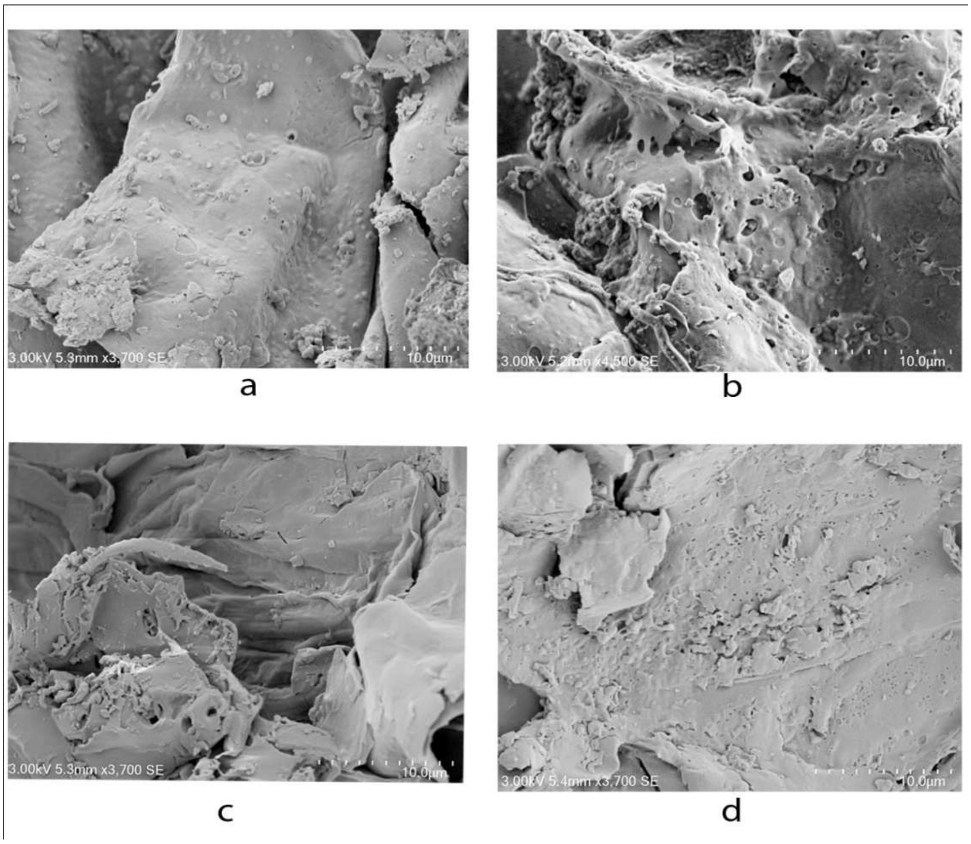


**Figure 3. SEM of *Nypa fruticans* before activation with a magnification of 3700X (a), after activation, 4500X (b), after the absorption of Pb(II), 3700X (c) and after absorption of Cu(II), 3700X (d)**

### Effect of Agitation

Metal ion absorption by varying the stirring speed of 30-250 rpm. Figure **6** shows the effect of stirring speed on the absorption capacity. Based on the picture above the metal ion absorption capacity rose only slightly with increasing rotational speed of 30-150 rpm, and the metal ions absorption capacity decreased slightly from the rotational speed of 200-250 rpm. Stirring speed was not a significant influence on the absorption capacity. In this work used the stirring speed of 150 rpm. According to Nazaruddin et al., 2014 maximum mixing speed with *Nypa fruticans* Merr shells were sampled at 150 rpm, because all of the active site on the surface biosorbent adequate to absorb metal ions. Biosorbent layer thickness decreases with increasing stirring speed which results in a reduction in the surface membrane resistance. Therefore, the metal ions adsorbed on the biosorbent surface easily. At the time of high-speed stirring, the mixture of metal ions with unhomogeneous biosorbent thus lowering biosorption. Similar results were also obtained with Phanerochaete chrysosporium biosorbent in absorption of Pb (II) ions with a rotational speed of 150 rpm [14].

### Effect of biosorbent dosage.

Total biosorbent mass is greatly affect the absorption capacity of the metal ion, because the greater the number biosorbent used the more active sites containing in it, as the interaction of the metal ion absorption process. In

Figure **7** it can be seen that the decrease in the absorption capacity of the metal ions with an increasing biosorbent dosage. Absorption capacity decreased from 4.9215 mg/g to 0.3978 mg/g for Pb(II) and Cu(II) ions of 4.7705 mg/g to 0.3956 mg/g. The increasing of the number of biosorbent cause an agglomeration of cells and continuous in reduction the distance between the intracellular will produce a screen effect between layers of cells that leads to protection against active sites. An decreasing in the absorption capacity of the metal ions are also reported in the study of absorption using Marine Algae [15] and waste paper [16].

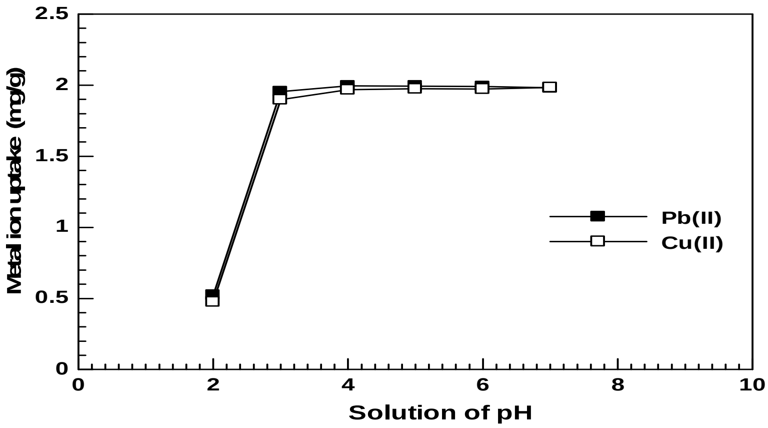


**Figure 4. Effect of pH on Pb(II) and Cu(II) biosorption by *Nypa fruticans* husk ; 25 mL metal solution; initial concentration = 20 mg /L: mass biosorben = 0.25 g; contact time = 90 min; stirring speed = 100 rpm**

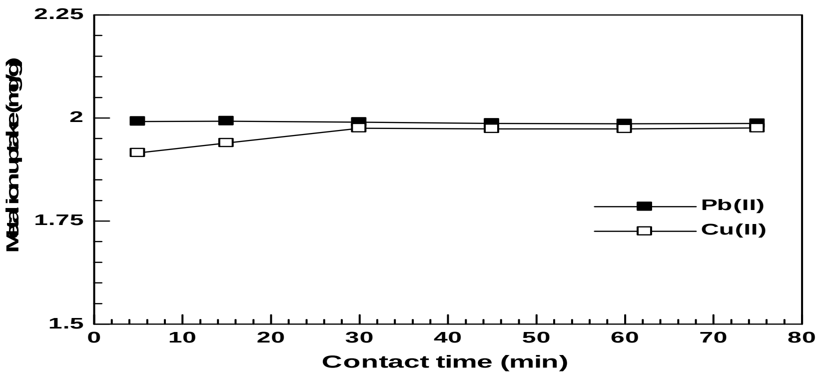


**Figure 5. Effect of contact time on Pb(II) and Cu(II) biosorption by *Nypa fruticans* husk ; pH of Pb(II) = 4 and Cu(II) = 5; 25 mL metal solution; initial concentration = 20 mg /L: mass biosorbent = 0.25 g; contact time = 90 min; stirring speed = 100 rpm**

### Effect of initial metal ion concentration

The concentration of Pb(II) and Cu(II) ions greatly affects the absorption capacity. Figure **8** shows that the absorption capacity of the Pb(II) ions continued to increase in the concentration of 30 mg/L to 100 mg/L, the optimum concentration of metal ions is at 100 mg/L with the absorption capacity of 20.8250 mg/g, while the Cu(II) ions concentration absorption capacity of 60 mg/L of 7.519 mg/g. The amount of adsorbed metal will increase with increasing the initial concentration of metal ions, this was due to an increase in the electrostatic interactions of metal ions with low affinity. Decrease the amount of metal ions adsorbed with increasing concentration of active groups describe saturation contained in biosorbent, this is because the amount of metal ions while the more active groups available fixed [15]. At low concentrations, all the metal ions in solution can interact with the active group biosorbent thus obtained higher adsorption percentage. While high concentrations of low adsorption results, this is due to the saturation of the active sites existing in the biosorbent surface because the more the number of metal ions [17].

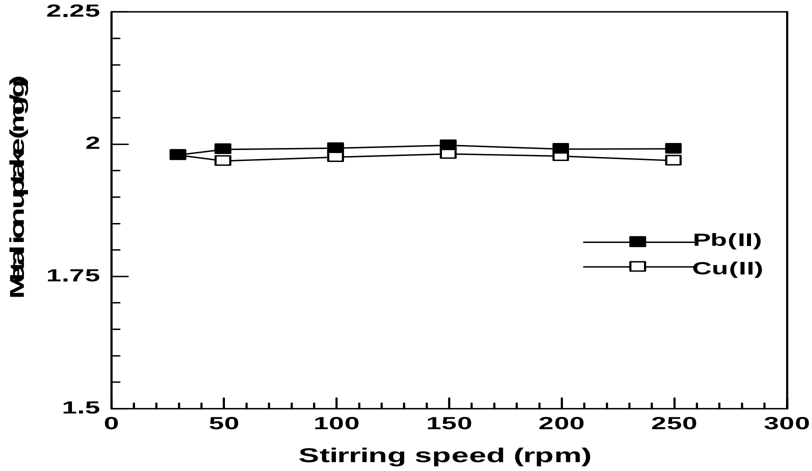


**Figure 6. Effect of stirring speed on Pb(II) and Cu(II) biosorption by *Nypa fruticans* husk ; pH of Pb(II) = 4 and Cu(II) = 5; contact time of Pb(II) = 5 min and Cu(II) = 30 min: 25 mL metal solution; initial concentration = 20 mg /L: mass biosorben = 0.25 g**

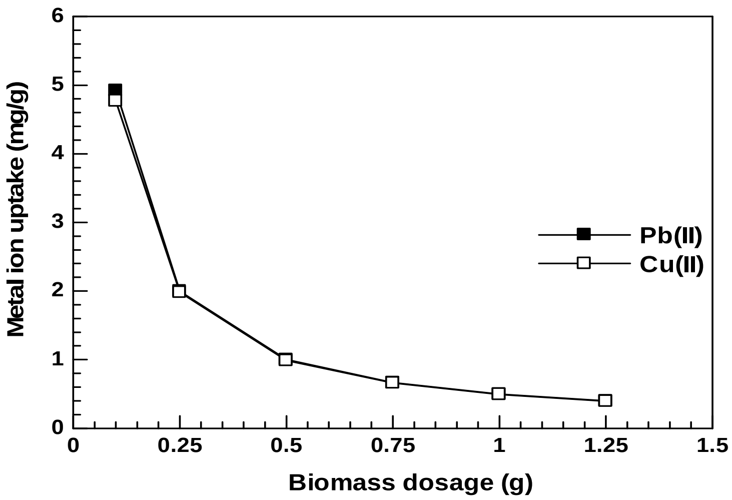


**Figure 7. Effect of biomass dosage on Pb(II) and Cu(II) biosorption by *Nypa fruticans* husk; pH of Pb(II) = 4 and Cu(II) = 5; contact time of Pb(II) = 5 min and Cu(II) = 30 min: stirring speed = 150 rpm for Pb(II) and Cu(II); 25 mL metal solution; initial concentration = 20 mg /L**

**Biosorption in mixed-metals system**

Metal ion absorption by the biomaterial is influenced by the amount and type of metal ions contain in the solution. In Figure **9** shows the visible effect of the addition of Cu(II) ions with various concentration of 0-20 mg/L in the uptake of Pb(II) ions with a fixed concentration of 20 mg/L. The optimum absorption capacity of Pb(II) ions in a solution of a single ion is 4.9215 mg/g (Figure **8**). While the solution absorption capacity bicomponent as 4.9513; 4.9169 and 4.7939 mg/g in the concentration of Cu(II) ions of 10, 15 and 20 mg/L. While the absorption capacity of Cu(II) ions of the concentration of 0-20 mg/L is always an increase in the concentration of Pb(II) ions remains. Based on these results indicate the existence of competition between Pb(II) and Cu(II) ions at the time of mixing and even though there are ions of Cu(II) as a bully metal ions does not affect the absorption of Pb(II) ions by *Nypa fruticans* husk powder.

The same treatment was also performed for the Cu(II) wherein the metal ion concentration of Cu(II) ions remains, the concentration of Pb(II) ions varied between 0-20 mg/L. From Figure **10** it can be seen that the absorption capacity of the Cu(II) metal ion almost constant while the Pb(II) ions continues to increase. This illustrates that the lack of effect of mixing Pb(II) ions on the absorption capacity of Cu(II) ions.

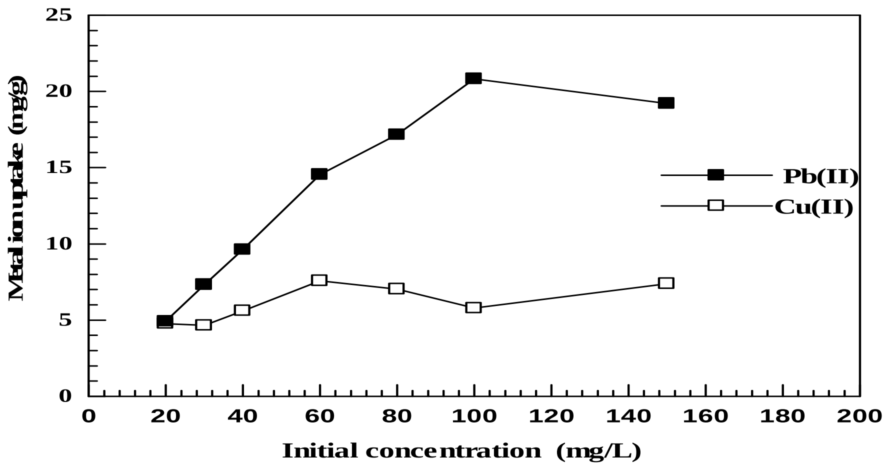


**Figure 8. Effect of initial metal ions concentration on Pb(II) and Cu(II) biosorption by *Nypa fruticans* husk; pH of Pb(II) = 4 and Cu(II) = 5; contact time of Pb(II) = 5 min and Cu(II) = 30 min: stirring speed = 150 rpm for Pb(II) and Cu(II); mass biosorben 0.1 g; 25 mL metal solution**

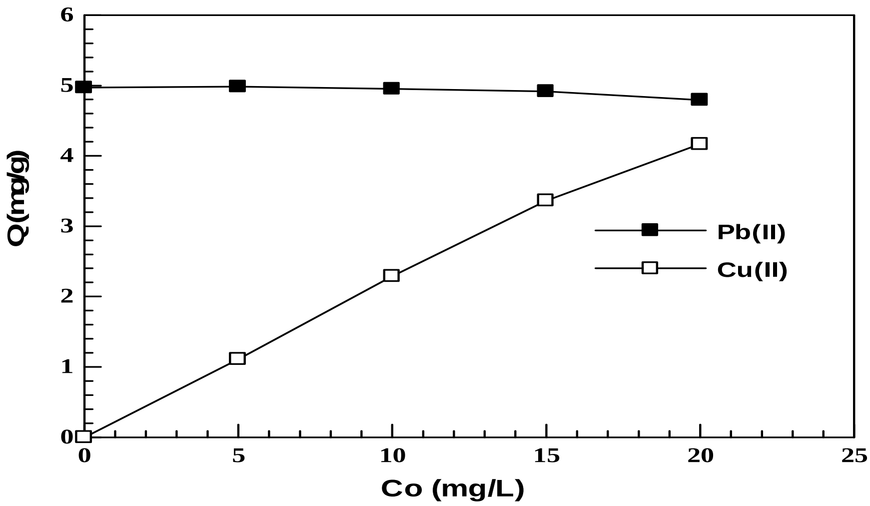


**Figure 9. Adsorption isotherms of Pb(II) in the presence of Cu(II) by *Nypa frutican* husk powder; 25 mL of Binary metal solution; pH = 4; contact time = 5 minutes; stirring speed = 150 rpm; the initial concentration of metal ions : Pb(II) = 20 mg/L; Cu(II) = 0, 5,10,15,20 mg/L**

A certain amount of biomaterials will produce a limited active side, and then the active side will experience burnout as a result of competition of metal ions, especially at high concentrations. In addition, the ability of these two metal ions to compete to fill the active side of the biomaterial [14].

**Adsorption isotherms**

Adsorption isotherms describe how the adsorbed molecules distributed between solid phase and liquid phase during the adsorption process reached an equilibrium. In determining the adsorption isotherm can be used several models including the Langmuir isotherm and Freundlich isotherm. Langmuir isotherm assumes the monolayer adsorption and adsorption energy constant, which is related to the absorption isotherms homogeneous. While the Freundlich isotherm is associated with heterogeneous absorption [5].

Langmuir isotherm can be described by the eqn (2):

$$Q_e = \frac{C_e\, B. Q_m}{1 + B. C_e}$$

Figure **11** is a plot Langmuir curve linearity between Ce (mg / L) with Ce / Qe (g / L).

Freundlich isotherm following equation (3):

$$\ln Q_e = \ln K_F + \frac{1}{n}. \ln C_e$$

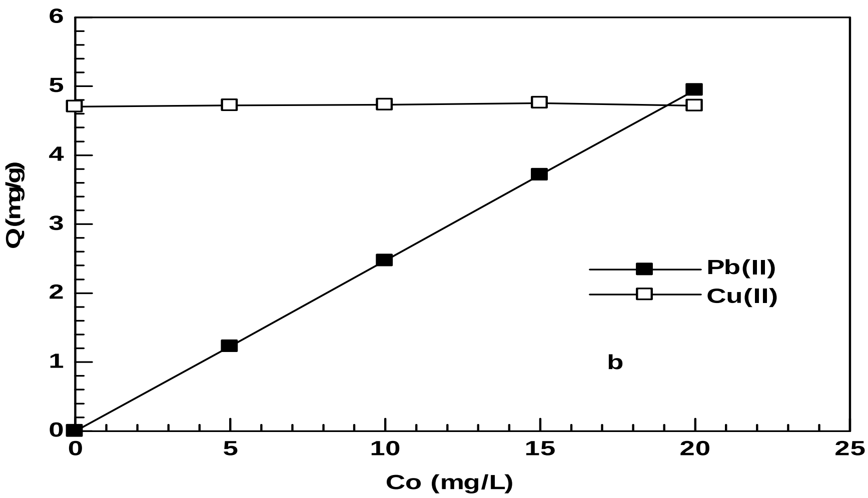


**Figure 10. Adsorption isotherms of Cu(II) in the presence of Pb(II) by *Nypa frutican* husk powder; 25 mL of Binary metal solution; pH = 5; contact time = 30 minutes; stirring speed = 150 rpm; the initial concentration of metal ions : Cu(II) = 20 mg/L; Pb(II) = 0, 5,10,15,20 mg/L**

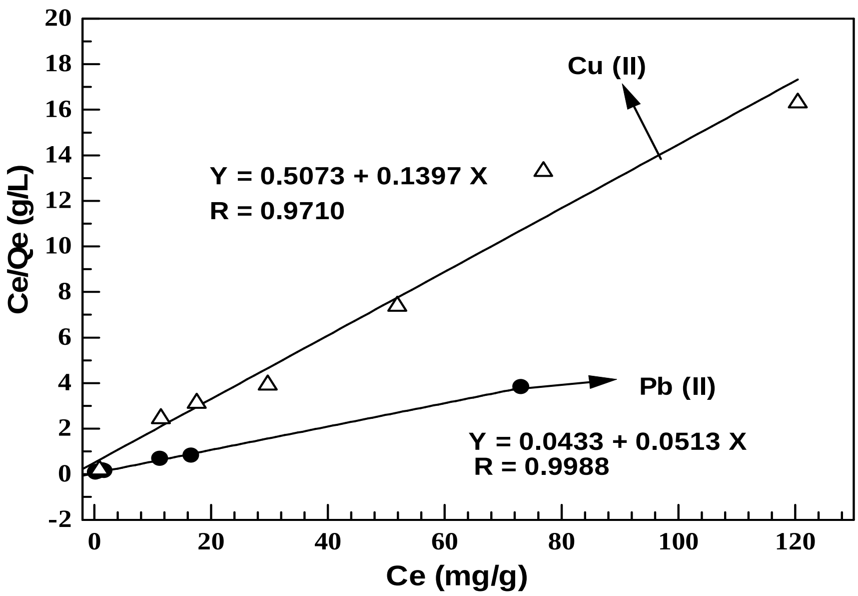


**Figure 11. Langmuir isotherm for ion absorption of Pb (II) and Cu (II) by *Nypa frutican* husk powder**

Figure **12**. Freundlich isotherm linearity curve is the relationship between ln Qe with ln Ce .. Where KF is the Freundlich isotherm constants of.

Evaluation of correlation values of the isotherm at the same temperature where is the value of Qmax, B, KF, n and $R^2$ can be seen in Table **1**. Of the $R^2$ value indicates that the Langmuir isotherm is better than the Freundlich isotherm in the uptake of Pb(II) and Cu(II) ions with palm fruit husk powder biosorbent, because its value is close to 1. [18] studied the uptake of Pb(II) and Cu(II) ions with Sophora japonica biosorben pods powder found that the adsorption isotherms of Langmuir better than the Freundlich isotherm.

Comparison of ion absorption capacity of Pb(II) and Cu(II) with other biomaterials can be seen in Table **2**. In the table shows that the absorption capacity of the Pb(II) and Cu(II) ions is almost close to the value of the same capacity despite different biomaterials, means *Nypa fruticans* husk powder can be used as biomaterials alternatives to harmful metal ion absorption

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

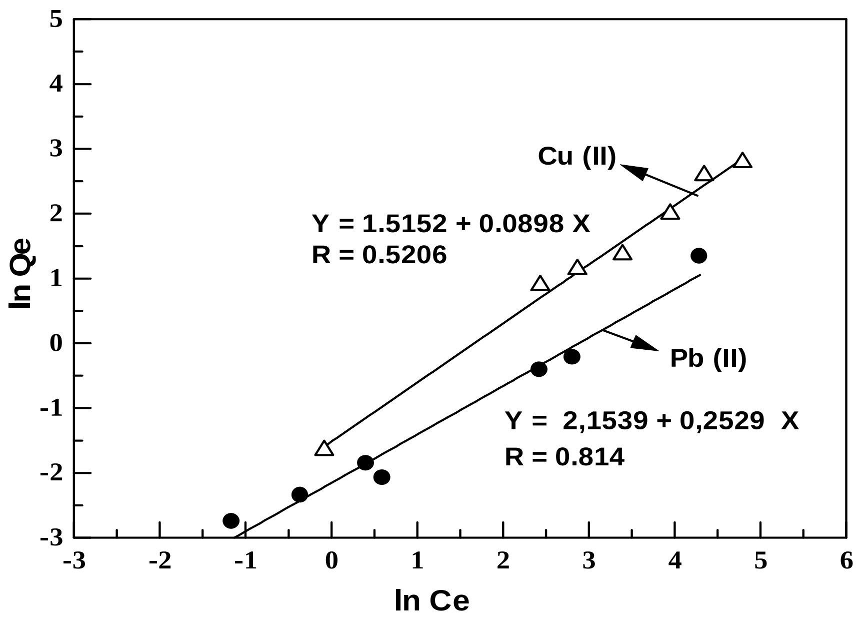


**Figure 12. Freundlich isotherm for ion absorption of Pb (II) and Cu (II) by *Nypa frutican* husk powder**

## CONCLUSION

This present work is concerning the biosorption of lead(II) and copper(II) in aqueous solution by using *Nypa fruticans* biomass as biosorbent. The parameters studied in the absorption of the metal ions include pH, contact time, stirring speed, biosorbent weight and concentration of metal ions.

*Nypa fruticans* husk can be used as an alternative biomaterial in the absorption of the metal ions. Absorption of both metal ions tends to follow the Langmuir isotherm with optimum absorption capacity for Pb(II) and Cu(II) ions respectively of 20.8250 mg/g and 7.5719 mg/g. *Nypa fruticans* husk powder can be made as biomaterials alternatives to absorb the toxic metal ions.

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