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Palm Fruit (*Arenga pinnata*) Shell as Biosorbent for the Removal of Cu(II), Co(II), Ni(II), and Pb(II) from Aqueous Solution.

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ABSTRACT

Sorption behaviour of Cu(II), Co(II), Ni(II) and Pb(II**)** by Palm fruit (*Arenga pinnata) shell* fruit shell was investigated. The experiment, were conducted in a glass column. Some variable that affect the sorption capacity such as solution of pH, particle size, flow rate, amount of weight biomass and metal ion concentration has been investigated. Using the optimum conditions, sorption capacity of metal ions Cu(II), Co(II), Ni(II) and Pb(II) were 1.48, 1.49, 1.16 and 1.66 mg/g, respectively. More over the sorption capacity using multi elements by Arenga pinnata fruit shell, will decrease due to the competition between the metal ions. Regeneration of metal in sorpted by diluted nitric acid, obtained that the maximum regeneration percentage for all metals at initial pH of 1. An FTIR examination revealed changes between the natural and heavy metals-loaded biomaterial. Scanning electron micrograph (SEM) also revealed changes in the surface morphology of the biomass as a result of heavy metal adsorption. Based on these results, it can be concluded that the *Arenga pinnata* is effective in removing heavy metal from aqueous solution and merits consideration for scaled-up trials.

Keywords: *Arenga pinata shell,* heavy metal, biosorption, AAS, FTIR, and SEM

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INTRODUCTION

The increase in the contamination of the aquatic system with heavy metals through industrial activities has initiated the search for economic strategies for their removal [1]. The pollution of water due to heavy metals is an issue of great environmental concern. Heavy metals and other metals ions exist as contaminants in aqueous waste streams of many industries, such as tanneries, mining operations, electronics, electroplating, batteries and petrochemicals industries [2,3]. Some metals associated with these activities are Pb, Cu, Co and Ni. Toxic metals are released into the environment in a number of ways. They have harmful effects on human physiology and other biological systems when they exceed the tolerance levels. Exposure to lead and cupper can cause brain and bone damage. It is therefore necessary to remove these heavy metals from industrial effluents [4]. The removal and recovery of heavy metal ions from wastewater involve many techniques such as ion exchange, evaporation, precipitation and membrane separation, but they are suitable for high concentrationw of metals [5-10]. These common techniques also are too expensive to treat low levels of heavy metals in wastewater.

Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising techniques and inexpensive biomaterial uses [11,12]. The removal of heavy metals ions using low-cost agricultural wastes which are abundantly available adsorbents in Indonesia such as rice husk [13], mangostana shell [14], snake fruit shell[15] were used and investigated. The materials usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohol, aldehydes, ketones, carboxylic, phenolic and ether groups [16]. These groups have the ability to some extent to bind heavy metals by donation of electron pair from these groups to form complexes with the metal ions in solution. The major merits of biosorption technology are the effectiveness in reducing the concentrations of heavy metals ions to low levels and the inexpensive nature of the materials because they are readily available at little or no cost [17].

The aim of the present research is to study the capability of Arenga pinnata shell as biosorption material to remove Cu(II), Co(II), Ni(II) and Pb (II) ions from aquesous solution.

MATERIALS AND METHODS

Preparation of Arenga pinnata shells

Arenga pinnata shell was collected from Puncak Pato district, Batusangkar, West Sumatra Province, Indonesia. The Arenga pinnata shell coleected then washed exhaustively with water to remove dirt, sand, clay and the particulate material from their surface and finally with deionized water. After washing then dried under the sunlight. Dried Arenga pinnata shell was cuted, ground in a pestle and mortar and then screened to particle size 150-425μm. The powder than collected in a bottle for use as a sorbent.

Chemicals and apparatus

All reagents ued were of analytical grade obtained from Merck (Darmstad, Germany). The apparatus used were screener Octagon 200 (Endcots,London, England), an analytical balance (KERN 220-4M, Germany), FTIR (FTIR-460 plus, Jasco, Japan), Scanning Electron Microscope (SEM) and atomic absorption spectrometer (AAS, Raylight WFX-320, BRAIC, China). Working standard solution of Cu(II), Co(II), Ni(II) and Pb (II) ions was made from a 1,000 mgL^{-1} stock standard solution. All reagent used were of analytical grade obtained from Merck (Darmstad, Germany).

Biosorption Studies

Dried Arenga pinnata shell used were soaked with 0.1 molL^{-1} nitric acid for ca. 48 hours and then were filtered and finally washed until neutral by using distilled water and then filtered and dried at room temperature.

Working standard solution made from stock standar solution of Cu(II), Co(II), Ni(II) and Pb (II). Adsorption experiments were carried out at various particle size, solution of pH, shell doze, initial concentration and flow rate of solution under dynamic methods and regeneration process.

The pH of the solutions was adjusted to the required value (range from 2-8) by adding buffer solution at indicated solution of pH. After equilibrium, the final concentration were measured by atomic absorption spectrophotometric method.

Fourier transform infrared spectroscopy analysis

For the FTIR studies, 5% (w/w) of powdered and dried of Arenga pinnata were presessed to form KBR disc. The FTIR spectra of sample before and after loaded with Pb(II) were recorded in the range of 4000-400 cm^{-1} spectral range.A total of 128 scans were averaged for each sample with a resolution of 2 cm^{-1}.

Scanning electron microscopy analyis

The study of morphology of biosorbent Arenga pinnata shell was ued by masuring SEM images of sample before and after loaded with Pb(II) were recorded with two different magnifications, i.e. 100 and 5000 times.

Desorption sudies

Metal ions that have been absorbed by biosorbent at optimum conditions eluted to use 20 ml of nitric acid with pH 1, 2, 3, and 4. Results measured elution with SSA.

Data evaluation

To determine the capacity of metal ion uptake by the arenga pinata shell. calculated using the Langmuir isotherm equation with a value of :

$$Q = \frac{Ci - Cf}{m} \times V$$

Where : Q = capacity of absorption (mg metal ion/g biomaterials) ; Ci = initial concentration of metal ion (mg/L) ; Cf = final concentration (mg/L), V = volume of metal ion/solution ; m = mass biosorbent/biomaterial (g) Percent regeneration of the acid solution be calculated by the formula :

$$\% \ Regeneration = \frac{C \ filtrat \ after \ regeneration}{C \ sorption} \ x \ 100\%$$

RESULTS AND DISCUSSION

FTIR measurements

FTIR characterization was carried out to analysis the major functional group such as carboxyl, amide, hydroxyl groups which exists in Arenga pinnata. The sorption process depend on various factors such as the number of functional groups, process interactions, chemical structures, and affinity (the ability to receive metal ions) between the Arenga pinata shell and of metal ions. The results are shown in Figure 1 a before sorption and 1 b after. Identification of functional groups involved in the absorption of pure Arenga pinnata powder commpared with that have interacted with the metal ions. From the results it can be concluded that sorption of Pb (II), Cu (II), Co (II) and Ni (II) shifted transmittance values. Wavenumber shift from 3434 cm^{-1} (before interaction with Cu (II), Pb (II), Ni (II) and Co (II)), 3429 cm^{-1} after interact with Cu (II), 3435 cm^{-1} for Pb (II), 3433 cm^{-1} interaction with Ni (II) and 3431cm^{-1} with Co (II). The results almost similar when rice straw [18] has been used as sorption material. From the data it can be concluded that the results was assigned to the strehing of O-H groups due to inter- and inta- molecular hydrogen bonding of polymeric compounds, such as alcohol, occasionally phenols, and carboxylic acid.The data also prove the existence of lignin and cellulose compounds that play a role in the uptake of metal ions.
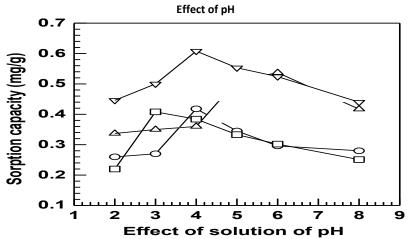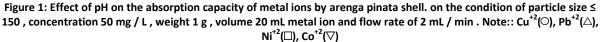
FE - SEM measurements

Roof structure of the fruit skin surface before absorption (A and B 5000X magnification 100X magnification) and after absorption of metal ions Pb (C and D 5000X magnification 100X magnification) viewed using FE - SEM tool turns surface structure forms arenga pinata shell have difference. Time before contacted with metal ions, arenga pinata shell does not flake fibers which can be seen in Figure B (red circles), while after contacted with metal ions Pb appears there lining the surface of the arenga pinata shell (image D in red circle). In the current 100X magnification before contacted with metal ions visible arenga pinata shell evenly split (image A red circle) after contacted with different fruit rind flake arenga pinata shell linked to each other and overlap (Figure C red circle). This prove functional groups contained in the arenga pinata shell has been interacting with metal ions where the metal ions Pb adsorbed on the surface of the roof of the fruit skin. Isaac (2011) explains that the skin of the fruit composition arenga pinata shell compounds containing lignin and cellulose. Functional groups present in lignin and cellulose is the one who interacts bind metal ions.

Effect of pH on Metal Ion Absorption

From Figure 1 note that the optimum pH for metal ion Cu (II), Pb (II), Co (II) and Ni (II) is in the range of pH 3-6 , the absorption capacity of each 0.418 mg/g at pH 4 ; 0.537 mg/g at pH 6 ; 0.608 mg/g at pH 4 and 0.426 mg/g at pH 3 . Almost the same results for the effect of pH was also reported by other researchers (Jafari et al, 2012; Yalcin et al, 2012; Prakash et al, 2011; Gazem et al, 2012) where the influence of pH for cationic metal ions in the range 3-6. This is also in accordance with the opinion Ramelow and Harris that the zero point charge or isoelectric point at pH 3 functional group wherein the pH less than 3 active group has a positive charge. While the pH is greater than 3 active group has a negative charge. This causes the electrostatic attraction between the positively charged cations with active groups on the negatively charged cell walls.

Figure 1: Effect of pH on the absorption capacity of metal ions by arenga pinata shell. on the condition of particle size ≤ 150 , concentration 50 mg / L , weight 1 g , volume 20 mL metal ion and flow rate of 2 mL / min . Note:: Cu^{+2}(○), Pb^{+2}(△), Ni^{+2}(□), Co^{+2}(▽)

If associated with competition occurring between the metal cations with H$^+$ for adsorbed on the active side of the arenga pinata shell. Arenga pinnata containing heteropoly saccharide complexes that can provide amino, carboxyl, and sulfate. At low pH, the protonated functional groups and limiting metal ion uptake due to competition with H. Along with the increase in pH, functional groups such as amino, phosphate, and carboxyl group will open and carry a negative charge so that the adsorbed metal ions will (Prakas et al , 2012). While at high pH above 6 came into being metal hydroxide solution or hydroxide anions that complex metal ions formed biosorption limiting the occurrence of the metal (Onwuka et al, 2011) .

Effect of Particle Size on Metal Ion absorption

Maximum absorption for metal ions Co (II), Ni (II) and Cu (II) contained in the particle size ≤ 150 μm, whereas for maximum absorption of Pb metal ions contained in the particle size of 151-180 μm. based on the data thus obtained the optimum particle size that is used here is ≤ 150 μm. This is consistent with the theory

that the large particle size decline in the capacity for absorption due to the decrease in the surface area of the arenga pinata shell.

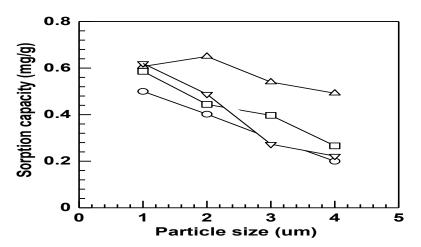**Effect of Particle Size of the Arenga Pinata Shell**

Figure 2 . Effect of particle size of the arenga pinata shell. at optimum pH conditions , the concentration of 50 mg/L, weight 1 g, volume 20 mL metal ion and flow rate of 2 mL/min. Note : Cu^{+2}(○), Pb^{+2}(△), Ni^{+2}(□), Co^{+2}(▽) dan 1 (≤150 μm), 2 (151-180 μm), 3 (181-250 μm), 4 (251-425 μm)

Mechanism of heavy metal ion uptake by biomaterial is due to the biomaterial composition of common chemical compounds are compounds of cellulose and lignin (Zhang et al . , 2012). Lignin is an aromatic polymer compound which serves to carry water from the roots to the leaves and to protect plants so as not degraded. Functional groups present in the lignin alcohols, aldehydes, ketones, carboxylic acid, phenol and ether.

Effect of Concentration on Metal Ion Absorption

In this research it appears that the maximum concentration set at a maximum adsorption of metal ions Cu (II), Pb (II), Ni (II) and Co (II) at a concentration of 100 mg/L. Can be seen to increase the absorption capacity still means active groups metal ions are still able to receive until later at saturation point. Langmuir explained that the biomaterial surface active group whose numbers are proportional to the surface area of biomaterials.
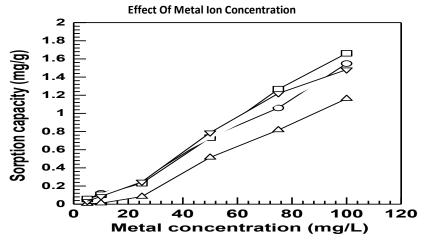

Figure 3. Effect of metal ion concentration on the absorption capacity of the arenga pinata shell. at the optimum pH, particle size ≤ 150, weighing 1 g, volume 20 mL metal ion and flow rate of 2 mL/sec. Note : Cu^{+2}(○), Pb^{+2}(△), Ni^{+2}(□), Co^{+2}(▽).

Langmuir Isotherm

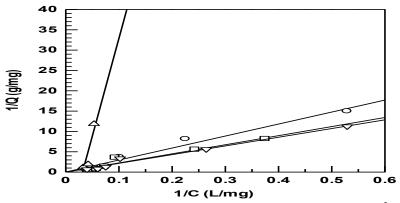**Figure 4. Langmuir isotherm of the metal ion is absorbed by the arenga pinata shell. Note : Cu^{+2}(○), Pb^{+2}(△), Ni^{+2}(□), Co^{+2}(▽)**

To study the relationship between the concentration of the metal ion absorption capacity used Langmuir isotherm. Figure 4 shows that the greater the concentration of metal ions , the greater the absorption capacity. Adsorption processes that occur between the metal ions {Cu (II), Pb (II), Ni (II) and Co (II)} and adsorbent arenga pinata shell Langmuir isotherm is assumed to follow a pattern, so that the determination of adsorption capacity as study thermodynamic used Langmuir equation. Langmuir adsorption isotherm can be expressed by the equation :

$$1/Q = 1/Qm + 1/bQmC$$

Where C is the concentration of metal ion (mg/L) , Q is the amount of substance adsorbed per gram of adsorbent (mg/g), and Q m is the adsorption capacity (mg/g). relationship between capacity and concentration of metal ions penyerepan can dilperoleh by plotting the data obtained from the results of research to chart 1/C with 1/Q produces a straight line with slope and intercept 1/bQm 1/Qm. Obtained from the calculation of the maximum absorption capacity for metal ion Cu (II) 90.9 mg/g (R2=0.974), Pb (II)-0.01 mg/g (R2=0.979), Ni (II) 76.92 mg/g (R2=0.936) and Co (II) 142.85 mg/g (R2=0.979).

Effect of Flow Rate Speed on Metal Ion Absorption

In Figure 5, the metal ions Pb (II) and Ni (II) the faster the flow rate decreased absorptive capacity, according to the theory of the faster flow rate, the smaller the interaction between the ions that occur so that the absorption capacity decreases. When the metal ions through the material in the column will be the interaction between the metal ions with the arenga pinata shell., the length of time the interaction will affect the amount of metal ions on the surface of the absorption arenga pinata shell.
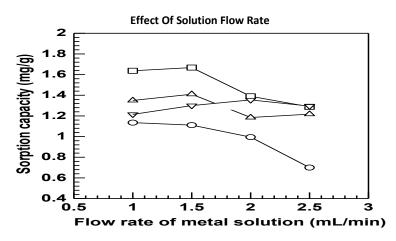

Figure 5. Effect of solution flow rate of the metal ion uptake capacity arenga pinata shell (at the optimum pH, particle size ≤ 150, the concentration of 100 mg/L, 20 mL volume of the metal ion and a weight of 1 g. Note: Cu^{+2}(○), Pb^{+2}(△), Ni^{+2}(□), Co^{+2}(▽)
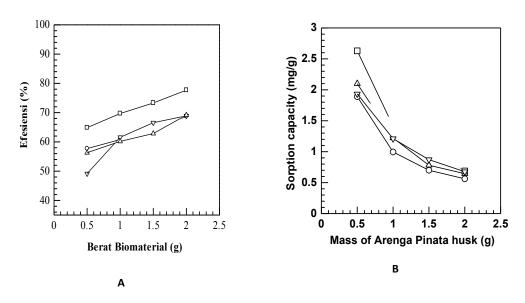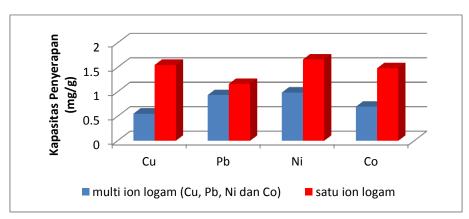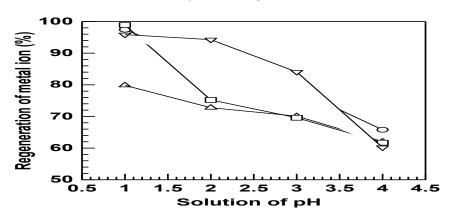
A

B

Figure 6. Heavy influence arenga pinata shell (A. Efficiency absorption, B. The absorption capacity) At optimum pH conditions, particle size ≤ 150, the concentration of 100 mg/L, 20 mL volume of the metal ion and flow rate of 2 mL/min. Note : Cu^{+2}(○), Pb^{+2}(△), Ni^{+2}(□), Co^{+2}(▽).

Multicomponent Metal Ion Absorption Capacity

Figure 7. Multicomponent metal ion absorption capacity on the arenga pinata shell at the optimum pH, particle size ≤ 150, the concentration of 100 mg/L, 1 g weight, and a flow rate of 2 mL/min.

Effect Of pH On The Regeneration

Figure 8. Effect of pH on the regeneration of the metal ion is absorbed by the arenga pinata shell. Note : Cu^{+2}(○), Pb^{+2}(△), Ni^{+2}(□), Co^{+2}(▽).
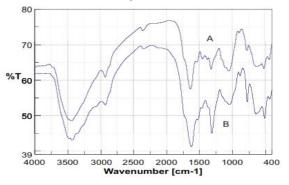
FTIR Arenga Pinata Shell

Figure 9a. FTIR arenga pinata shell. before (A) and after (B) uptake of metal ions Cu (II)
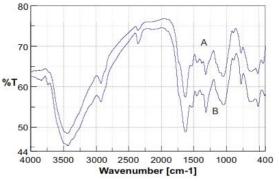

Figure 9b. FTIR arenga pinata shell. before (A) and after (B) uptake of metal ions Pb (II)
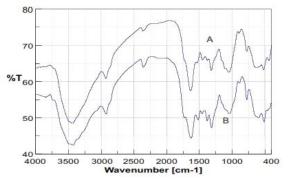

Figure 9c. FTIR arenga pinata shell before (A) and after (B) uptake of metal ions Ni (II)
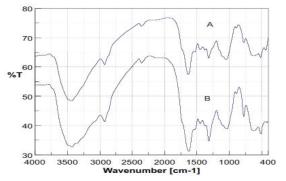

Figure 9d. FTIR arenga pinata shell before (A) and before (B) absorption of metal ions Co(II)

Similar results were also found by Saatcilar (2001), using Cibacron Blue F3GA as biosorben to absorb metals Cd (II), Cu (II), Pb (II) and Zn (II) with the column method. Flow rate range used is from 0.5 to 10 ml/sec. At fast flow rates the capacity of absorption decreases, this is because the contact time between the metal ions with biosorbent shorter so that the absorption capacity decreases.

FE - SEM

Figure 10. FE - SEM of the Arenga pinnata with 100X magnification (A), 5,000 X (B) and after absorption of metal ions Pb (II) 100 X (C) and 5000X (D)

Effect of weight of biomass on the metal ion biosorption

Weight variation arenga pinata shell used for absorption of metal ions Cu (II), Pb (II), Ni (II) and Co (II) were 0.5, 1.0, 1.5 and 2.0 g. Heavy influence on the arenga pinata shell. skin absorption capacity was found that the uptake of metal ions unit weight decreases with increasing weight biosorbent. On the other hand the absorption efficiency increases with increasing weight biosorbent. Due to the weight of the highest biosorben surface area also increased. (Vankar et al, 2011). The same thing also happened on Onwuka study (2011) which showed a decrease in the adsorption capacity with increasing weight of adsorbent.

In general, the presence of other metal ions in a solution of biomaterials affect the absorption capacity. From this data it can be concluded that metal ions compete in getting active on Arenga pinnata side so that the absorption is reduced. This could be explained where the saturation of the active biosorben the concentration of metal ions in excess of the capacity of active group. If done on the condition of low concentration of small

possibility of competition. Conversely, if the concomitant increase in the concentration of metal ions, scramble competition between the active side of the metal so that the metal which has a high selectivity towards biomaterial absorption is large (Karaca, 2008). This is what happens to ions Pb (II) and Ni (II) which has a high selectivity towards biomaterials arenga pinata shell.

Regeneration

Regeneration of metal ions by H^+ ions from HNO_3 occurs through ion exchange process resulting metal ions on biosorbent carried. Where the results of research into shows that at pH 1 to regenerate the metal ions Cu, Pb, Ni and Co the highest metal ion, respectively 97.43 %, 79.83 %, 98.87 % and 95.86. Of the image can be seen the smaller the pH the greater the percentage of metal ions was obtained due to the H^+ ions from HNO_3 that is strong to replacing metal ions bound to the biomaterial arenga pinata shell.

In the process of biosorption reactions that occur are reversible, this was observed when the metal ions are bound to biosorbent be treated with dilute HNO_3 called desorption process. Results obtainable from the data that the process desopsi increased at low pH, it is because the smaller the pH the greater the concentration of HNO_3, so that metal ions will quickly dissolve in the low pH HNO_3. In the desorption process, the H^+ ions displace metal ions Pb (II), Cu (II), Co (II) and Ni (II) on biomaterials, by way of cation exchanger (Singha & Kumar, 2012). Where Singha also obtain maximum results for desorption is 95.76 % on coconut fiber biomaterial.

CONCLUSION

From the study it can be concluded that the roof pods can be used as an absorbent material metal ions Pb (II), Cu (II), Ni (II), and Co (II). Pieces of the roof can be regenerated using pH 1 with HNO_3 maximum outcome for metal ion Cu (II), Pb (II), Ni (II) and Co (II), respectively 97.4 ; 79.8 ; 98.8 and 95 , 8 %.

ACKNOWLEDGEMENTS

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