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Batch Method for the Removal of Toxic Metal from Water Using Sugar Palm Fruit (*Arenga pinnata* Merr) Shell.

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ABSTRACT

The use of *Arenga pinnata* fruit shell as absorbent material for ion Cr (III), Cr (VI), Cd (II) and Zn (II) has been investigated using batch method. Several variables such as effect of solution of pH, contacting time, concentration of toxic metals solution, stirring time and agitation speed on the absorption capacity of metals ion has been investigated. All metals ion concentration has been measured by using atomic absorption spectrometry. On the other hand the fungsional groups present on the shell was measured using Fourier Transform Infra Red spectroscopy.
Keywords: Biosorption, heavy metal, *Arenga pinnata* Merr shell, atomic absorption spectrometry, fourier transform infra red spectroscopy.

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INTRODUCTION

Recently, biosorption has emerged as a treatment methods as an alternative technology to the conventional used ones for the wastewater treatment. There are various secondary and tertiary treatment techniques for the removal of heavy metals from aquaeous solution [1]. However, these processes are having technical and or economical constraints [2]. Biosorption has emerged as an alternative to these methods with the major advantage such as low cost, high efficiency, minimization of chemical and or biological sludge, regeneration of biosorbent and possibility of metal recovery [3,4].

Various biosorbents such as agricultural by products and microorganisms such as rice husk, algae, citrus peels, grape stalks, cocoa shell, mangostana fruit shell, have been reported for the removal of toxic metal from environmental water [4, 5-10]. Biosorption refers to different modes of non-active metal binding, where metal sequestration by cell wall can take place through adsorption, ion exchange and complexation. Numerous functional groups namely, sulphydryl, carbonyl, hydroxide amino, thiol, carboxyl and amide moieties are possible for the binding metal ions [3,4,11]. Sugar palm fruit shell has earlier been reported fir its biosorption properties for a number of metal ions including mechanism prediction by using artificial neural network [12-13].

The present study is focused to explore the ability of environmentally friendly agricultural by product such as sugar palm fruit shell for the removal of Cr(III), Cr(VI), Cd(II) and Zn(II) from aqueous solutions under batch or static methods. Experimental parameters affecting the biosorption process such as pH, contact time, stirring speed, solution pH ion, size and multielement particles. stirring speed, solution pH ion, size and multielement particles. stirring speed, solution pH ion, size and multielement particles has been investigated to calculate the biosorption capacity of the sugr palm.

MATERIAL AND METHODS

Equipment and Materials

Field Emission Scanning Electron Microscope / FE-SEM (Inspect F50, FEI Company, USA), atomic absorption spectrophotometer (WFX-320 Raylight, BRAIC, China), FTIR (FT/IR-460 Plus, Jasco, Japan), a digital balance (KERN 220-4M, Germany), pH Universal (Merck), blender, filter paper, and other glassware. Materials used *Arenga pinnata* Merr shell which taken in the summit area Pato, Batusangkar, West Sumatra, ZnCl2 (Merck), CdCl2 (Merck), CrCl3.6H2O (Merck), K2Cr2O7 (Merck), HNO3 65% (Merck), NaOH (Merck), ethanol distillation, and the distilled water.

Implementation Research

The experiment was conducted in three phases. The first is the creation of adsorbent the *Arenga pinnata* Merr shell. The second is testing the ability of the metal ion uptake of Cr (III), Cr (VI), Cd and Zn with time varying stirring, agitation speed variation of metal ion solution, the concentration of HNO_3, and pH to determine the optimum conditions using batch sorption method. The third is to regenerate by using multicomponent solution in optimum condition resulting from the previous stage.

Adsorbent of Arenga pinnata fruit shell

Arenga pinnata Merr shell were taken in Puncak Pato, cleared of rocks and mud that sticks, then washed with water and dried in the open air. Once dried and then crushed by crushed with pestle and sieved with a sieve based particle size to be used is 150μm. The *Arenga pinnata* Merr shell in a solution of 0.1 M HNO3 for 2 hours while stirring occasionally. Results filtered then washed with distilled water. After it was soaked with ethanol for 2 hours, then dried again.

Determination of Optimum Conditions

Determination of optimum conditions performed for each metal ion Cr (III), Cr (VI), Cd (II) and Zn (II). For each treatment using 1 g of biomaterial.

Effect of pH

Arenga pinnata Merr shell put into a flask with a particle size of 150 μm was then added 20 mL of Cr (III) 50 mg / L at pH variation 2, 3, 4, 5, 6 and 8, then those are shaked for 60 minutes with a rotation speed of 150 rpm. Equal treatment for solution of Cr (VI), Cd (II) and Zn (II) has been done. The resulting filtrate was analyzed by atomic absorption spectrophotometer.

Effect of Particle Size

Biomaterial put into each flask with a size of 150, 180, 250 and 425 μm, then added with 20 mL of Cr (III) 50 mg / L at pH optimum, then solution are shaked for 60 minutes with a rotation speed of 150 rpm, equal treatment for solution of Cr (VI), Cd (II) and Zn (II) were carried out. The resulting filtrate was analyzed by atomic absorption spectrophotometeric detection.

Effect of Concentration

Arenga pinnata Merr shell put into a flask with optimum particle size, then added 20 mL of Cr (III), respectively 5, 10, 25, 50, 75 and 100 mg / L with a pH optimum. The solution then are shaked for 60 minutes with a rotation speed of 150 rpm. Equal treatment for solution of Cr (VI), Cd (II) and Zn (II) has been done. The resulting filtrate was analyzed by atomic absorption spectrophotometer.

Effect of Contact Time

Adsorbent with a particle size of 150 μm weighed 1.0 grams. Then added a solution of 20 mL of metal ion and dishaker for 60, 120, 180 and 240 minutes with a rotation speed of 150 rpm. After it was filtered and the resulting filtrate is collected and analyzed by atomic absorption spectrophotometer.

Effect of Agitation Speed

Adsorbent with a particle size of 150 µm weighed 1.0 grams. Then added a solution of 20 mL of metal ion and dishaker for 120 and 180 minutes with an agitation speed of 50,100, 150 and 200 rpm. After it was filtered and the resulting filtrate is collected and analyzed by atomic absorption spectrophotometer.

Multicomponent for total Cr, Zn (II) and Cd (II)

The optimum particle size of 150 µm and each metal concentration of 100 ppm. Solution set according to the pH optimum pH is pH 4 and passed into the column as much as 20 mL. The resulting filtrate was analyzed by atomic absorption spectrophotometer.

Regeneration

Metal ions have been absorbed by biosorben in optimum condition eluted using 20 ml of nitric acid with pH varasi 1, 2, 3 and 4. Elution results measured by AAS.

RESULTS AND DISCUSSION

FTIR is an important analytical technique, which detects the vibration characteristics of chemical functional groups existing on the surface of adsorbent. Some characteristic peaks obtained from the functional groups proteins and polysaccharides. Functional groups contained in *Arenga pinnata* Merr shell be shown in Fig. 1a-1b

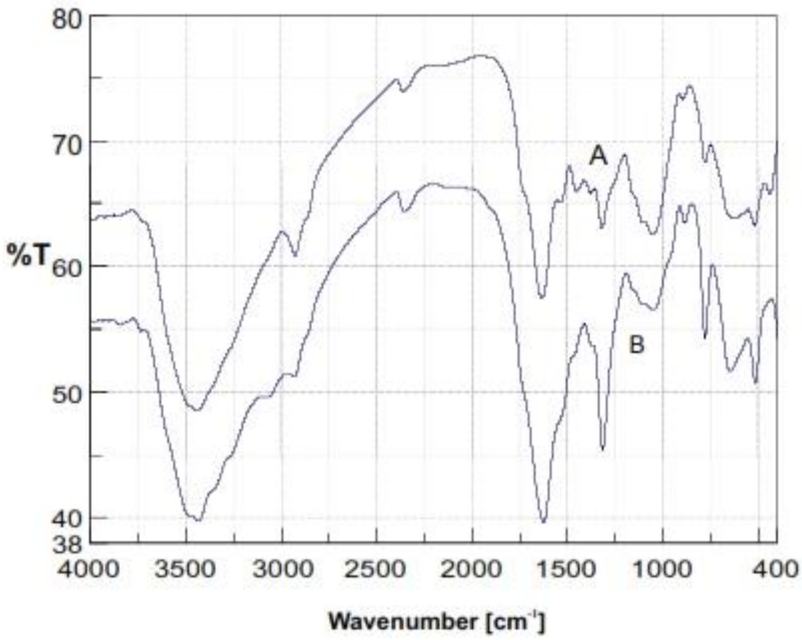

Figure 1a. FTIR of *Arenga pinnata* fruit shell before (A) and before (B) absorption of metal ions Cd (II).

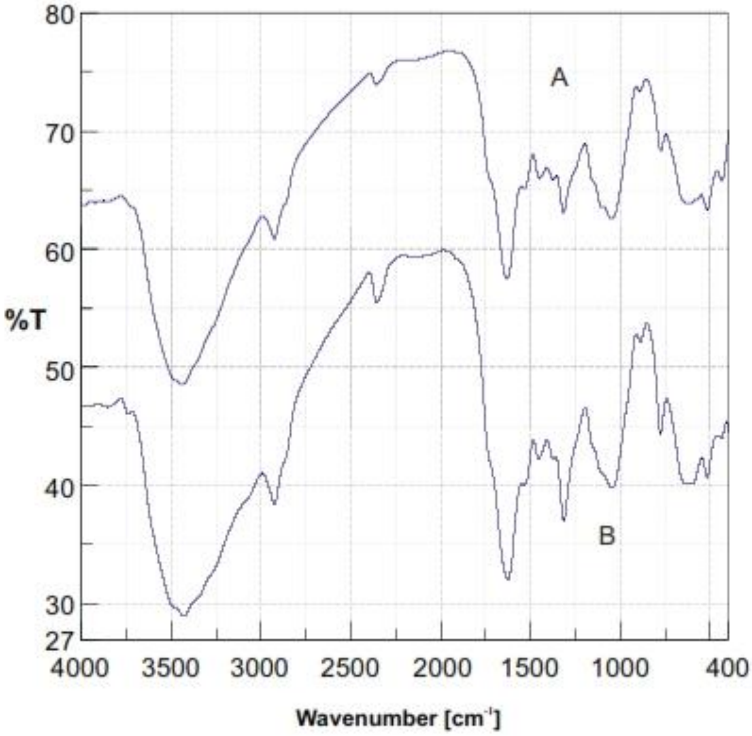

Figure 1b. FTIR *Arenga pinnata* fruit shell before (A) and after (B) absorption of metal ion Zn (II)

The spectrum can be seen in the shift of the transmittance values of functional groups contained in the *Arenga pinnata* Merr shell.

Effect of Contact Time

Figure 2 shown that the absorption capacity of the largest found in metal ion Zinc (II) and Chromium (VI) with stirring time of 120 minutes and 180 minutes. At the time of 120 minutes for Zinc (II) and 180 minutes for the Chromium (VI) interaction between metal ions and active groups biosorben the more and the greater the possibility of absorption capacity. When metal ions mixed with the material in the flask will be an interaction between the metal ions with active the *Arenga pinnata* Merr shell, the length of time the interaction will affect the amount of metal ions adsorbed on the surface of the skin off the *Arenga pinnata* Merr shell. Absorption increases with the length of time to interact and reach equilibrium at the optimum time. It also occurs on the metal ion Chromium (III) and cadmuim (II), but not the absorption capacity of metal ions Chromium (VI) and Zinc (II).

Effect of Agitation Speed

While the metal ions is passed into the pumpkin will be the interaction between the metal ions with the active side of *Arenga pinnata* Merr shell flour, stirring speed interaction will affect the amount of metal ions adsorbed on the active surface of the fruit peel flour

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roof. From figure 3, agitation speed 100 and 150 rpm maximum absorption occurs for Cr (VI) and Zn (II)

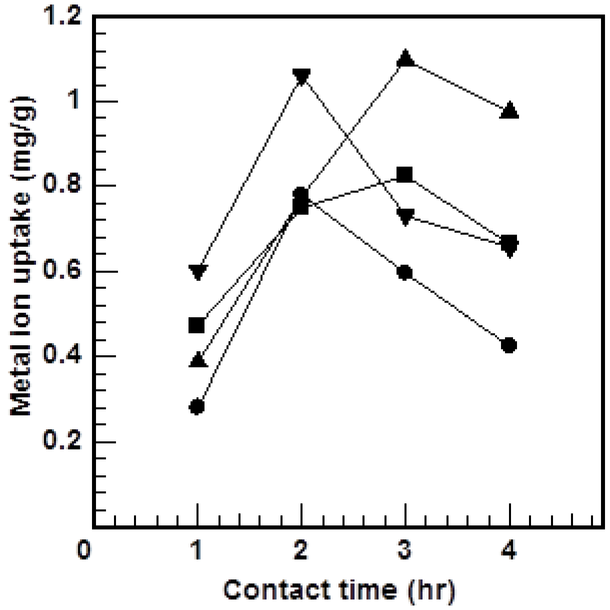

Figure 2: Effect of contact time between metal ions and biomaterial on chromium (III)(●), chromium (VI) (▲), cadmium (II)(■) and Zinc (II) (▼) adsorption by *Arenga pinnata* shell.

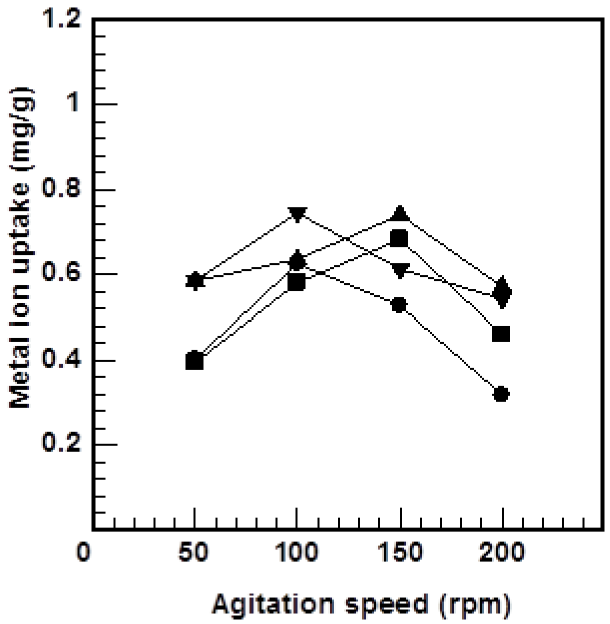

Figure 3. Effect of agitation speed between metal ions and biomaterial on chromium (III)(●), chromium (VI) (▲), cadmium (II)(■) and Zinc (II) (▼) adsorption by *Arenga pinnata* shell.

Effect of Concentration of HNO_3

The image can be seen the smaller the pH the greater the percentage of the metal is obtained due to the H^+ ions from HNO_3 that is strong enough to replace the metal ions bound to the biomaterial the *Arenga pinnata* Merr shell. The results showed that at pH 1 for the regeneration of total Cr, Cd and Zn metal highs respectively 98.40%, 94.41% and 50.69%. Regeneration can be used to re-release metal ions that have been absorbed by the roof rind (Arenga pinnata) using nitric acid to pH variations 1, 2, 3 and 4 to elute the metal. Regeneration of metal ions by H + ions from HNO_3 occurs through ion exchange process that resulted in the metal ion biosorben carried. The results is shown in Figure 4.

Adsorption Isotherms

Uptake of metal ions by biomaterials can be described by Langmuir Isotherm. Langmuir describe absorber on the surface there are a number of active centers is proportional to the surface area of the absorbent. Each center is only a single active molecule that can be absorbed. Bonding between substances that are absorbed by the absorbent material must be strong enough to prevent the movement of molecules have been absorbed along the attack on the surface. Chemical adsorption is due to the interaction between the active adsorbent with adsorbate involving chemical bonds. Chemical interactions only occur at a single absorption layer surface of the cell wall of the adsorbent. To study the relationship between the concentration of the metal ion absorption capacity used Langmuir isotherm. Langmuir isotherm curves of metal ions that are absorbed by the *Arenga pinnata* Merr shell may be seen in Figure 5. This figure shows that the greater the concentration of metal ions, the greater the absorption capacity.

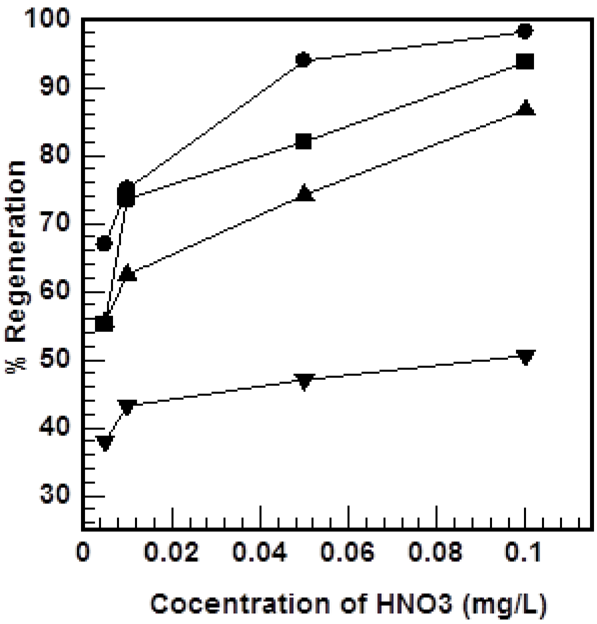

Figure 4. Effect of cocentration of HNO_3 between metal ions and biomaterial on chromium (III)(●), chromium (VI)(▲), cadmium (II)(■) and Zinc (II) (▼) adsorption by *Arenga pinnata* shell.

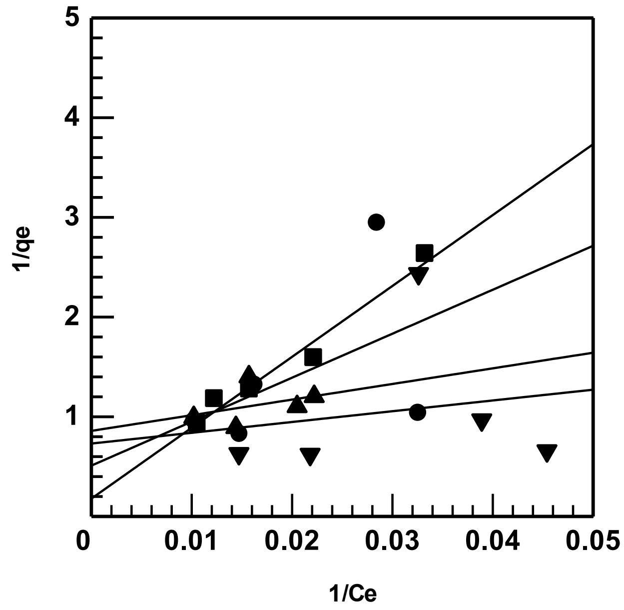

Figure 5. Langmuir isotherm curve of chromium (III)(●), chromium (VI)(▲), cadmium (II)(■) and Zinc (II) (▼) adsorption by *Arenga pinnata* shell.

Adsorption Kinetics

Adsorption patterns change over time requires a kinetic model approach. This model is used to explain the dynamics of the sorption process and obtain the values of the two order parameters Pseudo a model developed based on the mechanism of metal sorption on the surface of the *Arenga pinnata* Merr shell. This model can be seen in Figure 6. The image is the longer the contact time the greater the absorption of metal ions that cause changes in the pattern of adsorption of the time stated adsorption of Cr (III), Cr (VI), Cd and Zn adhere to the following.

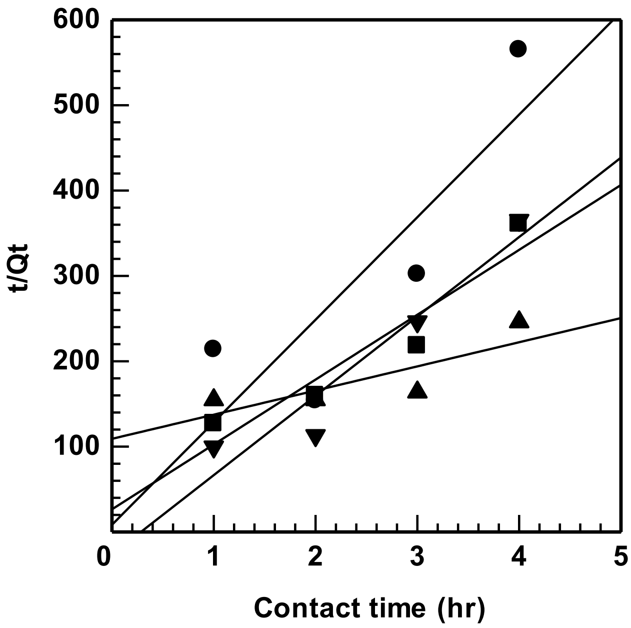

Figure 6. Pseudo second order kinetic models of chromium (III)(●), chromium (VI)(▲), cadmium (II)(■) and Zinc (II) (▼) adsorption by *Arenga pinnata* shell.

Effect of multielemen

In Figure 7 can be observed conditions of the solution of the metal ion absorption capacity of metal ions Cd (II) and Zn (II), respectively 1,106 and 1,651 mg / g. While the condition of multielemen absorption capacity of each metal ion Cd (II) and Zn (II) to 0994 and 1119 mg / g. The absorption capacity of the total Cr metal ion is 0.969 mg / g which showed an increase in the absorption capacity for metal ions Cr (III) or Cr (VI). These data indicate the existence of competition between the metal ions that would result in a decrease in the capacity of each metal ions. Where metal ions interact with functional groups that exist on the surface biosorben. In Figure 7 can be observed conditions of the solution of the metal ion absorption capacity of metal ions Cd (II) and Zn (II), respectively were 0.65 and 0.70 mg / g. While the condition of multielemen absorption capacity of each metal ion Cd (II) and Zn (II) to 12:40 and 12:55 mg/g. Absorption capacity of the total Cr metal ion is 0.950 mg / g which indicates an increase in the absorption capacity for metal ions Cr (III) or Cr (VI). These data indicate the existence of competition between the metal ions that would result in a decrease in the capacity of each metal ions. Where metal ions interact with functional groups that exist on the surface biosorben.

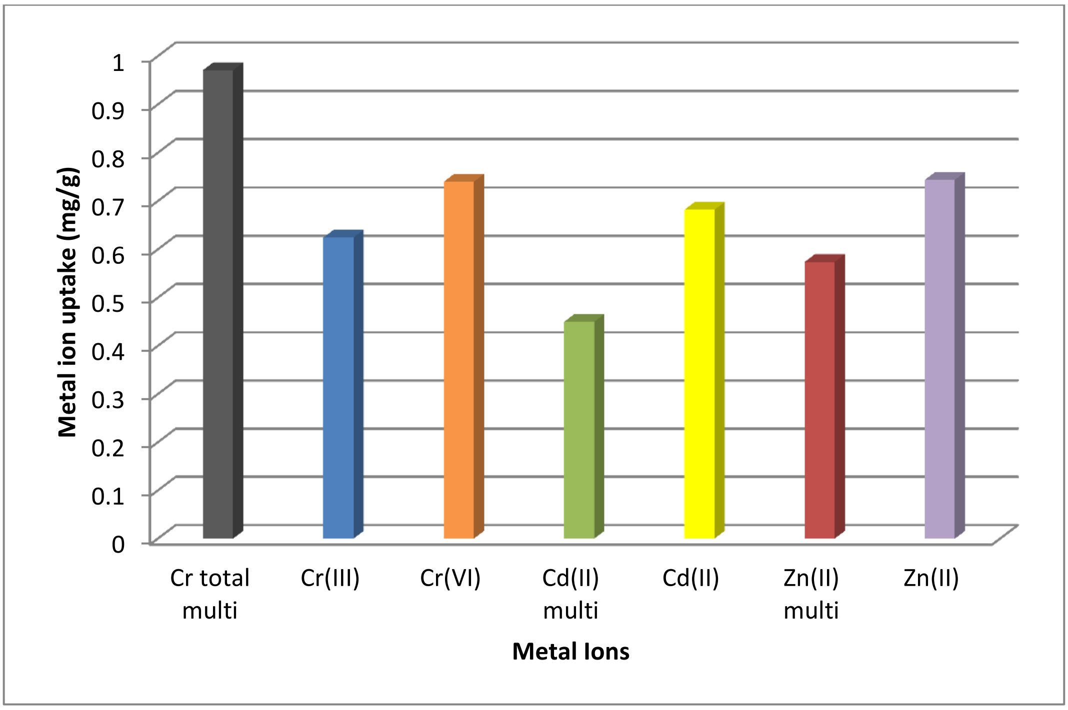

Figure 7. Effect of multielemen between metal ions and biomaterial on chromium (III), chromium (VI), cadmium (II) and Zinc (II) adsorption by *Arenga pinnata* shell.

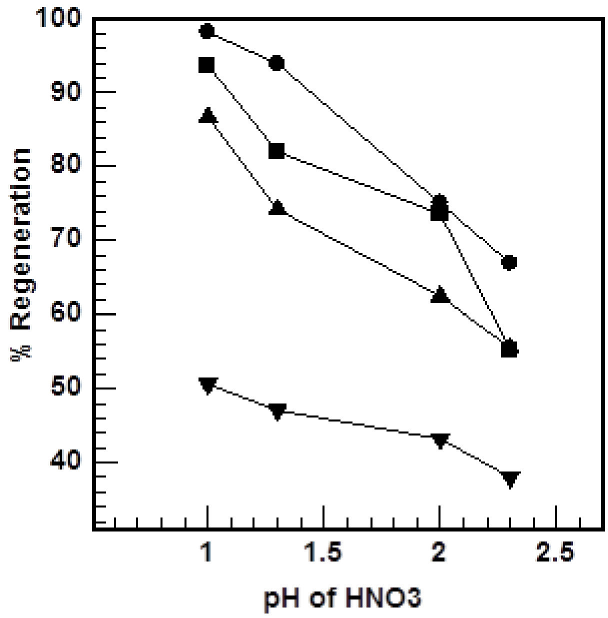

Fig 8. Effect of pH of HNO_3 between metal ions and biomaterial on chromium (III)(●), chromium (VI)(▲), cadmium (II)(■) and Zinc (II) (▼) adsorption by *Arenga pinnata* shell

To release metal ions that have been absorbed by the *Arenga pinnata* Merr hell using nitric acid to pH variations 1, 2, 3 and 4 to elute the metal. Regeneration of metal ions by H + ions from HNO3 can occur through ion exchange process that resulted in the metal ion biosorben carried as shown in Figure 8. The results showed that at pH 1 for the regeneration of total Cr, Cd and Zn metal highs respectively 98.2%, 94% and 52%. Of the image can be seen the smaller the pH the greater the percentage of the metal is obtained due to the H + ions from HNO3 strong enough to replace the metal ions bound to the biomaterial the *Arenga pinnata* Merr shell.

Biosorption process the reaction is reversible, this was observed when the metal is bound to biosorben treated with dilute HNO3 called desorption process. From the results obtained 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 of HNO_3.

CONCLUSION

FTIR spectra results known that functional groups that cause the absorption (ion exchange) on the OH group interacts with metal ions Cr (III), Cd (II) and Zn (II) which is a cation. While the anion is metal ions Cr (VI) to interact with the group R-NH3 *Arenga pinnata* Merr shell can be used as an absorbent metal ions Cr (III), Cr (VI), Cd (II) and Zn (II). Absorption capacity of the largest found in the metal ion Chromium (VI) and Zinc (II) with stirring time of 120 minutes and 180 minutes. At the time of 120 minutes for Zinc (II) and 180 minutes for the Chromium (VI) interaction between metal ions and active groups biosorben the more and likely getting besar. Agitation speed of absorption capacity 100 and 150 rpm maximum absorption occurs for Zn (II) and Cr (VI).

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