ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

The use of Snake Fruit *(Salacca sumatrana)* Seeds Powder for the Removal of Cd(II), Cu(II) and Zn(II) Ions from Environmental Water.

Edison Munaf*, Fitra Hayuni, Rahmiana Zein and Hamzar Suyani.

Department of Chemistry, Faculty of Mathematic and Natural Sciences, Andalas University, Padang 25163, Indonesia.

ABSTRACT

The ability of snake fruit *(Salacca sumatrana)* seeds powder to remove cadmium, cupper and zinc ions from environmental water has been investigated using batch method. Several parameters that can influence metals uptake such as pH, contact and stirring time, mass of biosorbent as well as initial metals concentration were described. Langmuir isotherm is used to study the adsorption mechanism. More over characterization of snake fruit seeds was investigated using FTIR. All metals ion concentration were measured using atomic absorption spectrometric. At the optimum conditions, the cadmium, cupper and zinc ions removal from environmental, waters are 62.79%, 90.69% and 63.09%, respectively. After the biosorption of metals ion, the analyte retained in the snake fruit seed powder could be recovered almost completely by eluting with dilute nitric acid. The method was applied to the removal cadmium, cupper and zinc ions present in Batang Arau river water of Padang city, Indonesia.

Keywords *:* Snake fruit seed powder toxic metal, environmental water, atomic absorption spectrometry and fourier transform infra red spectroscopy.

***Corresponding author**

INTRODUCTION

Since the number of health problem asscociated with toxic metal contamination continues to rise, stringent environmental regulations required the treatment of wastewater to remove toxic heavy metals [1-3]. The conventional physical-chemical techniques such chemical precipitation, ion-exchange and membrane separation process may present difficulties in the metal uptake from environmental water as they proved to be costly for midle and small scall industries [4-6]. In the last few years, biosorption process has been suggested as a potential alternative to the existing physico-chemical technologies for the detoxification and heavy metal uptake from wastewater [7].

In recent years a number of materials such as manggostana fruit shell, marine algae and rice husk has been investigated to removal of heavy metals from wastewater [8-10]. Metals uptake by non living cell (dead biomass) are believed to occur through sorption process involving the functional groups associated with proteins, polysacharide, lignin and other biopolimers found in the cell or cell walls. Biomaterial from dead biological plants can contain numerous functionalities including amino, carboxylate, hydroxide and imidazole. Other advantageous of this kind biosorbent is that they can be regenerated and reused.

This work reports on the use of snake fruit seed powder for removal of cadmium, copper and zinc ion from environmental water. The method has been applied to the removal metals ion from Batang Arau river of Padang city, Indonesia.

MATERIAL AND MTHODS

Treatment of snake fruit seeds

Snake fruit seeds commonly called as Medan's salak, collected from flea market of Padang city. Seeds were washed with clean water followed with an excess of pure water. Dried at room temperatur for a week. Then ground and screened within the particle size 180-425 µm. To remove the trace amounts of metal ions indigenous to seed powder, The seed powder is rinsed with nitric acid 0.01 mol/L for 2 hours and then washed with deionized water. After the washing solution is discharded, the seed powder dried at room temperature before used.

Chemicals and apparatus

All reagents employed in this work were analytical reagent grade and obtained from E-Merck (Darmstadt, Germany). Aqueous standard solution of metals chlorides, namely, Cd(II), Cu(II) and Zn(II) were prepared from the stock solution (containing 1,000 mg/L of each metal). Experiments were conducted using batch system. All metal ions concentration were analyzed by using Varian model Spetra AA (Europe) atomic absorption spectrometer. Where as to determine functional groups involved in the biosorption process of metal ion were conducted by using Thermo scientific model Nicolet-iS1 (Germany) fourier transform infra red spectroscopy.

Procedure

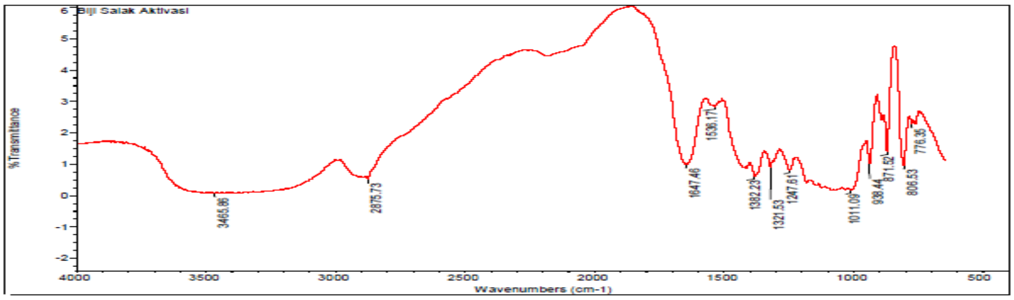
Some amounts of treated snake fruit seeds powder was inserted into the beaker glass. Then added with standard solution of metal ions investigated. String, and filtered. Filtrate containing metal ions then measured with atomic absorption spectrometer.

Several paramater that influence the biosorption capacity such as solution of pH, contact time, mass of biosorbent and initial concentration of metal ions have been studied. After the adsorption was completed, the adsorbed metal ions were eluted with diluted nitric acid, then washed with water and could be reused.

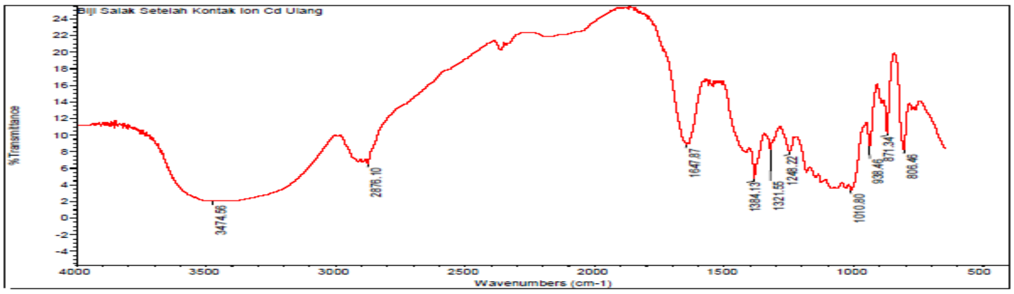
RESULTS AND DISCUSSION

Characteristics of snake fruit seed

The infrared spectral analysis was carried out to determine the type of functional group involved in the biosorption process. FTIR spectra before and after snake fruit seed powder uptake of metal ions is used to determine the type of functional groups contained in the seed and to look the changes of the intensity of the functional groups after the absorption of the metal ion**.** The spectrum was measured at a wave number range 500 - 4000 cm^{-1} and the results expressed in Figure 1. Carboxyl groups showed uptake -C = O appeared at 1647 cm^{-1} and OH absorption emerging as a broad band at 3465 cm^{-1}. Peak at 1321 cm^{-1} was the peak -C-O of the alcohol. -CH was observed at 2875 cm^{-1}. Sulfonyl group is characterized by the presence of S = O bands who rose to 1384 cm^{-1} after the absorption of the metal ion. FTIR analysis showed the presence of functional groups (carboxyl, hydroxyl and sulfonyl) shifted wave numbers, this is due to changes in the atomic vibrations after the ion exchange reaction between functional groups with ions.



(a)



(b)

Figure 1. FT-IR spectrum of salak sheed before (a) and after (b) removal of Cu(II) ions.

The streching 3400 cm^{-1} (Fig. 1a) was shifted to 3420 cm^{-1} (Fig. 1b) after metal ions biosorption, indicating the involvement of free hydroxyl groups in the biosorption process. The enhancement of the intensity at the all peaks region indicates the involment of O-H, C-H and C-O groups in the adsorption process. From the results shown in Figure 1, it is clear that these functional groups acquire a positive charge when protonated and may interact with the negatively charged metal complexes.

Effect of solution of pH on metal ion removal

It is well known that adsorpiton behaviour of metal ions by solid substrates much depends on pH of the solution. Figure 2 shows the effect of pH on Cd(II), Cu(II) and Zn(II) adsorption by snake fruit see powder. As can bee seen from Figure 2, when the pH solution was changed from 3 to 8, the snake fruit seed powder showed the favourable sorption in the pH range of 4 to 6. Solution of pH will influenced both aqueous metal ions and surface binding of the snake fruit seed. At pH lower than 4, the surface of the sorbent would surrounded by the hydronium ion (H^+) which would hinder the metal ions from reaching the binding sites of the sorbent caused by repulsive force. At the pH higher than 6, the metal ions investigated start to precipitate. For this reason the solution of pH ranging fromo 5 to 6 was selected. The maximum uptake of Cd(II) and Zn(II) at solution of pH 6 are 0.93 and 1.1 mg/g. More over, maximum uptake of Cu(II) ion by snake fruit seed powder is 1.93 mg/g at solution of pH 5.

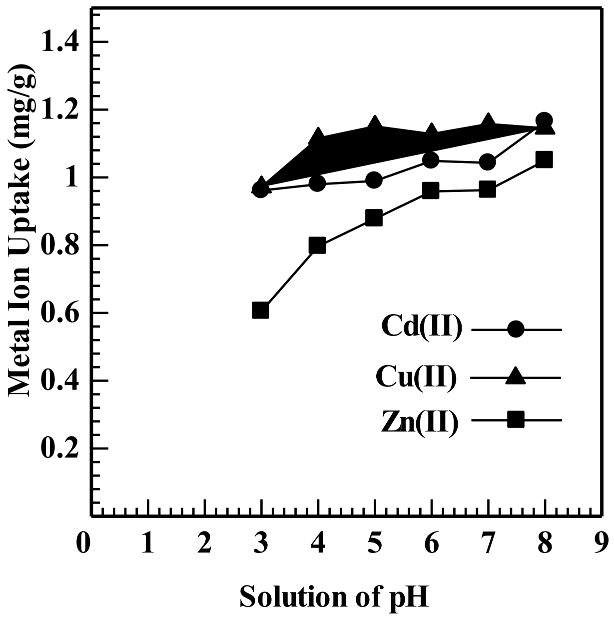


Figure 2. Effect of pH Solution on the metals ion removal by Salak Seeds.

Effect of contact time on metal ion removal

Figure 3 shows the effect of contact time with the metal ion biosorben. Studies the variation of the contact time in the range of 15-120 minutes has been carried out to see how long it takes to reach optimum absorption. The length of contact time on Cd metal ions on the absorption capacity decreased with increasing contact time between the metal ions with biosorben. The optimum contact time for Cd metal ion is 15 minutes which indicates that the metal ions Cd uptake is rapid. Cd metal ion absorption capacity decreases when the metal ion is contacted longer due to the release of metal ions bound to the Cd is already active side biosorben. The optimum contact time for Cu metal ion is 30 minutes with a lower absorption capacity compared with Cd(II). While for Zn(II), optimum absorption requires a longer time is 45 minutes with a lower absorption capacity than the ion Cd(II) and Cu(II). This can be attributed to electropositive of two metal ions, Cd ions with larger electropositive then do not take a long time to bind to the active site than the Zn ion [7,8].

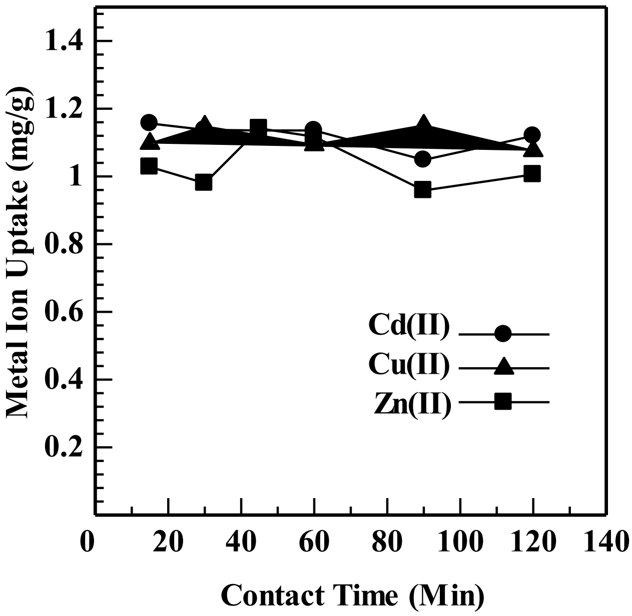


Figure 3. Effect of contacting time on the Cu(II), Cd(II) and Zn(II) removal by Salak Seeds.

Effect of stirring speed on metal ion removal

The effect of stirring speed on the removal of Cd(II), Cu(II) and Zn(II) ions shown that Cd(II) and Zn(II) ions reach the optimum removal at the speed of 50 rpm while for Cu (II) ion at the speed of 150 rpm. This is attributed to the nature electropositive each metal ion, where the Cd(II) is more electropositive than Zn(II) and Cu(II). Ties Cd(II) and Zn(II) with functional groups are stronger than Cu(II) with functional groups, therefore the absorption capacity of Cd(II) and Zn(II) is greater with lower stirring speeds than Cu(II). Conversely, if the stirring speed is too large will cause the metal ions released from the surface biosorben (desorption).

Effect of metal ion concentration on metal removal

Figure 4 shows the effect of metal ion concentration on metal ion removal capacity of Cd (II), Cu(II) and Zn(II). The figure shows that the greater the concentration, the greater the absorption capacity of the metal ions. This is because the greater the concentration of metal ions, the more will compete to bind to the functional groups of biosorben. But at some point will be found that the absorption capacity decreases with increasing initial concentration of metal ion solution because biosorben surface has been saturated [12-13].

The optimum removal of Cd(II), Cu(II) and Zn(II) ions are at the concentration of 150 mg/L, 75 mg/L, and 50 mg/L, respectively with absorption capacity of each metal ion was 3.0833 mg/g, 2.4270 mg/g and 2.4791 mg/g. This suggests that the metal ions Cd(II) has a high absorption capacity with optimum high concentrations, due to Cd(II) ions has a radius greater than Cu(II) and Zn(II) ions, so that more Cd(II) ion bound with the charged functional groups biosorben negative on the surface.

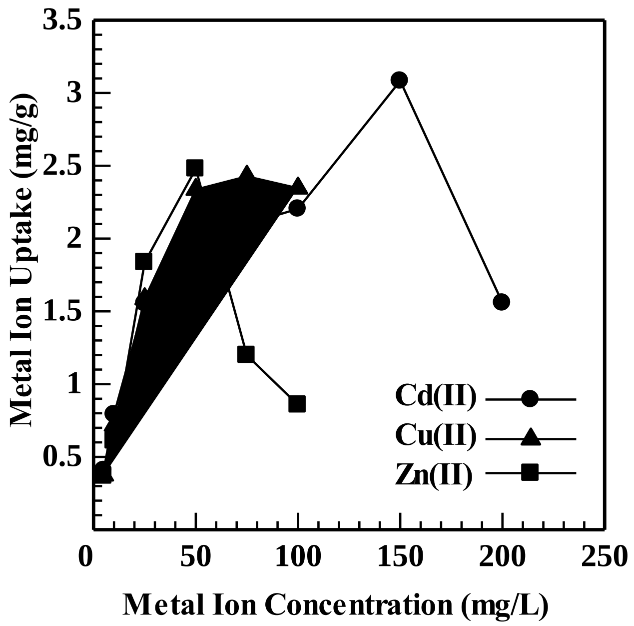


Figure 4. Effect of Cu(II), Cd(II) and Zn(II) ions concentration on the metals ions removal by Salak Seeds.

Effect the solution of multicomponent on metal ion removal

The effect of a multicomponent solution of the metal ion uptake capacity of Zn. The image above shows the effect of a multicomponent solution on metal ion uptake capacity of Zn, which in this experiment added metal ions Cd(II) and Cu(II) with various concentrations of 25 mg/L and 50 mg/L. It can be observed that the greater the concentration of other metal ions are mixed, the smaller the metal ion uptake capacity of Zn(II). This is because the competition between the metal ions that will go into the active site functional groups. The more types of metal ions and the greater the concentration of other metals in the solution of the target metal ion concentration will be smaller [13-15].

Adsorption isotherms

Figure 5 is a plot between 1/Ce with 1/Qe by Langmuir isotherm models to determine the maximum absorption capacity constants associated with Qmax and KL which is obtained from the intercept and slope. Meanwhile Freundlich isotherm models are shown in figure 10 with the plot between log Ce log Qe to get the value of the intercept and slope n KF. From the table it can be seen that the value of the maximum absorption capacity (Qm) ion Cu(II) is greater than Cd(II) and Zn(II). But this does not mean the absorption of Cu is better because the value of KL is smaller ions indicates affinity between ions Cu with salak seed lower than ion affinity Cd and Zn.

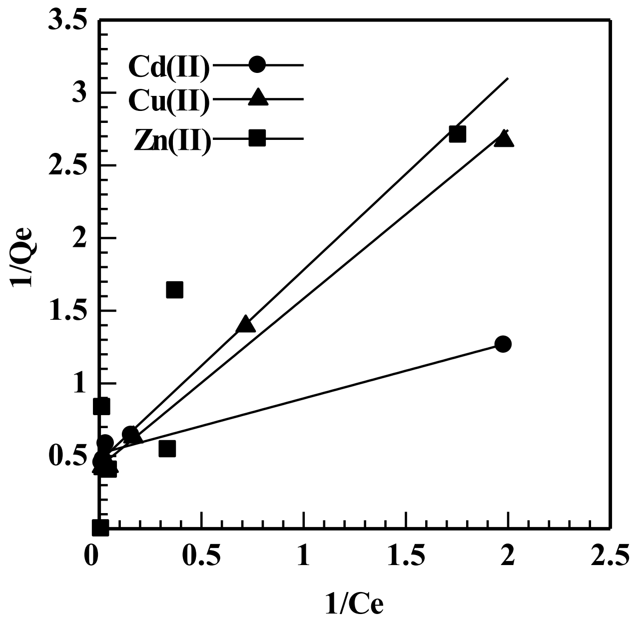


Figure 5. Isotherm Langmuir of Cd(II), Cu(II) and Zn(II) ion removal by Salak Seeds.

Correlation coefficient value / R^2 both isotherm models (Table 1) shows that the experiment is likely to follow the Langmuir isotherm than Freundlich isotherm. This suggests that the active side dispersed homogeneously in the salak seed where the ions Cd(II), Cu(II) and Zn(II) cover the sorbent surface by forming a single layer (monolayer) and tied to the side of the salak seed chemically active. Besides the main character of the Langmuir isotherm is Separation factor (RL) and surface coverage (Θ). RL stated value types based on the characteristics of the absorption isotherm biosorben surface fraction covered by metal ions studied from Θ vs concentration plot. RL values and Θ the variation of ion concentration Cd(II), Cu(II) and Zn(II) is expressed in Figure 5. RL values for all three metal ions (Fig. 11a) are in the range 0 - 1 , it is stated that the salak seed is effective for absorption biosorben ion Cd(II), Cu(II) and Zn(II) at low concentrations . The smaller the value of RL at higher concentrations, which means that the metal ions Cd(II), Cu(II) and Zn(II) with a high concentration of well absorbed in salak seed. Θ greater value with increasing concentrations of the two metal ions. Increased concentrations of metal ions to cause more surface coated salak seeds metal ions. At high concentrations Θ value increased slightly . This indicates that the surface of the grain bark almost completely covered by metal ions Cd(II), Cu(II) and Zn(II).

Regeneration

Figure 6 shows the effect of pH solution 0.01 mol/L pf HNO_3 on salak seed regeneration. Regeneration of metal ions by H^+ ions from HNO_3 occurs through ion exchange process that resulted in the metal ion biosorben carried. The metals are absorbed by the salak seed eluted with dilute nitric acid with a pH of 1, 2, 3, and 4. Where results showed that at pH 1 for Cd metal regeneration, the highest Cu and Zn, 86.32%, 22.10% and 54.07% respectively.

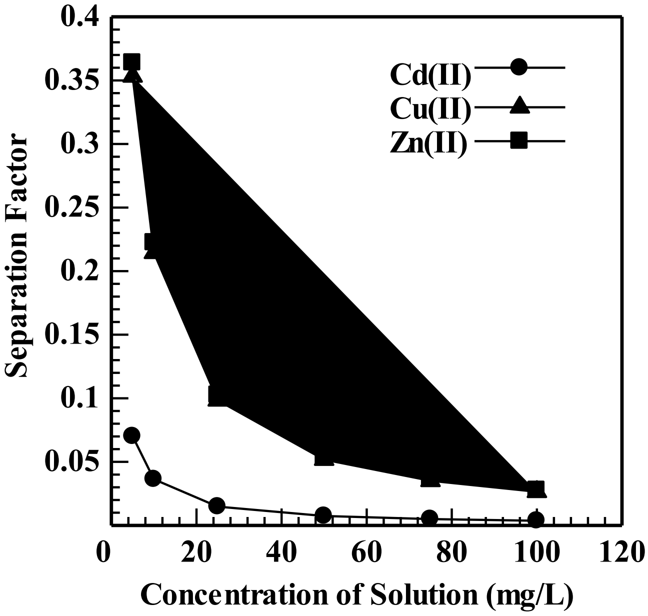


Figure 6. Regeneration of metal ions behaviour by using diluted nitric acid.

Applications to the removal of metal ions present at Batang Arau River water samples

Based on previous research it has been found the optimum conditions of each metal ion. Therefore, the salak seed applied biosorben this field to Batang Arau River water so that we can know biosorben to water absorption capacity of the river. Before the seeds tested, measured first initial pH and concentration of metal ions Cd(II), Cu(II) and Zn(II) in water samples. The treatment of Batang Arau River water with salak seeds biosorben indicates that the efficiency of absorption of Cu(II) ion is higher than Cd(II) and Zn(II). On the absorption of Cu(II) ion absorption efficiency obtained was 90.69% with the absorption capacity of 0.013 mg/g while the Cd(II) ion was 62.79% with the absorption capacity of 0.0045 mg/g and Zn(II) ion by 63, 09% to the absorption capacity of 0.0056 mg/g.

CONCLUSION

Based on the research that has been done can be concluded that the bark can be used as a seed biosorben metal ions Cd(II), Cu(II) and Zn(II). The optimum conditions for the absorption of metal ions Cd is at pH 6, contact time of 15 minutes, stirring speed of 50 rpm, the concentration of 150 mg/L with the use of 0.3 g biosorben and particle size of 180 µm. For ion Cu at pH 5, contact time 30 min, stirring speed 150 rpm, the concentration of 75 mg/L with the use of 0.3 g biosorben and 180 µm particle size. While for ions Zn at pH 6, contact time 45 min, 50 rpm stirring speed, concentration of 50 mg/L with the use of 0.3 g biosorben and 180 µm particle size. At multi component and more types of metal ions and the greater the concentration of other metals in the solution of the target metal ion concentration will be smaller, the effect is related to the application of the waste in the environment where there is one type of metal ions contained in the waste. Regeneration of Cd(II), Cu(II) and Zn(II) ions at pH 1, are 86.32%, 22.10% and 54.07% respectively.

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