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The use of *Terminalia catappa L.* fruit shell as biosorbent for the removal of Pb(II), Cd(II) and Cu(II) ion in liquid waste

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ABSTRACT

Terminalia Catappa L. fruit shell, an agricultural waste as a low cost adsorbent has been studied for removing of Pb(II), Cd(II) and Cu(II) ions. The optimum adsorption condition of Pb(II) and Cu (II) ion onto Terminalia Catappa L. fruit shell was occurred at pH 5, 100 rpm in 0,1 g biomass with each contact time was 45 and 75 minutes, metal ion concentration was 150 mg/L and 100 mg/L with adsorption capacity was 12.6700 mg/g and 5.4400 mg/g . The optimum adsorption conditions of Cd (II) ion was occurred at pH 6, 100 rpm in 0,1 g biomass with contact time was 60 minutes, metal ion concentration was 150 mg/L and adsorption capacity was 16.4625 mg/g. The metal ion concentration was analyzed by Atomic Absorption Spectrophotometry (AAS) method. FTIR spectra analysis might revealed that carboxyl, hydroxyl and carbonyl groups were dominant in the process of metal ions uptake. SEM analysis the morfology of biosorbent before and after treatment. Aplication to liquid waste obtained that adsorption efficient of Terminalia catappa L. fruit shell to adsorp Pb(II), Cd(II) and Cu(II) ion was 55.879 %, 86.375% dan 41.565% respectively.

Keywords: biosorption, heavy metal ion, *Terminalia catappa* L fruit shell, adsorption isotherm.

INTRODUCTION

Heavy metals can enter the environment through mining activities of oil, coal, electric power plants, pesticides, ceramics, metal smelting, fertilizer plants and other industrial activities. Some techniques for waste treatment of heavy metal ions has been developed by experts such environment using chemical methods, membranes, ion exchange and solvent extracts. However, the method requires high costs, long process and solvents that much that it becomes a new problem in the disposal system [1] . Industrial waste and the result of human activity has led to heavy metal ions in water. Presence of heavy metals in water is toxic, even in low concentrations. Without realizing the heavy metal ions can accumulate in the human body, because the consumption of water and food (rice, vegetables, fish and shellfish) contaminated with heavy metals, which can cause metabolic disorders, neurological disorders and decreased intelligence, the causes of cancer and even death.

In recent years, a material derived from biology has attracted the interest of many researchers. Including agricultural waste, fruit leather, algal biomass, and fishery products. The most commonly used are natural biosorben low cost, renewable and handling does not involve risks. Researchers environment then look for a cheap method, friendly to nature, and effective for the absorption of the metal ions in water or wastewater and adsorption technique was discovered. Biosorption is the absorption process that uses biological materials as biosorbent, where the ions in solution will bind to the existing functional groups on the biomaterial. The functional groups include carboxylate groups, carbonyl, hydroxyl, amine, ester, sulfhydryl and others.

The results of the research have been widely reported that agricultural waste can be used as an absorber of heavy metal ions such as: mangosteen peel [2] , loquat bark [3] , green coconut shell [4] , wheat bran [5] , rice straw [6] , soursop seed [7] , active carbon from *Adatodha vasica* [8] kind of herbs and walnut shell [9] .

Ketapang *(Terminalia catappa)*, sometimes referred as katapiang by Minang language, widely grown around the beach, on the edges of the road and planted as a shade tree in the garden or around campus. Ketapang is a multipurpose plant from the roots, stems, leaves and fruit has been used. Ketapang seeds can be used for cake maker, bread, noodles, jams and tempeh. While the shell of the fruit ketapang usually discharged or not utilized. Study from literatures to absorption of heavy metal ions more use ketapang leaves [10,12] . While the shell ketapang made briquettes and active carbon [13] absorber made of Co, but still expensive to use. Therefore, this study tried to take advantage of the fruit shells of Ketapang and search for the optimum condition of the fruit shell ketapang as absorbent metal ions Pb (II), Cd (II) and Cu (II) that can be used to reduce heavy metals in waste water.

EXPERIMENTAL SECTION

Ketapang fruit shells in Fig.1.were collected around the campus of Andalas University, Padang, West Sumatera , Indonesia. Then dried in oven at temperature $60^{\circ}C$ for 24 h [14]. The shell is broken, crushed with grinder and sieved [15]to 180 μm (Standard solution of $Pb(NO_3)_2$, $Cd(NO_3)_2$ and $Cu(NO_3)_2$ 1000 mg / L in 0.5 M HNO_3 M from Merck). 25 g samples were soaked for two hours in 100 ml of HNO_3 0.01 mol/L. Washed with distilled water, filtered, wind dried and ready to determination optimum absorption of metal ions. 25 ml solution of Pb (II) 10 mg / L inserted into 50 ml erlenmeyer. Then adjust the pH using HNO_3 and NaOH 0.1 M, added biosorbent 180 μm of 0.5 g and shaked for 90 minutes at 100 rpm. The solution was filtered and the metal ion concentration was determined by AAS. The same is done for Cd(II) and Cu(II) ion, so that later obtained the optimum pH solution, contact time, stirring speed, initial metal ion concentration, biosorbent dosage of each metal ion absorption by the shell of ketapang. The adsorption capacity obtained from equation :

$$Qe = \frac{(C_0 - C_e)\,V}{m} \qquad (1)$$

RESULTS AND DISCUSSION

Effect of pH solution on absorption capacity

Effect of pH is one of the most important parameters in the absorption of the metal ions, because the pH determines the surface charge of the adsorbent and adsorbate ionization rate.

In Figure 2 can be seen that optimum conditions ketapang fruit shells to absorb metal ions Pb (II) and Cu (II) occurs at pH 5 with the absorption capacity was 0.4262 mg/g and 0.4058 mg/g while the metal ions Cd(II) on pH 6 with the absorption capacity of 0.4151 mg/g. At pH 2 absorption capacity of Pb (II), Cd (II) and Cu (II) was low, due to the metal ions must compete with many H^+ ions dissociate in acidic conditions, to bind to biosorben active side. However, an increase in the capacity of a very sharp absorption of pH 3-4 because of reduced competition between the metal ions with H^+ ions on the active side biosorben. At alkaline pH, depending on the concentration of metal ions is feared more tends to form a hydroxide salt [16] with OH^- ions to form $Pb(OH)_2$, $Cd(OH)_2$ and $Cu(OH)_2$ so that the metal ions do not bind to the active site biosorben. The same condition also occurs in *Desmostachya bipinnata* [17] which can absorb metal ions optimum at pH 6 to pH 5 for Cd and Cu.

Effect of contact time on Absorption Capacity

In Figure 3 shows the effect of contact time with the metal ions biosorben ketapang fruit shells. Time contact was made with variation 5 minutes to 90 minutes to see how much time it takes biosorben optimum contact to absorb metal ions. Metal ion absorption capacity will decrease if the metal ion is contacted longer than the optimum time, because the release of metal ions that are already bound to the active side biosorben. The optimum contact time for the metal ions Pb(II) is 45 minutes with the absorption capacity of 0.4290 mg / g, which is faster than ions Cd(II) and Cu(II). This caused the Pb(II) ion have a larger radius than Cd(II) and Cu(II) ion were 1.75 A^o, 1.54 A^o and 1.28 A^o respectively. So that the ions Pb(II) more electropositive and binds more rapidly with the active side biosorben [14] . While the optimum contact time for the metal ions Cd(II) was 60 minutes with the absorption capacity of 0.4319 mg/g and Cu(II) required a longer time was 75 minutes with the absorption capacity of 0.4089 mg/g.

Effect of stirring speed on absorption capacity

Metal ion absorption capacity by ketapang fruit shells carried by the stirring speed variation of: 50, 100, 150, 200 and 250 rpm. In figure 4 showed that the optimum stirring speed on the absorption of metal ions Pb(II), Cd(II) and Cu(II) were 100 rpm with the absorption capacity of each was 0.5078 mg/g, 0.4319 mg/g and 0.4089. Increasing the stirring speed exceeding the optimum speed can cause the desorption of metal ions than adsorption, resulting in the decrease of absorption capacity.

Effect of metal ion concentration against absorption capacity

The influence of variations in the concentration of metal ions on the absorption capacity can be seen in Figure 5. The greater concentration of metal ions, the greater the absorption capacity of the metal ion. It caused of the greater concentration, the more metal ions that will compete to be bound with the functional groups of biosorben. Absorption capacity will decrease with an increase in the initial concentration of the metal ion solution for surface biosorben already saturated. Optimum absorption both of metal ions Pb(II) and Cd(II) occurs at concentration 150 mg/L, but for Cu(II) at a concentration of 100 mg / L with the absorption capacity of each metal ion was 3.5695 mg/g , 2.0800 mg/g and 1.7640 mg/g.

Effect of mass biosorben on absorption capacity

Figure 6 showed the influence of the mass bisorben ion absorption capacity of Pb(II), Cd(II) and Cu(II). With increasing biosorben mass will caused a reduction in the absorption capacity of the metal ion. Instead absorption capacity will be greater if the mass of the smaller biosorben on biosorben mass of 0.1 g of the metal ion absorption capacity of Cd(II), Pb(II) and Cu(II), respectively was 16.4625 mg/g, 12.6700 mg/g, and 5.4400 mg/g. It caused that the ratio between metal ions and biosorben unbalanced, where the mass number biosorben clotting will occur which causes disruption on the active side biosorben. Besides, it can also be caused due to insufficient metal ions in solution with the active site available.

Adsorption isotherms analysis

Isoterm adsorption is used to characterize the interaction of ions Pb (II), Cd (II) and Cu (II) with ketapang fruit shells. Langmuir isotherm model is based on the assumption that the maximum absorption occurs when a dense monolayer of molecules that are available have saturated the adsorbent surface, the energy absorption constant and there is no interaction of adsorbate molecules around the adsorbent surface layer. Meanwhile Freundlich model is based on an empirical relationship where the energy absorption on the surface of the adsorbant metals depend on the surrounding has been filled or not.

Figure 7 was a plot of 1/Ce with 1/Qe based on the Langmuir isotherm models to determine the maximum absorption capacity associated with the constants Q_{max} and K_L are obtained from the intercept and slope.

$$\frac{1}{\mathrm{Qe}} = \frac{1}{\mathrm{Qm}\,.\mathrm{K_L}} \mathrm{x} \frac{1}{\mathrm{Ce}} + \frac{1}{\mathrm{Qm}} \qquad (2)$$

Meanwhile Freundlich isotherm models shown in Figure 8 with the plot between log Ce with log Qe to get the value of the intercept and slope K_F and n.

$$\log \mathrm{Q_e} = \log \mathrm{K_F} + \frac{1}{\mathrm{n}} \log \mathrm{C_e} \qquad (3)$$

In Table 1 can be seen that the correlation coefficient or R which is close to = 1, meaning there is a correlation between the metal absorption capacity of absorption in both models. While the coefficient of determination (R^2) can be concluded that the absorption of ions Pb (II) and Cu (II) tend to follow the Freundlich isotherm models while the ion absorption of Cd (II) followed the Langmuir isotherm, which means that the active side dispersed homogeneously in fruit shells ketapang where ions Cd(II) covering the surface of the sorbent to form a single layer (monolayer*)* and chemically bound. While the ions Pb (II) and Cu (II) absorption occurs in physics and heterogeneous.

In the Langmuir isotherm model grades K_L (affinity) ions Cd(II) is 0.1966 with a maximum absorption capacity (Q_m) is 1.4263 mg/g. Besides, the main character of the Langmuir isotherm is with the value of separation factor ($R_{L)}$ and surface coverage (Θ). The value of R_L declare the type isotherm based on the absorption characteristics. Biosorben surface fraction covered by the metal ions studied from Θ vs. concentration plot. The value of R_L and Θ the ion concentration variation of Pb(II), Cd(II) and Cu(II) is expressed in Figure 9. The value of R_L for metal ions Cd (II) in the range of 0 - 1 which means the preferred adsorption*(favorable).* While in figure 10, the Θ or closing value biosorben surface by metal ions greater with increasing concentrations of the three metal ions. Increasing the concentration of metal ions to cause more surface ketapang fruit shells coated by metal ions. This indicated that the surface of the fruit shells ketapang almost completely covered by metal ions Pb(II), Cd(II) and Cu(II).

Meanwhile Freundlich isotherm model in Table 1 indicated that the value of K_F is the ability of the adsorbent to absorb metal ions Pb(II) and Cu(II) of 1.3508 and 0.3725 with the value of n or metal adsorption intensity with biosorben good, were in the range of 1-10 in the amount of 2.8153 and 3.4165. Co metal absorption by leaves [15] of ketapang modified with acetic acid also follow Freundlich isotherm model.

FTIR analysis
Analysis of FTIR (Fourier Transform Infra Red) aims to identify functional groups of biosorben used to absorb metal ions and changes of intensity the functional group after absorption of the metal ions. The spectrum was measured at wave numbers 400 - 4000 cm^{-1} and the results can be seen in Figure 11.

In figure 11 showed that the fruit shells ketapang having a hydroxyl group in the presence of O-H stretching vibration absorption at the wave number 3448.15 cm^{-1}, which is an intramolecular hydrogen bonds polymeric compounds such as alcohols, phenols, and carboxylic acids are commonly found in cellulose, hemicellulose and lignin. C-H stretching vibration was observed at 2919.42 cm^{-1} and at 2360.20 cm^{-1}. The peak around 1735.18 cm^{-1} indicates the presence of a carbonyl group C = O stretching vibration strengthened by the presence of C = O in the range of 1000 - 1300 cm^{-1} which showed the presence of alcohol and carboxylic acid [14-15].

SEM analysis
Analysis of SEM (Scanning Electron Microscope) aims to see morfology of the surface ketapang shell before and after treatment. In the figure 12.a can be seen that the surface of the fruit shell ketapang before being treated is still in the closed state of the pores. The image 12.b. biosorben activated by nitric acid which aims to open up the pores of biosorben, activate the functional groups and removing metal or other cations are still bound by biosorben so that later can be the target metal ion absorption maximum, and this was evident in Figure 12.c. that surface biosorben already begun covered after the absorption of the metal ions.

Applications ketapang fruit shells to wastewater
Under optimum conditions obtained on the metal ion absorption by fruit shells ketapang, the optimum conditions are applied to the liquid waste in laboratorium Environmental Chemistry, University of Andalas.

Before the tested, the pH samples was pH 2.31 and concentration metal ion Pb(II), Cd(II) and Cu(II) in the sample solution. Subsequently the samples were treated in accordance with the conditions of optimum absorption of each metal ion and obtained the percentage uptake of metal ions and ion absorption capacity of Pb(II), Cd(II) and Cu(II) in the sample.

$$\% \text{ Sorption } = \frac{(C_0 - C_e)}{C_0} x100\ \% \qquad (4)$$

In Table 2 can be seen that the efficiency of absorption of metal ions Pb(II), Cd(II) and Cu(II) by ketapang fruit shells were respectively 55.87%, 86.375% and 41.565%. Absorption is not up to 100% due to the influence of other metal ions which caused the metal ions in the competition [18] and also the mixing of sewage waste with compounds or other organic solvents so biosorben not optimal in absorbing metal ions Pb(II), Cd(II) and Cu(II). However, the efficiency of absorption and absorption capacity of the metal ions by ketapang fruit shells already synchronized with the optimum conditions in which the study of absorption capacity and the percentage of ion uptake of Cd (II) ions more higher than Pb (II) and Cu (II).

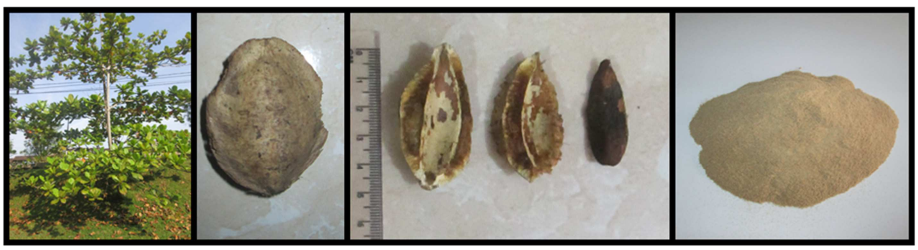

Fig. 1. (a) Ketapang *(Terminalia catappaL.)* tree. (b) Ketapang fruit. (c) Ketapang shell and seed (d) Ketapang shell powder in 180 µm

Effect of pH solution on absorption capacity

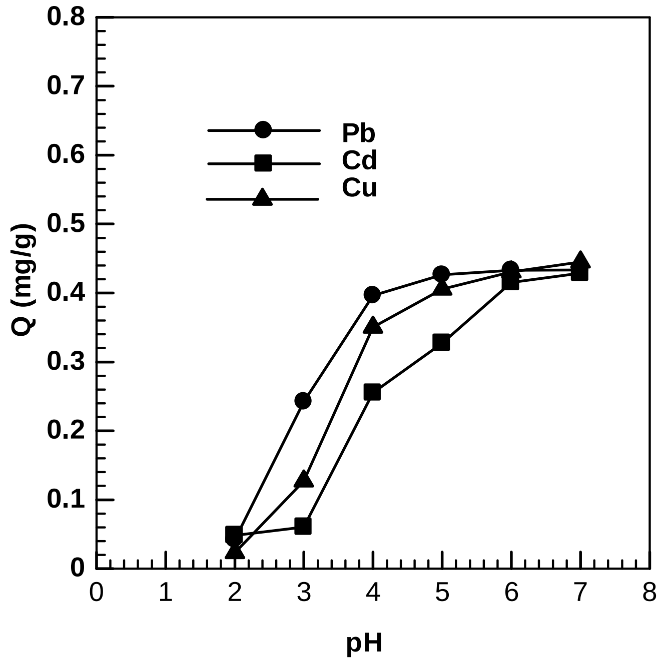

Fig. 2. Effect of pH on Pb(II) , Cd (II) and Cu(II) biosorption by *Terminalia Catappa L*. fruit shell; 25 mL metal solution; concentration = 10 mg/L; mass of biosorbent = 0.5 g; contact time = 90 min; stirring speed = 100 rpm

Effect of contact time on absorption capacity

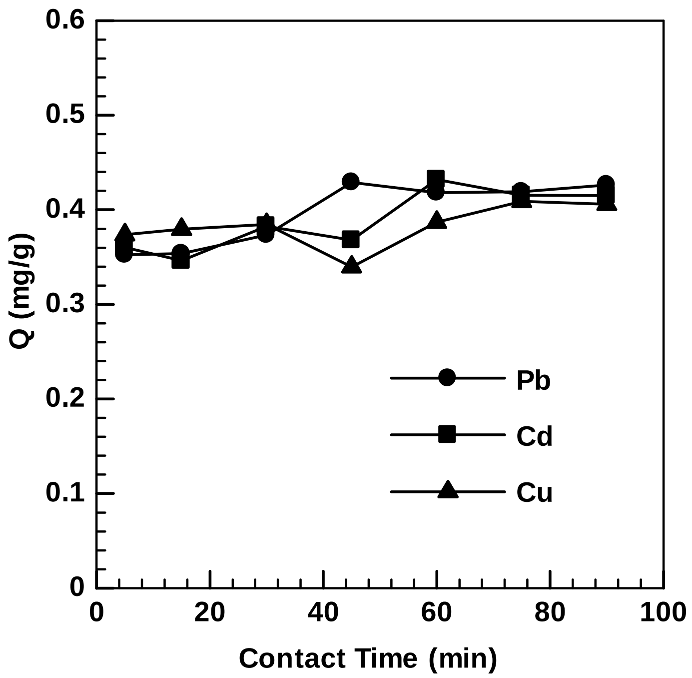

Fig.3. Effect of contact time on Pb(II), Cd (II) and Cu(II) biosorption by *Terminalia Catappa L*. fruit shell ; 25 mL metal solution; concentration = 10 mg/L; pH of Pb(II) = 5, Cd (II) = 6 and Cu(II) = 5; mass of biosorbent = 0.5 g; stirring speed = 100 rpm

Effect of stirring speed on absorption capacity

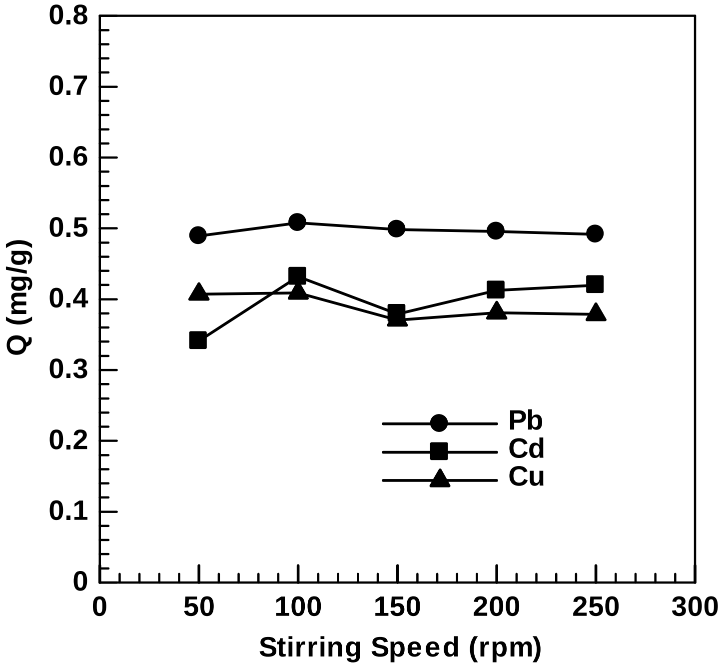

Fig.4. Effect of stirring speed on Pb(II), Cd (II) and Cu(II) biosorption by *Terminalia Catappa L.* fruit shell ; 25 mL metal solution; concentration = 10 mg/L; pH of Pb(II) = 5, Cd (II) = 6 and of Cu(II) = 5; mass of biosorbent = 0.5 g; contact time = 45 min for Pb(II), 60 min for Cd(II) and 75 min for Cu (II)

Effect of metal ion concentration against absorption capacity

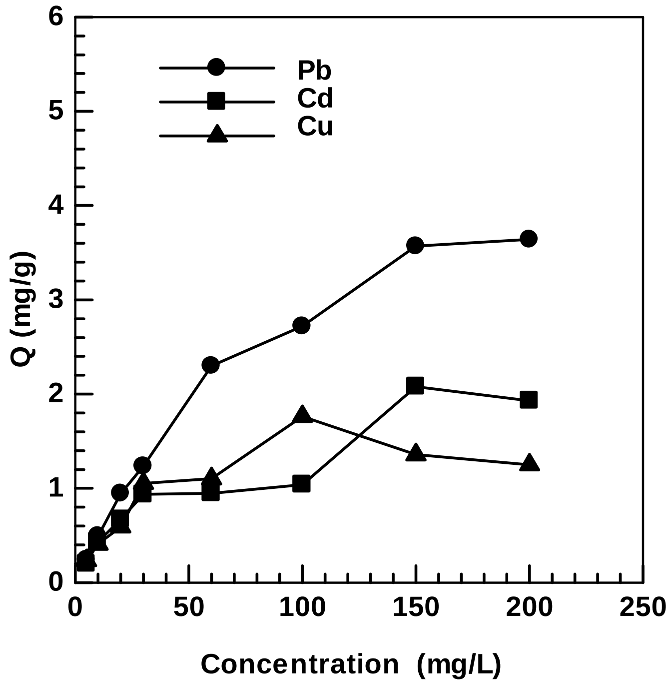

Fig. 5. Effect of metal ion concentration on Pb(II), Cd (II) and Cu(II) biosorption by *Terminalia Catappa L.* fruit shell; 25 mL metal solution; pH of Pb(II) = 5, Cd(II) = 6 and Cu(II) = 5; mass of biosorbent = 0.5 g; contact time = 45 min for Pb(II), 60 min for Cd(II) and 75 min for Cu(II) ; stirring speed =100 rpm for Pb(II), Cd (II) and Cu(II).

Effect of mass biosorben on absorption capacity

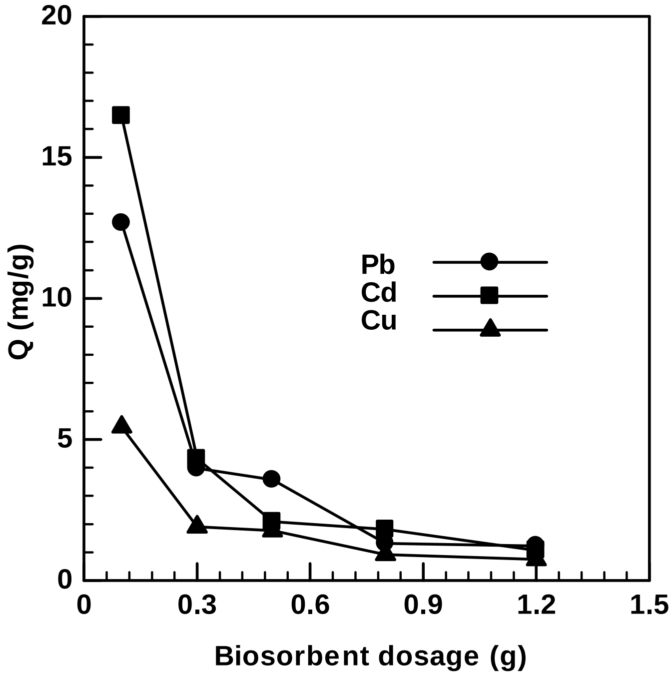

Fig. 6. Effect of biosorbent dosage on Pb(II), Cd (II) and Cu(II) biosorption by *Terminalia Catappa L.* fruit shell ; 25 mL metal solution; pH of Pb(II) = 5, Cd (II) = 6 and of Cu(II) = 5; contact time = 45 min for Pb(II), 60 min for Cd(II) and 75 min for Cu(II), stirring speed = 100 rpm for Pb(II), Cd (II) and Cu(II), concentration 150 mg/L for Pb(II), 150 mg/L for Cd and 100 mg/L for Cu(II)

Adsorption isotherms analysis

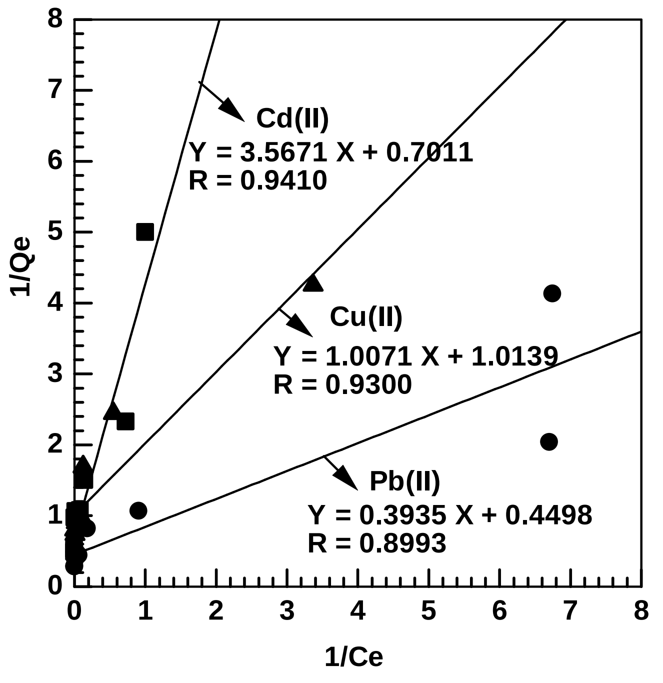

Fig. 7. Langmuir isotherm for ion absorption of Pb (II), Cd (II) and Cu (II) by ketapang fruit shells

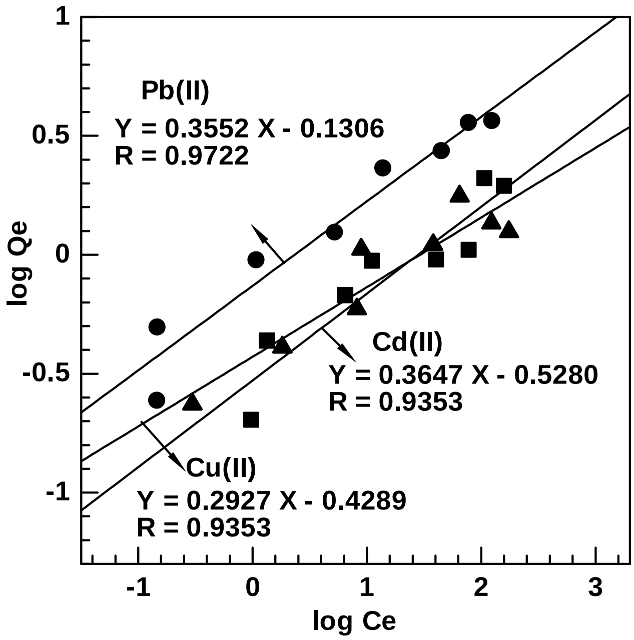

Fig 8. Freundlich isotherm for ion absorption of Pb (II), Cd (II) and Cu (II) by ketapang fruit shells

Table 1. Langmuir and Freundlich isotherm coefficient on ion uptake of Pb (II), Cd (II) and Cu (II) by ketapang fruit shells

Metal Ion	Langmuir isotherm				Freundlich isotherm			
	K_L (L / mg)	Q_m (Mg / g)	R	R^2	K_F (L / mg)	n	R	R^2
Pb (II)	-	-	0.8993	0.8087	1.3508	2.8153	0.9 722	0.9452
Cd (II)	0.1966	1.4263	0, 9410	0.8855	-	-	0, 9353	0.8748
Cu (II)	-	-	0, 9300	0.8649	0.3725	3.4165	0, 9353	0.8748

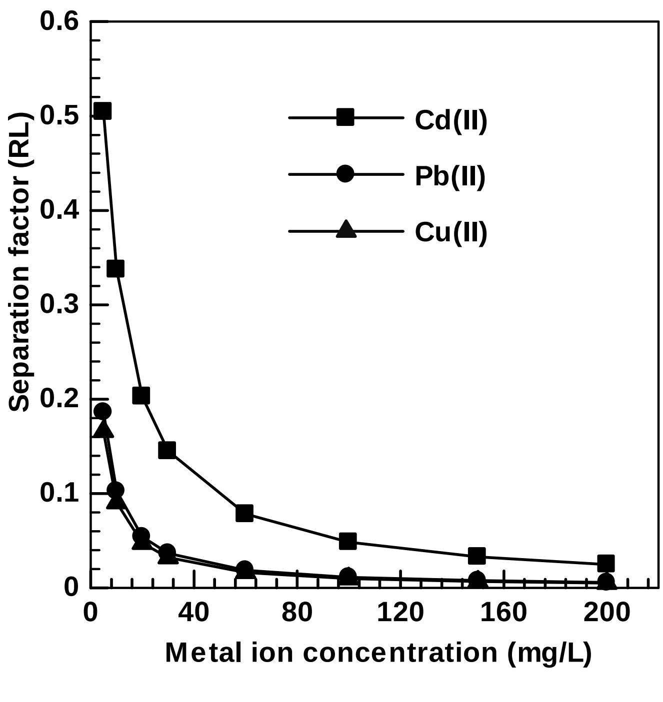

Fig. 9. Plot of the concentration of metal ions Pb (II), Cd (II) and Cu (II) to the separation factor (R_L)

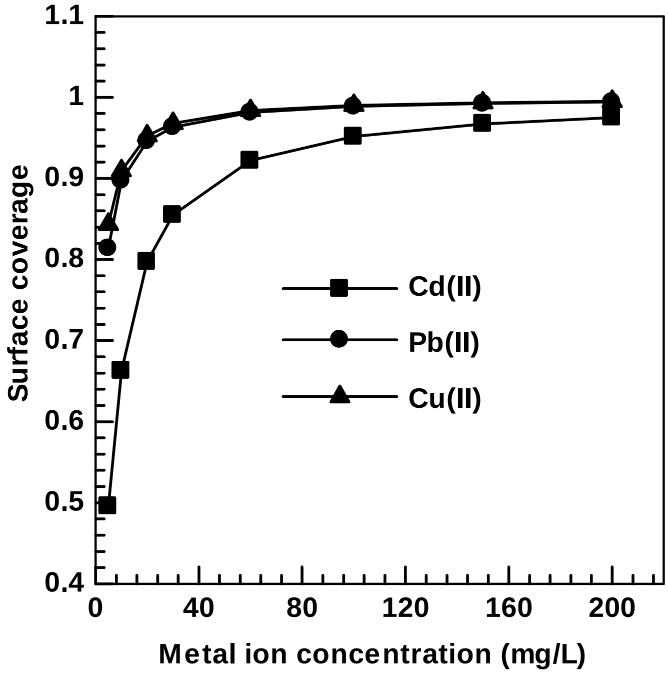

Fig. 10. The plot between the concentration of metal ions and Pb (II), Cd (II) and Cu (II) to the surface of the closure (Ө)

FTIR analysis

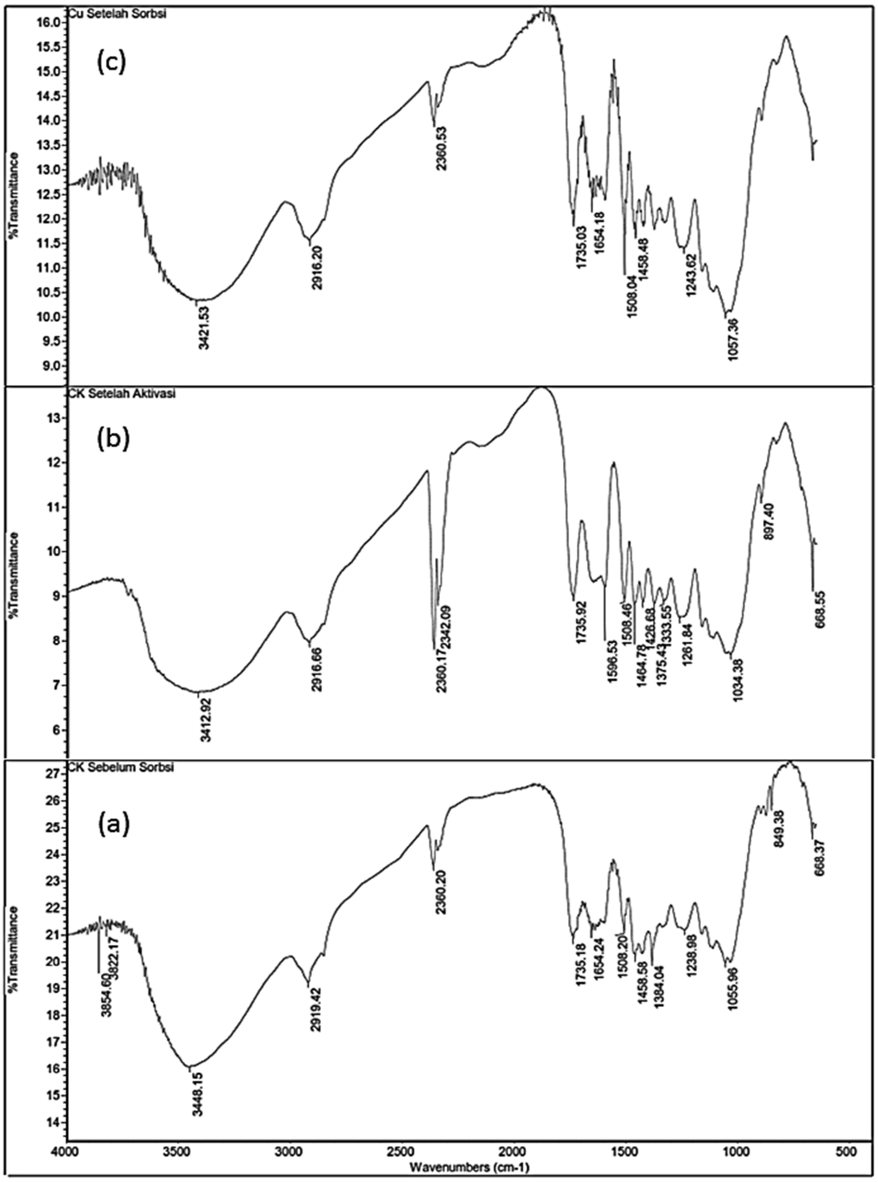

Fig. 11. FTIR of fruit shells ketapang . (a) Before activation. (b) After activation with HNO_3. (c) Once activated and absorb metal ions

SEM analysis

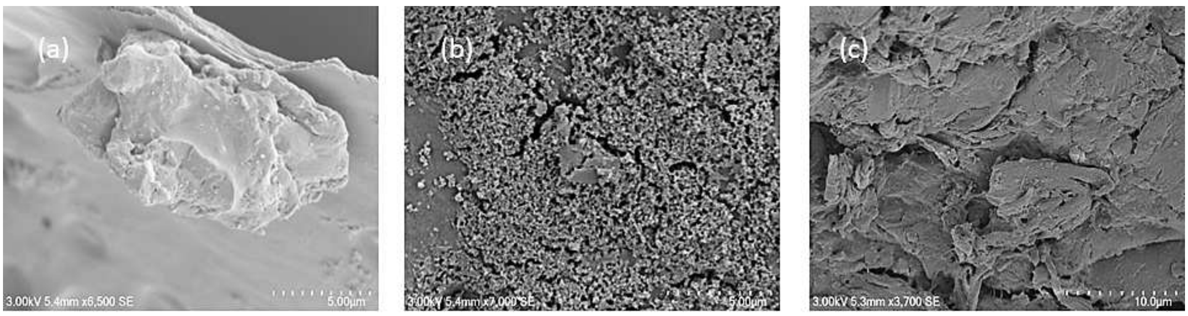

Fig. 12. SEM of ketapan fruit shells. (a) Before activated with HNO_3. (b) once activated, and (c) once activated and load of metal ion

Applications ketapang fruit shells to liquid waste

Table 2 .
The capacity of absorption and% uptake of metal ions Pb (II), Cd (II) and Cu (II) on Laboratorium Waste Environmental Chemistry Unand, Padang.

Metal Ion	Kons.Awal (mg/L)	Kons. End (mg/L)	Q (absorption capacity) mg/g	% Absorption
Pb (II)	3,334	1.471	0.466	55.879
Cd (II)	4.285	0.830	0,806	86.375
Cu (II)	2.211	1.292	0.230	41.565

CONCLUSION

From the study of the absorption of metal ions Pb(II), Cd(II) and Cu(II) by ketapang fruit shells that had been activated with HNO_3 0.01 N can be concluded that: Ketapang fuit shells can be biosorbent to remove Pb(II), Cd(II) and Cu(II) ion. The optimum conditions uptake of metal ions Pb (II) by ketapang fruit shell was at pH 5, 45 minutes contact time, conconcentration of 150 mg/L and ions Cd(II) at pH 6, the contact time of 60 minutes, the concentration of 150 mg/L and Cu(II) at pH 5, a contact time of 75 minutes, the concentration of 100 mg/L, which is obtained each treatment using 0,1 g mass, particle size of 180 μm and a stirring speed of 100 rpm.

Adsorption isotherm models on ion uptake of Pb(II) and Cu(II) is more suitable with Freundlich isotherms and uptake of metal ions Cd(II) fit to the Langmuir isotherm. The results of FTIR spectra showed the presence of functional groups (carboxyl, carbonyl and hydroxyl) on the surface of the fruit shells ketapang which serves as the active site for absorption or cation exchange process. The optimum conditions obtained from the research applied to liquid waste of Laboratorium Environmental Chemistry Andalas University, the absorption efficiency of metal ions Pb(II), Cd(II) and Cu(II) by ketapang fruit shells are respectively 55.87%, 86.375% and 41.565%.

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