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# Biosorption of Cadmium and Zinc by Tanjung Fruit Husk (*Mimusops elengi* L.)

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## ABSTRACT

*Biosorption of Cadmium and Zinc by Tanjung Fruit Husk (Mimusops elengi L.) has been studied. Some parameters were donesuch as pH effect, solution concentration, contact time, biosorbent mass, and particle size. The optimum conditions for Cd ion were at pH 5, concentration 900 mg/L, contact time 15 minutes, biosorbent mass 0.1 g, particle size 32 µm, at room temperature. The optimum conditions for Zn ion were at pH 6, concentration 1000 mg/L, contact time 30 minutes, biosorbent mass 0.1 g, particle size 32 µm, and heat temperature of biosorbent 25 $^oC$. Adsorption capacity ($q_e$) at the optimum condition for Cd and Zn ion were 6.95 mg/g and 14.51 mg/g, respectively. Adsorption isotherm for both metal ions followed Freundlich isotherm mechanism model with $R^2$ for Cd and Zn ion were 0.8851 and 0.9202, respectively.Analysis of functional group in biosorbent was used FTIR that might revealed –OH stretching, C-H stretching, C=O stretching, and C-O stretchinggroupwith wave numbers were 3419.97; 2922.60; 1617.47; and 1034.99 $cm^{-1}$. Morphology of biosorbent surface was analyzed using SEM.*

**Keywords :** biosorption, *Mimusops elengi* L., cadmium, zinc, and Freundlich isotherm.

## INTRODUCTION

Waste water containing heavy metals produced from a variety of industries. The process of electroplating and metal surface treatment of the waste produced by the quantity of heavy metals significantly (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) of the various uses. Another source is the timber industry to produce contaminant metals chromium, copper and arsenic. Industries that manufactures inorganic pigments produce a contaminant-containing compounds of chromium and cadmium sulfide. Petroleum refining processes produce contamination resulting from the conversion catalyst consisting of nickel, vanadium, and chromium. Field of photography on the film production process using silver and iron cyanide concentrations are high. Everything is a source of the greatest heavy metal waste that can be categorized as a hazardous waste and require extensive special treatment [1].

Heavy metals can cause serious effects on health, for example, inhibits the growth and development, cancer, organ damage, nervous system damage, even death. Exposure to some metals, such as mercury and lead, can lead to the development of autoimmunity, in which a person's immune system attacking its own cells[2]. As was the case in Japan's Minamata Bay in 1953, due to people were ate fish exposed to mercury, making it difficult to control the body, known as Minamata syndrome[3].

Biosorption isadsorption process using biomaterials. Biosorption is the ability of biomolecules (e.g biomass) to bind certain ions or other molecules from solution. Biosorption by biomass (molecules that have an active group) is passive and is based on the affinity between the biosorbent and sorbate[4]. Biosorption emerged as a superior method to remove the metal. Removal process is rapid, lasting a few minutes, and in normal pressures and temperatures. Biosorption method is one alternative method removes metals that can be considered from the economic side. The advantage of biosorption is lower operational costs because using biomass or agricultural by product, minimizing volume of chemical matter, high efficiency in detoxifying wastes very dilute, no specific composition requirements, the biosorbentcan be regenerated[5].

Several studies to absorb heavy metals by using biomaterials have been carried out such as by using *Garcinia mangostana* L. fruit shell[6], *Annona muricata* L. Seed[7], rice husk[8], *Muntingia calabura* L. Leave[9], sugar palm fruit shell[10], herbal plant of mahkota dewa[11]and *Nypa fruticans* Merr shell[12]. In this research, ion biosorption of Cd and Zn by utilizing the waste from the Tanjung fruit husk (*Mimusops elengi* L.).

The aim of the present research is to study the capability of Tanjung fruit husk for biosorption of cadmium and zinc ion.

## MATERIALS AND METHODS

All chemical used in this experiment namely $Cd(CH_3COO)_2.2H_2O$, $ZnSO_4.7H_2O$, NaOH, $HNO_3$, NaOH, and $CH_3COOH$ are analytical grade and obtained from E-Merck (Germany) unless other wise noted. Distilated water are obtained from laboratory. A cruiser, blender, pH meters, analytical balance, rotary shaker, AAS (spectraAA-240 VARIANT), Oven, FTIR (NICOLET is10), SEM was used in this experiment. Tanjung fruits were collected from Andalas University campus in Padang City, West Sumatra,Indonesia.

**Preparation of Biosorbent:** Tanjung fruitshusk washed with water, then dried at room temperature, and ground in pestle and mortar screened to particle size 32 –425μm (Fig.1 c) and soaked with 0.01 mol/L $HNO_3$ for three hours, filtered then rinsed with distilled water until neutral. The biosorbent was dried and ready to used.


**Fig. 1.(a) *Mimusops elengi* L. Fruits and leaf, (b) *Mimusops elengi* L. Fruit, (c) dry powder of *Mimusops elengi* L. Fruit Husk**

**Batch Adsorption:** Powder of Tanjung fruit husk(biosorbent) was entered into 10 mL solution containing Cd or Zn ion, and stirred using shaker for several minutes. The experiments were conducted with variety of pH solution, concentration, contact time, biosorbent mass and particle size.

To determine the amount of Cd or Zn ion adsorbed by Tanjung fruit husk, the formula used is:

$$q_e = \frac{(C_o\text{-}C_e)}{m} \times v$$

where Co is the initial concentration of metal ions (mg/L), Ce, final concentration at equilibrium state (mg/L), m, biosorbent mass(g) and *v* is volume solution (L).

## RESULTS AND DISCUSSION

**Effect of pH solution:** The pH solution is one important factors. The pH of solution had a significant impact on the removal of heavy metals, since it determined the surface charge of the adsorbent (has carboxylate, phosphate and amino group) and its degree of ionization [7].pH was varied with the range 3-6 for Cd ionand3-7 for Zn ion.

Fig. 2 showed the optimum biosorption of Cd and Zn ion occurred at pH 5 and 6, respectively. The dependence of metal uptake on pH is related to both the surface functional groups on the cell walls of the Tanjung fruik husk and the metal chemistry in solution.When pH was further increased up to 5forCd and up to 6forZn,the adsorption capacity was decreased. At pH 5 to 6 the adsorption capacity of Cd ion and at pH 6 to 7 the adsorption capacity of Zn ion were reduced, respectively.The same research was obtained by Hajar [13] using *Sargassum* Sp., Njouku *et.al.*, [14]using cocoa pod husk, Coelho *et.al.*, [15] using cashew nut shells, Hamza *et.al.*, [16] using *Saccharomyces cerevisae* and Deli *et.al.*,[9] using*Andrographis paniculata* leaves.

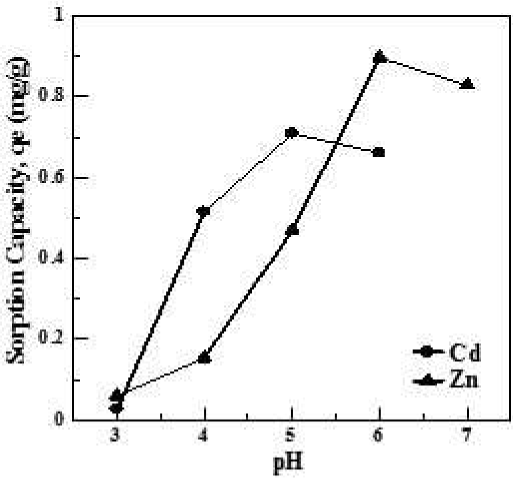


**Fig. 2.Effect of pH on Zn and Cd ion biosorption by on Tanjung fruit husk. Experimental condition: concentration = 10 mg/L, biosorbent mass = 0.1 g, stirring speed = 200 rpm, contact time = 15 min, and particle size = 160 µm**

**Effect of Concentration:**The initial concentration of metal ions were studied to determine the ability of the active site of biosorbentto bind [15]. The Cd ion concentration varied 10-1000 mg/Land Zn ion 10-2000 mg/L.

Fig.3 showed that the equilibrium sorption capacity seems to increase essentially linearly with an increase in the initial concentration up to 900 mg/L for Cd ion and 1000 mg/L for Zn ion. The distribution of solute, Cd and Zn ion between the liquid phase and solid phase can be described by several mathematical relationships such as the standard Freundlich and Langmuir isotherm models.

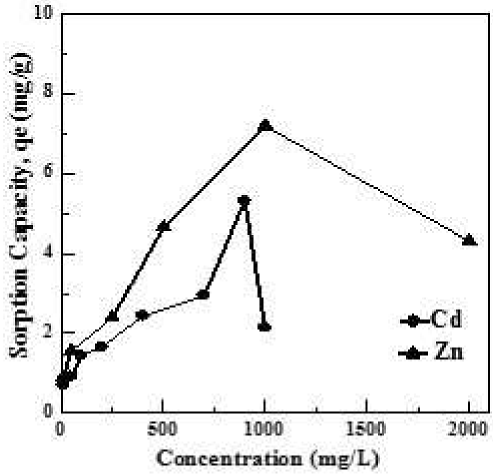


**Fig. 3. Effect of concentration on the sorption capacity of Cd and Zn ions on Tanjung fruit husk. Experimental condition: pH solution of Cd = 5, pH solution of Zn = 6,biosorbent mass = 0.1 g, stirring speed = 200 rpm, contact time = 15 min, and particle size = 160 µm**

**Effect of contact time:**The contact time on the biosorption of metal ion was useful to identify how long biosorbent bind metal ions on the active sides. Contact time were varied at 15, 30, 60 and 90 minutes.Fig**.** 4 showedthat the optimum condition of Cdand Zn ion by powder of Tanjung fruit husk were obtained at 15 and30 min, respectively. This shows that the sorption capacity of Cd ion rather than Zn ion.

Coelho *et.al.*,[15] also found the sorption capacity is fast during the initial time contact; it slowly increases at larger time contact till reaching equilibrium at 60 min, with insignificant variations thereby.Hamza *et.al.*,[16] and the Meitei, *et.al.*,[17] stated that the process of metal ion adsorption by the biosorbent in a batch system occured in two stages: the initial stage of rapid (passive uptake) and it needed short duration for about 5- 30 minutes, followed by much slower (active uptake) with the duration was 120 minutes.

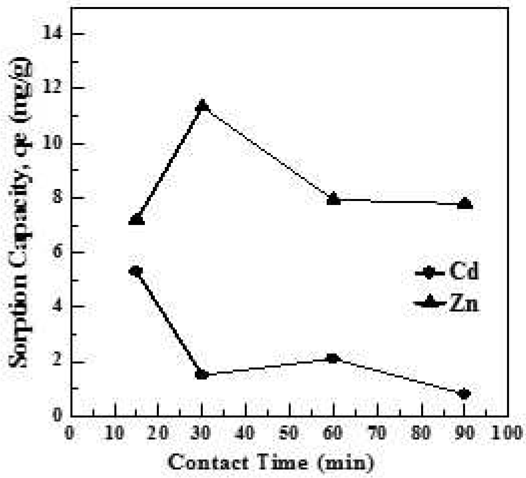


**Fig. 4. Effect of contact time on the sorption capacity of Cd and Zn ions on Tanjung fruit husk. Experimental condition: pH solution of Cd = 5, pH solution of Zn = 6, Cd ion concentration = 900 mg/L, Zn ion concentration = 1000 mg/L, biosorbent mass = 0.1 g, stirring speed = 200 rpm, and particle size = 160 µm**

**Effect of Biosorbent mass:**Biosorbent mass is an important parameter in the biosorption process to evaluate the adsorption capacity of metal ions on the biosorbent. Biosorption of metal ions depends on the type of adsorbent surface and on the ion forms that metals find in the water solution[15]. The mass of biosobent was varied at 0.1, 0.3, 0.6, 0.9 gram. Fig.5showed the optimumbiosorbent mass of Cd and Zn ion byTanjung fruit huskin the aqueous solution. According to Kurniawan *et.al.*,[7]showed that the adsorption capacity decreased with increasing the amount of biomass.The optimum biosorbent mass for Cd and Zn ions found in mass 0.1 gram.

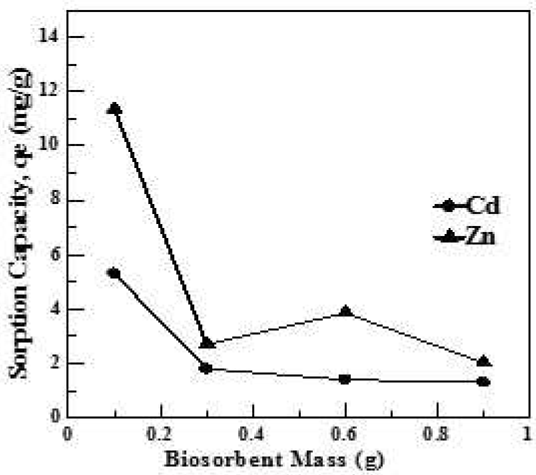


**Fig. 5. Effect of biosorbent mass on the sorption capacity of Cd and Zn ions on Tanjung fruit husk. Experimental condition: pH solution of Cd = 5, pH solution of Zn = 6, Cd ion concentration = 900 mg/L, Zn ion concentration = 1000 mg/L, contact time of Cd = 15 min, contact time of Zn = 30 min, stirring speed = 200 rpm, and particle size = 160 µm**

**Effect of Paticle Size:**The particle size was varieted from 32 – 425 µm. Fig.6 showed that the particle size has adsorption capacity of Cd and Zn ion weredecreased from 32 – 425 µm. The optimum particle size was found on 32 µm.

According to Song *et.al.*, [20] reported that since the biosorption capacity of small size biosorbent showed little increase than the medium and big ones,it is very likely that, in the practical application, the biosorbent in bigsize would achieve similar performance with the small andmedium ones with less cost of pretreatment.

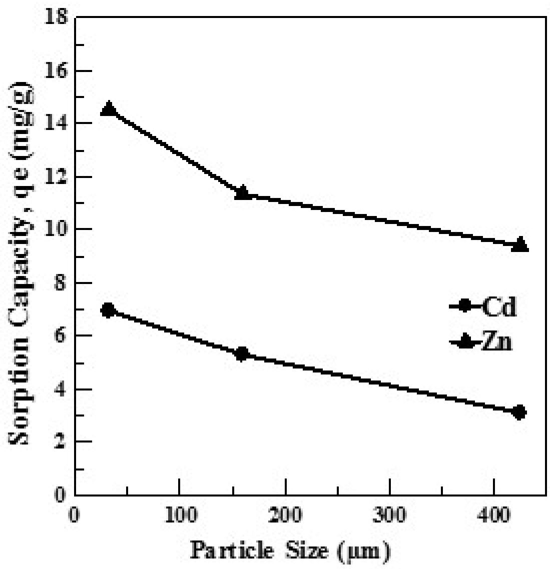


**Fig. 6. Effect of particle size on the sorption capacity of Cd and Zn ions on Tanjung fruit husk. Experimental condition: pH solution of Cd = 5, pH solution of Zn = 6, Cd ion concentration = 900 mg/L, Zn ion concentration = 1000 mg/L, contact time of Cd = 15 min, contact time of Zn = 30 min, biosorbent mass = 0.1 g, and stirring speed = 200 rpm**

**Adsorption Isotherm:**An adsorption isotherm describes the relationship between the amount of adsorbate taken by the adsorbent and the adsorbate concentration remaining in solution. This isotherm was derived from equilibrium constant of the interaction of adsorbate with adsorbent [7].In this research, the equilibrium data for biosorption process of Zn and Cd ions on Tanjung fruit husk evaluated by the Freundlich andLangmuirisotherm models.

Table 1, fig. 7 and fig. 8 described some information related to biosorption processof Cd and Zn ions on powderof Tanjung fruit husk i.e. (1) The value of correlation coefficient ($R^2$) for both metal ions was closer to 1 in the Freundlich isotherm than Langmuir isotherm, it indicated that the adsorption process for both metal ions followed the Freundlich isotherm model, (2) the slope of linear function (n) both metal ions greater than 1 (n> 1), so the adsorption process through physical processes (physisorption), (3) the value of separation factor ($R_L$) for Langmuir isotherm for both metal ionsat ranges between 0 and 1 ($0 < R_L < 1$), it can be concluded that the adsorption process was going well, (4) the value $Q_{max}$ (mg/g) obtained from Langmuir isotherm equation showed that the uptake of Zn ions greater than Cd ions

**TABLE 1 Data Models Freundlich And Langmuir Adsorption Isotherms**

| Ion | Freundlich | | Langmuir | | |
|---|---|---|---|---|---|
| | n | $R^2$ | $Q_{max}$ (mg/g) | $R_L$ | $R^2$ |
| Cd | 3,459 | 0,8851 | 1,938 | 0,005 - 0,3 | 0,7909 |
| Zn | 3,879 | 0,9202 | 3,107 | 0,001 - 0,2 | 0,8821 |

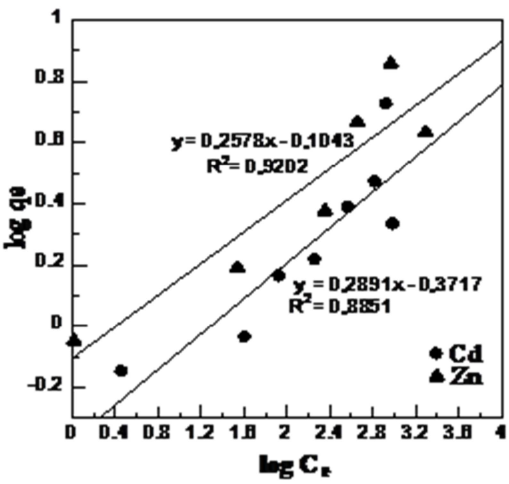


**Fig. 7. Freundlich isotherm model for Cd and Zn ions biosorption on Tanjung fruit husk**

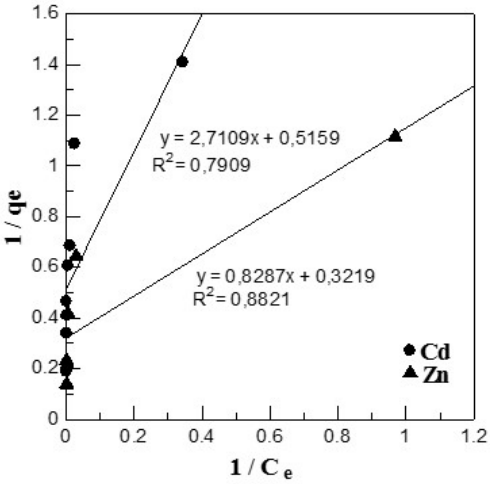


**Fig. 8.Langmuir isotherm model for Cd and Zn ions biosorption on Tanjung fruit husk**

**Fourier Transform Infra Red (FTIR) Spectroscopy Analysis:** FTIR is an important analytical technique, which detects the vibration characteristics of chemical functional groups existing on the surface of adsorbent [12].

From comparison four spectra in Fig. 9 wave numbers seen in all four groups, namely -OH stretching, shifting wave number was from 3419.96 became 3438.46; 3447.95 and 3422,98cm$^{-1}$, -CH stretching, shifting wave number was from 2922.37 became 2922.60 and 2920.98 cm$^{-1}$, C=O stretching, shifting wave number was from1624.71 became 1617.47; 1636.63 and 1617.96 cm$^{-1}$, and C-O stretching, shifting wave number was from 1034.99 became 1032.15; 1034.69 and 1032.08. It can be concluded the the four functional groups played a role in the process of metal ion biosorption.

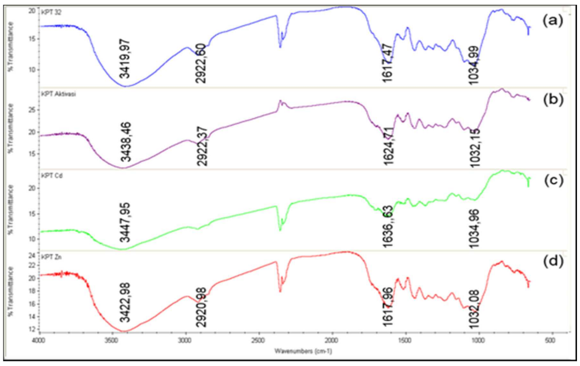


**Fig. 9. FT-IR spectrum of Tanjung fruit husk powder**

**Scanning Electron Micrograph (SEM) Analysis:**SEM was used to see the morphology of biosorbent surface. The influence of biosorbent morphological was investigated because it was related to the efficiency of adsorption of the metal ions in the biosorbent particles [21].

Fig. 10 showed the change was not very significant, it was in accordance with the adsorption capacity (qe) of metal ions on the biosorbent that were quite small on the surface of the biosorbent. From the biosorbent surface morphology on fig.10 known that the biosorbent surface morphology was irregular, rough and not homogeneous.

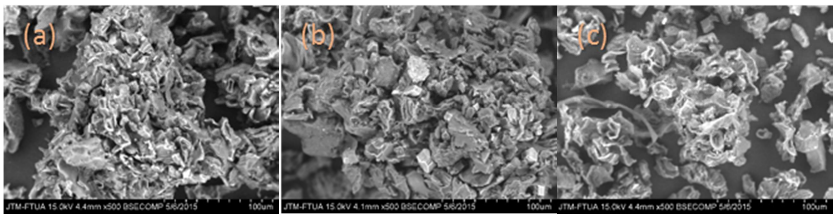


**Fig. 10. Scanning electron microscope husk of Mimusops elengi L. before sorption (a), after Zn ion sorption, and after Cd ion sorption (c). Magnification 500 times**

## CONCLUSION

The powder of Tanjung fruit husk *(Mimusops elengi* L.) can adsorb Cd and Zn ions present in water sample at optimum condition for Cd ions at pH 5, the concentration is 900 mg/L, the contact time is15 minutes, the mass of biosorbent is 0.1 g, and the particle size is 32 µm with the adsorption capacity (qe) is 6.95 mg/g. On the other hand, the adsorption of Zn ions at pH 6, the concentration is 1000 mg/L, contact time is 30 minutes, the mass of biosorbent is 0.1 g, and the particle size is 32 µm with the adsorption capacity (qe) is 14.51 mg/g. Adsorption isotherms for both the metal ion adsorption mechanisms follow Freundlich isotherm models with $R^2$ to ion Cd and Zn respectively are 0.8851 and 0.9202. Analysis by Fourier Transform Infrared Spectroscopy (FTIR) obtained functional groups that play a role in the adsorption process is the -OH stretching, C-H stretching, C = O stretching, and C-O stretching seen with the shift wave number of the functional groups. Analysis of the morphology of the surface of the biosorbent carried out by Scanning Electron Microscope (SEM) showing the surface of the powder of Tanjung fruit husk is irregular, rough and not homogeneous.

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