

Biosorption of Zn (II) Metal Ion by Ca-Alginate Immobilized Durian (*Durio Zibethinus*) Seed

*Intan Lestari*¹, *Desy Kurniawati*², *Rahmiana Zein*³, *Hermansyah Aziz*⁴

¹Department of Chemistry Faculty of Science and Technology Universitas Jambi, Jambi 36361 Indonesia

²Laboratory of Environmental Analytical Chemistry, Universitas Negri Padang, Indonesia

^{3,4}Laboratory of Environmental Analytical Chemistry, Universitas Andalas Indonesia

Abstract. Heavy metal biosorption by alginate immobilized durian seed has been done. The immobilization of durian seed powder to Ca-alginate was able to improve biomass adsorption process, increase uptake capacity, ease separation from solution, generate and repeat biosorbent. In this experiment the effect of pH, contact time, concentration and temperature on the uptake capacity of metal ions Zn(II) in solution were studied. Biosorption was done batch methods and result was studied Langmuir and Freundlich adsorption isotherm. The adsorption of heavy metal was optimum in pH 5 with 75 mins contact time and Zn(II) ion under the concentration of 250-300 mg/l. The adsorption isotherm data was characterized using Langmuir and Freundlich equation. The equilibrium biosorption isotherm showed that alginate immobilized durian seed process has high affinities with adsorption capacities of 25.05 mg/g. All results showed that alginate immobilized durian seed is an alternative low cost biosorbent for heavy metal ion removal from aqueous solution.

Keyword: Biosorption, Durian seed (*Durio zibethinus*), heavy metal, immobilized

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1 Introduction

Heavy metal contamination in waters is increasing with waste disposal to water-bodies (Sari A, 2009). This issue is being paid big attention to because heavy metals are nondegradable in the environment and dangerous for the species in the water. They are able to bring toxic effect to human, animals and plants in the environment, even at a very low concentration (Das et al, 2007). Heavy metals are accumulated in the food chain and affecting human health.

Various of chemical and physical methods have been used to remove heavy metal ions from solutions in the past few decades. These methods involved filtration, precipitation, solvent extraction, coagulation, ion exchange, evaporation, reverse osmosis, electrolysis and membrane process (Sari A, 2009; Abbas et al, 2014; Tijani et al, 2013). However, the application of those

*Corresponding author at: Department of Chemistry Faculty of Science and Technology Universitas Jambi, Jambi and Indonesia

E-mail address: ilestari_15@unja.ac.id

processes are often limited by technique and cost factors. Ion exchange and adsorption, for instance are very effective. However they required expensive adsorbent materials and complicated processes (Das et al., 2001). Nevertheless, ion exchange and adsorption, also solvent extraction, are the most commonly used among those methods mentioned.

New study to remove heavy metals from waste directs to biosorption technique which is based on metal bonds in biological materials. Biosorption is a relatively new process that has shown a significant contribution for the removal of contaminants from aqueous effluents. Biosorption can be defined as the removal of metal or metalloid species, compounds and particulates from solution by biological materials or a by-product or waste material from another industry (Coelho, Laus, Mangrich, de Favere, & Laranjeira, 2007; Gadd, 1993). Biosorption process is fast and the reaction can be reversible from the metals bind with biomass. Biosorption mechanism shows that lignocellulose has absorption ability and generally acts as adsorbent with its structure and polymer compounds (Osman, 2010, Pehlivan et al, 2012)

Immobilized biomass is the stage needed to scale up biosorption in industrial scale. Durian seed biomass in powder (native) form is less preferred as it cannot stand in acidic solution that leads to difficulties during the separation after biosorption process. The advantages of biomass immobilized in alginate are to improve biomass performance in dynamic absorption, increase absorption capacity and ease biomass separation from the solution. (Kacar , Y., et. al , 2001) Biosorbents are able to be regenerated without damaging the structures of biomass and can be used for repetitively (regenerate) (Aksu et al, 1998).

This study aims to immobilize durian seed powder to Ca-alginate polymer matrix in bead forms in order to be used as a relatively strong mechanical biosorbent which is able to stand in aqueous solution media. Moreover, the study is to determine the maximum absorption capacity of Zn(II) ion.

2 Materials and Methods

2.1 Tools and Materials

Field Emission-Scanning Electron Microscope (FE-SEM) (Inspect F-50 FEI Company USA), Atomic Absorption Spectrophotometry (AAS WFX -320 Ray light, Braigh China, FTIR (FT/IR-460 Plus, Jasco Japan), analytical balance, durian seed from durian sellers in Padang. Biosorption experiment was done by stock standard solution (1000 mg/L) from Zn(NO₃) Merck (Germany), Na-alginate, CaCl₂, HNO₃ and NaOH and aquadest. Zn(II) standard solution was made fresh from the mother liquor.

2.2 Durian Seed Preparation and Characterization

Durian seed preparation is referred to the previous research (Lestari et al 2016). The dried durian seed powder was immobilized to Ca-alginate as the procedure in Mahamadi and Zambara (2010).

Polymer alginate 2% solution was made by solving 2 g alginate into 100 mL deionized solution and followed by agitation for 4 – 6 hours using magnetic stirrer at 100 rpm. To make homogenized polymer solution, 2 g durian seed powder biomass was mixed into 100 mL of 2% alginate. Next, the mixture was formed into beads by dripping the mixture to CaCl₂ 0.1 M solution by gravimetry with a syringe. Beads formed were hardened in CaCl₂ 2% solution for 24 hours and washed with distilled water while stirred at 100 rpm for 30 minutes. It is repeated for 3 – 5 times until neutral pH was reached. The bead was dried at room temperature and stored at a sealed container.

2.3 Biosorption Experiment

Biosorption experiment was done by mixing 0.1 g durian seed powder biosorbent or Ca-alginate immobilized durian seed beads with 20 mL Zn(II) 10 mgL⁻¹ solution. The mixture was shaken for 60 minutes at 150 rpm and filtered. The concentration of Pb(II) ion in the solution was analyzed by Atomic Absorption Spectrophotometry AAS (spectra 20 variant) . The optimum conditions learned are effect of pH, contact time, Zn(II) concentration and temperature. The total of metal ion absorbed per gram biomass for biosorption capacity can be calculated by the equation below:

$$Q_e = \frac{C_o - C_e \cdot V}{M}$$

Where C_o and C_e are the initial concentration of metal ions in the solutions and equilibrium (mgL⁻¹) respectively, V is the volume of Zn(II) ion metal solution and m is the mass of biosorbent. The characterization of biosorbent's functional groups was done by FTIR and surface morphology analysis by SEM-EDX.

3 Results and Discussion

3.1 The Influence of pH on Zn(II) Absorption

The initial pH of a solution is one of the important parameters to study metal biosorption process (Ting Fan et al, 2008). The results show that the maximum capacity of Zn(II) absorption obtained using Ca-alginate immobilized durian seed biosorbent is at pH 5, with adsorption capacity of 2.01 mgg⁻¹ (Figure 1). Previous study also obtained pH 5 for durian seed (Lestari et al, 2015).

Absorption capacity increases with the increase of solution's pH from 2 to 5 and decreases at pH 6 – 7. In low pH, competitions occur between ion H^+ and metal ion at absorption active side, with a big total of hydrogen ion limiting on metal ion absorption (Saikaew,2010., Sari dan Tuzen, 2009).

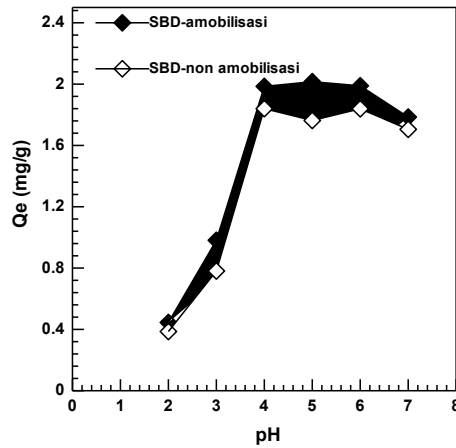


Figure 1 : The influence of pH on solution towards Zn(II) absorption capacity. (Initial concentration = 10 mgL^{-1} , volume = 20 mL, mass = 0.1 g, contact time = 60 minutes)

3.2 The Influence of Contact Time on Zn(II) Biosorption

The contact time in Zn(II) biosorption learned in Ca-alginate immobilized durian seed biosorbent learned is between 15 – 120 minutes. The maximum absorption capacity obtained at 120 minutes gave Q_e value = 2.875 mg/g . The results of Zn(II) absorption capacity can be seen in Figure 2.

Figure 2 shows that the increase of contact time length has resulted in the increase of Zn(II) absorption and finally constant at 75 minutes. Generally, metal ion reached equilibrium at 15 – 60 minutes and after that it becomes saturated (Adeel, 2013). In the initial condition, absorption took place fast as there is a big availability of active sides on the surface and it reached equilibrium afterwards.

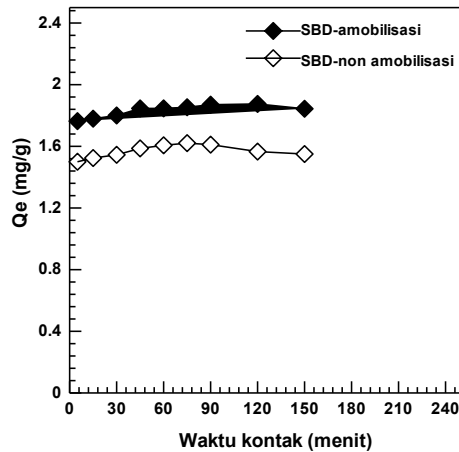


Figure 2. The influence of contact time on Cd absorption capacity, pH 4 at non-immobilized and pH = 5 at SBD-immobilized, biosorbent mass = 0.1 g, initial concentration = 10 mgL⁻¹, stirring rate = 150 rpm.

3.3 The Effect of Zn(II) Initial Concentration

The influence of initial concentration of Zn(II) absorption at concentration range of 1 – 300 mg/L Zn(II) can be seen in Figure 3. The higher the concentration of Zn(II), the higher the absorption capacity. The maximum biosorption of Zn(II) ion obtained is at concentration of 250 mg/L with $Q_e = 25.05$ mg/g.

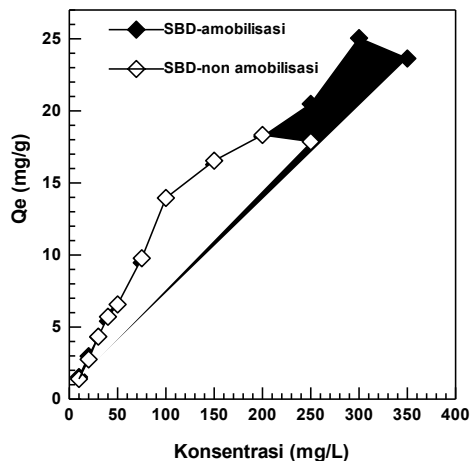


Figure 3 : The influence of solution concentration on Zn(II) biosorption by immobilized and non-immobilized biosorbent (pH Zn solution = 5, volume = 20 mL, mass = 0.1 g, contact time SBD – immobilized = 90 minutes and SB-non immobilized = 45 minutes)

The higher the concentration, the bigger the thrust force of metal ion to move to the surface of cell walls. Consequently, absorption capacity increases (Fun et al, 2008).

Table 1 : Metal ions biosorption capacity value by Ca-alginate immobilized biosorbent

Alginate Immobilized Biomass	Metal ion	Q _{max} (mgg ⁻¹)	Reference
Micro alga <i>Senedesmus quadricauda</i>	Cu ²⁺	75.6	Bayramoglu and Arica, 2009
	Zn ²⁺	55.2	
	Ni ²⁺	30.4	
<i>Mentha arvensis</i>	Cu ²⁺	104.48	Hanif <i>et al</i> , 2009
	Zn ²⁺	107.75	
<i>Penicillium sp</i>	Cu ²⁺	17.2	Misra, 2013
	Zn ²⁺	19.1	
<i>Solanum nigrum</i> L	Zn ²⁺	144.72	Indrasti and friends, 2009
Alga <i>Chlorella kessleri</i>	Cu ²⁺	37.24	Horvathova <i>et al</i> , 2009
	Zn ²⁺	40.23	

3.4 Adsorption Isotherm

The analysis to determine the absorption equilibrium between solid biosorbent and Zn(II) metal ion was done by Langmuir and Freundlich adsorption model isotherm.

3.5 Langmuir Isotherm

Langmuir model assumes one layer at adsorbents surface layer with limited total from the same part (Nawaz, *et al.*, 2011). Langmuir equation can be written as follow:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} \cdot K_L} + \frac{C_e}{Q_{max}}$$

Where Q_e = total metal ion absorbed at equilibrium per unit adsorbent mass (mg/g). Q_{max} is maximum adsorption capacity for metal unit per adsorbent mass unit (mg.g). C_e is equilibrium concentration of metal ion in the solution (mg/L) and K_L shows Langmuir constant. Langmuir adsorption isotherm for Zn(II) ion at various temperatures can be seen in Figure 4. The plot of C_e/Q_e value against C_e values produce a straight line with $1/Q_{max}$ slope and $1/Q_{max} \cdot K_L$ intercept.

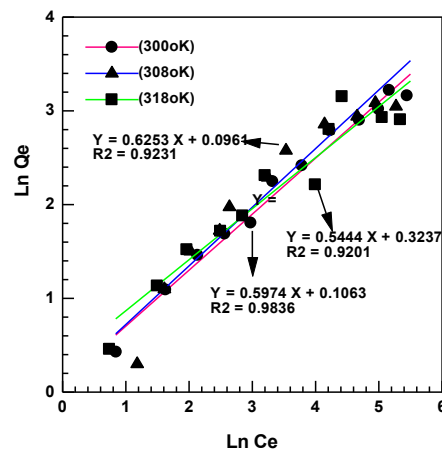
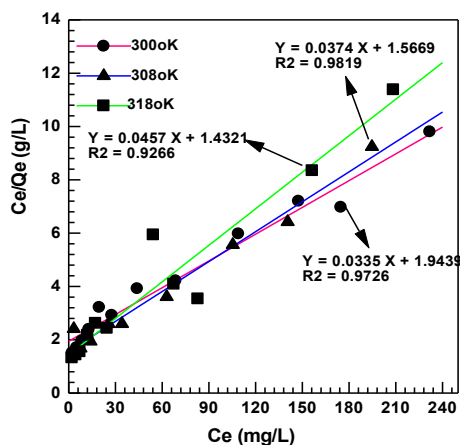


Figure 4A. Langmuir isotherm adsorption curve Figure 4B. Freundlich isotherm adsorption curve

Figure 4A and 4B show that temperature affects isotherm constant and maximum adsorption capacity. The correlation coefficient value (r) is more linier at 300 oK with $r^2 = 0.982$.

3.6 Freundlich Isotherm

Freundlich isotherms is empirical equation based on the adsorption at multilayers (heterogenous) surfaces (Kurniawan et al, 2014). Freundlich isotherm can be applied at multilayer adsorption. The linier equation of Freundlich isotherm can be written as: $\ln Q_e = \ln K_F + 1/n \ln C_e$, where K_F and n are Freundlich constant which can be determined by plotting $\ln Q_e$ against $\ln C_e$. The linier plot of Freundlich isotherm can be seen in Figure 4B.

3.7 Biosorbent Characterization with FTIR

FTIR spectra analysis done before and after metal ion biosorption is used to observe the functional groups in the biosorbent and the interaction with the metal ion after adsorption process. FTIR analysis in SBD-alginate immobilized biosorbent before and after Zn(II) biosorption can be seen in Figure 5. From the analysis, biosorbent with alginate immobilization has got several functional groups that can be seen at the stretched peak in wavelength 3424.20 cm^{-1} which is hydroxyl (-OH) or amine (-NH₂). The band at 2925 cm^{-1} is marken with C – H stretching vibration and at 1636.91 cm^{-1} is the stretching of bonds between carbonyl C = O and amide. The peak at 1158.86 cm^{-1} and 1023.65 cm^{-1} are marked by the vibrations of stretching alcohol.

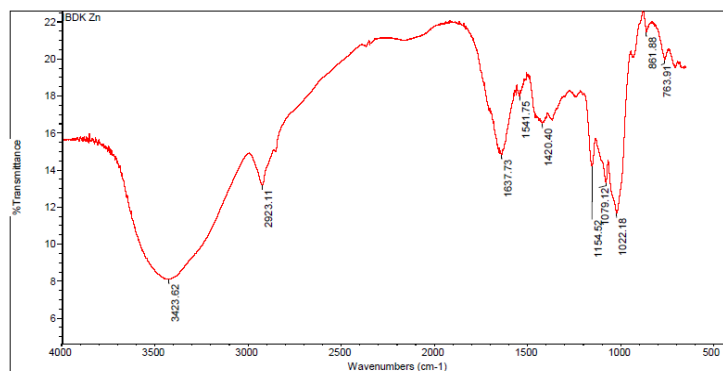


Figure 5 : FTIR Spectra for Ca-alginate immobilized durian seed biosorbent before absorption

The shift of wavelength took place after Zn(II) metal ion absorption which can be seen in Figure 5b. The spectra shows the shifts at 3423.20 cm^{-1} and 3423.62 cm^{-1} which care marked by -OH or -NH₂ functional groups intensity with adsorbates. Next, the peak at 2925 cm^{-1} to 2923.11 cm^{-1} is marked by stretching vibration of C – H. Then the peak at 1636.91 cm^{-1} to 1637.73 cm^{-1} is marked in stretching vibration of carbonyl C = O group. From biosorption FTIR spectra of metal ion Zn(II) biosorption took place involved carboxyl, carbonyl, hydroxyl and amine

functional groups at the surfaces of biomass. The same functional groups were also obtained at Cu(II) biosorption in *Trametes versicolor* biomass (Subbaiah et al, 2011).

4 Conclusion

In this study, Ca-alginate immobilized durian seed (*Durio zibethinus*) biosorbent has been used as one of the potential biosorbents to absorb Zn(II) in a solution. The biosorption characteristics learned are by various parameters like pH, contact time, solution concentration and temperature. The optimum conditions are at pH 5 with 75 minutes contact time, initial concentration of 250 – 300 mgL⁻¹ in room temperature. The research data was analyzed by Langmuir and Freundlich isotherm. Equilibrium data follows more of Langmuir adsorption model with $r^2 = 0.9726$. The maximum biosorption capacity obtained was $Q_e = 25.05$ mgg⁻¹.

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