Isotherm and Kinetics of Cd(II) Adsorption by Durian (*Durio zibethinus*) seed Immobilized into Ca-alginate

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Abstract

Purpose – The purpose of this paper to immobilization provides biosorbent particle with density and mechanichal strength, immobilization can save the cost of separating from biomass, can be regeneration and to increase adsorption capacity for metal ions.

Design/Methodology/Approach – The parameters affecting the adsorption, such as initial metal ion concentration, pH, contact time, and temperature, were studied. The analysis of biosorbent functional group was carried out by Fourier Transform Infrared Spectroscopy, SEM-EDX, for elemental analysis.

Findings – Optimum pH condition for biosorption Cd(II) was pH 5, contact time was 45 min, and initial concentration was 250 mg/L. Biosorbent analysis was characterized using SEM-EDX and FTIR analysis. Kinetics adsorption was studied and analyzed in terms of the pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetics models. The result showed that the biosorption for Cd(II) ion followed the pseudo-second-order kinetic model. Biosorption data of Cd(II) ion at 300°K, 308°K, and 318°K was analyzed with Temkin, Langmuir, and Freundlich isotherms. Biosorption of Cd(II) by durian seed immobilization in alginate according to the Langmuir isotherm equation provided a coefficient correlation of $r^2 = 0.939$ and maximum capacity biosorption of 25.05 mg/g.

Keywords Biosorption, *Durio zibethinus* seed, Ca-alginate, immobilization

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1. Introduction

Contamination of aquatic environments by heavy metals is caused by the disposal of industrial wastewater. Some heavy metals are quite dangerous, such as Pb, Cd, and Hg. Cadmium is an unnecessary element for plants and animals, and is not degradable and transferable through the food chain. Waste stream from smelting, alloying, pigments, batteries, plastics, mining, and refining processes are the main sources of cadmium release into the environment. Cadmium is a toxic metal that contaminates the environment and does not degrade naturally, causing serious problems in the environment. Therefore, cadmium ion must be removed from the industrial waste.

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There are several chemical and physical methods used to reduce cadmium, including precipitation method, membrane process, adsorption, ion-exchange floating, and others (Kefala *et al.*, 1999; Selatnia *et al.*, 2004). However, several methods have such limitations as being less efficient, resulting in further disposed secondary sludge and expensive operating costs (Ahluwalia *et al.*, 2005). One alternative technique is biosorption (Volensky, 2007), in which some types of biomaterial can bind metals even at very dilute concentrations (Martinez *et al.*, 2006).

Some biological materials have been studied in the biosorption of heavy metal ions in water, such as seaweed, algae, fungi, and microorganisms, both living cells and nonliving cells (Volensky, 2007).

Some of the agricultural waste used as heavy metal biosorbents include jackfruit seeds for Pb(II) (Okolo *et al.*, 2012), soursop fruit (*Annonamuricata*) for Cd(II) and Zn(II) ions (Rahmadani *et al.*, 2013), durian skin for Cd(II) (Saekaew, 2010), and durian seeds for Zn(II) biosorption (Lestari *et al.*, 2015).

Durian seed was selected as a biosorbent because it is an agricultural waste present in abundance. Durian (*Durio zibethinus*) seed consists of holocellulose (26.4%), cellulose (60.5%), and hemiselose (13.1%) (Ahmad *et al.*, 2014); these characteristics can be utilized as biosorbent metal ions.

Alginate is an anionic copolysaccharide consisting of residues of β-1-4-D-manuronate (M) and α-L-guluronate (G). Alginate is a natural polysaccharide commonly present in the cell walls of all species of brown algae (*Phaeophyceae*), nontoxic, degradable, and biocompatible (Verma *et al.*, 2013). The purpose of this study was to immobilize durian seeds with Ca-alginate and use them for adsorption of Cd(II) ion from aqueous solutions by batch experiment and evaluate the effects of contact time, pH variable, initial concentration cadmium ions, and temperature of the solution.

2. Methods

2.1. Biosorbent preparation

Durian seeds were collected from a local market durian located in the Padang City, West Sumatra, Indonesia. Durian seed sample was processed by washing with deionized water. The washed material was cut into small pieces (1–2 cm) and then dried in an oven at 60°C until it reached a constant weight. The dried sample was finely grounded using a grinder, saturated with a particle of 71 μm, and activated with HNO_3 0.1 M for 2 h, filtered, and dried again.

2.2. Immobilization of durian seeds in Ca-alginate

The procedure used is based on the reference method of Lestari *et al.* (2016). Biosorbent durian seeds immobilized into Ca-alginate were characterized before and after sorption by FT-IR Spectrometer (Perkin Elmer System, 2000). Surface morphology of biosorbent was analyzed by a scanning electron microscopy (SEM), and the photograph was taken using the JSM-JSM-5410 LV model.

2.3. Batch biosorption experiment

2.3.1. Effect of pH solution. The effect of the pH solution was determined from a pH of 2 to 7, with agitation of 0.1 g biosorbent and 20 mL Cd(II) with a 10 mg/L concentration by using a shaker. Contact time of agitation was 60 min with an agitation rate of 150 rpm at 25°C. pH was adjusted by adding 0.1 N NaOH or 0.1 N HNO_3.

2.3.2. Effect of contact time. The contact time was determined by stirring 0.1 g biosorbent and 20 mL Cd(II) with a concentration of 10 mg/L by using a shaker at pH 5. The contact time of agitation was set to 5–120 min with a stirring speed of 150 rpm at 25°C.

2.4. Isotherm experiments

Equilibrium isotherm was determined by stirring 0.1 g biosorbent with Cd(II) at a concentration of 10–250 mg/L using a shaker at pH 5. The agitation contact time was 45 min, with a constant agitation rate of 150 rpm and a temperature of 25–45°C. The absorption capacity of Cd(II) was determined by using a mass balance. The adsorption capacity of Cd (II) can be calculated as:

$$Q_e = (C_i - C_e).V \tag{1}$$

where Qe = uptake capacity Cd(II) at the equilibrium (mg/g), V = volume of Cd(II) (mL) solution, m = biosorbent mass (g), C_i = initial concentration Cd(II) (mg/L), and Ce = concentration Cd(II) at equilibrium (mg/L).

3. Results and discussion

3.1. Result

3.1.1. Effect of pH. pH is an important parameter in the biosorption process (Wan Ngah *et al.*, 2002). Effects of pH on the uptake capacities of Cd(II) on alginate immobilized durian seed were investigated (Lestari *et al.*, 2016).

3.1.2. Effect of contact time. Speed of biosorption is an important process for design experiment designed in batch. The adsorption capacity of Cd(II) ion can increase with increasing time and can reach an equilibrium state at 45 min with an adsorption capacity, which is is 1,9108 mgg^{-1} (Figure 1).

3.1.3. Biosorption kinetics. The adsorption kinetics depends on sorbent–sorbate interaction and the operating conditions. Some of the kinetics models are used to study the properties of the adsorbent and the adsorption mechanism (Subbaiah, 2011). Biosorption balance data were analyzed by using kinetic adsorption pseudo-first order and pseudo-second order. The pseudo-first order can be written in the following linear form:

$$\text{Ln} \quad (Qe - Qt) = \text{Ln} \quad Qe - k_1(t) \tag{2}$$

where Qe and Qt (mg/g) = the amount of Cd(II) ion at the equilibrium and at time t (min), and k_1 = biosorption of speed constant.

Linear equations for pseudo-second order can be written in linear form:

$$\frac{t}{Qt} = \frac{1}{k_2 Qe_2} + \frac{1}{Qe}.t \tag{3}$$

where k_2 (g/mg min) is the second-order constant, and Qe (mg/g) and Qt are the biosorption capacities at equilibrium and at time t.

Kinetics of Cd(II) ion can be seen in Figure 2. Kinetics of Cd(II) ion on biosorption of Ca-alginate can follow pseudo-second-order kinetics with $r^2 = 0.999$.

3.1.4. Effect of concentration of Cd(II) ion. Effect of concentration on adsorption capacity of Cd(II) ion on biosorption was studied with an initial concentration of 10–300 mg/L at 25°C. Effect of concentration on adsorption capacity of Cd(II) ion can be seen in Figure 2. The amount of metal ions adsorbed per unit of biosorbent mass increases with increasing solution concentration and is optimum at 250 mg/L. At a high concentration, the adsorption capacity increases due to of influence of the thrust force on metal ions toward the surface of cell wall (Fun *et al.*,2008). The maximum Cd(II) adsorption capacity was 25,05 mg/g.

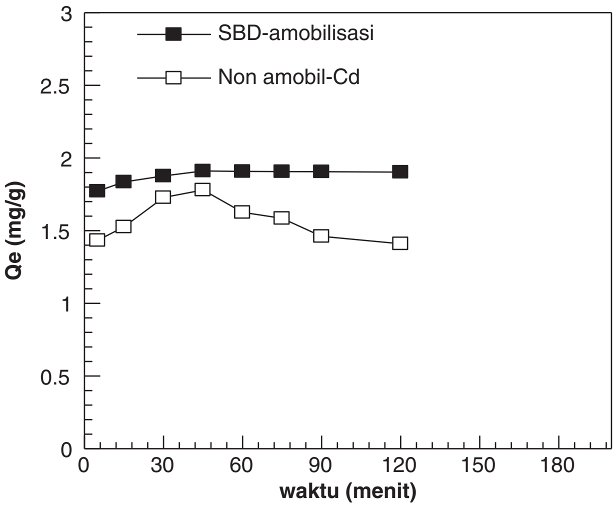

Figure 1.
Effect of contact time on Cd(II) uptake capacity (pH = 5, initial concentration = 10 mg/L, stirring rate = 150 rpm)

3.1.5. Isotherms adsorption ion Cd(II) The biosorption isotherm adsorption of Cd(II) is fundamental providing the essential information needed to design the adsorption process. In this research, we use the isotherm adsorption analysis by Langmuir and the Freundlich model.

3.1.6. Isotherm langmuir. Adsorption isotherm Langmuir assumes that biosorption occurs in the monolayer and can be written with the following equation:

$$\frac{Ce}{Qe} = \frac{1}{K_{max}} + \frac{1}{Qe}.Ce \tag{4}$$

where K_L is the Langmuir constant associated with the adsorption energy, and Qe and Q_{max} are the adsorption capacities at the equilibrium and the maximum state.

3.1.7. Freundlich isotherm. Freundlich's isotherm model describes that adsorption occurs in heterogeneous layers with interactions between adsorbate molecules. Freundlich's equation suggests that the adsorption exponential energy decreases at the adsorption center side. Freundlich isotherm empirical equation in linear form can be written as follows:

$$\text{Log} \quad Qe = \text{Log} \quad K_F + 1/n \quad \log \quad Ce \tag{5}$$

where K_F is the Freundlich related with the bond energy and n is the degree of adsorption linearity. Freundlich's isotherm is determined from the plot of linear log Qe versus log Ce. The value n denotes the degree of nonlinearity between the concentration of the solution and the adsorption as follows: if n = 1, then linear adsorption; if n <1, then chemical adsorption process; and if n> 1, then adsorption process occurs physically.

3.1.8. Characterization of biosorbent. The FT-IR spectrum shows wave number of peaks, indicating the properties of the adsorbent. Spectra are seen at the following bands: 3424.25 cm^{-1} (OH stretching vibration), 2925.51 cm^{-1} (OH stretching vibration), 1636.91 cm^{-1} (C = O

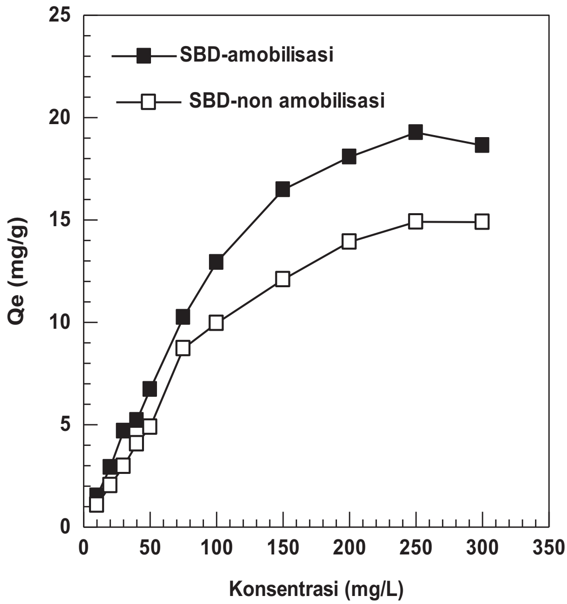

Figure 2. Effect of concentration on adsorption capacity Cd(II) (pH Cd = 5, volume solution = 20 mL, mass = 0.1 g, contact time = 45 minutes)

stretching of carboxylic acid vibration), 1420 cm^{-1} (C = C vibration stretch), and 1158, 1023.5 (COH stretching).

4. Conclusion

Durian seed was immobilized in Ca-alginate as a potential biosorbent Cd(II) ion in aqueous solution. Adsorption properties of a biosorbent are influenced by pH, concentration, contact time, and temperature of the solution. Isotherm adsorption at equilibrium fitted well in the Langmuir isotherm model with a maximum adsorption capacity of 25.05 mg/g. Adsorption kinetics followed the pseudo-second-order model. Characterization of the biosorbent with FT-IR spectra showed that functional groups involved in biosorption are carboxyl, hydroxyl, and carboxyl and amine groups. Durian seed immobilized in Ca-alginate can be a potential candidate for Cd(II) biosorption and further research is needed to study the biosorption process dynamically.

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