



Biosorption characteristics of Cd(II) ions using herbal plant of mahkota dewa (*Phaleria macrocarpa*)

Ali Napih Nasution¹, Yasherly Amrina², Rahmiana Zein², Hermansyah Aziz² and Edison Munaf^{2*}

¹Department of Tropical Medicine, Faculty of Medicine, the University of Prima Indonesia, Medan, Indonesia

²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Padang, Indonesia

ABSTRACT

The efficacy of herbal plant Mahkota Dewa (*Phaleria macrocarpa*) fruit namely seed and flesh as an alternative low cost biosorbents for the removal of Cd(II) ions from aqueous solution was investigated. Batch biosorption studies were carried out to evaluate the effects of solution of pH, initial Cd(II) ion concentration, contact time and biosorbent mass on biosorption capacity. The optimum biosorption condition was found at pH 6,0 for both seed and flesh. Initial concentration at 3,000 mg/L, contact time 30 min for flesh and 45 min for seed and 0.1 g biosorbent dose for both seed and flesh of mahkota dewa herbal plant. The biosorption data were fitted to the Langmuir isotherm. The maximum biosorption capacities (Q) estimated from Langmuir isotherm model for Cd(II) ion were 21.4592 mg/g and 24.7629 mg/g for seed and flesh of mahkota dewa, respectively. Cd(II) ion concentrations were measured by using Atomic Absorption Spectroscopy detection, while the characterisation studies were performed using Scanning Electron Microscope (SEM) and Fourier Transform Infra Red spectroscopy (FT-IR). Interaction of Cd(II) ion with the functional groups of seed and flesh of mahkota dewa led to the formation of discrete aggregates on the biosorbents surface. Indicated the Cd(II) ion bond to the active sites of the biosorbent of mahkota dewa through either electrostatics attraction.

Key words: Biosorption; Mahkotadewa (*Phaleriamacrocarpa*) fruit; Cd(II) ion; Biosorption capacity. Electrostatics interaction.

INTRODUCTION

The increasing concentration of heavy metals in water has become a major issues all over the world, because heavy metals concentration in water often exceed the admissible value. Heavy metals is a serious problem that led to some environmental problems and human health issues [1,2]. Toxic metals could contaminate surface and underground water as a life source of humans, plants, animals and aquatic biota. This causes heavy metals found in several waters, food chains, accumulate in the body and affect health [3,4]. Cadmium and other heavy metals are commonly used in various industries. Cadmium is a non-essential metal for human life and could give severe damage to health [5,6].

Biosorption is a process that provides the removal of heavy metal ions by living or dead biomass. This method has been developed for an easy, environmentally friendly and utilize agricultural waste as a low cost biosorbent [2-8]. Mahkota Dewa (*Phaleria macrocarpa*) is a traditional medicinal plants in Indonesia and used to cure various diseases [9-11], its secondary metabolites can be considered as potential candidates for heavy metal adsorption. Lots of materials have been studied as heavy metals biosorbents such as *Annona muricata* L. seeds [7,12,13], *Lansium domesticum* Corr fruit peels [14] and seeds [15], Eggshells [16], Peanut shells [17], Coconut corr [18], rice husk [19] and others.

The aim of the present work was to investigate the potential of mahkota dewa (*Phaleria macrocarpa*) herbal plant as an antidote for the cadmium toxicity to human health.

EXPERIMENTAL SECTION

Chemicals and Equipments

All chemical used in this experiment namely $ZnSO_4 \cdot 7H_2O$, $Cd(CH_3CO_2)_2 \cdot 2H_2O$, HNO_3 , $NaOH$, HCl , CH_3COOH , CH_3COONa , NH_4OH and NH_4Cl are analytical grade and obtained from E-Merck (Germany) unless other wise noted. Distilated water are obtained from laboratory made. A cruiser, Mortal grinding, pH meters, analytical balance, rotary shaker, AAS (spectraAA-240 VARIANT), Oven, FTIR (NICOLET is10), SEM were used in this experiment. Herbal plant of Mahkota Dewa fruits were collected from home garden in Padang City, West Sumatra, Indonesia.

Preparation of Biosorbent

Mahkota Dewa fruit of herbal plant was collected from home garden in Padang city, West Sumatra, Indonesia. The fruit of mahkota dewa was then washed with water and were separated between seed and flesh. Then dried at room temperature, and smoothed by using a cruiser to form powder. Powder sieved to $450 \mu m$ and soaked with 0.01 mol/L HNO_3 for two hours, filtered then rinsed with distilled water until neutral. The biosorbent were dried and ready to be used.

Batch Adsorption

Powder of seed and flesh of mahkota dewa biosorbent was entered into 10 mL solution containing Cd(II) ions, and stirred using a shaker for several minutes. The experiments were conducted by varying pH solution, initial concentration, contact time, biosorbent mass and heating temperature of biosorbent.

Data Analysis

To determine the amount of Cd(II) ion adsorbed by Mahkota Dewa seeds and flesh, the formula used is:

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

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

RESULTS AND DISCUSSION

Effect of pH solution

pH solution plays an important role in the biosorption process. This parameter affects the chemical properties of heavy metals and the ability of biosorbent to adsorb metal ions [5]. Fig.1 shows the effect of pH solution for the adsorption of Cd(II) ions by seeds and flesh of mahkota dewa fruit in the pH range 3-8.

The net charges of present on the surface of seed and flesh of biosorbent surface, greatly depend on the initial pH. This is perhaps the most important parameter influencing the effect of solution of pH on the biosorption process of Cd(II) ions. The results in Fig.1 indicate, for both seed and flesh of mahkota dewa fruit was ineffective at $pH < 3$. At the pH 3 to 6, can reasonably be ascribed to a decreased H^+ concentration in the solution and consequently increasing the number of negative charge on the biosorbent surface, This situation automatically increasing the electrostatic attraction and sorption of positively charge Cd(II) ions and then increased the amount of metals ion sorbed [20]. At the $pH > 6$ precipitation of insoluble hydroxides of Cd(II) ion was occurred in the solution. This optimum pH value = 6 was used in all the further experiments carried out to explore the effects of the other operating variable.

Effect of Initial Concentration

Kinetics of Cd(II) ion sorption onto seed and flesh of mahkota dewa fruit was investigated at different initial concentration of Cd(II) ions, ranging up to 4,000 mg/L. Adsorption capacity increased by the increasing of metal ions concentration up to 3,000 mg/L as shown in Fig. 2. Its high amount of metal ions adsorption were caused by several factors such as the collision between the metal ions with the metal surface and the ability to diffuse on the biosorbent surface. This high capacity is due to the availability of active sites on the biosorbent surface, when the number of active sites is greater than the metal ions adsorbed, the adsorption capacity will increase until the amount of the active site is equal with the number of Cd(II) ions, decreasing occurred after the equilibrium is reached [19]. High initial metal concentration accelerate the driving force and reduce the mass transfer resistance. From the results in Fig. 2, indicate that seed of biosorbent having a high sorption capacity compare with the flesh of biosorbent

Effect of contact time

Adsorption capacity of the metal ions were studied as a function of contact time for 15–120 min range. Fig. 3 shows that the optimum condition of the metal ion adsorption of Cd(II) ions by seed of mahkota dewa fruit was obtained at the contact time of 30 min and tend to decrease until 120 min, while for the flesh biosorbent obtained at the contact time of 45 min. This shows that the uptake of Cd(II) ions by seed faster than by flesh.

Effect of Biosorbent dosage

The adsorption capacity for a given initial concentration of adsorbate was defined by biosorbent dosage, which was one of significance parameters. The effect of seed and flesh dosage of mahkota dewa fruit was examined by varying dosage at the range from 0.1 to 1.0 g. The results is shown in Fig. 4. This experiment shows that the biosorbent mass which can bind maximum metal ions for both seed and flesh biosorbents are 0.1 g. The decreasing of adsorption capacity were caused by the saturation and particle interactions such as aggregation by an increasing in biosorbent mass [19].

Adsorption Isotherm

Langmuir adsorption isotherms model were studied from previous initial concentration of Cd(II) ions and shown in Fig. 5. The adsorption isotherm describes the process of adsorption of molecules distributed between solid phase and liquid phase when adsorption reached the equilibrium and used to describe the interaction between the metal ions with biosorbent [14].

The adsorption of metal ions by mahkota dewa seeds and flesh tend to follow Langmuir isotherm models with determination coefficient for Cd(II) ions is 0.9846 for seed and 0.9532 for flesh biosorbents. This indicates that the for both biosorbents, adsorption process occurs in a homogeneous surface with a monolayer adsorption. Chemical adsorption is explained by the interaction between the active adsorbent with adsorbate involving chemical bonds, so the Langmuir isotherm models explain the process of chemical biosorption [8].

However, based on the value of N in Freundlich isotherm models, it can also be said that the adsorption of both biosorbent shows physical adsorption process, because it has a value of $N > 1$. The value of N indicates the degree of non-linear between solution concentration and adsorption, where $N = 1$, is the linear adsorption, $N < 1$, adsorption through chemical processes and $N > 1$ adsorption through physical process [20].

Fourier Transform InfraRed (FTIR) spectroscopy Analysis

FTIR analysis of Mahkota Dewa seeds were shown in Fig. 6. Strong and dense ribbon at $3500\text{--}3200\text{ cm}^{-1}$ shows the OH stretch group resulted by inter and intramolecular hydrogen bonds of alcohols, phenols and carboxylic acid [21]. Adsorption band at $3000\text{--}2850\text{ cm}^{-1}$ were assigned to be of C–H stretch while C = O stretch were shown at $1760\text{--}1690\text{ cm}^{-1}$. Band at $1500\text{--}1400\text{ cm}^{-1}$ is a group of C–C stretch or C–H bend. C–O stretch functional groups and C–H rock encountered at wave number $1320\text{--}1000\text{ cm}^{-1}$. Spectrum (a), (b) and (c) shows the adsorption band shift and indicates the change of functional groups with metal ions. The results of the same study also take place at the use of metal ion adsorption by *Annona muricata* L. by M.I. Kurniawan [11].

Scanning Electron Micrograph (SEM) Analysis

The surface morphology of the biosorbents before and after Cd(II) ion adsorption by seed and flesh was observed using SEM analysis. There are significant changes to the surface morphology of the biosorbent, as well as the formation of discrete aggregates on their surface following Cd(II) ions adsorption. The SEM images of seed and flesh before and after Cd(II) ions sorption at 1,000 x magnification are shown in Fig. 7. As presented in Fig. 7 seed displayed a dense and porous surface texture then flesh. Interaction of seed with Cd(II) has resulted in the formation of flake-like deposits on its surface (Fig. 7 a, b) meanwhile, cube like deposits were observed on the surface of seed after Cd(II) ion sorption. Flesh had a smooth and dense surface texture. Interaction with Cd(II) ion changes the surface morphology of flesh texture.

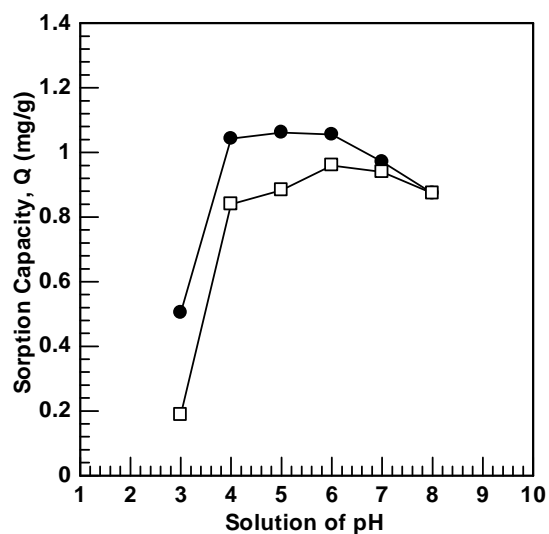


Fig. 1. Effect of solution of pH on the biosorption capacity of Cd(II) ions on seed (\square) and flesh (\bullet). Experimental condition: Initial concentration = 10 mg/L, biosorbent dose = 0.1 g, stirring speed = 200 rpm and contact time = 15 min

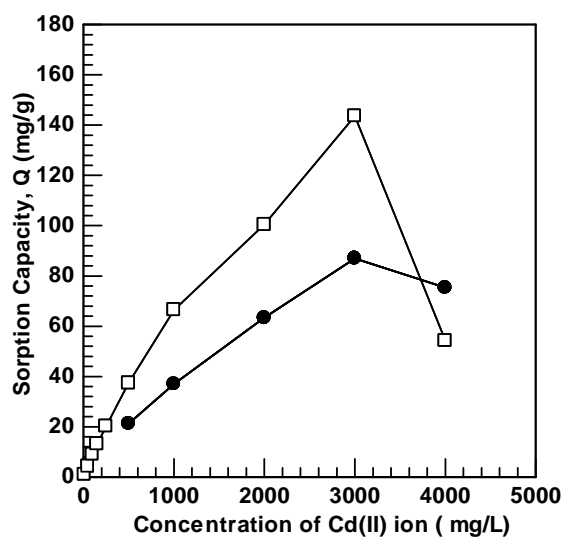


Fig. 2. Effect of initial concentration on the biosorption capacity of Cd(II) ion on seed (\square) and flesh (\bullet). Experimental condition: solution of pH = 6, biosorbent dose = 0.1 g, stirring speed = 200 rpm and contact time = 15 min

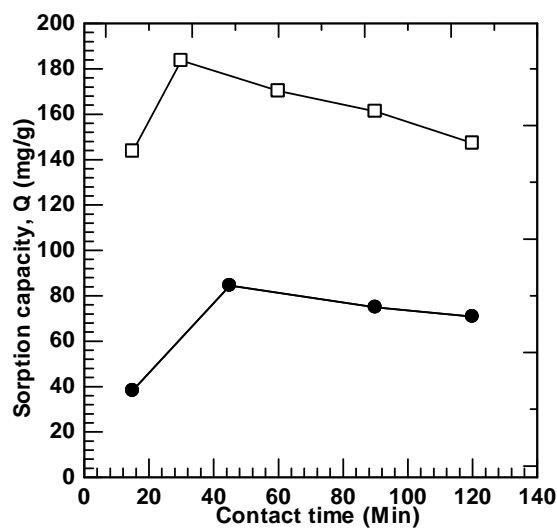


Fig. 3. Effect of contact time on the biosorption capacity of Cd(II) ion on seed (□) and flesh (●). Experimental condition: Cd(II) ion concentration = 3000 mg/L, solution of pH solution = 6, biosorbent dose = 0.1 g and stirring speed = 200 rpm

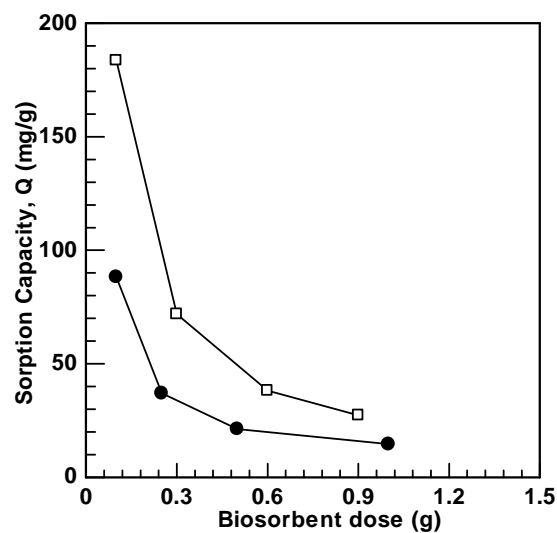


Fig. 4. Effect of biosorbent dose on the biosorption capacity of Cd(II) ion on seed (□) and flesh (●). Experimental condition: solution of pH = 6, initial concentration = 3000 mg/L and contact time = 30 min

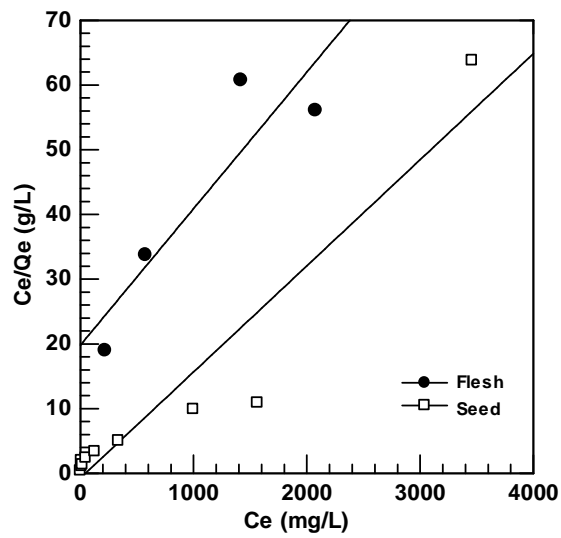


Fig. 5. Langmuir isotherm model for Cd ion biosorption on on seed (□) and flesh (●)

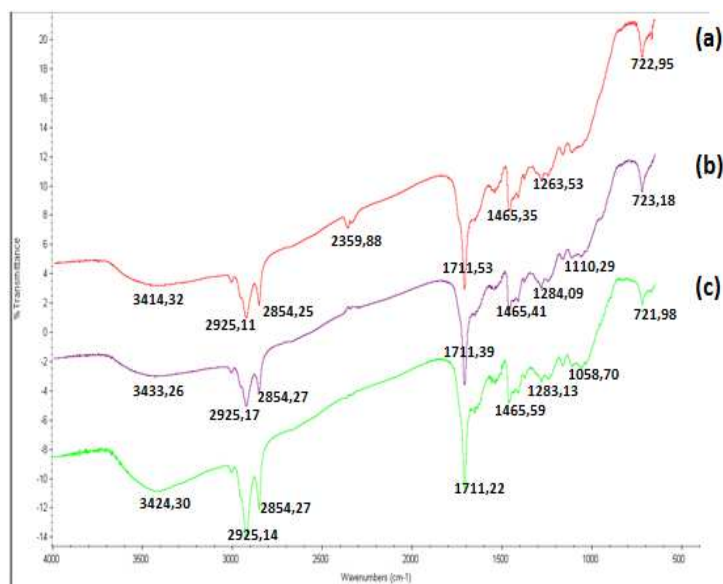


Fig. 6. FT-IR spectrum of Mahkota dewa seed powder

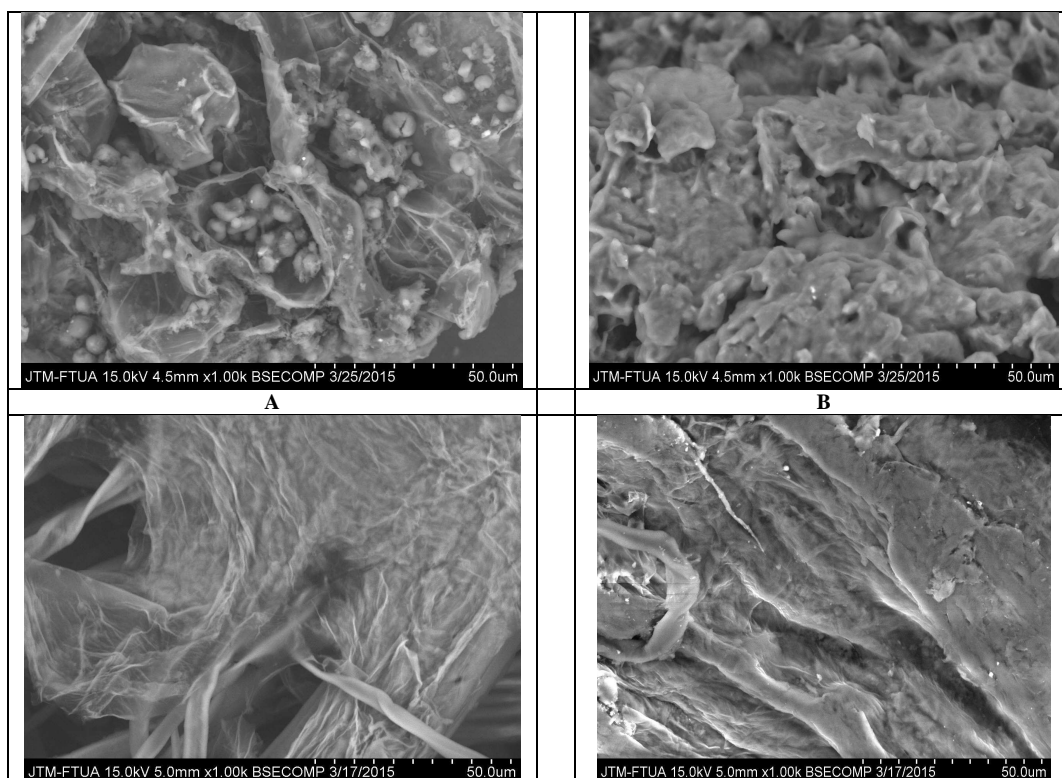


Fig. 7. Scanning electron microscope of seed (above) and flesh (below) of *Phaleria macrocarpa* before (A) and after Cd ion sorption. Magnification 1,000 times

CONCLUSION

Based on this research, it can be conclude that, the herbal plant of mahkota dewa fruit either seed and flesh can be used to adsorp Cd(II) ion present in sample either in water and organ sample. Therefore it is a potential herbal plant to adsorp Cd(II) ion in case of Cd(II) ions present in molecular of animal organ.

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