The Feasibility Study of Brown Marine Algae toward Cadmium Ions as a Low Cost Biosorbent

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***Abstract*—The adsorption study on removal of cadmium ions from aqueous solution by modified brown marine algae namely Padina sp. was performed under batch experimental conditions. The effect of initial concentration of metal ion solution, contact time, and biosorbent dosage has been investigated using the batch adsorption technique. The data obtained were used to analyzed by using pseudo-first order and pseudo-second order model. The result show that pseudo-second order obey the assumptions. The optimum removal of cadmium ions by initial concentration of 50 ppm. While 60 minutes contact time of biosorbent was resulting maximum adsorption of cadmium ions with 1.0 g dosage of biosorbent under 150 rpm of agitation speed.**

***Index Terms*—cadmium, brown algae, *Padina* sp., biosorbent, biosorption, heavy metal, kinetic studies**

I. Introduction

Cadmium is an element naturally presence in the earth and also come from electroplating, smelting, alloy manufacturing, plastic, mining and refining industries [1]. It is highly toxic and easily accumulates in the environment [2]. The presence of excess cadmium may have an adverse effect to human health by accumulating in food chain as well as bringing up harmful effects to the flora and fauna [3]. Therefore, it is crucial to remove the cadmium that exists in the environment.

Biosorbent is one of techniques that use to remove heavy metal from the polluted area. This technique is based on the affinity between biosorbent and the sorbate. Biosorbent have low cost, environmental friendly, high efficiency to remove heavy metals, easy to handle and gaining interest due to relative abundance [4].

Previously, brown marine algae such as *Sargassum* sp., *Laminaria* sp. and *Fucus vesiculosus* were widely used in removing metal ions [5]-[10]. The present study was used *Padina* sp. as a potential biosorbent to remove cadmium. The adsorption process was investigated as function of biosorbent initial concentration, contact time and dosage.

II. Experimental

A. Preparation of Biosorbent

The dried brown macro algae *Padina* sp. was washed with tap water repeatedly for removing undesired materials. Then, it was placed in an oven over night at 60 ℃. Next, the biomaterial *Padina* sp. was ground and sieved between 150-250 μm sizes. 1% NaCl solution was prepared and 50 g of dried *Padina* sp. was immersed into the solution. The function of NaCl solution is to remove dirty from the biomaterial. After that, it was washed with deionized water until neutral pH and dried. 100 mL poly (allyamine hydrochloride) (PAA/HCl) solution was added into 1 g of biomaterial *Padina* sp. Then, 1 mL of epichlorohydrin (ECH) was mixed with PAA/HCl-treated biomaterial and the mixture was stirred. NaOH was used to neutralize the portion of HCl groups of PAA/HCl to provide free NH_2 sites for the ECH cross-linking. After that, the slurry of biomaterial-ECH-PAA/HCl are centrifuged to separate liquid and solid and then washed with distilled water for several time. Then, it was dried and stored for the future used. The purpose of this method is to modified the surface of biomaterial to encourage more functional group exist on the surface. Thus, it was inceased the uptake of metal ions by biosorbent.

B. Metal Solution

Metal solution standard supplied by Perkin Elmer was diluted with mili-Q water at desired concentration and pH of the solution was measured and recorded.

C. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The verification vibration frequency of the functional groups on the surface of the treated biomaterial *Padina* sp. was performed by FTIR analysis.

D. Batch Biosorption Studies

Metal ions solution was mixed with biosorbent and the adsorption capacity of metal ions was studied. The concentration of cadmium before and after adsorption was measured by using Inductive Couple Plasma Microscopy (ICP-MS) supplied by Perkin Elmer. The variables used in the study are initial concentration, contact time and biosorbent dosage. The biosorption percent of cadmium ions was calculated by using formula below:

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$$q_e = \frac{c_i - c_f}{m} V \quad (1)$$

$$\% \, Adsorption = \frac{c_i - c_f}{c_i} \times 100 \quad (2)$$

where; q_e is metal uptake at equilibrium, V is volume, m is the amount of biosorbent, C_i and C_f are metal ions for initial and final concentration respectively.

III. Result and Discussion

A. FTIR Analysis

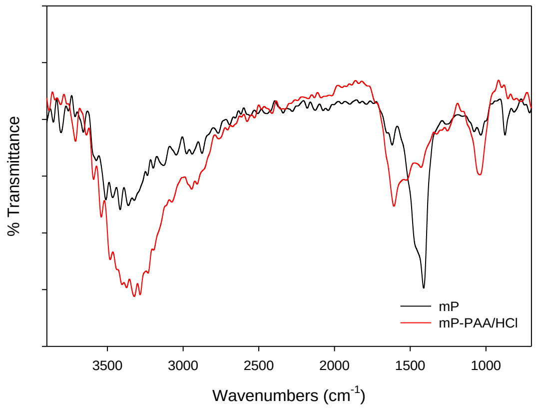

Figure 1. FTIR analysis of *Padina* sp. after chemical treatment with PAA/HCl

The verification vibration frequency of the functional groups on the surface of the biosorbent was performed by FTIR analysis and the spectra were registered at range 4000 cm^{-1} to 400 cm^{-1}

From the Fig. 1, the strong, high intensity and broad peak of *Padina* sp. modified with PAA/HCl (mP-PAA/HCl) was observed at 3322.78 cm^{-1}. These peaks were produced due to the reaction of PAA/HCl on the algae. Besides that, N-H group also seen at the region of 1607.52 cm^{-1} and it was confirmed that PAA/HCl has encouraged more O-H and N-H group presence on the surface of algae. Thus, it increases the number of active site for metal binding. The peak at 2943.68 cm^{-1} could be assigned to the C-H stretch and 1040.11 cm^{-1} is corresponding to the C-N. The functional groups recommended here were established with those reported in other studies on infrared spectra of biomaterial [7], [11], [12].

B. Influence of Initial Concentration

Fig. 2 shows the influence of initial concentration toward adsorption of cadmium ions. The initial concentration was varied from 1 ppm to 100 ppm. While pH, contact time, dosage and agitation speed are constant. The experimental data indicates that increase the initial concentrations of solution were increased the adsorption capacity of biosorbent and it is become constant at 100 ppm of initial concentration as illustrated in Fig. 2. This phenomenon is due to the driving force which occurred because of the huge different concentration of cadmium ions and biosorbent. Therefore, as the concentrations increase the mass transfer resistance would be decrease between cadmium ions and biosorbent. Similar results have been reported by other studies [7], [11], [13]-[15].

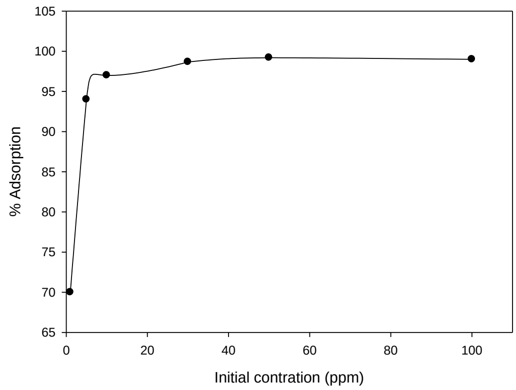

Figure 2. Influence of initial concentration on the adsorption of cadmium at constant pH (6), contact time (60 minutes), dosage (0.3 g) and agitation speed (150 rpm)

C. Influence of Contact Time

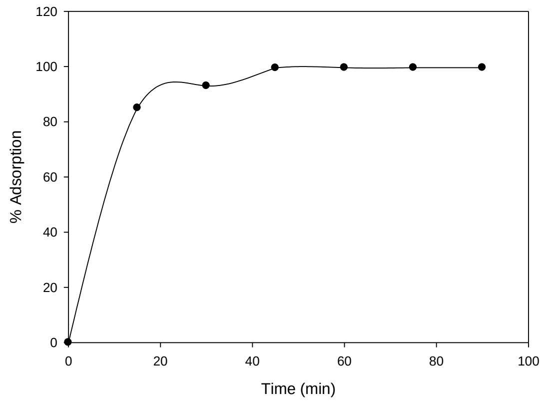

Figure 3. Influence of contact time at constant pH (6), initial concentration (50ppm), dosage (0.3g) and agitation speed (150 rpm).

The study of contact time was investigated in order to determine the adsorption capacity of cadmium ions onto biosorbent. From the Fig. 3, the graph was showed the adsorption between biosorbent and cadmium ions occurred rapidly with 15 minutes of contact time. The phenomenon happened because at the initial of contact time, the active sites are open for cadmium attached. At this time, cadmium ions is compete each other for the active sites of biosorbent and it was resulting the adsorption rate is faster. Then, the rate of adsorption becomes slower and finally no more adsorption of biosorbent is noted beyond 60 minutes of contact time. It is because the active sites were mostly occupied by cadmium ions and then become saturated. Thus, it was preventing for further adsorption of cadmium ions. This trend was related with others study on the adsorption of metal ions by green algae waste biomass, *Bael* tree leaf and brown algae [6], [16], [17].

D. Influence of Dosage

The influence of biosorbent dosage onto adsorption was studied by varying 0.1 g to 1.0 g of biosorbent. The removal by percent of cadmium ions as function of adsorbent dosage was shown in Fig. 4. Percent adsorption increased as the increases of dosage from 0.1 g to 1.0 g. This is because larger dosage of biosorbent could be provides greater surface area and automatically would increase the number of active sites. Thus, it is enhancing the adsorption of cadmium ions due to more active sites is available to attach. The others studies have been reported the related result [11], [13], [18], [19].

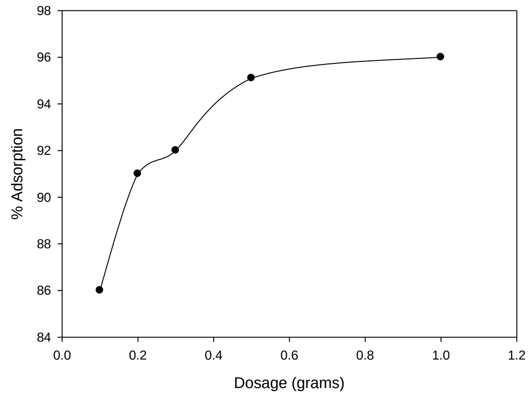

Figure 4. Influence of biosorbent dosage at constant pH (6), initial concentration (50 ppm), contact time (60 minutes) and agitation speed (150 rpm).

E. *Kinetic Modeling*

In order to investigate the mechanism occurred on the biosorbent, pseudo first order and pseudo second order were tested to fit the kinetics experimental data.

The sorption kinetics may be described by a pseudo-first order equation. The differential equation is the following;

$$\left(\frac{d_q}{d_t}\right) = k_1(q_e - q) \tag{3}$$

Linear form of equation (3):

$$log(q_e - q_t) = log\, q_e - \frac{k_1}{2.303}\, t \tag{4}$$

where q_e and q_t are the amount of metal ions adsorbed at equilibrium and at time t respectively and k_1 is the rate constant of the pseudo first order adsorption process (min-1).

The adsorption kinetics may also be described by a pseudo-second order equation. The differential equation is the following:

$$\left(\frac{d_q}{d_t}\right) = k_2\,(q_e - q)^2 \tag{5}$$

Linearized form of equation (5):

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}\, t \tag{6}$$

where q_e and q_t are the amount of metal ions adsorbed at equilibrium and at time t respectively and k_2 is the rate constant of the pseudo second order adsorption process (min^{-1}).

k_1 and k_2 are represent constant equilibrium for both pseudo-first and pseudo-second respectively. R^2 is correlation coefficient which is summarized together with constant equilibrium in Table I. Values in Table I are obtained from the linear plot of log (q_e-q_t) vs t and of t/q_t vs t for pseudo-first order and pseudo-second order as parameter respectively.

Pseudo-second order kinetic model has higher correlation coefficient to be compared with pseudo-first order kinetic model and the value of calculated q_e from pseudo-second order close to q_e experimental value. Therefore, this model is better in describing the kinetic of biosorbent for this study.

The pseudo-second order kinetic model is based on the assumptions of chemical interaction between functional groups of biosorbent and cadmium ions, the rate controlling step in the biosorption process and identical characterization have been reported for a few types of algae biosorbent [7], [17].

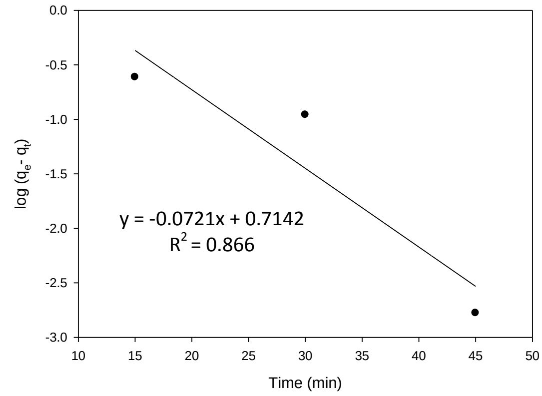

Figure 5. Pseudo-first order for the adsorption of cadmium ions onto biosorbent at room temperature and pH 6.

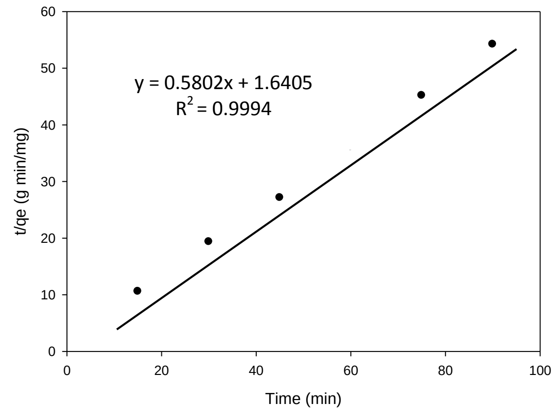

Figure 6. Pseudo-second order for the adsorption of cadmium onto biosorbent at room temperature and pH 6.

TABLE I. PSEUDO-FISRT AND PSEUDO–SECOND OF RATE CONSTANT AND EQULIBRIUM FOR CADMIUM IONS BY BIOSORBENT

q_e experimental		1.4167
Pseudo-first order	k_1	0.1660
	q_e calculated	5.1780
	R^2	0.8660
Pseudo-second order	k_2	0.2052
	q_e calculated	1.7235
	R^2	0.9994

IV. CONCLUSION

This study exhibits the operating variables that affect the adsorption of cadmium ions in the aqueous solution. The optimum adsorption at initial concentration of 50 ppm is due to the highest driving forces that overcome the mass transfer resistance. The maximum adsorption at 60 minutes was the best duration for this study. Besides that, the data obtained used to describe the pseudo-first second order and pseudo-second order. Pseudo-second obey all the assumption and has better correlation coefficient with 0.9994. Biosorbent dosage is proportional to the number of active sites and it has a great influence on adsorption process. As a conclusion, the present study revealed that the *Padina* sp. was result a great potential to remove cadmium ions.

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