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Biosorption of copper ions from aqueous solution using *Kappaphycus striatum*

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Abstract. Biosorption is an eco-friendly alternative technology for the removal of heavy metals from industrial waste and effluents using low-cost and effective biosorbent. Abundant of natural materials like agricultural biomass, industrial waste, and microbial biomass can be used as a promising biosorbent. In the present study, red algae *Kappaphycus striatum* biomass will be used for the adsorption of copper ions in aqueous solution. The free (non-immobilized) and immobilized form of red algae *Kappaphycus striatum* biomass and biosorption rate were investigated for the adsorption process. The maximum biosorption of copper ions was achieved when immobilized form of algae biomass were used at the condition pH of 5, biomass dosage, 0.25 g/L, contact time of 90 minutes, and at the temperature of 50 ℃ with a 65.8% of removal. The experiment data for biosorption rate with time also was used to evaluated two kinetic models (pseudo-first-order and pseudo-second-order) and two isotherm models (Langmuir and Freundlich). The results reveal that metallic ions biosorption on the immobilized *Kappaphycus striatum* followed the pseudo-second-order kinetic model with a $R^2=0.9996$ and Langmuir isotherm model with a $R^2=0.9999$. The present work shows that the red algae of *Kappaphycus striatum* as a potential biosorbent for the removal of heavy metal ions from aqueous solution.

1. Introduction

Wastewater can be classified into three types, municipal wastewater, sewage, and industrial wastewater. Industrial wastewater has gained paramount consideration among all the wastewater, as it may consist of a huge amount of poisonous substance and heavy metal. Heavy metal can enter the human body through food, water, air, or skin absorption and it can be toxic to humans if they are not metabolized by the human body. The natural environmental and human activities are the two major sources of heavy metals present in wastewater. The natural reasons involve volcanic eruption, soil erosion, and particulate aerosols, while human factors involve metal grinding, electroplating, and manufacturing factories [1].

Techniques that are widely used for sequestration of heavy metals from industrial wastewater are involving ion-exchange, coagulation-flocculation, adsorption, and precipitation. However, these methods are usually expensive and inappropriate for treating highly diluted solutions [2]. The

biosorption process has been regarded as a promising suitable, eco-friendly, and cost-effective method for removing pollutants from wastewater which utilized dead biomass. Besides, this process provides several advantages compared with conventional methods. The abundant nutrient demand, supply, high sorption capability lower amount of sludge to be disposed of, large surface area to pore depth, and the potential for metal regeneration and recovery, has made the researchers to focused on the use of algae as a biosorbent [3]. The *K. striatum* red algae are one of the most important economic sources of carrageenan and it also has numerous therapeutic and industrial uses [4]. The amount of production for red algae *K.striatum* was reported 10,493,540 tons in the year 2016 from Asia (Philippine, Malaysia, and Indonesia)[5]. This abundant amount of red algae available has made a new interest to become as a promising biosorbent for the adsorption of heavy metals from industrial effluent.

A recent study has suggested that immobilized form biomass in alginate form can removed a lot of heavy metal from aqueous solution. They have observed that immobilization enhanced the biosorption ability and enable it to re-used [6][7]. However, there is a limited literature report on the effectiveness of immobilized red algae *K.striatum* in removing heavy metal from aqueous solution. Thus, the research aimed to identify the performance of both free cells (non-immobilized) and immobilized cells in the adsorption of heavy metal from aqueous solution. The kinetic and isotherm models were carried out by biosorption rate with time.

2. Methodology

2.1 Preparation of aqueous solution
Copper stock solution with 100 %(w/v) concentration was prepared by dissolving 3.93 g of copper (II) sulfate pentahydrate in 1 L of distilled water. The solution was prepared by using a volumetric flask. The 100 %(w/v) of the working solution was prepared by diluting the copper stock solution with distilled water.

2.2 Immobilization of red algae K.striatum
3% (w/v) sodium alginate was prepared and mixed with 0.25 g of dry algae. The alginate alga mixture was then introduced into a 3% (w/v) calcium chloride ($CaCl_2$) solution by using a syringe. The alginate beads were formed and stirred together with the magnetic stirrer at 3500 rpm and leave for 1 hour. Then removed the alginate bead from the calcium chloride solution and wash with distilled water to remove the remaining $CaCl_2$. The beads were dried by using filtered paper and left it to expose to the air for 30 minutes [6].

2.3 Biosorption experiment procedure
The biosorption experiments have identified the effectiveness of free cell (non-immobilized) and immobilized algae with sodium alginate in removing copper ions from aqueous solution. The best fit of kinetic and isotherm was be defined by biosorption rate with time. The experiment was undergoing in optimum condition, which the solution in pH 5 and a 50 ℃ operated on the shaker with 250 rpm for 90 minutes.

2.3.1 Biosorption of kinetic and isotherm models.
Adding 0.25g of algae biomass with immobilized by alginate into Erlenmeyer flask containing 100 ml of the 100 %(w/v) of working copper solution with a pH 5. Then put the solution into an incubator shaker with the temperature 50 ℃ and 250 rpm for 100 minutes. The 5 ml sample was collected every 10 minutes. The experiment data were fit to the equation for both kinetic model (Pseudo-first-order and Pseudo-second-order) and isotherm model (Langmuir and Freundlich) as shown in Table 1.

The biosorption capacity (q_e) and heavy metal removal in percentage were calculated by using equation (1) and equation (2) respectively [8][9].

$$q_e = \frac{(C_i - C_f)}{m} \times v \qquad (1)$$

$$\text{Metal removal, R (\%)} = \frac{c_i - c_f}{c_i} \times 100\% \qquad (2)$$

where C_i and C_f (mg/g) is the concentration of a metal ion in aqueous solution at initial and after adsorption respectively, m is the mass of biosorbent used in the process (g) and V (L) is the volume of metal solution used.

Table 1. Equation of the kinetic model and isotherm model used in the study

Model	Equation	Reference
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - \dfrac{K_1}{2.303}.t$	[10]
Pseudo-second-order	$\dfrac{t}{q_t} = \dfrac{1}{K_2.q_e^2} + \dfrac{t}{q_e}$	[6]
Langmuir	$\dfrac{C_e}{q_e} = \dfrac{1}{q_{max}K_L} + \dfrac{1}{q_{max}}C_e$	[11]
Freundlich	$\log q_e = \log K_F + \dfrac{1}{n}\log C_e$	[12]

3. Result and discussion

3.1 Effectiveness of free cell and immobilized algae

The result indicates that the treatment of aqueous solution containing copper ions with immobilized *K. striatum* in sodium alginate beads removal 65.8% of copper ions at an initial concentration of 100 mg/L for 90 minutes, which is significantly higher than the removal presented using free cell biomass in only 25.38%. Figure 1 shows the percentage of biosorption of copper ions using free-cell and immobilized *K. striatum* biosorbent.

The technique used to immobilize biosorbent in this study is entrapment with sodium alginate. Entrapment refers to capture biosorbent within a polymeric matrix to strengthen the cell wall of biosorbent from a high shaking rate (250 rpm) in the biosorption process. The polymeric matrices allow the copper ions to pass through and reached the binding site of biosorbent on the cell wall [13]. The behavior of immobilization biosrobent is more effective in biosorption of heavy metal compared to the free cell as the immobilized are more stable in biosorption process and permeable for copper ions to the binding site of biosorbent [14]. Similar results have been reported by other researchers [6][7][15] for biosorption of different metal ions onto different biosorbents used.
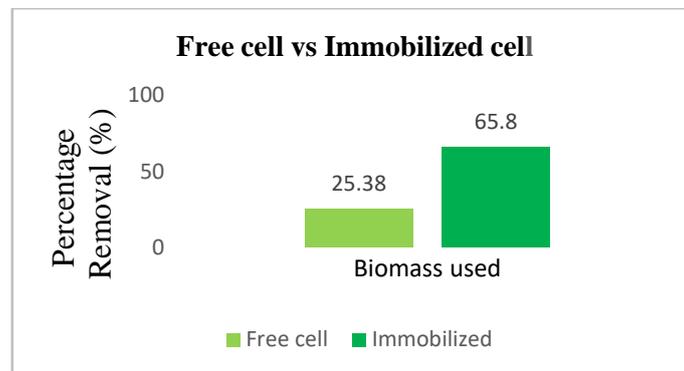
Figure 1. Comparison of the effectiveness of free cell and immobilized cells in copper ions removal.

3.2 Biosorption rate with time

The biosorption rate of copper ions on the immobilized *K.striatum* biomass was obtained by the decrease in the concentration of a metallic ion in the copper solution with time. As shown in Figure 2, the biosorption rate of copper ions was rapid initially, this is because most of the metal-binding sites are vacant and available for metal ion biosorption. The equilibrium was achieved after 60 minutes. It has indicated that the biosorption process became slow during the later stage. This is happened because during the initial stage of biosorption process a large quantity of unmanned binding sites was available for the copper ions to compare to that in the later stages when the rest of the vacancies binding site were inaccessible in the cell membranes due to the saturation point of biosorption. The maximum uptake of copper ions was reached up to 66.33% in 100 minutes. The result has the same agreement with the previous studies by [16] on the biosorption of heavy metal using *K.striatum.*
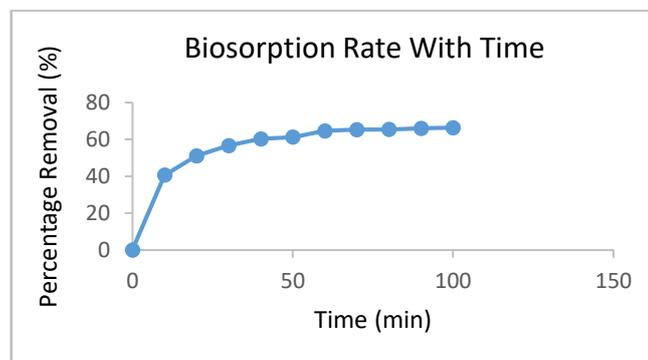
Figure 2. Percentage of removal of copper ions with time.

3.3 Kinetic model

The mechanism of biosorption includes processes such as pore diffusion, mass transfer, and chemical reaction. To define the behaviour of the mechanism, the experimental data were fit to both pseudo-first-order and pseudo-second-order. Data on contact time effect on the number of copper ions absorbed were used in this study. The pseudo-first-order is used to predict the sorption kinetics, while the pseudo-second-order is used to analyze the rate of metal sorption uptake [17]. The best-suited model was defined based on the linear regression correlation coefficient (R^2) as well as compared the value of equilibrium from experiment and calculation.

3.3.1 Pseudo-First-Order. To analyze the mechanism of biosorption process, the experiment data at optimum conditions were fitted to the equation of the pseudo-first-order kinetic model. From the calculation, as shown in Table 2, the pseudo-first-order model did not suit the experimental data satisfactorily. The difference between the experimental value of adsorption equilibrium, $q_{e,exp}$ 2.8360, were higher than the calculated adsorption equilibrium, $q_{e, calc}$ 2.2208. As shown in Figure 3, the plot of log $(q_e - q_t)$ versus t was a non-linear dependency. Thus, it is also proposed that the pseudo-first-order model is inadequate to describe the kinetic sorption of the experimental metal ions on dried biomass of *K. striatum.* A similar result was reported by [17], biosorption of Co^{2+} on *E. spinosum.*

3.3.2 Pseudo-second-order. The value of the correlation coefficient for the pseudo-second-order model was the highest ($R^2 > 0.99$) from the plot compared to the pseudo-first-order model as shown in Figure 4. The qe, $_{calc}$ value calculated from the model are close to the value of $q_{e,exp}$ as shown in Table 2. The rate constant, k_2 for pseudo-second-order is referred to as the rate constant of adsorption and it was determined as 0.0386 from the model. The half-adsorption time, $t_{1/2}$ (min) specified as the time needed for the adsorption to take up a half amount of the equilibrium metal ions was found in 8.1399 suggesting a strong affinity between the adsorbate and adsorbent molecules [16]. Base on the calculation and graph, it can be concluded that the experimental data was the best fit for the pseudo-second models. The results indicate that the biosorption mechanism is a process of chemisorption involving the exchange or sharing of electrons between metal ions and various functional groups in the biosorbent [16]. The result has the same agreement with [10].
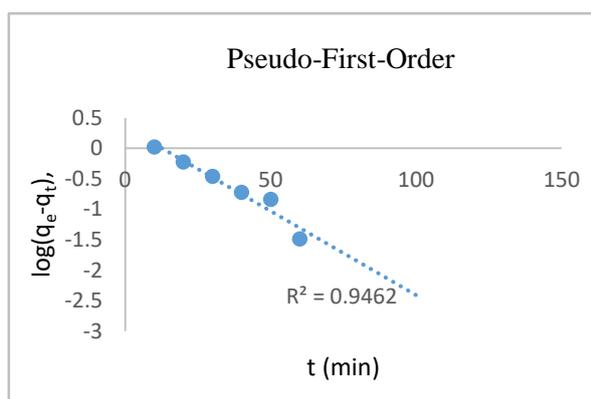
Figure 3. Pseudo-first-order model for the copper ions biosorption onto *K.striatum.*
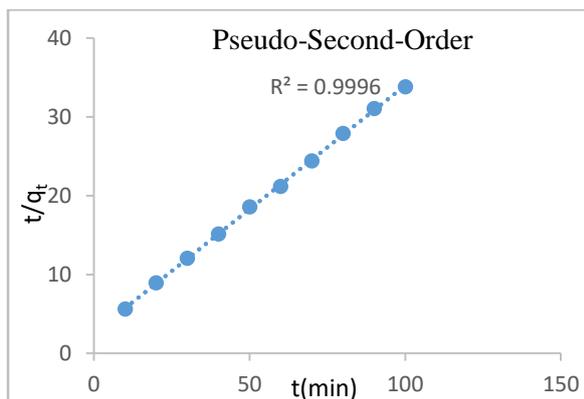
Figure 4. Pseudo-second order model for copper ions biosorption onto *K.striatum.*

Table 2. Kinetic model parameters for the copper ions biosorption onto *K.striatum*

Model	Parameter	
	$q_{e,exp}$ (mg/g)	2.8360
Pseudo-first order	K_1 (min)	0.0636
	$q_{e,calc}$ (mg/g)	2.2208
	R^2	0.9462
Pseudo-second order	K_2 (g/mg.min)	0.0386
	$q_{e,calc}$ (mg/g)	3.1827
	$t_{1/2}$ (min)	8.1399
	R^2	0.9996

3.4 Isotherm model

The adsorption isotherm is the essential requirement for the design and optimizes the biosorption process. Freundlich and Langmuir adsorption isotherms are the most widely used isotherm for the adsorption process. The data from isotherms can be used to compare the biosorptive capacities of the biosorbent for different pollutants.

3.4.1 Langmuir isotherm model. The empirical model predicts the maximum capacity of biosorption corresponding to complete monolayer coverage on the biomass surface with a homogeneous distribution of a sorbate binding site [18]. Langmuir model can be used to determine the capacity of maximum biosorption (q_{max}) and affinity (K_L) value from the intercept and slope of the linear equation.

The parameter of model isotherm and the regression coefficient is represented in Table 3. The plot of c_e/q_e versus c_e is shown in Figure 5. The maximum adsorption capacity of sorbent, q_m for the copper ions is 2.8090 and the Langmuir isotherm constant, K_L, is 0.0413. This may be due to carboxylate polysaccharides in algae that exhibit preferential cation binding with broad ionic radii for the copper ion is 1.190. This has the same agreement with [16], the higher the electronegativity of the ions the stronger the attraction for their electrons, and the greater the attraction to the negative charge of the biomass ligands. The result indicates that the Langmuir isotherm model with $R^2 = 0.99$ was very well to define for biosorption process.

3.4.2 Freundlich isotherm model. Freundlich isotherm applies to the biosorption process that occurs on the multilayer (heterogeneous surface) of the active site in biosorbent [19]. The strength of biosorption and the degree of heterogeneity can be determined by calculated n-value from Freundlich isotherm [18]. The larger n (n>1) value indicates the metal ions and heterogeneity of biomass surface are favourable and intensively biosorbed by the dried biomass under experimental conditions.

Figure 6 shown the plot of log q_e versus log C_f. The constant K_F is indicated the capacity of adsorption copper ions by biosorbent. The value of n and K_F for *K. striatum* are 1.2299 (n>1) and 8.5684 respectively, it is illustrated that copper ions are favourable to the heterogenous *K. striatum* surface under experimental condition. However, the values of the correlation coefficients (R^2) obtained from

the Freundlich isotherm model are lower than those obtained for the Langmuir isotherm model as shown in Table 3, which suggests that the Freundlich model is not adequate to describe the process of biosorption of Cu^{2+} on red algae waste biomass. The results have the same agreement with [20] for the biosorption cadmium using *U.lactuca.*
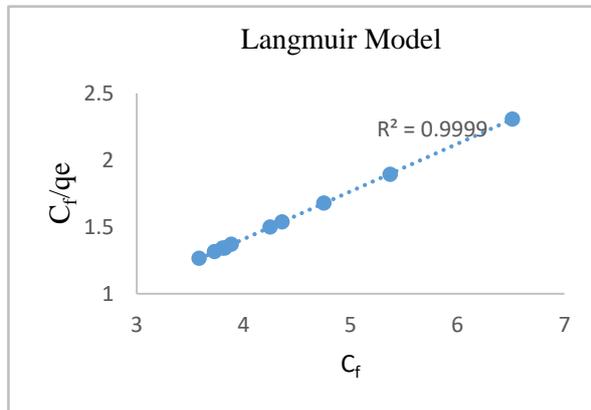
Figure 5. Langmuir isotherm model for copper ions biosorption onto *K. striatum*.
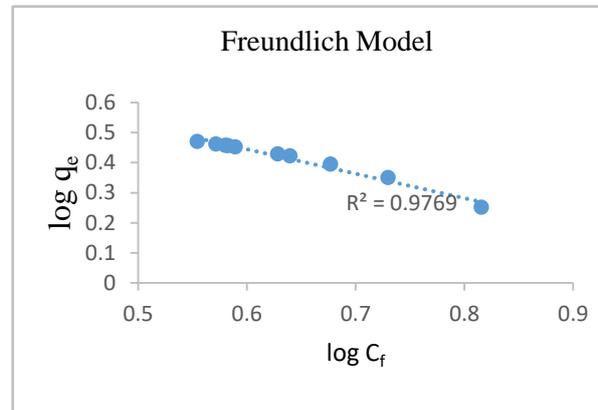
Figure 6. Freundlich model for copper ions biosorption onto *K.striatum*

Table 3. Biosorption isotherm model parameters for the copper ions biosorption onto *K.striatum*

Model	Parameter	
Langmuir isotherm	Q_m (mg/g)	2.8090
	K_L (L/mg)	0.0413
	R^2	0.9999
Freundlich isotherm	K_F (mg/g)(L/mg)$^{1/n}$	8.5684
	N	1.2299
	R^2	0.9769

3.5 Fourier Transform Infra-red Spectroscopy (FT-IR) Analysis

The FTIR spectra of pure *K. striatum* biomass was contrasted with spectra of immobilized algal biomass before and after biosorption, to identify and describe any detectable variations related to the interaction of metallic ions with a functional group. The literature has suggested the functional group presented in the cell wall of algae are carboxyl-, hydroxyl-, amino, and sulfate group. The spectra for the FTIR were taken in between 400-4000 cm^{-1} as shown in Figure 7.

The strong board peak observed in raw biosorbent at peak 3438.2 cm^{-1} corresponds to the O-H stretching band from cellulose and N-H stretching bond from protein in the algae [9]. This band was shifted to a lower peak before and after the immobilization of biosorption. The peak at 2919.7 cm^{-1} from raw biosorbent corresponds to medium C-H stretching bond vibrations of aliphatic groups. It is shifted

to the lower wavenumber when biosorbent was immobilized and after biosorption. It is defined that the aliphatic group was responsible for the copper ions adsorption.

The two strong peaks at 1650 cm^{-1} and 1267.7 cm^{-1} from raw biosorbent can refer to strong C=O stretching bond and C-O stretching bond vibrations to the carboxylate group. These peaks change dramatically before and after immobilization of biosorbent for metal binding, it indicates that carboxylic groups played a major role in the biosorption of heavy metal through complexation mechanism [21]. Absorbance peaks lead to S-O stretching bands of sulfonate groups at 928.65 cm^{-1} and 848.88 cm^{-1}. These bands were dropped dramatically and disappeared before and after immobilization of biosorbent for metal binding, which was characteristic of the complexation of sulfonate groups through dative interaction of experimental metal ions [22].
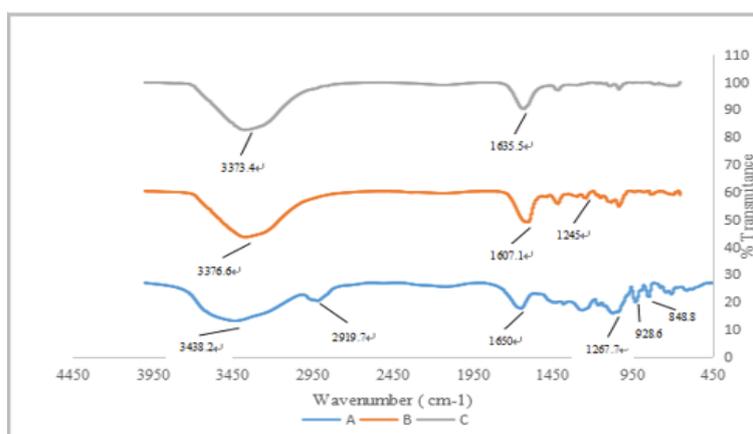
Figure 7. FTIR spectra of *K.striatum* biosorbent for (A) raw biosorbent, (B) immobilization biosorbent before adsorption, and (C) immobilization of biosorbent after adsorption.

4.   Conclusion

This research is implemented to compare the performance of free cells and immobilized *K. striatum* in biosorption process and studied the kinetic and isotherm models. Free cell and sodium alginate immobilized dried algae biomass of *K. striatum* have been effectively been shown to be potentially useful for copper ions biosorption from aqueous solution. The result indicates that immobilized algae biomass in alginate beads may increase the biosorption of metal ions compared to the free cell of biomass. *K. striatum* for kinetic reaction shows that the data matched well with the pseudo-second-order kinetic model implying the chemosorption mechanism. The Langmuir model gives the best fit to the biosorption equilibrium results, indicating that the biosorption mechanism occurs in a homogeneous surface-active site. The FTIR analysis showed the involvement of carboxylic, sulfonate, and aliphatic groups in the biomass cell wall matrix responsible for the absorption of metal ions.

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