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Egypt. J. Chem. **Vol. 64**, No10, pp. 5437- 5442 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Biosorption of Copper (II) Ion from Aqueous Solution Using Algae Biomass *Oscillatoria sp.*

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Abstract

Biosorption is the method of removing heavy metal from the aqueous solution. *Oscillatoria sp* microalgae were used to adsorb copper ion in this study. The maximum biosorption capacity was obtained 4.9 mg/g at pH of 9 with an efficiency of 99%. The algae dosage in 0.1 g gave the maximum capacity of 12.33 mg/g. The maximum contact time occurred at 60 minutes with an adsorption capacity of 19.87 mg/g. Adsorption Cu^{2+} by microalgae *Oscillatoria sp* followed by the Langmuir and Freundlich isotherms. According to the Langmuir models the value of q_m is 217.39 mg/g , K_L = 8.8 x10^{-4} L/mg, and R^2 = 0.9999. The Freundlich model showed the coefficient correlation R^2 = 1, 1/n = 1.0162, and Kf = 5.39. The model of pseudo-second-order with q_e = 4.98 mg/g, k_2 = 81.38 g mg^{-1} h^{-1}, and R^2 = 1.

Key words: Biosorption, Cu^{2+}, isotherms adsorption, *Oscillatoria sp*

1. Introduction

Water pollution is an important problem in environment because the presence chemical compounds can change the quality of the aquatic system. Heavy metals are inorganic pollutants that can accumulate in organisms because they are non-biodegradable. Heavy metal such as copper can pollute the environment. Copper toxicity may cause anemia, intravascular hemolytic, and diarrhea [1]. The removal of copper is important issue to protect against environmental damage. There are several methods for the removal of copper from the aquatic environment such as precipitation, adsorption, reverse osmosis, ion exchange, [2-5], membrane filtration, ultrafiltration, and electrocoagulation [6-9].

The new technology to eliminate Cu from aqueous solution by using biosorption process. Biosorption can involve the mechanism of physical adsorption, chemical adsorption, and ion exchange. Biosorption is a passive process that occurs at a faster rate than bioaccumulation [10]. The component in the cell wall of algae is very important in the biosorption process because it has groups of carbonyl, sulfate, and hydroxyl [11,12]. Microalgae biosorption has advantages such as cultivation is easier, safe, cheaper, has a higher production yield, higher efficiency, and specific biosorption area [13,14]. There are some research reports of the copper biosorption by algae biomass such as *Sargassum sp* [15-17], *Cytoseira Indica* [18], *Chlamydomonas reinhardtii* [19], *Gracilaria corticate* [20], and *Ulva lactuca* [21,22].

This experiment will study is to the removal of copper using algae biomass of *Oscillatoria sp*. Adsorption variation include of pH, weight of adsorbent, initial concentration and incubation time. The kinetic models, isotherm Langmuir and Freundlich models were studied in this paper.

2. Materials and Methods

2.1. Chemical and reagents

The reagents used in this experiment was $CuSO_4$. 5 H_2O p.a (Merck), M HCl with concentration of 0.1M, and NaOH with concentration of 0.1M.

2.2. Prepared the material

This experiment uses microalgae *Oscillatoria sp*. The cell is well grown at 25°C under fluorescent

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Receive Date: 24 December 2020, Revise Date: 15 May 2021, Accept Date: 22 May 2021

DOI: 10.21608/EJCHEM.2021.54959.3148

light intensity at pH 8. The harvested in exponential phase after 14 days of growth by centrifuged at 6000 rpm for 30 minutes. The algae were washed with distillation water and then used for the adsorption process.

2.3. Analytical method

Determination of Cu concentration of Cu was carried out using atomic absorption spectrophotometer (SHIMADZU A6000) with graphite furnace with λ = 324.8 nm.

2.4. Adsorption study

The effect of pH was tested using A series of experiments, with 25 mg/L Cu (II) was conducted under different pH. The algae dosage was 0.25 g. The pH was adjusted from 3.0 to 9.0 with HCl or NaOH. The contact time for 60 minutes and 150 rpm agitation. The effect of biomass dosage used a different weight of biomass (0.1-0.6 gram) was mixed and shaker with 25 mL of solution at pH 9 for 60 minutes.

The effect of contact time was conducted at contact times ranging from 15-90 minutes. The constant weight of algae (0.25g) was added to Cu (II) of 25 mg/L. The solution was filtered after and the concentration was analyzed. The effect of concentration was done with the concentrations at 10-50 mg/L was examined at pH 9, contact time of 60 minutes with 250 rpm agitation, and algae dosage of 0.25 g.

2.5. Adsorption capacity and efficiency adsorption

The adsorption capacity and efficiency can be measured by this equation.

$$qe = \frac{(Co-Ce)V}{m} \quad (1)$$

$$Metal\ removal\ (\%) = 100\ \frac{(Co-Ce)}{Co} \quad (2)$$

Where:
qe = Adsoprtion capacity (mg/g),
Co = Initial concentration (mg/L).
Ce = Concentration at equilibrium (mg/L),
m = Weight of biosorbent (g)
v = Volume (L).

2.6. Adsorption isotherms

The isotherm adsorption uses the Langmuir model according to this equation:

$$\frac{Ce}{qe} = \frac{1}{q_m.K_l} + \frac{Ce}{q_m} \quad (3)$$

Where
Ce = Concentration at equilibrium (mg/L)
K_L = Constant of Langmuir (L/mg)
qe = Amount of copper at equilibrium (mg/g)
qm = Maximum adsorption capacity(mg/g)

The Freundlich isotherms is given as:

$$\ln q_e = \frac{1}{n}\ln Ce + \ln Kf \quad (4)$$

Where Kf and 1/n are the Freundlich constant.

2.7. Adsorption kinetic

Adsorption kinetics for Cu (II) was evaluated at pH = 6. Adsorbent dosage of 0.25 g was added to Cu solution (50 mL) with concentration of 25 mg/L. The variation of time was 15, 30, 45, 60, 75, and 90 minutes were examined for Cu concentration.
The pseudo-first-order for kinetic models:

$$\ln q_e - k_1 t = \ln(q_e - q_t) \quad (5)$$

Pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where
q_t = Adsorption capacity at certain time t (mg g^{-1})
q_e = Adsorption capacity at equilibrium (mg g^{-1})
k_1 = Constant of first-order kinetic (mg^{-1} h^{-1})
k_2 = Constant of second-order kinetic (mg $g^{-1}h^{-1}$).

Result and Discussion

2.8. Adsorption parameters

The effect of pH on adsorption of Copper can be seen in Figure 1

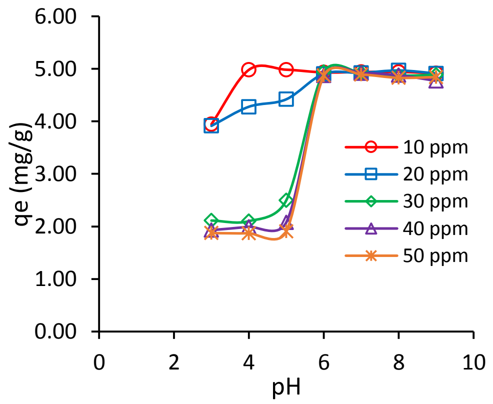

Fig 1. Variation of pH Vs adsorption capacity

The effect of pH on the adsorption of Cu (II) by *Oscillatoria sp* was carried out with a variation of 3-9 and can be seen in Figure 1. The significant adsorption increased at pH 6 and after that, the adsorption capacity was more stable until pH 9. Variation in initial Cu concentration showed the increase of Cu concentration caused the decrease of adsorption capacity in the range of pH 3 until 5. Adsorption capacity at pH of 6-9 showed the increase of Cu concentration was not influenced by adsorption capacity. The significant adsorption capacity was 4.9 mg/g with the efficiency of 99 %. The maximum adsorption of Cu was occurred at pH 9. Weak adsorption of metal ions occurred in pH range 3-5. This due to the competition between H_3O^+ ions and active sites for algae. The H_3O^+ ions increase the ability to establish links between the metal cation and ligan [14].

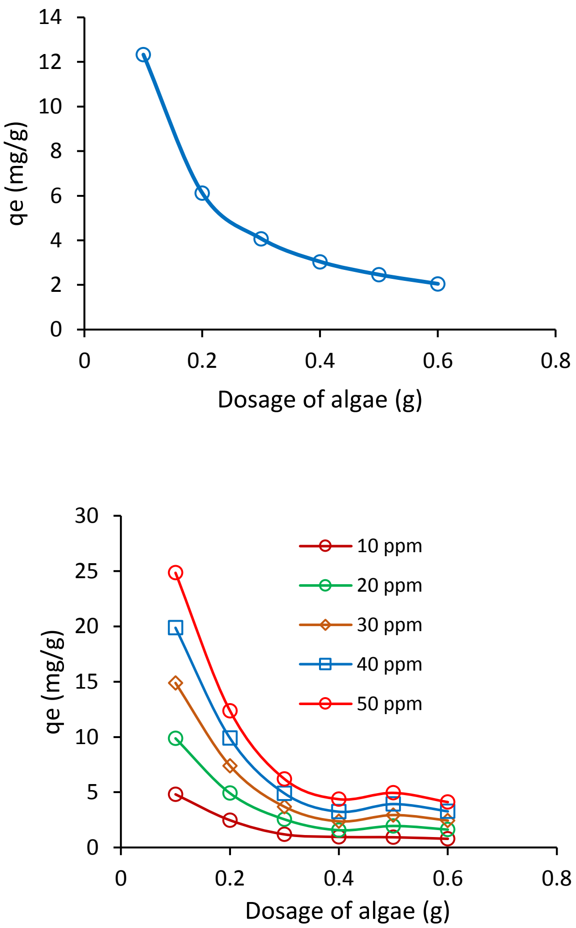

Fig 2. Effect of algae weight on copper adsorption by *Oscillatoria sp.*

The effect of algae dose was carried out in the range from 0.1-0.6 g and the volume solution was 25 mL. The biosorbent dosage is an important factor because it can determine the capacity of biosorbent for a given initial metal ion concentration [23]. Fig. 2 showed the effect of algae dosage on a desorption capacity by *Oscillatoria sp*. The experiment showed the increase of algae dosage caused the decrease of adsorption capacity. The maximum adsorption capacity occurred at a dosage of 0.1 g with an adsorption capacity of 12.33 µg/g.

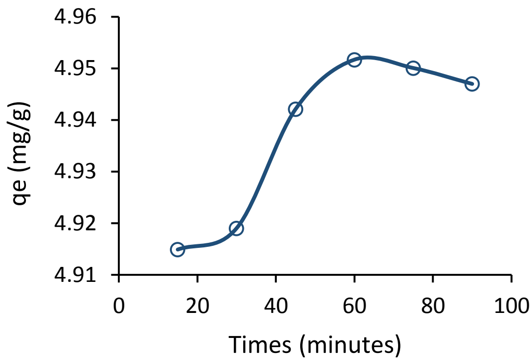

Fig 3. Effect of contact time on adsorption of Cu (II) by *Oscillatoria sp.*

The effect of contact time on the adsorption of Cu (II) was displayed in Fig. 3. The experiment was done with a variation of 15 to 90 minutes. The optimum contact time happened on 60 minutes with an adsorption capacity was 19.87 mg/g and efficiency adsorption of 99.34%. The higher biosorption related to the driving force of heavy metal ions into the algae surface.

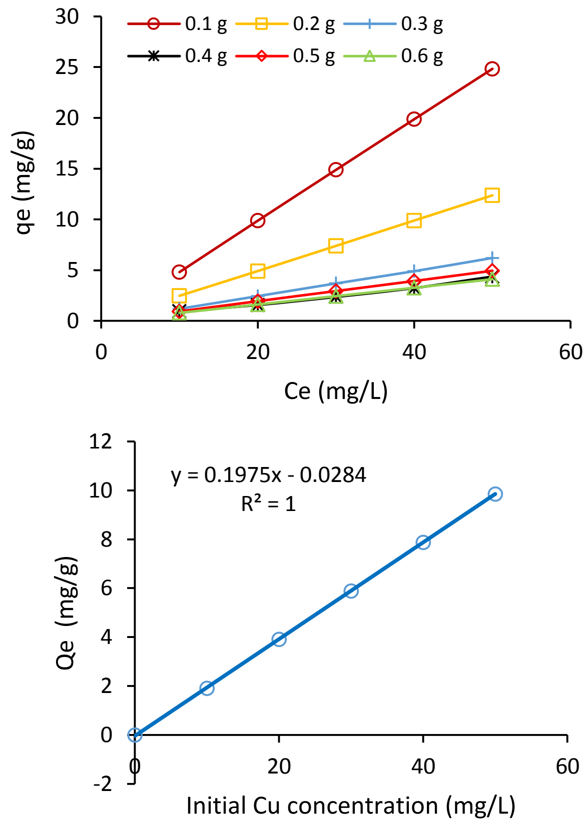

Fig 4. Effect of copper concentration to adsorption capacity.

Figure 4 showed the effect of the initial concentration from copper to adsorption capacity. The experiment resulted in the increased Cu concentration, the increased adsorption capacity with the ranged of 10- 50 mg/L. There was a linear correlation between the concentration of Cu versus adsorption capacity with R^2 = 1.00 and the equation of y = 0.1975x-0.0028. Depended on the initial concentration of Cu with adsorption capacity in different dosages of algae resulted in a linear correlation. In different algae dosage showed the increase of algae dosage resulted from decrease of biosorption capacity. The increases of the initial concentration related to the increased biosorption capacity [14].

2.9. Adsorption Isotherms.

The isotherms adsorption of Cu (II) by algae can be seen in Figure 5

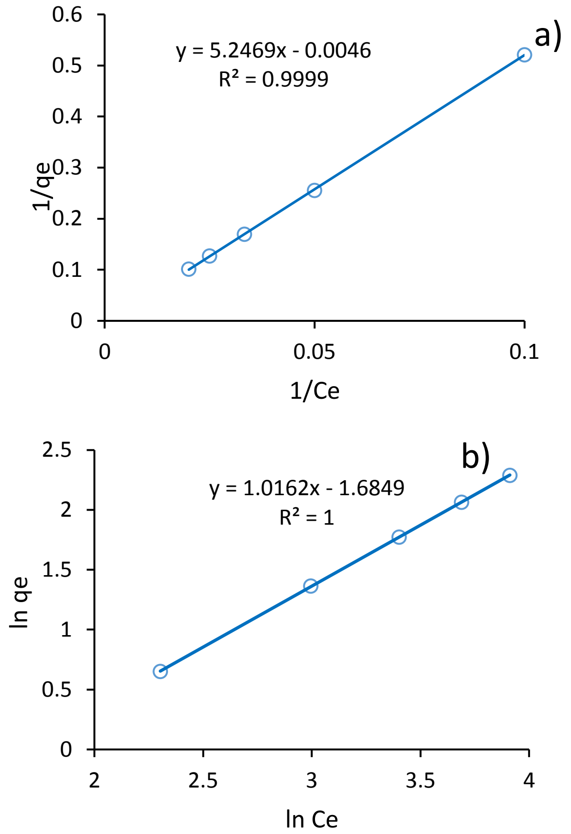

Fig 5. Isoterms adsorption a) Langmuir isotherms adsorption b) Freundlich isotherms adsorption

Figure 5 shows the Langmuir and Freundlich isotherms for Cu adsorption. The Langmuir isotherm is homogeneous distribution on the adsorbent surface. The Langmuir model was also evaluated through equation y = 5.2469x-0.0046. A high R^2 (0.9999) was obtained from the plots of ln 1/Ce versus ln 1/qe. The maximum Cu adsorption capacity with a value q_m of 217.39 mg/g. The Q_{max} value indicates the biosorption intensity.

The Freundlich constant (1/n) is related to the sorption interest of sorbent. Based on the result 1/n value of 1.0162 was observed for Cu^{2+}. It shown that the uptake of Cu by algae was very good [23]. The Freundlich constant (Kf) was 5.39. The parameters Langmuir and Freubdlich isotherm can be seen in Table 1.

Table 1. The Langmuir and Freundlich isotherm adsorption

Langmuir models			Freundlich models			
Q_m	K_L (L/mg)	R^2	1/n	K_f	N	R^2
217.39	8.8×10^{-4}	0.999	1.0162	5.39	0.9840	1

The equilibrium data at 25°C were correlated successfully to the Freundlich and Langmuir model isotherms with a R^2 = 0.9999 and 1 respectively and the Langmuir maximum biosorption capacity is 217.39 mg/g. Freundlich model is occurred on the heterogeneous adsorbent surface [24].

2.10. Adsorption Kinetic

The adsorption kinetic of Cu by *Oscillatoria sp.* can be seen in Figure 6.

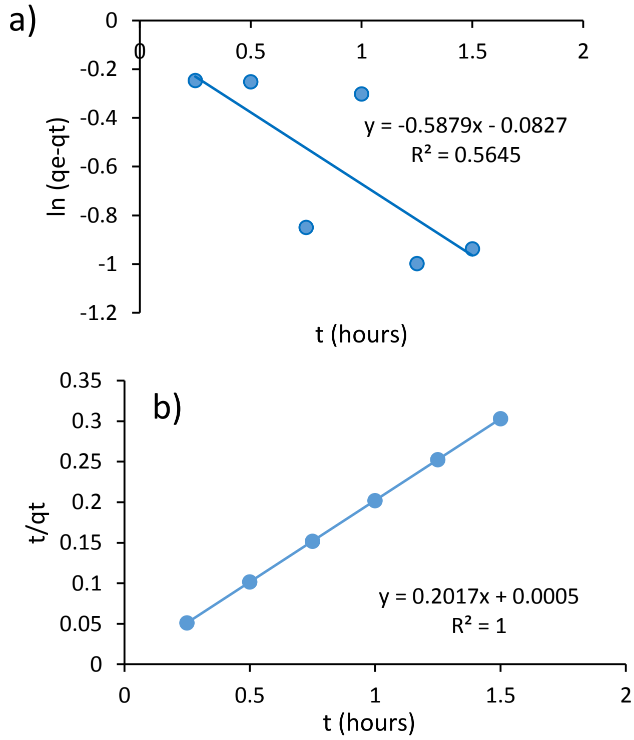

Fig 6. Kinetic model of Cu adsorption by *Oscillatoria sp*

Based on Figure 6 showed the low correlation between *t* versus ln (q_e-q_t) in pseudo-first-order model for adsorption of Cu with R^2 = 0.5645 indicated that sorption is not occurring exclusively on-site per ion [25]. The high correlation of the pseudo-second-order model for Cu adsorption by *Oscillatoria sp* with coefficient correlation R^2 = 1. The second-order kinetic involved the exchange of electron between particle especially for polar functional group [25, 26]. The relative of pseudo-first-order and pseudo-second-order were shown in Table 2.

Table 2. Kinetic models from adsorption of Cu by *Oscillatoria sp*

Pseudo-first-order			Pseudo-second-order		
qe (mg g^{-1})	k_1 (h^{-1})	R^2	qe (mg g^{-1})	k_2 (g mg^{-1} h^{-1})	R^2
0.92	0.59	0.56	4.96	81.38	1.00

Constant k_1 (0.59 h^{-1}) was calculated from the slope of plotting ln (q_e-q_t) versus *t*. Constant k_2 (81.38 g $mg^{-1}h^{-1}$) from the intercept of plotting t/q_t versus *t*. From Table 2 it can be seen the R^2 from the second-order-kinetic was higher than the first model. This model gave the information of the kinetics rates [27].

The use of microalgae as copper ion biosorption is an economically effective solution in reducing pollution of the aquatic environment. This biosorption method efficiently reduces the concentration of heavy metals in waters. Physical and chemical methods to deal with metal contamination are very expensive in terms of chemicals, involve a large use of energy, and produce toxic deposits or sediments. This is different from the use of living things such as microalgae which can be produced cheaply, can be renewed, grow very fast, are sustainable and in abundance so that they have the ability to overcome a very large area of pollution, work with high selectivity in removing and removing, reduce additional costs due to chemical or precipitate treatment.

3. Conclussions

Oscillatoria sp was prepared and characterized by sorption Cu^{2+}. The maximum adsorption of Cu by *Oscillatoria sp* was observed at pH 9, the weigt of algae (0.1 g), Cu concentration (10 mg/L), and contact time (60 minutes). The equilibrium followed the isotherms of Langmuir and Freundlich models. The adsorption kinetics based on the model of pseudo-second-order.

4. Acknowledgments

The study was supported by the Politeknik AKA Bogor, Indonesia.

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