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Biosorption of Cu(II) onto algae biomass (*Oscillatoria Splendida*) isolated from swamp water ecosystem in Palembang, South Sumatera

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Abstract. Studies of adsorption of Cu(II) on algae biomass (*Oscillatoria Splendida*) isolated and cultured from algae swamp ecosystem in South Sumatera have been carried out. These studies included determination of pH and kinetic biosorption at various contact time, isotherm and biosorption capacity of interaction between Cu(II) onto algae biomass (Oscillatoria Splendida). The result showed that the optimum pH was 5, and the optimum contact time was 30 min. Biosorption capacity of algae biomass (*Oscillatoria Splendida*) toward Cu (II) was 55.15 mg/g and agree to Pseudo-Seconds-Order kinetic model with the rate of reaction k_2 is 0.00642 mg g^{-1} min^{-1} and the adsorption thermodynamic agree to the Langmuir's model.

1. Introduction

Oscillatoria is known as one of the parameters for determining air quality, often defined as one of the cyanobacteria in a typical freshwater ecosystem. Algae and especially *Oscillatoria* are important in monitoring water sources, which are known as three Oscillatoria species that live in fresh water, namely, *Oscillatoria chlorina* (above), *Oscillatoria putrid*a (middle) and *Oscillatoria lauterbornii* (bottom) [1]. In this study the sample was taken from swamp water found in the vicinity of Palembang, South Sumatera. The condition of the aquatic environment where water samples are taken is shown in the figure 1.A total of 24 samples from 8 different locations around Palembang city were collected, characterized and screening to obtain the algae culture material. In this study the focus is on the *Oscillatoria* because of its potential as an adsorbent of heavy metal ions that are quite well approved by the previous study[2].

Biosorption using microorganism biomass has been approved by researchers and is one of the effective and economical technologies to remove and reduce concentrations of heavy metal ions from wastewaters. Where metals are important one of the water pollutantbecause it can be concentrated and accumulate in the aquatic environment[3,4]. Heavy metals also can cause harmful effectseven at very low concentrations in the aquatic environment and have potential to accumulate in living organisms through the food chain. So the research on the potential for adsorption or reduction in the concentration of heavy metals using micro algae is very important [5,6,7].

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2. Experiment

2.1. Chemicals

The analytical grade reagents of Cu(II) standard solutionand diphenyl carbazide as complexing agentwere used directly after purchase from E. Merck., Germanyfor adsorption studies without prior purification. Biosorbent of *Oscillatoria Splendida* was taken from swamp water ecosystem in Palembang, South Sumatera isolated and cultured in laboratory with environmenal condisionas show in **figure 1**. After harvesting, the biosorbent of *Oscillatoria Splendida* was drying in the oven at ±55°C for 24 h [2]. After drying process, the dried algae biomass was crushed using a mortar and sieved to select the particles sizes of 50 mesh and the dried algae biomass powder was stored in a vacuum desiccator.

Figure 1. Swamp ecosystem situation on sampling location and cultured step to obtain dried algae biomassof *Oscillatoria Splendida.*

2.2. Equipment

The Cu(II) concentration in aqueous solution samples were measured using UV-Vis model biobase BK-UV1800PC spectrophotometer. The functional groups of dried algae biomass was characterized using FTIR Shimadzu Prestige-21 with KBr plate.

2.3. The adsorption kinetic parameter studies

The kinetical adsorption parameter of Cu(II) onto dried algae biomass *Oscillatoria Splendida* was studied inbatch system. For the determination of reaction rate of Cu(II) biosorption by dried *Oscillatoria Splendida.* Amount of 0.01 mg dried *Oscillatoria Splendida* was interacted with 20mL of 100 mg/L Cu(II) in aqueous solution in 100 mL conical flask the contact time were 10, 20, 30, 60, 90, 100, 120, 150, 175 minutes, respectively and agitation by rotated shaker at 80 rpm. The mixture then filtered by Whatman No.41 filter paper, the supernatant wasanalyzed using UV-Vis model biobase BK-UV1800PC spectrophotometer to determine the remaining Cu (II) concentration in aqueous solution at various contact time.

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2.4. The adsorption thermodynamic parameter studiesthrough initial concentration and temperature

The effect of initial Cu(II) concentrations was studied using Cu(II) aqueous solution 50, 60, 70, 80, and 100 mg/L, respectively. The equilibrium time wasused for the interaction time with 0.01 mg dried *Oscillatoria Splendida* in conical flask 100 mL and the temperature effect on biosorption was carried out at various temperatures at 303, 310, and 320 K, respectively. After agitation by rotated shaker at 80 rpm the mixture then filtered using Whatmanfilter paper No.41, the supernatant was analyzed for residual Cu(II) remain in solution.

3. Results and Discussion

3.1. The characterizationof dried algae biomass

The functional group of algae biomass was characterized using a spectrophotometer FT-IR with a frequency area of 4000 to 400cm^{-1}. The functional groups of *Oscillatoria Splendida*in figure 2 exhibitthe presence of carbonyl, hydroxyl, and aliphatic chains.

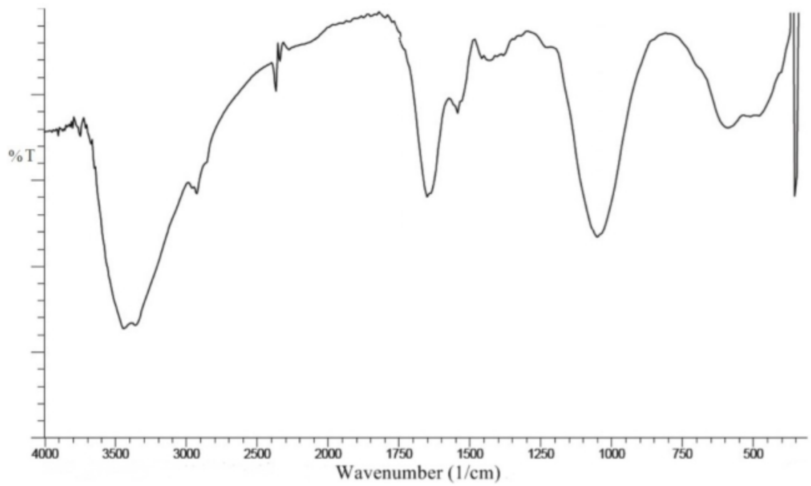

Figure 2. The FT-IR spectra of dried algae biomass *Oscillatoria Splendida*

The band position at 3405 cm^{-1} was attributed to the water ν(O-H) stretching and the protein ν(N-H) stretching of amide in biomass [8]. The bands in the range of 2913 and 2854 cm^{-1}indicate the presence of aliphatic C−H stretching of lipid - carbohydrate indicated by $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ stretching [9]. The bands in the range of 1645 to 1390 cm^{-1} considered of −C=O stretching for aldehydes oramide. The adsorption peaks 1100 cm^{-1} indicate of carbohydrate ν(C-O-C) of polysaccharides. These functional groups are important for dried algae biomass to bind the metal ion because it characterization act as ligand [10,11].

3.2. The adsorption kinetic parameter

The adsorption kinetic parameterswere studied trough the effects of contact time on percentage adsorption of Cu(II) onto biosorbent dried *Oscillatoria Splendida.* The contact time of 10 to 175 min, using 0.01 mg dried *Oscillatoria Splendida* were used for interaction between adsorbent and adsorbate with 20 mL of 100 mg/L Cu(II) in aqueous solution and 80 rpm rotation shaking speed. The mixture condition was made of Cu(II)metal concentration at pH 5, based on the stability of Cu(II) ion in aqueous solution at various pH showed in Figure 3(a), while the temperature of interaction was at 303K. The kinitic data of adsorption of Cu(II) ions onto the *Oscillatoria Splendida* showed that the contact time of 30 mins wasthe time that the equilibrium kinetically begins to occur. The adsorption of Cu(II) onto dried *Oscillatoria Splendida* did not significantly changeat further additional contact time

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as shown in Figure 3(b). The optimum adsorption concentration of Cu(II) metal ion adsorbed by biosorbent dried *Oscillatori asplendida* was 53.683 mg/L.

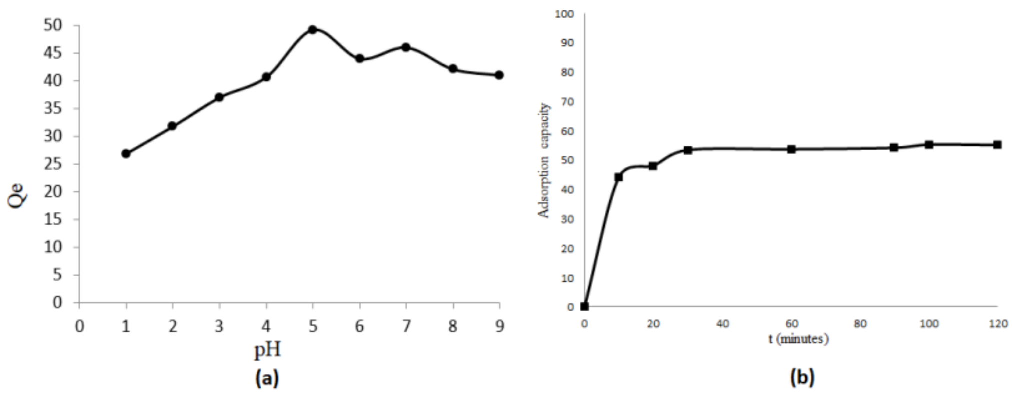

Figure 3. (a) The stability of Cu(II) ion in aqueous solution at various pH. (b) The effect of contact time on the adsorption of dried algae biomass *Oscillatoria Splendida* to ward Cu(II) ion in aqueous medium.

The contact time of Cu(II) adsorption onto biomass *Oscillatoria Splendida* determined by varying the time of interaction between the adsorbent and the adsorbate so the optimal time is obtained when graph slope became stable that indicates equlibrium of interaction of Cu(II) with biomass *Oscillatoria Splendida*. An equilibrium state characterizes the optimum interaction between the concentration of Cu(II) and the adsorbent. Based on Figure 3(b) the amount of Cu(II) ionadsorbedat 10 mins initial time relatively rising gradually then to achieve interaction stabilityat 30 mins. Adsorption of Cu(II) ion on biomass *Oscillatoria Splendida* occurat a rapid rate of adsorption at the begining and became stable when the adsorbent site active has filled by adsorbate and resulting the saturation of adsorption and the reactivity of interaction was decreased.

The adsorption kinetics is used to determine the adsorption rate constant (k). The adsorption kinetics model applied on this research using Langmuir-Hinshelwood model. The pseudo-first order rate of reaction kinetics expressed as follow:

$$\log(q_e - q_t) = \log q_e \frac{k_{1,ads}}{2.303}\, t \qquad (1)$$

where qt (mg/g) is show the amount of Cu(II) ion were adsorbed onto the site active of adsorbent dried biomass *Oscillatoria Splendida* at equilibrium time (t), while the pseudo-first order rate of reaction constant (k_1). The kinetic parameters of the interaction between dried biomass *Oscillatoria Splendida* and Cu(II) ionare given in Table 1.

Table 1. Kinetical parameters of the adsorption of Cu(II) ion onto biomass *Oscillatoria Splendida*

Kinetic model	Parameters	Cu(II) metal ion
Pseudo-first-order	qe experiment (mg/g)	55.147
	qe count (mg/g)	9.3040
	k1 (min^{-1})	0.0281
	R^2	0.7531
Pseudo-Seconds-order	qe experiment (mg/g)	55.147
	qe count (mg/g)	56.3899
	k2 ($mg\ g^{-1}\ min^{-1}$)	0.00642
	R^2	0.9997

The kinectical pseudo-second order equation model can be expressed as equation 2.

$$\frac{1}{q} = \frac{1}{k_{2,ads}\, {q_e}^2} + \frac{1}{q_e}\, t \qquad (2)$$

Where, the rate constant of second order of adsorption k_2 (g mg^{-1} min^{-1}). The kinetic parameters in Table 1. The linear correlation coefficient (R^2) of kinetical pseudo-second order adsorption model was show relatively higher than to the pseudo-first order, thus can concluded that the kinetics model for adsorption of Cu(II) on dried biomass *Oscillatoria Splendida* agree to the pseudo-second order of kinetical adsorption model [12].

3.3. The effect of adsorbent initial concentration

The initial metal ion concentration effect on the adsorption of Cu(II) ion ontodried algae biomass *Oscillatoria Splendida*from aqueous solution was studied using Cu(II) solution concentration 50, 60, 70, 80, and 100 mg/L, respectively. The equilibrium time 30 mins from kinetic data was used for the interaction time with 0.01 mg biosorption. The result showed in table 2.

Table 2. Isotherm and thermodynamic parameters of the adsorption of Cu(II) ion onto biosorbent dried *Oscillatoria Splendida*

Parameters	T= 303 K	T= 313 K	T= 323 K
Langmuir			
Qmax	77.5194	52.4553	34.8269
KL	0.0295	0.0351	0.0492
R^2	0.8512	0.9106	0.9123
Freundlich			
Kf	13.9516	5.5757	6.8167
n	1.9452	2.1785	2.98
R^2	0.7885	0.808	0.5256

The effect ofinitial concentration and temperature at the interaction of Cu(II) ion as adsorbed on biosorbent dried *Oscillatoria Splendida* showed in Table 2. The higher of initial temperature and concentration not increasing the amount of Cu(II) where adsorbed onto dried *Oscillatoria Splendida*. From equilibrium data, this adsorption provides insight into the protection and endothermic interaction properties because the increase in reaction temperature does not affect the equilibrium of the reaction. The adsorption of Cu(II) on biosorbent dried *Oscillatoria Splendida* agree to the Langmuir equilibrium isotherms equation with R^2 0.8512, Qmax 77.5194 at 303 K, respectively.

4. Conclusion

The studies of biosorption of Cu(II) metal ion onto algae biomass *Oscillatoria Splendida* have optimum pH was 5, and the optimum contact time was 30 mins. The isothermand thermodynamic parameters of interaction of *Oscillatoria Splendida* to ward Cu (II) agree to Pseudo-Seconds-Order kinetic model with the rate of reaction $k_2$was 0.00642 mg g^{-1} min^{-1} and the adsorption thermodynamic agree to the Langmuir's model with biosorption capacity was 55.15 mg/g.

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