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Kinetic and Thermodynamic Study Removal of Co(II) Using Biosorbent *Spirulina* sp. in Aqueous Solution

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Abstract

Kinetic and thermodynamic adsorption study of Co(II) ions from aqueous solutions by dried *Spirulina* sp. biomass was investigated in the batch system. The *Spirulina* sp. was isolated and cultured from algae swamp ecosystem in South Sumatera. The adsorption properties of Co(II) onto dried *Spirulina* sp. biomass was studied by the influence of contact time, initial metal ion concentration and reaction temperature. The experimental results were the rate of adsorption followed the second-order kinetic model with the rate of reaction k_2 is 0.023 g mg^{-1} min^{-1} and the thermodynamic studies showed that the adsorption was well fitted to the Langmuir's model, and the amount of Co(II) removed from solution increased with increasing Co(II) concentration with the higher adsorption energy was 10.38 kJ/mol at 30 °C.

Keywords: *Spirulina* sp, Co(II), adsorption, algae swamp, South Sumatera

Abstrak (Indonesian)

Studi kinetika dan termodinamika adsorpsi Co(II) oleh biomassa *Spirulina* sp. dalam medium air telah dilakukan dalam sistem batch. *Spirulina* sp. diisolasi dan dari kultur algae yang berasal dari ekosistem rawah di sekitar Provinsi Sumatera Selatan. Karakteristik adsorpsi Co(II) pada *Spirulina* sp diamati dengan pengaruh waktu kontak, konsentrasi awal ion logam dan termperatur. Dari hasil penelitian diperoleh reaksi mengikuti mekanisme reaksi orde dua dengan kecepatan reaksi k2 0,0023 g mg^{-1} min^{-1} dan secara termodinamika mengikuti model isoterm Langmuir dengan energi adsorpsi terbesar adalah 10,38 kJ/mol pada temperatur 30 °C

Kata Kunci: Spirulina sp, Co(II), adsorpsi, alga rawa, Sumatera Selatan

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INTRODUCTION

Heavy metal pollution in the aquatic system is one of the most important environmental problems. They impose serious health risks via their accumulation in living tissues throughout the food chain. The majority of toxic metal pollutants are waste products of industrial and other environmental sources. One method to reduce heavy metal pollution in the environment is by the process of adsorption [1]. There are many materials that have been used by scientists and researchers as the adsorbent material in the process of adsorption of heavy metals in the environment. In the previous research, we investigated the potential of natural biomass derived from algae as a heavy metal adsorbent by characterizing the composition of chemical compounds contained in spirulina sp. algae biomass [2].

However, other researches have revealed that inactive/dead microbial biomass can passively bind metal ions via various physicochemical mechanisms. Therefore, researches on biosorption have become an active field for the removal of metal ions or organic compounds could be potential especially in South Sumatera region that have large area cover by swamp ecosystem that as naturally as habitat of swamp algae that potentially as adsorbent materials for remove heavy metal ions in aqueous system [3]. The mechanisms responsible for biosorption of Cobalt (II) ion, although understood to a limited extent, may be one or combination of ion exchange, complexation, coordination, adsorption, electrostatic interaction[4].

MATERIALS AND METHODS

***Chemicals*:** Analytical grade reagent or solution Co(II) was used to prepare standard solutions for the adsorption studies directly used after purchase from E. Merck., Germany. Biosorbent of *Spirulina* sp. preparation according to Hilda et.al (2016) [5]. The collected biosorbent was soaked for 10 minutes with 0.1 M nitric acid filtered and washed continuously with distilled water until neutral pH to remove all mineral and impurities. The biosorbent was then kept on a filter paper and dried in an oven at 60 °C for 24 h to reduce water content. Subsequently, it was ground on an agate stone pestle mortar and sieved, to select the particles of 100 µm mesh sizes.

Equipment: The Co(II) concentration in sample were measured using Atomic Absorption Spectro-photometer NOVAA 350 from Analytik Jena (Germany).

Effect of Intraction time: The adsorption kinetic studies for Co(II) onto dried *Spirulina* sp. was studied by batch system. For the determination of reaction rate of Co(II) biosorption by biomasses of dried *Spirulina* sp. Amount of 0.01 mg dried *Spirulina* sp. was interacted with 20 mL of 10 mg/L Co(II) solution in conical flask 100 mL the contact time were 10, 20, 30, 40, 50 minutes and agitation by shaker at 80 rpm. The mixture then filtered using whatman No.41 filter paper, the supernatant was analysed for residual Co(II) at various contact time.

Effect of adsorbent initial concentration: The effect of initial metal concentrations was studied with Co(II) concentration of 3, 5, 7 10, 20 mg/L. The equilibrium time was used for the interaction time with 0.01 mg dried *Spirulina* sp. in conical flask 100 mL. After agitation by shaker at 80 rpm the mixture then filtered using whatman No.41 filter paper, the supernatant was analysed for residual Co(II).

Effect of temperature: the temperature effect on biosorption was carried out at various temperatures at 30, 40, 45, 50 °C. Amount of 0.01 mg dried *Spirulina* sp. was interacting with Co(II) solutions (20 mL). The Co(II) concentration was varied 3, 5, 7, 10, 20 mg/L in conical flask 100 mL. After agitation by shaker at 80 rpm the mixture then filtered using whatman No.41 filter paper, the supernatant was analysed for residual Co(II).

RESULT AND DISCUSSION

The biosorbent dried *Spirulina* sp. was prepared from pevious work [5]. In this research the dried *Spirulina* sp. is applied as adsorbent of Co(II) and studied the kinetic and thermodynamic aspect of the adsorption of Co(II) onto dried *Spirulina* sp.

Figure 1. Biosorbent dried *Spirulina* sp.

Effect of contact time

The determination of adsorption kinetics of Co(II) onto biosorbent *Spirulina* sp. was performed at various interaction time to determine the adsorption rate. The contact times were 10, 20, 30, 40, 50 minutes. The adsorption kinetics is used to determine the value of the adsorption rate constant (k). The adsorption kinetics model applied on this research using Langmuir-Hinshelwood model [6]. The linear form of the pseudo-first order rate expressed as

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

where qt (mg/g) is the amount of Co(II) adsorbed by dried *Spirulina* sp. at equilibrium time t, k_1 is the pseudo-first order rate constant (min^{-1}). The graph of log (qe –qt) versus log qe is shown in Figure 2a and the kinetic parameters are given in Table 1.

Table 1. Kinetic parameters for the adsorption of Co(II) on biosorbent dried *Spirulina* sp.

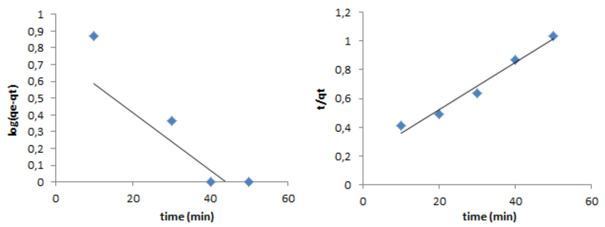
T (K)	First order kinetic		Second order kinetic	
	k_1 (min^{-1})	R^2	k_2($g\ mg^{-1}\ min^{-1}$)	R^2

303	0.027	0.213	0.023	0.928

The pseudo-second order model can be expressed in its linear form by the equation

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

where k_2 (g mg^{-1} min^{-1}) is the rate constant of second order adsorption. The graph t/q versus t is shown in Figure 2b, and the kinetic parameters in Table 1. The value of correlation coefficient for pseudo-second order adsorption model was found to be relatively high compare to the pseudo-first order, thus can concluded that the kinetics for adsorption of Co(II) on dried Spirulina sp. agree to the pseudo-second order adsorption model.



A B

Figure 2. First-order kinetic modeling (A) and Second-order kinetic modeling (B) of adsorption of Co(II) onto dried *Spirulina* sp.

From **Figure 3**. it can be seen that the absorption rate was increases at the initial time and tend to constant when the reaction was in equilibrium event more additional interaction time was applied. A graph was plotted with qe versus contact time was observed that the adsorption increased with increase in time, reached a constant value at which no further Co(II) was adsorb or removed from the solution by the dried *Spirulin*a sp as biosorbent.

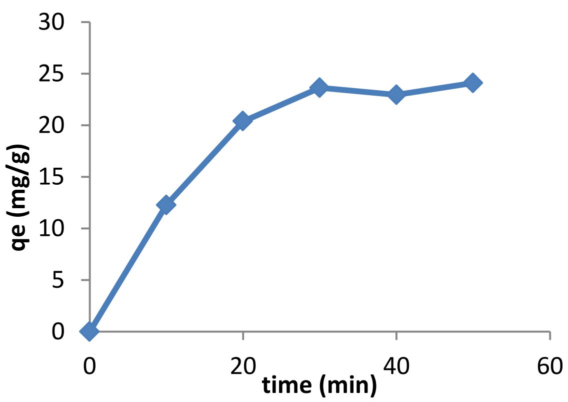


Figure 2. Effect of contact time on the biosorption of Co(II) by dried *Spirulina* sp.

The maximum adsorption took place within 30 min as shown in **Figure 3**. The fast sorption at initial stage may be due to the presence of large number of negative charged surface active sites responsible for adsorption of Co(II) on dried *Spirulina* sp. and after the additional time the rearangement of intraction between Co(II) ion on the site active of dried *Spirulina* sp. was cause the rate of reaction become slower until reach the equilibrium [7].

Adsorption Isotherm

Isotherm adsorption is used to determine the adsorption capacity. In this research, adsorption isotherms by various initial concentration of Co(II) interacted with biosorption dried *Spirulin*a sp.

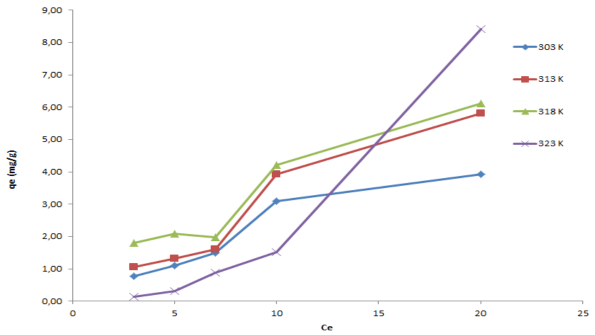


Figure 4. Adsorption isotherms of Co(II) onto biosorbent dried *Spirulina* sp. at different temperature

The initial concentration used in this study 3, 5, 7 10, 20 mg/L and the effect of temperature on Co(II) adsorbed onto biosorption dried *Spirulina* sp. was investigated by taking four different temperatures (303, 313, 318, and 323 K) as shown in **Figure 4**.

Table 2. Thermodynamic parameters for the adsorption of Co(II) on biosorbent dried *Spirulina* sp..

T (K)	b (10^{-3} g/mg)	E(kJ/mol)	ΔH° (kJ/mole)	ΔS° (kJ/mole/K)
303	42.9	10.38	-71.400	0.231
313	44.1	9.20	-62.637	0.203
318	30.5	7.36	-17.567	0.052
323	2.8	8.12	-26.114	0.085

With an increase in temperature there were a decrease in adsorption shows that adsorption is exothermic. This phenomenon can be understood as chemical reaction between adsorbate and the surface activity of biosorbent. The enthalpy, entropy and other thermodynamic parameter of adsorption of Co(II) onto biosorption dried *Spirulina* sp. were shown in **Table 2.** The adsorption isotherm equation can also be used to determine the amount of adsorption energy by using the equation ΔEads = RT ln K. From the results of this study it is found that the energy occurring at the binding of Co(II) to the biosorbent dried *Spirulina* sp. was varied defend on the temperature of reaction. The higher temperature the lower energy of adsorption and also the entropy, with the higher adsorption energy of 10.38 kJ/mole and enthropy 0.231 kJ/mole/K, respectively.

CONCLUSION

The used of biosorbent dried *Spirulina* sp. to adsorp of Co(II) was studied by the influence of contact time, initial metal ion concentration and reaction temperature. The experimental results were the rate of adsorption followed the second-order kinetic model with the rate of reaction k_2 is 0.023 g mg^{-1} min^{-1} and the thermodynamic studies showed that the adsorption was well fitted to the Langmuir's model, and the amount of Co(II) removed from solution increased with increasing Co(II) concentration. The reaction was occur exothermic indicated by increase in temperature will decrease in adsorption energy and enthropy with the higher adsorption energy was 10.38 kJ/mol.

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