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Research Paper

Kinetic and Thermodynamic Adsorption of Cr(VI) onto Dried *Oscillatoria Splendida* in Aqueous Solution

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Abstract
Kinetic and thermodynamic adsorption study of Cr(VI) ion in aqueous solutions by dried *Oscillatoria Splendida* biomass was investigated in the batch system. The *Oscillatoria Splendida* was isolated and cultured from algae swamp ecosystem in South Sumatera. The adsorption properties of Cr(VI) onto dried *Oscillatoria Splendida* biomass was studied by the influences of contact time, initial Cr(VI) ion concentration and temperature of reaction. The experimental results were the rate of adsorption followed the second-order kinetic model with the rate of reaction k2 is 0.00181 mg/g.min and the adsorption thermodynamic agree to the Langmuir's model with amount of Cr(VI) removed from aqueous solution increased with increasing Cr(VI) concentration with the higher adsorption energy was 8.46 kJ/mol at 50 °C.

Keywords
Oscillatoria Splendida, Cr(VI), adsorption, algae swamp

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1. INTRODUCTION

Algae is known as a major producer in water bodies, enriching nutrients in water through organic wastes can selectively stimulate the growth of algae species that produce a lot of growth, which in turn reduces water quality. However, certain algae that develop in water bodies contaminated with organic waste play an important role in self-purification of water. In fact, algae can play an important part of the aquatic life food chain. Recently, algae have become significant organisms for biological purification of wastewater because they are able to collect nutrients from pollutants, heavy metals, pesticides, organic and inorganic toxic substances, pathogens and radioactive things from the surrounding water by collecting and / or using them in their cells. In addition, research shows that algae can be used successfully for wastewater treatment because of their bioaccumulation ability (Alp et al., 2012).

Biological wastewater treatment systems with microalgae are very rapidly developing nowadays and it is widely accepted that wastewater treatment systems using algae are as effective as conventional care systems. These specific features have made wastewater treatment systems with algae a significant low-cost alternative to complicated expensive maintenance systems especially for urban wastewater purification (Mohadi et al., 2017). Algae support the oxidation of aerobic bacteria from organic matter that produces oxygen through photosynthesis while releasing carbon dioxide and nutrients in the use of aerobic oxidation for algal biomass growth (Kalesh and Nair, 2005). Algae that use nitrogen and phosphorus in growth can move nutrients to wastewater loads from a few hours to several days (N and C, 2009). Compared to general processing systems, oxidation ponds that support the growth of several species may be effective in removing nutrients. Increases dissolved oxygen concentration and causes pH for phosphorus sedimentation, removal of ammonia and hydrogen sulphur. High pH in algal ponds also leads to pathogen disinfection. Removal of the efficiency of heavy metals by algae shows changes between species. In fact, research shows that chromium by Oscillatoria, cadmium, copper and zinc by Chlorella vulgaris, led by Chlamydomonas and molybdenum by Scenedesmus chloreloides can be successfully removed (Aly, 2000).

In this study, the cultivation of Oscillatoria Splendida algae and dried biomass was carried out which was then interacted with a certain amount of chromium metal ion concentration which are known to have toxic properties to determine the adsorption rate and adsorption capacity of *Oscillatoria Splendida* biomass on adsorption of Cr (VI) metal ions in aqueous medium.

2. EXPERIMENTAL SECTION

Chemicals: Analytical grade reagent or solution Cr(VI) and diphenyl carbazide were used to prepare standard solutions for the adsorption studies and as complexing agent were used directly after purchase from E. Merck., Germany. Biosorbent of *Oscillatoria Splendida* preparation according to (Zulkifli et al., 2017). 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 Cr(VI) concentration in sample were measured using UV-Vis model biobase BK-UV1800PC spectrophotometer.

Effect of Intraction time: The adsorption kinetic studies for Cr(VI) onto dried *Oscillatoria Splendida* was studied by batch system. For the determination of reaction rate of Cr(VI) biosorption by biomasses of dried *Oscillatoria Splendida* Amount of 0.01 mg dried *Oscillatoria Splendida* was interacted with 20 mL of 100 mg/L Cr(VI) solution in conical flask 100 mL the contact time were 10, 20, 30, 60, 90, 100, 120, 150, 175 minutes and agitation by shaker at 80 rpm. The mixture then filtered using Whatman No.41 filter paper, the supernatant was analyzed for residual Cr(VI) at various contact time.

Effect of adsorbent initial concentration: The effect of initial metal concentrations was studied with Cr(VI) concentration of 50, 60, 70, 80, and 100 mg/L. The equilibrium time was used for the interaction time with 0.01 mg dried *Oscillatoria Splendida* 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 analyzed for residual Cr(VI).

Effect of temperature: the temperature effect on biosorption was carried out at various temperatures at 30, 40, 50 °C. Amount of 0.01 mg dried *Oscillatoria Splendida* was interact with Cr(VI) solutions (20 mL). The Cr(VI) concentration was varied 50, 60, 70, 80, and 100 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 analyzed for residual Cr(VI).

3. RESULTS AND DISCUSSION

3.1 Effect of Contact Time

The determination of adsorption kinetics of Cr(VI) onto biosorbent *Oscillatoria Splendida* was performed at various interaction time to determine the adsorption rate. The contact times were 10, 20, 30, 60, 90, 100, 120, 150, 175 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 (Zulkifli et al., 2017). The linear form of the pseudo-first-order rate expressed as:

$$log(qe-qt) = logqe - \frac{k1}{2.303}t \tag{1}$$

where qt (mg/g) is the amount of Cr(VI) adsorbed by dried *Oscillatoria Splendida* at equilibrium time t, k1 is the pseudo-first order rate constant (min^{-1}). The graph of log (qe −qt) versus log qe is shown in Figure 1a and the kinetic parameters are given in Table 1.

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

$$\frac{t}{qt} = \frac{1}{k2qe^2} + \frac{1}{qe}t \tag{2}$$

where k2 (mg/g.min) is the rate constant of second order adsorption. The graph t/q versus t is shown in Figure 1b, and the kinetic parameters in Table 1. The value of correlation coefficient for pseudo-second order adsorption model was found to be relatively high compared to the pseudo-first order, thus can conclude that the kinetics for adsorption of Cr(VI) on dried *Oscillatoria Splendida* agree to the pseudo-second-order adsorption model.

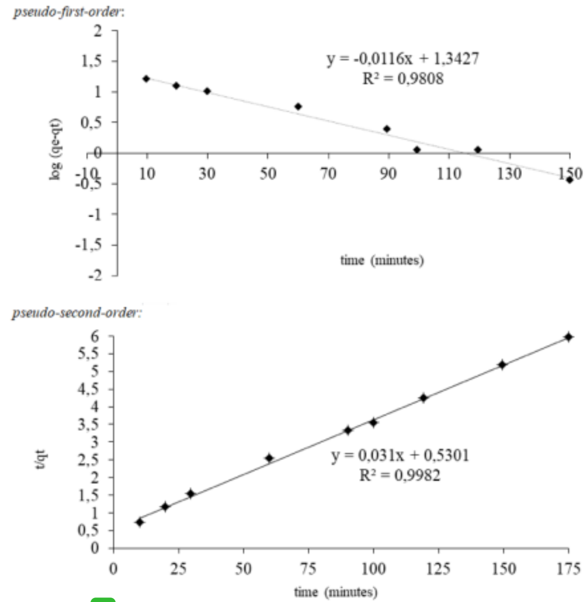

Figure 1. First-order kinetic modeling and Second-order kinetic modelling of adsorption of Cr(VI) onto dried *Oscillatoria Splendida*

From Figure 2. 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 Cr(VI) was

Table 1. Kinetic parameters for the adsorption of Cr(VI) on biosorbent dried *Oscillatoria Splendida*

T	First order kinetic model		Second order kinetic model	
(K)	k1 (min^{-1})	R^2	k2(mg/g.min)	R^2
303	0.027	0.981	0.0018	0.998

Table 2. Isotherm and thermodynamic parameters for the adsorption of Cr(VI) on biosorbent dried *Oscillatoria Splendida*

T (K)	Ce	Qe	Qe/Ce	Ln Qe/Ce	1/T	ΔS (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
303	42.04	7.96	0.19	-1.664	0.0033	0.209	-59.13	4.28
313	46.29	3.71	0.08	-2.523	0.003			6.37
323	47.88	2.12	0.044	-3.115	0.0029			8.46

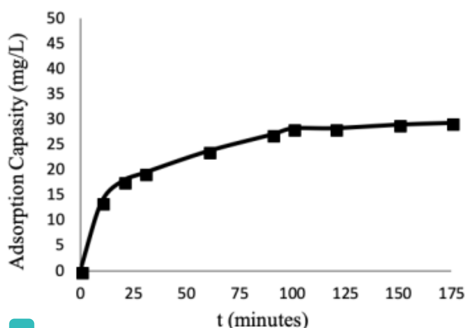

Figure 2. Effect of contact time on the biosorption of Cr(VI) by dried *Oscillatoria Splendida*

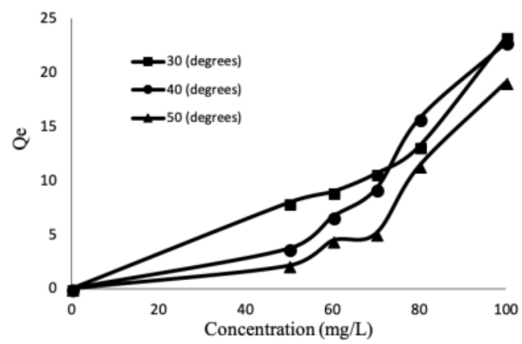

Figure 3. Adsorption isotherms of Cr(VI) onto biosorbent dried *Oscillatoria Splendida* at various temperature

adsorb or removed from the solution by the dried *Oscillatoria Splendida* as biosorbent.

The maximum adsorption took place within 100 min as shown in Figure 2. The fast sorption at initial stage may be due to the presence of large number of negatively charged surface active sites responsible for adsorption of Cr(VI) on dried Oscillatoria Splendida and after the additional time the rearrangement of intraction between Cr(VI) ion on the active site of dried Oscillatoria Splendida was cause the rate of reaction become slower interaction and reach the equilibrium (Zulkifli et al., 2017).

3.2 Adsorption Isotherm

Isotherm adsorption is used to determine the adsorption capacity. In this research, adsorption isotherms by various initial concentration of Cr(VI) interacted with dried *Oscillatoria Splendida*

The initial concentration used in this study 50, 60, 70, 80, and 100 mg/L and the effect of temperature on Cr(VI) adsorption onto dried *Oscillatoria Splendida* was investigated by taking three different temperatures (303, 313, and 323 K) as shown in 3. With an increase in temperature effect to decrease in adsorption shows that adsorption is exothermic. The enthalpy, entropy and other thermodynamic parameter of adsorption of Cr(VI) onto dried *Oscillatoria Splendida* 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. The binding energy of Cr(VI) to the dried *Oscillatoria Splendida* was varied defend on the temperature of reaction. The higher temperature the lower energy of adsorption and the entropy, with the higher adsorption energy of 8.468 kJ/mol and entropy 0.209 kJ/mol/K, respectively.

4. CONCLUSIONS

The used of biosorbent dried Oscillatoria Splendida to adsorp of Cr(VI) 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 k2 is 0.0018 mg/g.min and the thermodynamic studies showed that the adsorption was agree to the Langmuir's model, and the amount of Cr(VI) removed from aqueous solution increased with increasing Cr(VI) concentration. The reaction was occur exothermic indicated by increase in temperature will decrease in adsorption energy and entropy with the higher adsorption energy was 8.468 kJ/mol.

5. ACKNOWLEDGEMENT

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