Research Article

Adsorption of Cobalt Ion from Aqueous Solution Using Biomaterial of Microalgae

Oscillatoria sp Isolated from Teluk Jakarta

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Abstract: The adsorption of cobalt onto biomaterial of microalga Oscillatoria sp was investigated via batch experiment. Marine alga Oscillatoria sp was isolated from Teluk Jakarta Indonesia. The characterization of the functional group with FTIR spectrum showed microalgae have a functional group of O-H, C = O, COO, C-O-C, N-H, C-S, C-H and PO₄³⁻. Adsorption of cobalt ion was investigated as a function of time, pH, initial cobalt concentration, the dosage of biosorbent, salinity dan shaking. Equilibrium and kinetic adsorption were obtained from the batch experiment. The cobalt adsorption followed the Langmuir and Freundlich, isotherm models. The Freundlich constant (Kf) and n were 0.1186 (mg/g) (L.mol⁵/₂) and 8.43 mg/L, respectively. The maximum adsorption capacity was 4.71 mg/g at pH 8. Oscillatoria sp could adsorb cobalt even at a lower concentration, indicating a good affinity for metal. Kinetic studies showed that the adsorption of cobalt ion followed a pseudo-first-order with k₁ = 1.2×10⁻³ min⁻¹.

Keywords: Adsorption, biomaterial, cobalt, Oscillatoria sp

INTRODUCTION

The heavy metal contaminant is a problem in the aquatic environment because it can be accumulated in the human body and toxic above the tolerance level (Al-Rub et al., 2004). Cobalt is one of the heavy metal that must be reduced in the aquatic system. The higher of Co²⁺ solution was explored to remove Co²⁺ from solution (He et al., 2011). High-level cobalt concentration caused DNA damage (Simon sen et al., 2012; Leyssens et al., 2017). One technique to reduce cobalt contaminants in the aquatic is by adsorption technique using biosorbent. Biosorption is adsorption and accumulation process of pollutants from aqueous solution using the biological materials. Biosorption technique has an advantage in reducing heavy metal ions to a very low level (Feng and Aldrich, 2004). Many types of biomass have been studied for cobalt uptake as lemon peel (Bhatnagar et al., 2010), almond green hull (Ahmadpour et al., 2009) Blighia sapida (Jimoh et al., 2012).

Algae is one of the biosorbent in adsorb of toxic heavy metal because of it easy to grow and have a functional group in the wall cell. This functional group including carboxyl, sulfate and phosphate (Ahuja et al., 1999; Aravindhan et al., 2007). Many studies have shown that algae process high metal binding capacities (Deng et al., 2007). Oscillatoria sp, a kind of cyanobacteria microalgae, is widely distributed in eutrophic freshwater and marine environment. Several research has been used Oscillatoria as biosorbent to uptake of the heavy metal such as Cu and Zn absorption (Ahuja et al., 1997; Ahuja et al., 2001; Al-Shammary and Abdulhlay, 2016), Oscillatoria sp for adsorption of Cd (Azizi et al., 2012), Pb (Kumar et al., 2011).

In this study, we will explore the potential of microalgae Oscillatoria sp for the adsorb of cobalt (II) ion from aqueous solution. Marine microalg Oscillatoria sp was isolated from Teluk Jakarta, Indonesia. Effect of pH, adsorbent dosage, the concentration of cobalt, shaking and salinity will be performed in this study. Equilibrium isotherms for the adsorption of cobalt were measured experiment. Adsorption isotherms were determined with Langmuir and Freundlich equation.

MATERIALS AND METHODS

Prepared the material: Microalgae Oscillatoria sp obtained from an Indonesian culture collection, LIPI Cibinong. It was grown at 25°C and pH adjusted to 8. The algae were harvest after 14 days of growth. Thereafter, the algal pellet was washed with deionization distillation water and then used for metal
uptake experiment. Characterization of functional groups from the biosorbent using FTIR. The chemical reagents used in this study are analytical reagent grade. The cobalt solution was prepared by dissolving the Co(NO₃)₂·6H₂O salt in distilled water. The initial ion concentration range 5-50 mg/L. The pH of the solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH. The concentration of cobalt determined using Atomic Absorption Spectrometer (AAS) (SHIMADZU A6000). Adsorption reading was taken in 240.7 nm.

Adsorption study: The metal uptake experiment was performed in 250 mL Erlenmeyer flask containing 25 mL Co 50 mg/L and 0.25 g biosorbent. The solution becomes to 50 mL with added of demineralization water. The experiment was carried out in batches in different condition of time, concentration, pH, amount of biosorbent, etc. The biosorbent with a known weight was left in contact with 50 mL of cobalt solution (5-50 mg/L) at 150 rpm. The mixture was shaken for 60 min. The parameter adsorption consist of variation of contact time (30-120 min), dosage of biosorbent (0.1-0.6 g), initial concentration of cobalt (5-50 mg/L), shaker (50-200 rpm), pH (3-8) and salinity (0-30 g/L). Thereafter supernatant liquid was filtered and the concentration of cobalt was determined by AAS. The adsorbed quantities of cobalt ion were evaluated using the following equation:

\[
qe = \frac{(C₀-Cₑ) V}{W}
\]  \hspace{1cm} (1)

where,

\( q_e \) = The amount or concentration of cobalt adsorbed onto the unit amount of microalgae Oscillatoria sp (mg/g)
\( C₀ \) = The initial concentration of cobalt (mg/L)
\( V \) = The volume of solution (L)
\( W \) = The weight of biosorbent (Liu et al., 2010; Jeppu and Clement, 2012)

The adsorption percentage of cobalt was adsorbed by biosorbent used the equation below:

\[
\text{Adsorption (\%)} = \frac{(C₀-Cₑ)}{C₀} \times 100 \hspace{1cm} (2)
\]

where,

\( Cₑ \) = Cobalt concentration in solution
\( C₀ \) = The cobalt initial concentration

Adsorption isotherms: The Langmuir and Freundlich models were studies for equilibrium state. The Langmuir equation was shown below:

\[
\frac{Cₑ}{qₑ} = \frac{1}{q_{max}K₁} + \frac{1}{q_{max}}Cₑ
\]  \hspace{1cm} (3)

\[
\ln q = \ln k + \frac{1}{n} \ln C
\]  \hspace{1cm} (4)

The Freundlich equation is an empiric model based on heterogeneous adsorption (Boudrahem, et al., 2011):

\[
qₑ = k_f Cₑ^{1/n}
\]  \hspace{1cm} (5)

\[
\log qₑ = \log K_f + \frac{1}{n} \log Cₑ
\]  \hspace{1cm} (6)

where,

\( Ce \) = The solute concentration (mg/L) at equilibrium
\( qₑ \) = The amount of solute at equilibrium (mg/g)
\( q \) = Mon related to adsorption capacity
\( K \) = Langmuir constant

The Freundlich equation is an empiric model based on heterogeneous adsorption (Boudrahem, et al., 2011):

\[
\log(q₀ – qₜ) = \log qₑ - \frac{K₁}{2003} t
\]  \hspace{1cm} (7)

Where \( qₜ \) is the amount of adsorbate at time \( t \) (mg/g), \( qₑ \) is the adsorption capacity at equilibrium (mg/g) \( k₁ \) is the pseudo-first-order rate constant \( (\text{min}^{-1}) \) and \( t \) is the contact time (minute). The linearity second-order kinetic model is given as:

\[
\frac{t}{qₜ} = \frac{1}{k₂qₑ²} + \frac{1}{qₑ} t
\]  \hspace{1cm} (8)

Where \( k₂ \) is the equilibrium rate constant of pseudo-second-order adsorption \( (\text{g mg}^{-1}. \text{min}^{-1}) \).

RESULTS AND DISCUSSION

Characterization of biosorbent: Characterization of biosorbent was done using FTIR analysis. FTIR spectra of biosorbent Oscillatoria sp is shown in Fig. 1. IR spectroscopy has been the method of choice for studying structure and interaction of molecules with identified of functional group (Banyay et al., 2003). The identification of functional group from Oscillatoria sp can be seen in Table 1. The stretching vibration of C-H indicated the methyl group and usually found in organic compounds (Coates, 2006). The peak of C-H stretching usually occurs below 3000 cm⁻¹. The peaks 1510-1450 is an aromatic stretch (C=C) and 850 cm⁻¹ is C-H aromatic (Coates, 2006). Biosorption of metal ion depends on the component and functional group of the biosorbent. This component including cellulose,
Fig. 1: FTIR analysis of Oscillatoria sp

![FTIR analysis of Oscillatoria sp](image)

**Table 1: Identification of functional group of Oscillatoria sp**

| Wavenumber (cm⁻¹) | Functional group | Chemical group               |
|-------------------|------------------|------------------------------|
| 3272              | O-H              | Alcohol                      |
| 2925              | O-CH₃, C-H       | Hydrocarbon                  |
| 2087              | C-H, N-H, C=O    | Hydrocarbon, amine, carbonyl |
| 1634              | C-C              | Hydrocarbon                  |
| 1515              | C-H              | Hydrocarbon                  |
| 1449              | C-H, COO         | Hydrocarbon, carboxylate     |
| 1082              | C-N, C-O-C       | Amines                       |
| 853               | PO₄³⁻, C-O-P     | Phosphates                   |
| 596               | C-S, mineral     | Sulfur, Anorganic compounds  |

![Graph showing the relationship between pH and cobalt adsorption efficiency by Oscillatoria sp](image)

**Fig. 2: Effect of pH on the cobalt adsorption into Oscillatoria sp.**

**Adsortion study:** The cobalt sorption is depended on pH solution. The effect of initial pH on cobalt sorption capacity was studied at 25 mg/L cobalt initial concentration and the result is shown in Fig. 2. The uptake of cobalt in the pH range of 2-8 was determined in this experiment.

Figure 2 shows the relationship between pH and cobalt absorption efficiency by Oscillatoria sp. Biosorbent dosage of 0.25 g, the initial concentration of cobalt is 25 ppm and the volume of solution is 50 mL. An increase in pH caused an increase in the amount of cobalt absorbed. There is a linear correlation between pH and adsorption efficiency with a correlation of 0.9815 and equation y = 17.263x-47.855. The maximum efficiency is obtained at pH 8 with the adsorption of 23.58% and adsorption capacity of 4.71 mg/g. The pH solution can affect of metal-binding sites between cobalt and biosorbent. The cell wall ligands are closely associated with hydronium ion at the low of pH (Al-Rub et al., 2004). The increase of pH resulted in an increase in biosorption level because of influences of negative surface charge of the functional group. At the low pH occurred the competition between protons and metal ions in the adsorption process (Feng and Aldrich, 2004).

Shaking is carried out to homogenize the solution and regulate the process of absorption of cobalt by Oscillatoria sp. The stirring range is carried out with variations of 50-250 rpm. The effect of shaking on cobalt adsorption by Oscillatoria sp can be seen in Fig. 3. Based on the experiment, the optimum stirring was
Fig. 3: Effect of shaking on the cobalt adsorption into *Oscillatoria* sp.

Fig. 4: Effect of salinity on the cobalt adsorption into *Oscillatoria* sp.

Variation of salinity ion solution from 0-30 g/L. Figure 4 shows the greater the salinity, the smaller of cobalt absorbed by *Oscillatoria* sp. The optimum absorption was obtained in salinity = 0 with optimum efficiency is 28.72% and absorption capacity of 1.43 mg/g. Analytical isotherms equation such as Langmuir and Freundlich isotherms are widely used for modeling adsorption data (Jeppu and Clement, 2012). According to the Langmuir model, sorption occurs uniformly on the active site of the sorbent and once a sorbate occupies a site. These model isotherms can be seen in Fig. 5 to 7.

Figure 5 shows the effect of initial cobalt concentration on adsorption capacity onto *Oscillatoria* sp. The result showed a linear correlation between the initial cobalt concentration and absorption capacity with $R^2 = 0.976$ and equation $y = 0.1633x - 0.5312$. The adsorption isotherm showed the adsorption molecule between the solid and liquid phase on the equilibrium state (Hameed *et al.*, 2007). The applicability of the isotherm equation is compared with the correlation coefficient.

Fig. 5: Effect of concentration for the uptake of cobalt by *Oscillatoria* sp

Fig. 6: Freundlich adsorption isotherm

In the Freundlich model, the cases linear plots were obtained which reveal the applicability of this isotherm on cobalt adsorption process (Mittal *et al.*, 2007). The condition experiment was done in pH = 5, the amount of adsorbent = 2.5 g and time of 60 minutes. The correlation shown linear with $r = 0.9715$ and equation of $y = 0.1186x + 0.1411$. The linear plot in $Ce$ vs log $q_e$ shows that the adsorption of cobalt onto *Oscillatoria* sp follow the Freundlich isotherm model. The Freundlich
adsorption isotherm was also applied for the adsorption of cobalt onto *Oscillatoria* sp. Freundlich constant $k_f$ and $n$ were found to be $0.1186 \text{ (mg/g)}(\text{L.mol})^{1/n}$ and $8.43 \text{ mg/L}$, respectively.

Optimum adsorption capacity ($q_m$) biosorbent of cobalt to adsorb of cobalt according to Langmuir model was $6.24 \text{ mg/g}$. The slope and the intercept is $6.24 \text{ mg/g}$ and $0.01 \text{ L/mg}$, respectively, that it indicated $Q_{max}$ and $b$. The Langmuir parameters can be used to knowing the affinity between the biosorbent and adsorbate. It can be used to suggests of the adsorption process is monolayer (Kalavathy *et al.*, 2005; Ahalaya *et al.*, 2010). The linear isotherm model is an alternative mathematical approach to predict the overall adsorption behavior (Chen, 2015).

**Kinetic of adsorption:** The kinetic parameters were calculated by monitoring the effect of contact time, amount of adsorbent and concentrations of adsorbate solution on adsorption of cobalt. Figure 8 shows the effect of contact time on cobalt absorption by *Oscillatoria* sp. The increase in contact time shows the greater of cobalt absorbed. The optimum contact time is obtained by incubation for 120 min with an absorption capacity of $1.9338 \text{ mg/g}$. In can be inferred that the cobalt could ion could be adsorbed with a short time by using of *Oscillatoria* sp.

Figure 9 shows the effect of adsorbent dosage in cobalt adsorption by *Oscillatoria* sp. The algae dosage was $0.25 \text{ g}$ and the initial concentration of Co$^{2+}$ ion was approximately $25 \text{ mg/L}$. The experiment shows increasing biosorbent dose increasing of cobalt adsorption in solution. The dose of biosorbent in the range of $0.1-0.6 \text{ g}$ with the amount of adsorbent is $0.2983-0.3712 \text{ g}$. This adsorption involved in the mass transfer of ions from aqueous into the surface of biosorbent (Liu *et al.*, 2010).

The kinetics of adsorption describes the rate of cobalt ions uptake on *Oscillatoria* sp microalgae and this rate control by the equilibrium time. The kinetic model of cobalt adsorption can be seen in Fig. 10. The kinetic model indicates the behavior of the adsorbent in the adsorption process (Aravindhan *et al.*, 2007). The first-order rate, constant ($k_1$) and $q_e$ were determined from the slope and intercept of the plot $(q_0-q_t)$ versus time contact. Kinetic studies showed that the adsorption followed a pseudo-first-order. The first-order rate constant $k_1$ can be found in the experiment was $1.2\times10^{-3} \text{ min}^{-1}$.

**CONCLUSION**

The experimental result shows that microalgae of *Oscillatoria* sp is an alternative for the removal of cobalt was depend on contact time, pH, adsorbent dosage and initial cobalt concentration. Analysis of functional group from biosorbent shows the peaks of hydroxide, carboxyl and carbonyl ions. This functional group is an important role in the biosorption of cobalt ion. The adsorption models of cobalt ion with *Oscillatoria* sp followed the Langmuir and Freundlich isotherms. The kinetic rate shows the pseudo-first-order.

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CONFLICT OF INTEREST

No potential conflict of interest was reported by the authors.

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