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Characteristics of Cd(II) Biosorption into Streamer Biofilm Matrices

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Abstract. This study analyzed the characteristics of Cd(II) biosorption into the natural streamer biofilm matrices collected from the Brantas River in Indonesia to develop streamer biofilms as biosorbent pollutant ions. The biosorption features were studied by investigating the kinetics of adsorption and the adsorption isotherm of Cd(II) into the streamer biofilm. The adsorption sites of biofilms were investigated by analyzing the biofilms' electric charge characteristics and Fourier Transform Infrared Spectroscopy (FTIR) spectra. The results of this study suggest that the adsorption of Cd(II) to the biofilm streamer is a physicochemical process where the electrically charged sites promoted by ionization functional groups in the biofilm polymers functioned as adsorption sites. The adsorption of Cd(II) into streamer biofilm is well suited to the Langmuir adsorption pattern. Cd(II) adsorption's maximum capacity to the biofilm is estimated to be approximately 14.29 mmol/g, while the equilibrium constant is approximately 0.06 L/mmol. This study demonstrates the biosorption of Cd(II) using biofilm streamers that formed naturally in rivers in Indonesia, a phenomenon that had rarely been reported. This study's results reveal that the natural streamer biofilm formed in Indonesia's Brantas River is a promising biosorbent for Cd(II) removal in water pollution treatments.

Keywords: Adsorption; Aquatic ecosystem; Heavy metals; Microbial ecology; Water pollutant

1. Introduction

Water pollution has become a leading environmental problem in developing countries, including Indonesia (Chojnacka, 2010). Pollutants in the aquatic ecosystem include heavy metals such as Cd(II). This heavy metal is largely used for industrial purposes (Suprapto et al., 2020), such as in the coating and electrical industries (Chojnacka, 2010), and has become a primary battery component. Cd(II) is a cancer hazard and can cause lung and kidney diseases (Fomina and Gadd, 2014; He et al., 2016; Nasir and Faizal, 2016; Yi et al., 2017; Locosselli et al., 2018). The quality standard for Cd(II) concentration in aquatic ecosystems, such as rivers in Indonesia, is a maximum of 0.01 mg/L. Excessive use of Cd(II) can pollute aquatic environments.

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Numerous technologies have been proposed to reduce water pollution. These technologies should be sufficient, inexpensive, and environmentally friendly (Julien et al., 2014; Fomina and Gadd, 2014; Jobby et al., 2018). One alternative technology is using biological materials, or biomass, to immobilize contaminants (Jawad et al., 2018a; Kusrini et al., 2018). Biomass-based technologies have many advantages because they use inexpensive and renewable materials and can recover pollutants (Jawad et al., 2016; Desmiarti et al., 2019). Biosorption is a biomass-based technology that is widely proposed as an alternative pollution treatment. The choice of biosorbents strongly influences the success of biosorption. The evaluation of various types of biosorbents to develop biosorption-based water pollution treatments has become one of the latest research themes related to biosorption (Olufemi and Eniodunmo, 2018).

The alternative biosorbents that have attracted many experts' attention are microbes in aquatic ecosystems (Gadd, 2009; Jimoh & Cowan, 2017; Cheng et al., 2018). The primary habitat of microbes in aquatic ecosystems is a biofilm (Flemming and Wingener, 2010; Kurniawan and Yamamoto, 2019). *Biofilm* is defined as a microbial community matrix attached to the substrate (da Silva et al., 2020). Biofilms that grow in river ecosystems are called streamer biofilms. Streamer biofilm matrices can attract and retain various pollutant ions from the surrounding waters, including heavy metal ions such as Cd(II) (Gadd, 2009; Volesky, 2007).

Although understanding the characteristics of Cd(II) biosorption by streamer biofilms can improve the development of water purification technology (D'Acunto et al., 2018; Rittman, 2018), studies remain limited about the biosorption of Cd(II) using biofilm streamers formed naturally in rivers. Most of the studies use single-species biofilms or laboratory-grown biofilms (Hiraki et al., 2009; Kurniawan et al., 2015; Gul et al., 2018).

The present study analyzed the biosorption of Cd(II) by the natural streamer biofilm matrices collected from the Brantas River in Malang City, Indonesia. This study suggested that the streamer biofilm matrices may adsorb Cd(II) through a physicochemical process. According to this study's results, the natural streamer biofilm matrices formed in the Brantas River may become a potential alternative biosorbent for Cd(II) removal from aquatic ecosystems.

2. Methods

This study investigated Cd(II) biosorption by biofilm streamers from rivers in Indonesia, which had been overlooked in previous studies. The results of this study support using streamer biofilm as a biosorbent for heavy metals, especially Cd(II), in flowing aquatic ecosystems. The biosorption of Cd(II) into natural streamer biofilm matrices was analyzed by investigating the kinetics of adsorption and the adsorption isotherm of Cd(II) using the natural streamer biofilm formed on the river stones. Moreover, the biofilm's electric charge was examined by measuring the biofilm's electrophoretic mobility (EPM). This study's detailed methodology is described below.

2.1. Sample Preparation

Biofilm samples were obtained from the surface of stones taken from the Brantas River in Malang City, Indonesia. The stones covered with biofilm (approximately 50 stones) were sampled from an approximate depth of 50 cm. The stones were placed in plastic containers filled with river water and then taken to the laboratory; the containers' temperature was maintained at 4°C. The biofilm was removed from the stone surface using a toothbrush and suspended in distilled water. The biofilm suspension was then centrifuged (8,000 × g at 4°C for 10 minutes), and the supernatant was discarded. Forty mL of distilled water was added to the pellet biofilm, then mixed vigorously using a Vortex-Genie 2 (M&S Instruments, Inc., Osaka, Japan) at 3,000 rpm for 1 minute. The resulting biofilm suspension was centrifuged

(8,000 × g at 4°C for 10 minutes), and the resulting supernatant was discarded. This step was repeated six times to wash the biofilm pellets. The washed biofilm pellets were stored at -40°C until used in the experiment.

2.2. Electrophoretic Mobility (EPM)

The biofilm pellet was placed in 40 mL of 10 mM NaCl solution (diluted reagent-grade chemical [Wako Pure Chemical Industries, Osaka, Japan] in distilled water). The biofilm suspension was centrifuged (8,000 × *g* at 4°C for 10 minutes), and the biofilm pellets were collected. Some of the pellet (0.03 g) was suspended in 1 mL of 10 mM NaCl solution (diluted reagent-grade chemical [Wako Pure Chemical Industries, Osaka, Japan] in distilled water). The resulting suspension was mixed using a Vortex-Genie 2 (M&S Instruments, Inc., Osaka, Japan) at 3,000 rpm for 5 minutes, then sonicated for 10 minutes (2510J-MT, Yamato Scientific, Tokyo, Japan; 42 kHz, 125 W), and finally vortexed for 10 seconds. The suspension obtained was mixed with 10 mM of phosphate buffer solution in a ratio of 1:19. Phosphate buffer was prepared by diluting reagent-grade chemicals (0.526 g of NaCl and 0.358 g of $Na_2HPO_4 \cdot 12H_2O$) (Wako Pure Chemical Industries, Osaka, Japan) into 1 L of distilled water. The biofilm suspensions were used as samples in the EPM measurement (ZETASIZER Nano-Z, Malvern Instruments, Ltd., Worcestershire, UK). Biofilm EPM was measured between pH 2 and 9. Twenty mM of HCl or NaOH solution (Wako Pure Chemical Industries, Osaka, Japan) was used to adjust the solution's pH.

2.3. FTIR Spectra Analysis

Biofilm pellet was dried at approximately 60°C until the constant weight was reached. The dry pellet was used as the sample in FTIR analysis. In order to record the FTIR spectra of biofilm, 0.01 g of the dry biofilm pellet was mixed with powdered KBr before compressing the mixture under high pressure. Under pressure, KBr melts and seals the compound into the matrix. The KBr pellet was then inserted into the sample holder and measured using a Shimadzu FTIR Spectrometer 84002 (Shimadzu Corporation, Japan).

2.4. Kinetics of Adsorption

Biofilm pellet (2.5 g) was resuspended in 270 mL of distilled water. Biofilm suspension was vortexed for 5 minutes, then sonicated for 10 minutes, and finally vortexed for 30 seconds. After that, 30 mL of 100 mM $CdCl_2$ solution was added to the biofilm suspension. An artificial $CdCl_2$ solution was used instead of water from the Brantas River. The $CdCl_2$ solution was prepared by dissolving a $CdCl_2$ reagent-grade chemical (Wako Pure Chemical Industries, Osaka, Japan) into distilled water. The suspension temperature was kept at 25°C with a water thermostat and stirred using a magnetic stirrer. Some of the suspension (1.5 mL) was taken after 5 to 300 minutes, then centrifuged (15,000 × g at 4°C in flash mode) to obtain the supernatant. The number of ions adsorbed by the biofilm was calculated from the ion concentration difference between the supernatant and the control ($CdCl_2$ aqueous solution without the biofilm). Cd(II) concentrations were measured using an Atomic Absorption Spectroscopy Shimadzu AA-6800 (Shimadzu Corporation, Japan). The experiment was repeated three times independently.

2.5. Adsorption Isotherm

As in the kinetics of adsorption experiment, an artificial $CdCl_2$ solution was used in the adsorption isotherm experiment instead of water from the Brantas River. Biofilm pellet (2.5 g) was added to 100 mL of $CdCl_2$ aqueous solution. The suspension was vortexed for 5 minutes, then sonicated for 10 minutes, and finally vortexed for 30 seconds. Twenty mL of the $CdCl_2$ solution, prepared by dissolving a reagent-grade chemical (Wako Pure Chemical Industries, Osaka, Japan) into distilled water, was added to the biofilm suspension. The final concentrations of Cd(II) were between 15 and 250 mM. The suspension was kept

homogeneous using a magnetic stirrer, and the temperature was kept at 25°C using a water thermostat.

After 10 minutes, the suspensions were centrifuged (15,000 × g at 4°C in flash mode) to separate the pellet and the supernatant. Cd(II) concentrations in the supernatants were measured using an Atomic Absorption Spectroscopy Shimadzu AA-6800 (Shimadzu Corporation, Japan). The Cd(II) adsorbed into the biofilm was calculated from the differences of Cd(II) concentration between the supernatant and the control ($CdCl_2$ aqueous solution without the biofilm). The experiment was repeated three times independently.

The biosorption of Cd(II) into the biofilm was analyzed using the Langmuir equation variant shown in equation 1 (Volesky, 2007; Jawad et al., 2018b).

$$\frac{C}{N} = \frac{1}{(N_{max})b} + \frac{C}{N_{max}} \quad (1)$$

Equation 1 is based on the dynamic equilibrium between the ions in the solution and the adsorbed ions (N) at the equilibrium concentration (C). The adsorption equilibrium constant (b) is the ratio of the adsorption and desorption rates. The value of b increases as the adsorption rate exceeds the desorption rate. Hence, plotting C / N against C produces a straight line with a slope of $1/Nmax$ and the y-intercept $1/(Nmax)b$. From this condition, the values of $Nmax$ and b can be estimated.

3. Results and Discussion

3.1. Electric Charge Properties of Biofilm Polymers

The biofilm's electric charge properties were estimated by measuring the EPM of the biofilm between pH 2 and 9 (Figure 1). The EPM of the biofilms ranged from negative to positive values, suggesting that the biofilm matrix has positively and negatively charged sites. These charged sites can attract oppositely charged ions from the surrounding water of the biofilm. In this case, heavy metal ions such as Cd(II) in the river water can be attracted by the biofilm's negatively charged sites.

The EPM values of the biofilm are negative when the pH is greater than 2. These negative values decrease when pH decreases, especially at around pH 4. The lower the pH, the more protons (H^+) are available in the water. The abundance of protons (H^+) resulted in the decreased ionization of the negatively charged functional groups in the biofilm (such as the carboxylic group, whose pKa is around pH 4), as illustrated in the following reaction:

$$R\text{-}COO^- + H_3O^+ \rightleftarrows R\text{-}COOH + H_2O$$

In the above condition, the biofilm matrix's negatively charged sites will become neutral, resulting in the decrease of negative values of the biofilm's EPM. The protonation rate of negatively charged sites increases sharply at pH 2, resulting in more significant numbers of positively charged sites than negatively charged sites (positive net charge). Thus, the positive value of the biofilm's EPM can be detected in the EPM measurement.

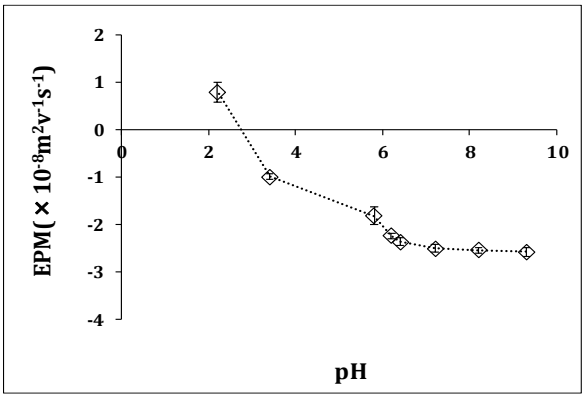

Figure 1 Result of EPM measurement of the biofilm matrices

3.2. FTIR Spectra

The EPM measurement results show that positive electric charge and negative electric charge are present in the biofilm matrix. This electric charge may derive from the ionization of functional groups present in the polymer biofilm. FTIR spectra of the biofilms were analyzed to determine the effect of the functional groups. FTIR spectra analysis of the biofilms detected various peaks (Figure 2).

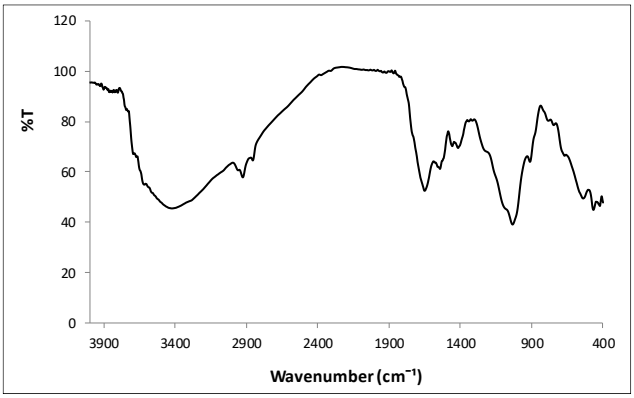

Figure 2 FTIR spectra of the biofilm matrices

The peaks between 1300 and 1600 cm^{-1} indicate the presence of carboxyl groups in the biofilm matrix. The carboxyl group's pKa of around pH 4 was also indicated in the biofilm by measuring EPM (Figure 1). The ionization of the carboxyl groups may result in the presence of negatively charged sites in the biofilm. Moreover, amino groups with a positive electric charge were also identified in the biofilm, characterized by C-N bending at 1414 cm^{-1}. The biofilm's positively charged sites may be caused by this amino group's ionization in the biofilm polymers.

3.3. Kinetics of Adsorption

The time course of Cd(II) biosorption to the biofilm matrices was analyzed (Figure 3). The results suggest that the amounts of adsorbed Cd(II) remained constant from 5 minutes to the end of the experiment. The biosorption of Cd(II) by the streamer biofilms seems to happen quickly. This type of process is a feature of the physicochemical mechanism that usually drives biosorption (Lewandowski and Beyenal, 2007). The biosorption of Cd(II) into the biofilm streamers may occur through a passive uptake process. The biosorption's primary driving force may be ion exchange mechanisms and attractive electrostatic interaction (Kurniawan et al., 2015; Ningrum et al., 2019).

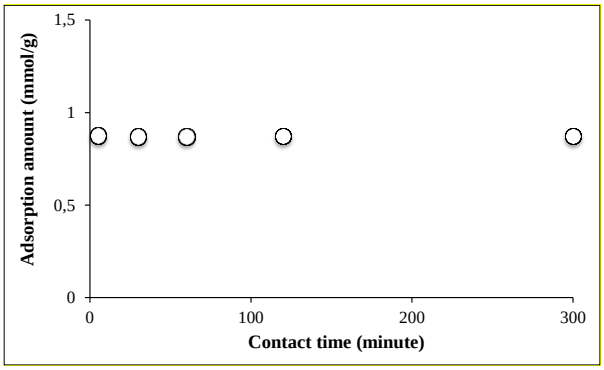

Figure 3 Time course adsorption of Cd(II) into the biofilm matrices

3.4. Adsorption Isotherm

The adsorption isotherm of Cd(II) into the streamer biofilms was analyzed (Figure 4). Based on the kinetics of adsorption experiments, the contact time used in the adsorption isotherm experiment was 10 minutes. The adsorbed amounts of Cd(II) increased with increased concentration and leveled off at a high concentration. At a lower concentration, the higher availability of the biofilm's charged sites for Cd(II) in the solution promotes a more significant accumulation of ions than at a higher concentration.

The efficiency of biosorption of Cd(II) using the biofilm matrix was estimated (Figure 5). The result indicates that the efficiency decreases along with the increase in Cd(II) concentration. Biosorption efficiency reaches more than 90% when the concentration of Cd(II) is ≤ 60 mM. The decrease in the adsorption efficiency at the high concentration may be caused by the decrease of available active sites in the biofilm for Cd(II) in the solution (Jawad et al., 2020). Determining the efficiency's limit is crucial in using the streamer biofilm matrix as a biosorbent for Cd(II) in water treatment technology.

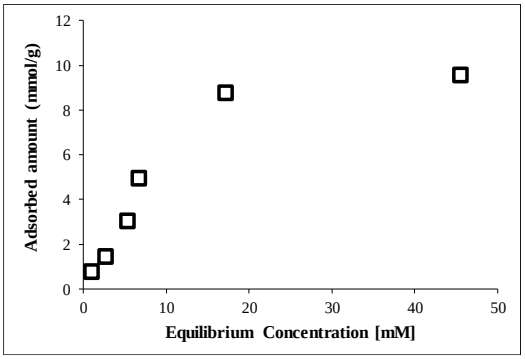

Figure 4 Adsorption isotherm model of Cd(II) into the biofilm matrices

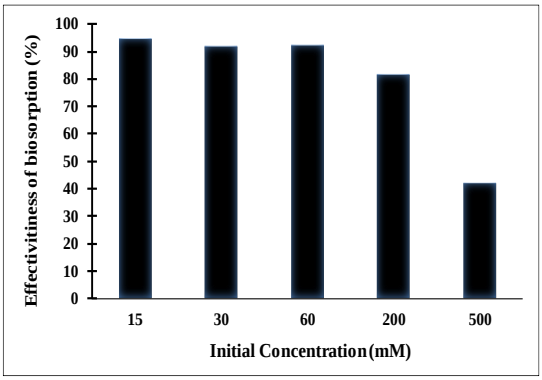

Figure 5 Efficiency of Cd(II) adsorption into the biofilm matrices

Characteristics of Cd(II) biosorption were elaborated in more detail using the Langmuir Isotherm Model (Figure 6). The ratio of the adsorbed amount of Cd(II) into streamer biofilm (N; mmol/g) in each equilibrium concentration (C; mM) were plotted to equilibrium concentrations (C; mM) in order to estimate the maximum capacity of biosorption (Nmax; mmol/g) and the adsorption equilibrium constant (b; L/mmol).

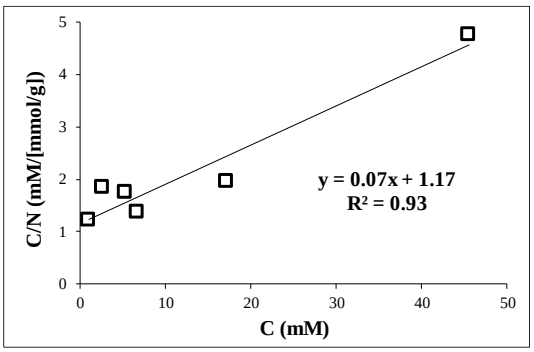

Figure 6 Adsorption isotherm model of Cd(II) into the biofilm matrices

Cd(II) biosorption by the streamer biofilm fitted well with the Langmuir Isotherm Model (R^2 = 0.93). Hence, the adsorption of Cd(II) into the streamer biofilm seems to occur in the monolayer form. Cd(II) adsorption to the streamer biofilm may be promoted by the attractive electrostatic interaction between Cd(II) and the negatively charged sites in the streamer biofilm.

In this study, the maximum amount of Cd(II) absorbed by the streamer biofilm (*Nmax*) is estimated to be 14.29 mmol/g. This capacity was comparable with the capacity of adsorbents reported in previous studies (Table 1). The result of this comparison indicates that the biofilm formed in the Brantas River shows promise for use in biosorption. The adsorption and desorption rates ratio represented by the value of the adsorption equilibrium constant (b) in this study is 0.06 L/mmol. A higher value of *b* indicates a stronger bond between Cd(II) and the biosorbent. In this study, the value of *b* of Cd(II) adsorption into the biofilm was relatively low compared to the other ions (Gadd, 2009). This result suggests that, once adsorbed into the biofilm matrix, Cd(II) may be easily removed from the biofilm matrix. Thus, it may be possible to reuse the biofilm matrix as a biosorbent.

Table 1 Cd(II) adsorption capacity of various adsorbents (converted into mmol/g)

Adsorbent	Nmax (mmol/g)	Reference
Biochar	0.58	Zhang et al., 2021
Ligand (Nano-composite materials)	1.3	Awal et al., 2018
Polyethyleneimine modified activated carbon	0.4003	Xie et al., 2019
Nanoscale zero-valent iron (NZVI)	0.43	Li et al., 2018
Modified chitosan beads	1.6	Sutirman et al., 2018
ZnO nanoflowers	0.64	Kataria and Garg, 2018
Modified hydrochar	0.81	Li et al., 2019
Biofilm from biotrickling filter	0.37	He et al., 2018
Magnetite nanocomposite	2.8	Alqadami et al., 2020
Magnetic silica gel	0.83	Guo et al., 2018
Guanyl-modified cellulose	0.46	Kenawy et al., 2018
Mesoporous cellulose biochar	3.3	Chen et al., 2018
Mercapto-modified bentonite	0.25	Ecer et al., 2018
Porous cellulose	0.48	Barsbay et al., 2018

4. Conclusions

The present study shows that biofilm streamers carry both positively and negatively charged sites. The streamer biofilm matrices can attract and adsorb heavy metal ions such as Cd(II) from the surrounding water. The streamer biofilms have been shown to quickly adsorb Cd(II) through a physicochemical reaction. The maximum biosorption capacity (*Nmax*) of the streamer biofilm matrix for Cd(II) is 14.29 mmol/g, and the adsorption equilibrium constant (*b*) is 0.06 L/mmol. According to this study's result, the streamer biofilm formed naturally in the Brantas River is a promising biosorbent in the removal of water pollutants. However, pollutants entering rivers include more than Cd(II). Hence, to develop river biofilms as biosorbent for river pollution, future studies will focus on the biosorption of other heavy metals by biofilm formed in the Brantas River.

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