Biosorption of Cu(II) by natural biofilm matrix of Lahor Reservoirs, Indonesia

A Kurniawan¹²³, L N Salamah¹², A A Amin¹² and A Yanuar¹²

¹ Microbial Resources and Biotechnology Research Group, Interdisciplinary Postgraduate Program, University of Brawijaya
² Coastal and Marine Research Centre, University of Brawijaya
³ Faculty of Fisheries and Marine Science, University of Brawijaya

*Corresponding author: andi_k@ub.ac.id

Abstract. Heavy metal pollution is a severe problem in aquatic ecosystems. Various technologies have been developed to overcome the problems. One of the proposed technologies is biosorption. The success rate of biosorption is largely determined by the selection of biosorbent. The biosorbent should have a high capacity to adsorb the contaminant as well as environmentally friendly. One of the alternative biosorbent in the biofilm matrix. This study analyzes the biosorption characteristics of Cu(II), as one of the common pollutants in the aquatic ecosystem, by biofilm matrix collected from Lahor Reservoirs in East Java, Indonesia. The kinetics of adsorption investigation in this study show that the biosorption of Cu(II) by the biofilm matrix reached the equilibrium state within 5 minutes. The adsorption isotherm investigation revealed that the biosorption of Cu(II) to the biofilm matrix fitted well to the Langmuir isotherm model. The maximum adsorption amount (Nmax) of Cu(II) by biofilm is around 33.3 mmol/gram, and the adsorption equilibrium constant is 0.03 L/mmol.

According to the result of this study, the biofilm matrix has the potentiality to become biosorbent in the treatment of heavy metal pollution in the aquatic ecosystem.

1. Introduction
Degradation of the aquatic ecosystem is one of the most serious environmental problems [1]. One of the pollutants causing degradation is heavy metal ions such as Cu(II) [2]. Cu(II) can cause various health problems for humans, such as kidney disorders or cancer [3,4]. Hence, various technologies are developed to solve the Cu(II) contamination. The technologies not only should be effective but also environmentally friendly.

Biosorption is one of the alternative technologies to solve heavy metal contamination in aquatic ecosystems [5,6]. One of the critical factors determined the success of biosorption is the biosorbent [7,8]. The selected biosorbent can come from various resources that can adsorb ions, including Cu(II) [9]. Biofilm matrices have been reported to have the ability to adsorb various ions, including pollutants such as Cu(II) [9,10]. Thus, the study regarding the biosorption process of Cu(II) by biofilm matrices is necessary.

Investigation of biosorption characteristics of Cu(II) by natural biofilm matrices, particularly formed in the reservoirs as one of the aquatic ecosystems in Indonesia, has been rarely reported. The biofilm matrices formed in the water reservoirs may provide the various function related to the water quality, such as the adsorption of water pollutants like heavy metals. Hence, the biofilm matrix can be
utilized in the treatment of heavy metal contamination if the adsorption characteristics can be understood. The present study investigated the biosorption characteristics of Cu(II) by the biofilm matrix collected from the Lahor Reservoirs in East Java of Indonesia. The results revealed that the biofilm matrix could be a potential biosorbent to solve Cu(II) contamination in the aquatic ecosystem.

2. Materials and method

2.1. Preparation of the sample of biofilm
Biofilms in this study were sampled from the surface of stones collected from Lahor Reservoir, Indonesia. The Lahor Reservoirs is a backup dam for the Sutami Reservoirs in East Java. The water in the Lahor Reservoirs will be channeled to the Sutami Reservoirs if the availability of water in the Sutami Dam shrinks. Stones were collected from a depth of 75 cm (30 stones from each sampling location) and brought back to the laboratory using a plastic container filled with the surrounding water. The temperature in the containers was maintained at 4°C. The biofilms were removed from the surface of the stones using sterilized toothbrushes and suspended in distilled water. The filtrates and biofilm pellets, prepared by centrifuging (8000×g at 4°C for 10 min) the biofilm suspensions.

2.2. Kinetics of adsorption
One wet-g of biofilm pellet was resuspended in 50 mL of distilled water. Then, 5.0 mL of 20 mM of a solution of reagent grade CuCl₂, prepared by dilute the chemical compound (Wako Pure Chemical Industries, Osaka, Japan) in distilled water, was added to the suspension and mixed well using a magnetic stirrer. The aliquots of the suspension were taken after 5 min – 300 min, then centrifuged (8,000 × g at 4°C at flash mode) to separate the supernatant and the pellet. The Cu(II) concentration in the solution was measured using an Atomic Absorption Spectroscopy Shimadzu AA-6800 (Shimadzu Corporation, Japan). The adsorption amounts of Cu were calculated from the concentration differences between concentrations of Cu in the supernatant and the control (the same aqueous solution without the addition of biofilm).

2.3. Adsorption isotherm
50 mL of CuCl₂ solution aqueous solutions (1 – 500 mM) was prepared by diluting reagent grade CuCl₂ in the distilled water. Then, one wet-g of biofilm pellet was added to each solution. After 15 minutes, the suspensions were centrifuged (8,000 × g at 4°C for 5 min) to separate the supernatant and the biofilm pellet. The Cu(II) concentration in the solution was measured using an Atomic Absorption Spectroscopy Shimadzu AA-6800 (Shimadzu Corporation, Japan). The adsorption amounts of Cu were calculated from the concentration differences between concentrations of Cu in the supernatant and the control (the same aqueous solution without the addition of biofilm).

3. Result and discussion

3.1. Time course of biosorption
Adsorption of Cu(II) by the biofilm matrix in various contact time (5-300 minutes) were investigated in this study (Figure 1). The adsorption amount of Cu(II) to the biofilm after 300 minutes was 1.8 mmol/wet-g. This amount is relatively the same as the adsorption amount of Cu(II) after 5 minutes (1.7 mmol/wet-g). The biosorption of Cu(II) to the biofilm seems to occur in the fast process where the equilibrium state had been reached within 5 minutes. This condition suggested that Cu(II) ions were adsorbed through a physicochemical process [11, 12]. The same process is reported as the typical process of ion adsorption to biofilms [1,10,13].
3.2. Adsorption isotherm
In order to analyze the biosorption characteristics of Cu(II) to the biofilm matrix, the adsorption isotherm characteristics of Cu(II) biosorption by the biofilm matrix were investigated (Figure 2). The adsorption amounts of Cu(II) by biofilm matrices were increased significantly in the low concentration of equilibrium states (<40 mM), and then, become relatively stable in high concentration (>40 mM). The adsorption amount of the ions to the biosorbent, including biofilm matrices, is a function of available adsorption sites and the ions concentration [7,13,14]. In this case, the adsorption amount will increase along with the increase of equilibrium concentration.

Slightly change of adsorption amounts of Cu(II) to the biofilm matrices in high concentrations (> 40 mM) in this study indicate that the adsorption amount is almost not affected by the increase of equilibrium concentration. This condition seems to occur because the adsorption sites in the biofilms were almost completely fulfilled by the Cu(II) resulted in the relatively stable adsorption amount [9].
The adsorption isotherm trend shows the adsorption of Cu(II) to the biofilm matrices is the L type of adsorption isotherm. The characteristics of adsorption in various equilibrium concentration and the L type of graph suggested that the adsorption of Cu(II) to the biofilm matrices occur in the monolayer form [9,12,15].

3.3. Biofilm in the biosorption of Cu (II)

The characteristics of Cu(II) biosorption to the biofilm matrices are analyzed by plotting the adsorption data using Langmuir Adsorption model [9]. The biosorption data of Cu(II) in this study is fitted well with the equation (R=0.96). It seems that the Cu(II) adsorption to the biofilm matrices occurs through physicochemical mechanisms such as ion exchange mechanism [16] and electrostatic interaction [17], [18]. This data also strengthens the estimation that the adsorption of Cu(II) occurs in monolayer, as explained above (Figure 2).

Based on the equation from figure 3, the maximum adsorption amount and the adsorption equilibrium constant for ion adsorption were calculated using a variant of the Langmuir isotherm equation [17], as described below:

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

(1)

The assumption in this equation is that a dynamic equilibrium exists between the adsorbed Cu(II) (N) and the free Cu(II) in solution (C). The adsorption equilibrium constant (b) was defined as the ratio of the adsorption and desorption rates. The value of b increases as the adsorption rate exceeds the desorption rate, relatively. The plot of C/N against C yields a straight line with a slope of 1/Nmax and a y-axis intercept of 1/(Nmax) b, and thus, the values of Nmax (the maximum amount of adsorbed ion; mmol dry-g–1) and b can be calculated.

The result of the analysis of Nmax and b show that the maximum adsorption amount of Cu(II) by the biofilm matrix in this study is 25 mmol/wet-g and the adsorption equilibrium constant is 0.03 L/mmol. The capacity of Cu(II) adsorption by the biofilm matrix in this study is comparable with the capacity of adsorption of Cu(II) by bottom ash of expired drug incineration [19], [20], activated carbon prepared from grape bagasse [19] or fixed-bed column [21]. These results suggested that the biofilm matrix can be a potential biosorbent to solve Cu(II) contamination in the aquatic ecosystem.

![Figure 3](image-url)

**Figure 3.** The results of plotting Cu (II) adsorption data into biofilms to the Langmuir Isotherm model. Bars represent standard deviation.

4. Conclusion
This study analyzed the characteristics of Cu(II) biosorption by the biofilm matrix collected from the Lahor Reservoirs. The results demonstrated: 1) the adsorption of Cu(II) to the biofilm was promoted by physicochemical interaction between the Cu(II) and the adsorption site in the biofilm matrix; 2) the biosorption of Cu(II) to the biofilm matrix occurs in the monolayer form; 3) the maximum adsorption amount of Cu(II) by the biofilm matrix in this study is 25 mmol/wet-g and the adsorption equilibrium constant is 0.03 L/mmol, and 4) the biofilm matrix can be a potential biosorbent to solve Cu(II) contamination in the aquatic ecosystem. According to the results of this study, the biofilm matrix formed in the Lahor Reservoirs may be utilized in the treatment of heavy metal contamination in the aquatic ecosystems.

References
[1] Kurniawan A and Yamamoto T 2019 Int. J. Microbiol. 2019 1-7
[2] Mary J, Karthik C, Ganesh R, and Kumar S S 2018 J. Environ. Manage. 217 56-70
[3] MacFarlane G R and Burchett M D 2002 Mar. Environ. Res. 54 65-84
[4] Kurniawan A 2018 J. Envi. Eng. Sust. Technol. 5 61-67
[5] Fomina M and Gadd G M 2017 Bioresour. Technol. 160 3-14
[6] Kurniawan A, Salamah L N, and Susanti Y A D 2019 IOP Conf. Ser. Earth Environ. Sci. 239 012026
[7] Kyzas G Z, Fu J and Matis K A 2014 Processes 2 419-440
[8] Kurniawan A, Salamah L N and Jayati P D 2019 J. Environ. Sci. 13 11-19
[9] Ulfa S M, Chamidah N and Kurniawan A 2019 IOP Conf. Ser. Earth Environ. Sci. 239 012008
[10] Kurniawan A 2019 J. Perik. 21 35-39
[11] Sinha S 1999 Environ. Monit. Assess. 57 253-264
[12] Ghazy S E, Samra S E and Mahdy A M 2003 Adsorp. Sci. Technol. 21 285-296
[13] Kurniawan A, Yamamoto T, Tsuchiya Y and Morisaki H 2012 Microb. Environ. 27 399-406
[14] Kurniawan A and Yamamoto T 2018 IOP Conf. Ser. Mater. Sci. Eng. 299 012004
[15] Kurniawan A and Sukandar 2017 Int. J. Sci. Res.73 185-190
[16] Gale P, Reddy K R and Graetz D A 1994 J. Environ. Qual. 23 370-377
[17] Kurniawan A, Musa M, Salamah L N, Yamamoto T, Prihanto A A and Amin A A 2019 Aquac. Aquar. Conserv. Legisla. 12 1951-1960
[18] Kurniawan A 2018 AIP Conf. Proceed. 2021 050001
[19] Benzaozi T, Selantnia A and Djabali D 2017 Adsorp. Sci. Technol. 36 114-129
[20] Fitratian A F, Rumhayati B and Kurniawan A 2019 J. Pure App. Chem. Res. 8 40–52
[21] Jodeh S, Abdelwahab F, Nidal J, Warad I and Jodeh W 2016 J. Assoc. Arab Univ. Basic Appl. Sci. 20 32–38