Enhancement Biosorption of Activated Sludge Process on Heavy Metals: Cadmium (Cd) And Nickel (Ni)

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Abstract. This study focuses on Activated sludge treatment is carried out by a continuous reactor. Merriotte tube capacity of 10L with a discharge of 10L/day as an inlet. Next to the 10L volume aeration tank where biological treatment occurs, pH 7 ± 0.2 and DO $\geq 3\text{mg/L}$ are the control variables. COD, Cd and Ni are taken for testing inlet and outlet. Artificial waste is used as an inlet with a nutrient ratio of C: N: P is 100: 5: 1. Seeding stage occurs 13 days to get an MLSS value $\geq 2000\text{mg/L}$. Acclimatization I for adapting microorganisms to the environment occurred for 27 days and acclimatization II for 11 days as microbial adaptation to heavy metals. Increasing the C/N ratio from 20 to 50 will reduce the efficiency of COD removal from 74.5% to 65.38%, Cd removal from 24.3% to 32.3% and Ni removal 13.8% to 28.5%. Initial metals reduced the efficiency of COD removal at low, middle and high levels by 82.5%, 71.75%, 55.875%, respectively. Initial metals at low, middle, and high levels were obtained Cd removal efficiency of 0%, 52.2%, 32.6% and Ni removal efficiency of 0%, 36.3%, 27%, respectively. Optimal response for COD removal is 68.5% with factor initial metal middle and ratio C/N 50.

1 Introduction

In the last few decades, heavy metal is one of the main environmental problems throughout the world. Biologically treating wastewater using activated sludge is one of the most frequently used processes because of its low cost and absorption of toxic substances including Cadmium (Cd) and Nickel (Ni) [1]. Microorganisms will form self-defense against toxic substances in the form of molecular layers called Extracellularly Polymeric Substances (EPS). Biosorption occurs when the process of exchanging heavy metal ions with functional groups found in EPS [2].

Microorganisms used in the removal of heavy metals are activated sludge from Penggaron Slaughterhouse microbial culture, Semarang. In describing the above problems, it is necessary to analyze the increase in biosorption of Cd and Ni heavy metals in wastewater without reducing the ability to degrade organic compounds. This research is about the

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correlation of C / N ratio and variation of heavy metal concentration with the absorption of heavy metals Cd and Ni so that it can determine the optimal biosorption capacity without reducing the efficiency of COD removal.

2 Methodology

The research method is divided into four stages, which are seeding, acclimatization and heavy metal biosorption experiment. Seeding aims to breed microbes and is done with a batch reactor that lasts 7-14 days [3]. While the acclimatization process and heavy metal biosorption experiments are carried out with a continuous reactor which designed as **Fig. 1**. Microbes will make adjustments to their environment during the acclimatization process [4]. Heavy metal biosorption experiments were carried out to find out the absorption capacity of Cd and Ni without reducing the ability of microbes in degradation of organic compounds represented by COD content.

Fig. 1. Design of Continuous Reactor

Seeding stage is carried out using batch reactor with pH 7 ± 0.2 , DO $\geq 3\text{mg} / \text{L}$ and 10L tank until get MLSS $\geq 2000\text{mg} / \text{L}$ [5]. Acclimatization I for adapting microorganisms to the environment and acclimatization II as microbial adaptation to heavy metals. Acclimatization and biosorption experiment using Merriote tube capacity of 10L with a discharge of 10L/ day as an inlet. Next to the 10L volume aeration tank where biological treatment occurs, pH 7 ± 0.2 and DO $\geq 3\text{mg} / \text{L}$ are the control variables. The clarifier tank designed with a volume of 8L is used to be settling basin and ends with an outlet. Inlet and outlet are taken for testing the soluble COD, Cd and Ni. Artificial waste is used as an inlet with a nutrient ratio of C: N: P is 100: 5: 1.

Biosorption experiment use additional bimetal heavy metals (Cd+Ni) and C/N Ratio as

factor. Variation of bimetal heavy metal (Cd+Ni) is 0+0ppm (low), 3+30ppm (middle), and 5+40ppm (high). The addition of heavy metal concentrations has an effect on EPS production. At certain concentrations, EPS production will increase and decrease dramatically [6]. Variation of C/N ratio is CN 20 and CN 50. Based on [5] shows that with C/N ratio 20 as a typical condition in activated sludge process.

3 Result and Discussion

1.1 Seeding

Seeding process lasts for 13 days and the MLSS results are ≥ 2000 mg / L on the 9th day.

Fig. 2. Plot Seeding Process

The growth curve equation based on data analysis using trend analysis with the Growth Curve Model method is $Y_t = 256.509 \times (1.1925^t)$. The Y_t variable represents the results of microbial development (mg / L) and t is time (days).

Fig. 3. Trend Analysis Plot for Seeding

Based on the results of the curve, it can be explained that the number of microbes will continue to grow every day according to the trend of analysis with the Growth Curve Model. The blue line represents actual data and the red line represents predictive data according to the growth curve equation. The analysis plot compares MLSS with time (days).

2.2 Acclimatization

Acclimatization I was carried out for microbial adaptation to the removal of organic compounds for 27 days and obtained a relatively constant number for the last 5 days. In acclimatization I, COD removal efficiency was found to be relatively constant at 87.20% with a standard deviation of 2.17%. The constant COD removal occurred on the 22nd - 27th day. The results of the COD test showed a significant decrease so as to obtain COD efficiency in the range of 49% - 90%.

Fig. 4. Plot COD Removal: Acclimatizes I

The acclimatization process II was carried out by the addition of heavy metals Cd and Ni each of 3ppm which lasted for 11 days and obtained a relatively constant number for the last 5 days. In acclimatization II the COD removal efficiency was relatively constant at 82.40% with a standard deviation of 2.08%. This process obtained COD efficiency with a range of 72% - 85%.

Fig. 5. Plot COD Removal: Acclimatizes II

The results of the COD removal data showed a decrease from the Acclimatization I to Acclimatization II process can be concluded that the addition of heavy metals during acclimation will reduce the COD removal.

3.3 Main Effect, Interaction, and Optimizer Factor

3.3.1 COD Removal

Increasing the C / N ratio from 20 to 50 will reduce the COD removal efficiency from 74.54% and 65.38%. It can be seen in Fig. 5. that the SVI value also increased from 88.58 to 113.83. When the C / N ratio increases it will reduce the element nitrogen so that the number of filamentous microorganisms decreases. The flock bond that is glued by the filament will get weaker which is represented by a high SVI value. Flocks will break easily because the bonds formed by the filaments between flocks are getting weaker [7]. Some of the flocks will go into the outlet or wash out, causing a relatively high COD out number, which will reduce the COD removal efficiency.

Fig. 6. Plot Main Effect COD Removal Efficiency

(a) (b)
Fig. 7. Plot Main Effect (a) SVI and (b) TSS

In Fig. 7. (a) the addition of heavy metals at low, middle, and high levels, respectively, obtained SVI values of 62.25, 76.87, and 161.30. When the C / N Ratios are at numbers 20 and 50, respectively, SVI values of 88.58 and 113.83 are obtained. The increase in SVI value is an indication of damage to activated sludge due to a small amount of sludge that can settle well due to poor deposition ability [7]. Thus, it can be concluded that the addition of heavy metal content and an increase in the value of the C / N ratio will increase the value of SVI. The results of the SVI value can be attributed to the efficiency of COD removal. In accordance

with the statement above, it can be concluded that the addition of heavy metal content and an increase in the value of the C / N ratio will reduce the efficiency of COD removal. When the SVI value is high, flocks easily destroyed that cause washed out at the outlet. Then the COD test at the outlet will get a high value. This statement can be supported by TSS data in **Fig. 7. (b)** which shows a graph pattern that is relatively the same as SVI. The higher the SVI value is directly proportional to the TSS value which also increases.

Fig. 8. Plot Interaction COD Removal Efficiency

In Fig.7. above can be seen as the lines look almost parallel so they have differences but not too large. Following the results of data analysis 2 Ways Interaction in the form of p-Value with a value of 0.073 which is greater than 0.05 then it is considered insignificant. From the two statements, it can be stated that there is no significant interaction between the Heavy Metal (Cd + Ni) factor and the C / N ratio to the COD removal efficiency response.

Based on the results of the optimization of the response analysis in Figure 8 obtained variations in the factors used are Heavy Metal (Cd + Ni) in the middle variation and C / N ratio at 50 so that the response or COD removal efficiency results of 68.50%.

Fig. 9. Plot Interaction COD Removal Efficiency

3.3.2 Heavy Metal Removal

Increasing the C/N ratio from 20 to 50 will increase the efficiency of Cd removal from 24.37% and 32.34%. It also increased the efficiency of the Ni allowance of 13.85% and 28.53%. Increased C/N ratio causes carbohydrate content in EPS to increase. Carbohydrates are an indicator of polymer release. The more carbohydrate content will increase the polymer exchange

with metal ions around microbes so that the absorption of metal ions (biosorption) increases.

Fig. 10. Plot Main Effect Cd (a) and Ni (b) Removal Efficiency

The addition of heavy metals at low, middle, and high levels, respectively, showed a Cd removal efficiency of 0%, 52.23%, and 32.65%. The addition of heavy metals at low, middle, and high levels, respectively, obtained Ni removal efficiencies of 0%, 36.35%, and 27%. EPS produced by microbes will absorb heavy metal ions. The more toxic substances are given, the more EPS is produced. However, the addition of heavy metals in high levels of microbial capacity to absorb heavy metals has exceeded the limit, namely when the levels of Cd are 5ppm and Ni40ppm.

Fig. 11. Plot Interaction Cd (a) and Ni (b) Removal Efficiency

In the allowance for Cd in Fig 10. that can be seen that many lines that are not parallel therefore have considerable differences. Following the results of data analysis 2 Ways Interaction in the form of p-Value with a value (*), it is considered significant. The influence of these two factors has the highest value when the Heavy Metal in the middle and the C / N ratio at 20 to get a Cd removal efficiency of 66.25%.

In the allowance for Ni in Fig 10. can be seen that many lines that are not parallel then have considerable differences. By the results of data analysis 2 Ways Interaction in the form of p-Value with a value (*), it is considered significant. The influence of these two factors has the highest value when Heavy Metal in the middle and C / N ratio at 50 so that the Ni removal

allowance is 44.43%.

Fig. 12. Plot Optimizing Responses Cd (a) and Ni (b) Removal Efficiency

Based on the results of the analysis of the response optimization in Fig. 12. the obtained variation of the factors used is Heavy Metal (Cd + Ni) in the variation of high and C/N ratio at 50 to get a response or the results of the Cd removal efficiency of 58.60%. The obtained variation of the factors used is Heavy Metal (Cd + Ni) in the variation of high and C/N ratio at 50 so that it gets a response or the results of the Ni allowance efficiency of 28.20%.

4 Conclusion

Breeding of microorganisms to reach MLSS 2000mg/L with nutrients C: N: P 100: 5: 1 and discharge of 10L /day occur for 9 days. Acclimatization of microorganisms to organic compounds lasts 27 days and heavy metals last for 11 days. The addition of heavy metals during Acclimatization II reduces the efficiency of CODremoval.

Increasing the C/N ratio will increase the SVI value. SVI value and COD allowance are inversely proportional. When the SVI value is high, flocks are easily destroyed and washed out at the outlet. Flock contains organic compounds that will increase the COD value at the outlet so that the COD removal efficiency decreases. Besides, the removal efficiency of heavy metals will increase because the carbohydrate content in EPS increases so that it will increase exchange with polymers or metal ions.

The addition of heavy metals increases the SVI value. Similar to the discussion of the C/N ratio factor, the COD removal efficiency will decrease. For the removal efficiency of heavy metals, there is an increase because the addition of heavy metals is directly proportional to EPS production. The more EPS, the higher the absorption of heavy metals. But at higher levels, it has decreased because it has exceeded the capacity of microorganisms to absorb heavy metal ions.

Variation factor of heavy metal addition (Cd + Ni) and optimal C/N ratio for COD allowance of 68.50% is middle with C/N 50, Cd allowance of 58.60% is high with C/N 50 and Ni allowance of 28.20% is middle with C/N 20.

References

[1] C. Lapik, “Biosorpsi Logam Berat Cr (IV) Dengan Menggunakan Biomassa *Saccharomyces Cerevisiae*,” no. Vi, (2017).

- [2] J. Laurent, M. Casellas, and C. Dagot, "Heavy metals uptake by sonicated activated sludge: Relation with floc surface properties," *J. Hazard. Mater.*, vol. **162**, no. 2–3, pp. 652–660, (2009), doi: 10.1016/j.jhazmat.2008.05.066.
- [3] Junaidi, "Pengaruh Gradient Kecepatan dan Dissolve Oksigen terhadap Penyisihan COD dan NH₃ dengan Simultaneus Nitrification Denitrification Pada Sistem Lumpur Aktif." (2008).
- [4] S. B. Ariyani, "Industri Jamu Dengan Metode Lumpur Aktif," no. 10, pp. 14–20, (2011).
- [5] B. Yuncu, F. D. Sanin, and U. Yetis, "An investigation of heavy metal biosorption in relation to C/N ratio of activated sludge," *J. Hazard. Mater.*, vol. **137**, no. 2, pp. 990–997, (2006), doi: 10.1016/j.jhazmat.2006.03.020.
- [6] G. S. H. Y. Z. Yue, "Production of extracellular polymeric substances from *Rhodopseudomonas acidophila* in the presence of toxic substances," pp. 216–222, (2005), doi: 10.1007/s00253-005-1990-6.
- [7] F. Ye, Y. Ye, and Y. Li, "Effect of C/N ratio on extracellular polymeric substances (EPS) and physicochemical properties of activated sludge flocs," *J. Hazard. Mater.*, vol. **188**, no. 1–3, pp. 37–43, (2011), doi: 10.1016/j.jhazmat.2011.01.043.