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Removal efficiency of Cd(II) in landfill leachate by immobilized *Skeletonema* sp.

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ABSTRACT

The objective of this study was to know the maximum cadmium (Cd (II)) removal efficiency and the optimum contact time in leachate from landfill using immobilized *Skeletonema* sp. *Skeletonema* sp. was immobilized by sodium alginate 0.65%. This study used 1, 2, 3, 4, 5, 6, and 7 days of contact time. The data were analyzed by statistical analysis through Anova One-Way ($\alpha = 0.05$) method, then continued with the Duncan test ($\alpha = 0.05$). The removal efficiency of Cd(II) was increased by increasing contact time. The highest removal efficiency of Cd(II) in leachate from landfill by immobilized *Skeletonema* sp. was at seven days of contact time with the 95.70% removal efficiency. The removal efficiency at 1, 2, 3, 4, 5, 6, and 7 days respectively was 45.88%; 47.25%; 64.18%; 77.23%; 92.53%; 93.81%; 95.70%. The highest result of removal efficiency of Cd (II) in landfill leachate was 95.70%. The optimum contact time was six days.

Key words: *Removal efficiency, Cd(II), Landfill leachate, Skeletonema sp., Immobilized*

Introduction

An increase in population will increase waste production. Waste in some are asisusually brought to a landfill (Ashar *et al.,* 2016). The waste in the landfill also consist of liquid which contain a chemical substance, organic and non-organic compounds, and pathogenic bacteria. This liquid is called leachate. Leachate contains decomposed organic matter and heavy metal (Himmah *et al.,* 2009). A heavy metal that usually found in leachate is lead (Pb), Cd (II) (Cd), copper (Cu), and Ferro (Fe) (Langmore, 1998). The existence of heavy metal in environment might cause health problem if it is ingested by eatable organism in long term period (Litaay *et al.,* 2018; Taba *et al.,* 2017; Sundari *et al.,* 2014; Sulastri and Tampubolon, 2019; Istiqomah *et al.,* 2019; Hermawati *et al.,* 2009; Eshmat *et al.,* 2014; Soegianto *et al.,* 2020)

Quality standards of total Cd (II) in landfill depend on "Peraturan Menteri Lingkungan Hidup dan Kehutanan Nomor 59 Tahun 2016" is 0.1 mg L^{-1}. Wulandari (2017) reported that the amount of Cd (II) metal in landfillsis 2,84 mg L^{-1}, and it has exceeded the quality standard. Based on that study, leachate treatment is needed before it discarded into the water. One such technique to remove Cd (II) from leachate is bioremediation. Bioremediation by microalga is widely used to treat pollution from water because of its abundant availability in the water, fast reproduction, extensive range toxicity, many types of waste can be remediated, and non-pathogen (Purnamawati *et al.,* 2015).

Microalga *Skeletonema* sp. has been known by bioremediation agents that could remediate heavy metals such as mercury (Hg), lead (Pb), and Cd (II) (Cd) (Soedarti, 2019). Immobilized microalga offers many advantages, including better reusability, high biomass loading, and minimal clogging in a continuous flow system. The immobilization technique also has an impact on increasing the removal efficiency of Cd (II). Immobilized cells can accumulate more metals ion than free cells (Riffiani, 2009). Based on that, it needs to know the removal efficiency of Cd (II) in leachate from landfill by immobilized *Skeletonema* sp.

Materials and Methods

This study used glass bottle (250 mL), aerator (Recent AA/350), lamp (40 Watt), autoclave, analytical balance, microscopy (Olympus), hand counter (Kw-Trio), bunsen, measuring pipette, micropipette, glass beaker, pH indicator paper (Merck), thermometer, refractometer, sample bottle 150 mL.

Materials used in this study were leachate from TPA Gedangkeret Jombang as a sample, *Skeletonema* sp. culture, sodium alginate, CaCl (2%), alcohol, and aquades.

Preparation

Tools and Material Preparation

Tools used in this reasearch had sterilized by autoclave. Sterilization was at 120 ^{o}C temperature for 2 hours. Sample of leachate analyzed before the bioremediation process by the AAS test. This research used 100 mL of leachate for one bioreactor.

Determination of Contact Time, Repetition, and Number of Cells *Skeletonema* sp.

Variation length of contact time used in this study determined 1, 2, 3, 4, 5, 6, and 7 days. Determination of replication used Replication of this study was determined by Federer statistical formula that could be seen in equation 1 below:

$$(t-1)(n-1) \geq 15 \quad .. (1)$$

Description: t was the number of variable treatments, and n was the number of repetitions. Based on the analysis result, the number of replication used in this research was three times of repetition. The number of cells used in this reasearch was 1500 x 10^4 cells at 100 mL sample for 2 mg L^{-1} of heavy metal concentration (Soedarti, 2017). Based on that calculation, this study used 2910 x 10^4 cells for each bioreactor.

Immobilization and Bioremediation

The concentration of the sodium alginate solution used is 0.65% (Permata, 2018). Solid sodium alginate 0,26 grams was dissolved in 40 mL of distilled water to get a 0.65% concentration of sodium alginate solution. *Skeletonema* sp. then added to the sodium alginate solution and homogenized. The solution of *Skeletonema* sp. in the sodium alginate then dropped into a 2% CaCl solution. Dropping was done by using a micropipette. This process formed a solution of *Skeletonema* sp. in sodium alginate into beads.

The bioreactor used a 250 mL sterilized glass bottle. Beads of *Skeletonema* sp. and 100 mL leachate put into the glass bottle, then aerated. The aeration process was for 24 hours without stopping. The duration time of the running process was according to the predetermined contact time, which is 1, 2, 3, 4, 5, 6, and 7 days. Harvesting was done after the specified contact time was over. The concentration of Cd (II) in leachate after the bioremediation process was analyzed used the AAS (Atomic Absorption of Spectroscopy) method.

Data Analysis

Removal Efficiency of Cd (II) (Cd)

The removal efficiency of Cd (II) counted by formula (2).

$$\text{Removal efficiency} = \frac{Co - C}{Co} \times 100\% \quad .. (2)$$

Description: C_0 = Cd (II) concentration before remediation (mg L^{-1}); C = Cd (II) concentration after remediation (mg L^{-1}).

Statistic Analysis

The data removal efficiency of Cd analyzed by One Way ANOVA. Before tested by by One Way ANOVA all data were tested their normality and homogeneity. Duncan post-test was used to know the difference of removal efficiency at variation length of contact time (α=0.05).

Results and Discussion

The result of the normality test showed that the data

of removal efficiency was usually distributed with a significance value of more than 0.05. The result of the homogeneity test also indicates that the data was homogenous so that Anova One-Way test could be performed. The result of the Anova One-Way test showed that data samples were significant. Based on that result, it could be concluded that there were significantly different in the data removal efficiency of Cd on leachate from landfill by immobilized *Skeletonema* sp. The result of removal efficiency of Cd from leachate by immobilized *Skeletonema* sp. at variation length of 1, 2, 3, 4, 5, 6, and 7 days of contact time showed in Figure 1.

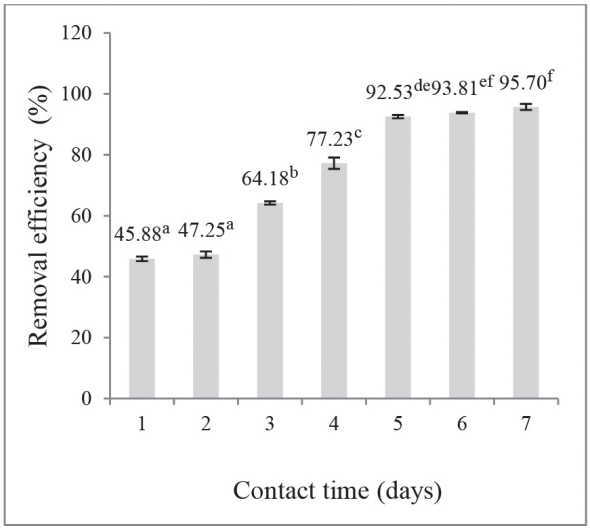

Fig. 1. The removal efficiency of Cd at variation length of contact time. The number followed by the same letter are not significantly different.

This graphic showed that the removal efficiency of Cd was increased by increasing contact time. The concentration of Cdon leachate before the bioremediation process was 3.88 mg L^{-1}. The result showed that the concentration of Cd on leachate was reduced after the bioremediation process. It showed that the bioremediation process could remove Cd from leachate, and there is influenced by variation length of contact time. The removal efficiency of Cd was increased by increasing contact time. According to statistical analysis, there is a difference between the removal efficiency of Cd at variation length of contact time. The results showed that the highest removal efficiency of Cd (II) in leachate from landfills by *Skeletonema* sp. was at 95.70% (seven days), but the optimum duration of contact was six days (93.81%). Microalgae *Skeletonema* sp. able to remove heavy metals Cd (II) from leachate because these microalgae have biosorption and bioaccumulation capabilities. The ability of biosorption possessed by microalga was able to bind and absorb heavy metal ions (Soedarti *et al.*, 2019), so the concentration of Cd (II) ions Cd(II) in leachate was reduced. The metal removal mechanism that occurred in the biosorption process by microalgae was thorough in several ways, physical absorption, ion exchange, and complex formation (Ahalya *et al.*, 2003).

Physical adsorption takes place with the help of van der Wall's force. Ion exchange occurs between ions found in the cell wall of Skeletonema sp. like K^+, Na^+, Ca^+, and Mg^{2+} with Cd^{2+} cations. Complex formation takes place by Cd^{2+} cation and functional groups in the cell wall of *Skeletonema* sp. These functional groups include carboxyl, hydroxyl, sulfate, phosphate, and amino groups (Abbas *et al.*, 2014). The carboxyl groups can form complexes with metal ions (M^{2+}) (Sembiring *et al.*, 2009). Carboxyl groups and amino acids are constituents of protein structure. *Skeletonema* sp. contains 51.77% protein content, 20.02% fat, 16.59% carbohydrate, and 5.20% ash (Hadiyanto and Azim, 2012). Thus, *Skeletonema* sp can absorb heavy metals.

This research used sodium alginate as a polymer to immobilize cells. The use of sodium alginate is one of the factors causing an increase in the removal efficiency of Cd. The alginate is a natural polymer extracted from brown algae and a linear polysaccharide consisting of β-D-Mannuronate (M) and α-L-guluronate (G). Naturally, sodium alginate contains carboxy, groups in each of its constituent residues. The carboxyl groups in these polysaccharides have a high affinity for divalent cations such as

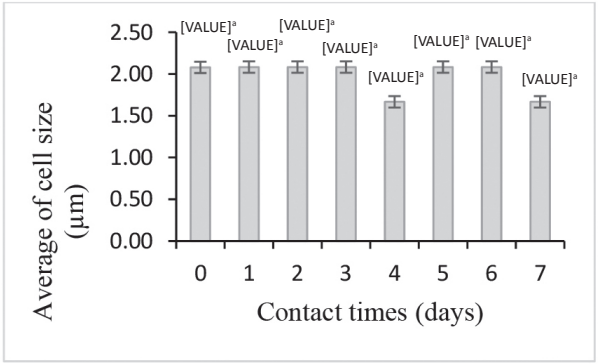

Fig. 2. The average cell size of *Skeletonema* sp. after melting beads immobilization based on the contact time

Pb(II), Cu(II), and Cd(II). That is why heavy metals ions easily bound to sodium alginate (Wang, 2016).

*Skeletonema*sp. immobilized that has been contacted with leachate at various contact times is melted to measure cell length. Figure 2 shows that the average size of the *Skletonema* cells is based on contact time. The size of the *Skeletonema* sp. cell did not differ significantly at various contact time variations. Musgrave *et al.* (1983) state that immobilization has a minimal effect on algal cell morphology.

Conclusion

Based on the research result, there is a difference in the removal efficiency of Cd (II) in the leachate at variation length of contact time. The removal efficiency of Cd was increased by increasing contact time. The highest result of removal efficiency of Cd (II) in landfill leachate was 95.70%. The optimum contact time was six days.

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