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Removal efficiency of total chromium in leachate from landfill using immobilized *Skeletonema* sp.

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ABSTRACT

This research aims to determine the difference in efficiency of Total chromium removal with variations in contact time. In this research *Skeletonema* sp. immobilized with sodium alginate through the cell coupling method. Data on total chromium removal efficiency was tested using One-Way ANOVA (α=0.05) and continued with Duncan test (α = 0.05). The results of the total removal efficiency of total chromium from landfill by immobilized *Skeletonema* sp. increased from day1 to day 7, (from 72.01%, 80.29%, 85.42%, 91.16%, 91.61%, to 94.59%); with the highest efficiency on day 7 is 96.11%. As contact time increases, sodium alginate can increase the ability of passive biomass immobilization. Immobilized *Skeletonema* sp has high capability to remediate total Crinleachate from landfill.

Key words: *Removal, Cr, Immobilized Skeletonema sp., Contact time, Leachate, Landfill.*

Introduction

The accumulation of garbage in a very large landfill will cause a natural decomposition process with rainwater to produce gases that will turn waste into organic fertilizer and cause byproducts such as leachate. There are various types of waste in the landfill, causing the entry of various chemicals contained in leachate water (Ginting *et al*., 2018). In addition to chemicals, there are also heavy metals which are elements that cannot be decomposed and can accumulate through the food chain with long-term adverse effects on living things (Sundari *et al.*, 2014; Irhamni *et al*., 2018). One of the heavy metals contained in leachate is total chromium (Cr) (Palar, 1994).

Through the food chain chromium can be deposited in the organ of living things which at a certain size can cause toxins (Tualeka *et al*., 2019). Generally, total chromium in nature consists of chrome with valence 3 (Cr^{3+}) which is still essential for living things and valence 6(Cr^{6+}) which is toxic due to its solubility and high mobility in the environment (Mulyana *et al*., 2015; Mudjari *et al*., 2019; Widia *et al.,* 2017; Rizky and Mukono, 2017). The impact of leachate on th eenvironment causes the need for leachate treatment which aims to reduce and prevent negative impacts on the environment (Palar, 1994; Larashati, 2004).

Bioremediation using microorganisms is an alternative method that can be used and the potential to reduce the concentration of heavy metals present in leachate (Soedarti *et al.,* 2019). The advantage in the bioremediation process is the relatively low cost, high efficiency, and its ability to reduce heavy metals and the resulting by products are very minimal because they do not use chemicals (Priadie, 2012).

This study uses *Skeletonema* sp. as a bioremediation agent because it has been proven its effectiveness in reducing heavy metals in a previous study by Soedarti *et al.* (2016). *Skeletonema* sp. is a diatomic microalgae or phytoplankton that belongs to the *Bacillariophycea* class which does not cause toxins, is easy to be cultured and grows relatively fast (Isnansetyo and Kurniastuti, 1995). *Skeletonema* sp. contains proteins composed of amino acids that consist of COOH functional groups. This functional group can bind to hydrogen ions because this group is negatively charged and is reactive to bind to total chromium, i.e. (Cr^{3+}) and (Cr^{6+}) which have a positive charge (Sembiring *et al.*, 2009).

The use of microorganism immobilization techniques with gel beads made of sodium alginate is a good method to maintain the viability of microorganisms, as aprotector so as to extend the life of microorganisms and also as nutrients for microorganisms. The advantage obtained from the immobilization technique is applied in this study in order to obtain a more optimal result of heavy metal reduction (Le-Tien *et al.*, 2004).

Based on this background it is necessary to conduct a series of studies to determine the ability of *Skeletonema* sp. immobilized as a total chrome (Cr) bioremediation agent based on variations in contact time.

Materials and Method

Tools and Materials

The tools and materials used in this study were reactor/treatment bottles with 335 mL, 1L glass bottles, centrifuge (Hettich / EBA 200), centrifuge bottles (IWAKI), 40 Watt lamps (Philips), magnetic stirrer hotplate (Thermo Scientific Cimarec), analytical scales (OHAUS), 50mL measuring cups (IWAKI), 100mL and 2000 mL beaker cups(IWAKI), lux meters, refracto meters, infrared thermometers Benetech/GS320), 10 mL volume pipettes (HBG), pump pipettes volume of 10 mL (Glasfirn), microscope (Olympus), Hemocytometer Neubauer (Assistant), hand counter (Kw- Trio), dropperpipette, 10 mm ocularmicrometer, 150 mL glass bottle (infusion), leachate from landfill, sodium alginate (Sigma) Aldrich/W201502), HNO_3 1M for decreased pH of leachate, $CaCl2.2H_2O$(2%) as amedium for the formation of beads from sodium alginate, distillated water.

Sodium Alginate Preparations Methods

The concentration of sodium alginate used in this study was 0.65%. The concentration is the concentration with the best absorption based on research by Izmila (2018). Sodium alginate in powder form was weighed as much as 0.26 g, then dissolved in 40 mL of distilled water using a magnetic stirrer with a speed of 50-60 rpm without heating. The sodium alginate solution that was ready, both of which had been mixed with *Skeletonema* sp., Was then dropped on a2% CaCl solution. 2% CaCl is obtained by dissolving 2 g of solid CaCl into 100 mL distilled water.

Absorption Efficiency Analysis

Total absorbed heavy metal chrome (Cr) concentration is carried out using the Langmuir method which can be seen in the following Equation:

$$\text{Absorption efficiency} = ((Co-C)/Co) \times 100\%$$

Note: Co = initial Cr concentration (mg/L); C = final Cr concentration (mg/L)

Skeletonema sp. Preparations Methods

Cell calculations using Neubauer hemocytometer and hand counter. Observation of *Skeletonema* sp. using a neubeuer hemocytometer under a microscope with a magnification of 100 times. The need for the number of cells needed is multiplied by the volume of *Skeletonema* sp. The number of cells *Skeletonema* sp. what is needed is 15000 cells (Soedarti *et al*., 2016). So the number of *Skeletonema* sp. what is needed in 100 mL of leachate with chromium (Cr) of 2 ppm is 15×10^6 cells/mL. One reactor bottle contains 100 mL of leachate water and 40 mL of alginate containing *Skeletonema* sp. Because the leachate water used contains 5.92 ppm Cr total, then what is needed for each treatment is 44.4×10^6 cells/100 mL.

Leachate from Landfill Preparations Methods

The pH parameters of the wastewater are observed first using a pH indicator, the temperature of the water with an alcohol thermometer and the salinity of the water with a refractometer. It is known that the pH of the leachate before treatment is 9. Sodium alginate can only maintain its solid form around pH 6, so that the leachate is acidified to reduce the pH to reach pH 6 by using HNO_3 of 1 Molar in order to be a good environment for sodium alginate. The volume of leachate used in the treatment was 100 mL per reactor.

Statistical Analysis

Before tested by One Way ANOVA all data were tested for 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

Statistical test results showed that the total Cr metal absorption efficiency data is normally distributed (with significant values > 0.05), and homogeneous (with significant values > 0.05). The One-Way ANOVA showed that a difference in total metal absorption efficiency between difference contact time. The result of the removal efficiency of total Cr from landfill leachate by immobilized *Skeletonema* sp. with variations in contact time can be seen in Table 1.

Table 1. Differences in total metal absorption (Cr) efficiency in leachate from landfill

No.	Contact Time	Efficiency (%)
1.	Day -1	72.013a ± 2.367
2.	Day -2	80.290b ± 0.961
3.	Day -3	85.416c ± 0.931
4.	Day -4	91.160d ± 1.271
5.	Day -5	91.610d ± 0.255
6.	Day -6	94.593e ± 0.444
7.	Day -7	96.113e ± 0.335

Note: The same letter shows no significant difference.

Duncan test showed the Cr absorption efficiency by *Skeletonema* sp. increased from day 1 to day 7. There was no significant difference in the efficiency of total Cr removal on day 4 with day 5, and on day 6 with day 7. The optimum contact time is the fastest contact time with the highest Cr absorption ability. So it can be concluded that the optimum contact time of this study is on the 6th day contact time with a total Cr absorption efficiency of 94.593%.

Increased efficiency of absorption of total Cr metal in leachate from landfill is due to the ability of *Skeletonema* sp. which is assisted by an immobilizing matrix, sodium alginate, which can help the absorption of heavy metals. Continual improvement despite increased contact time is due to the use of sodium alginate as an immobilizing agent which can also absorb heavy metals. This is consistent with the statement of Hidayati *et al*. (2013) which stated that the biosorption capacity of total Cr heavy metals by passive biomass immobilized by alginate would increase with increasing contact time. In this study, *Skeletonema* sp. does not interact directly with leachate water, but through sodium alginate.

Chrome both Cr (VI) and Cr (III) will first be bound by sodium alginate. This can also benefit *Skeletonema* sp. which can be protected from the carcinogenic properties of Cr (VI) and the environmental conditions of the leachate which is concentrated with other organic materials that can destroy *Skeletonema* sp.

Sodium alginate is a natural polysaccharide found in brown algae, having a molecular formula (C6H7NaO6) n with ion exchange properties. Ion exchange occurs when heavy metal ions replace the monovalent ion, sodium (Na). In the presence of sodium alginate, the bioremediation process occurs more effectively. Sodium alginate is only responsible for binding the heavy metals that occur in ion exchange. However, *Skeletonema* sp. is able to reduce and remediate heavy metal ions in the vacuole of the cell. Fitokelatin produced by *Skeletonema* sp. is a metalotion in class III peptide (MtIII) which functions to detoxify heavy metals. Cell vacuoles in living organisms are producing MtIII to control the cytoplasmic concentration of metal ions that cause toxic effects (Kumar *et al.,* 2015).

Phytocelatin in vacuoles make *Skeletonema* sp. hasa molecular mechanism that can distinguish essential and non-essential heavy metals because *phytocelatin* belongs to *Skeletonema* sp. contain metallothionein class III(MT III) which functions to detoxify toxic metals through absorption (Soedarti *et al.,* 2016). Metal lothionein is a metal binding protein that plays a role in the binding process of metals that can be toxic in cells such as essential metals (Cr^{3+}) and non-essential metals (Cr^{6+}).

Metallothionein contains thiol (-SH) groups in large enough quantities, this group is able to form very strong and efficient bonds with heavy metals, where 1 metal ion can be bound by 2 -SH residues or 3 -SH residues. Metallothionein has two domains involved in the binding of metal ions, namely the â (N-terminal) domain which plays a role in homeostatic essential metal ions, and the α (C-terminal) domain which plays a role in forming strong bonds with toxic metal ions (Anwar, 2008). Thus, *Skeletonema* sp. able to bind Cr (III) which is essential and bind Cr (VI) which is toxic and able to reduce total Cr in leachate from landfill.

The ability to bind the total Cr metal by sodium alginate and *Skeletonema* sp. this has been proven to produce the power to reduce total Cr from leachate. High efficiency suggests that this study is effective in remediating total Cr in leachate from landfill. The removal efficiency of total heavy metal Cr occurs very significantly and continues to increase until the contact time of the 7th day due to the presence of sodium alginate as a bioremediation agent and binder *Skeletonema* sp. as a passive biomass capable of accelerating the process of reducing total heavy metal Cr. The efficiency of absorption of total heavy metal Cr in leachate from landfill based on variations in contact time is influenced by several things, namely the environmental conditions of the sample or leachate, dissociation of Cr metal ionization species, absorption ability by *Skeletonema* sp. and also the ability of sodium alginate to help the absorption of total Cr.

Conclusion

The results showed that there were differences in the removal efficiency of total heavy metal chrome (Cr) by *Skeletonema* sp. immobilized in leachate from landfill in the variation of contact time of day 1 to day 4 and there was no significant difference in the total removal efficiency of chrome (Cr) on the 4th day to the 5th day, also on the 6th day by the 7th day.

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