Adsorption Efficiency of Lead by *Sargassum crassifolium* in Different Biomass Size and Dose

Lily Surayya Eka Putri[1], Eka Syafiqa[1] and Eka Apriliyani[1]
[1]*State Islamic University Syarif Hidayatullah Jakarta, Jl. Ir. H. Djuanda No. 95, Ciputat 15412, Indonesia*

Keywords: Adsorption, biomass size and dose, lead, *Sargassum crassifolium*

Abstract: Lead is the dominant water pollutants emerged in high concentration in a watershed of Jakarta, Indonesia. Biosorption using macroalgae is the efficient method used to eliminate heavy metals from liquid waste.*Sargassum crassifolium* is the original species of macroalgae from Indonesia that was used to analyze the ability of adsorption of lead (Pb) from industrial wastewater at different biomass size and dose.Samples collected at Pari and Kotok Besar Island, Seribu Island, North Jakarta, Indonesia were used to adsorb Pb from industrial wastewater with the biomass size of 10-50 µm and 25-500 µm and biomass dose of 0.1, 0.2,and 0.3 mg/L , using duplicate assessment. The adsorption of *S. crassifolium* on lead was higher in the size of 10-50 µm than in 250-500 µm, within 60 minutes oscillation at a particular pH. There was not a significant differentiation between biomass weight and adsorption capacity ($p>0.05$). Thus, *S. Crassifolium* can be used as an alternative biosorbent which has high efficiency for wastewater treatment, even in less biomass amount.

1 INTRODUCTION

Many industries whose materials are not widely used from processes such as discharge as high-color wastewater, biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, temperature, turbidity and toxic chemicals including heavy metals (Davies et al , 2003). all of that will be responsible for the release of heavy metals into the environment through the production process. the process of direct and indirect disposal of this waste water into water bodies pollutes water and affects aquatic organisms. Industrial wastes usually contain metals and a large number of potentially harmful compounds. This can cause environmental pollution and affect ecosystems (Hussein et al., 2004).

The treatment systems of industrial waste are many and most of them are physic and chemical processes. Less biological methods are chosen by industry to treat the wastewater. One of the biological methods is through biosorption process using macroalgae. Various macroalgae are found throughout the world's oceans including in Indonesian water which consists of three basic colors such as green, brown and red algae (Muhammad and Nwaedozie, 2011).

The presence of heavy metals in the environment is a major concern due to the toxicity effect to the aquatic living organisms (Romera, 2007). Thus, heavy metals recovery from industrial wastewater is becoming increasingly important in terms of neutralizing the hazards of heavy metals.

Many studies on heavy metal adsorption by macroalgae have largely been restricted to various species of brown macroalgae (Surjani, 2010; Al Homaida et al, 2011; Huang and Lin, 2015; Sweetly et al, 2014), microalgae (Putri et al, 2015), mushroom (Vimala and Das, 2009), and agriculture waste (Ashraf et al, 2011). In Indonesia, study of macroalgae as biosorbent of heavy metal is also developed which reported adsorption of Cu(II) on *Sargassum crassifolium* (Ronaldo et al, 2013), Cr(III) on *Euchema spinosum* (Sudiarta and Diantariani, 2008), Pb in *Eucheuma spinosum*, *Padina minor* and *Sargassum crassifolium* (Putri, 2016), and Pb(II) on *Sargassum duplicatum* (Buhani et al, 2006). However, those studies were experimented in aqueous solution, and less in industrial wastewater. Therefore, this study was done to evaluate the potential of brown algae *Sargassum carssifolium* to remove heavy metals from industrial wastewater. As biosorbent, *S. crassifolium* are widely found in Indonesian water and also has the important advantages including low

Eka Putri, L., Syafiqa, E. and Apriliyani, E.
Adsorption Efficiency of Lead by Sargassum crassifolium in Different Biomass Size and Dose.
DOI: 10.5220/0009935618091814
In *Proceedings of the 1st International Conference on Recent Innovations (ICRI 2018)*, pages 1809-1814
ISBN: 978-989-758-458-9

cost, the abundance distribution in water, size, high ability to accumulate metals through its cell wall (Ashraf et al, 2011).

However, the obstacle of the biosorption method carried out in previous studies was the availability of biosorbent raw materials in a relatively limited in the nature. It is known that to process 10 L of industrial wastewater it takes 100 g of dried weight of macroalgae or equal to 1000 g of wet weight of macroalgae. This means that it takes 1 kg of macroalgae to process 10 L of wastewater. Meanwhile, the amount of wastewater processed by an industry reaches thousands of liters, so a lot of macroalgae is needed. Accommodating this problem, the size and dose of biomass will be an important aspect. This study focused on the size and dose of *S. crassifolium* and analyzing the adsorption capacity on lead form industrial wastewater. A small amounts of biomass used will result in cutting costs for proper industrial wastewater treatment. In addition, it also conserves macroalgae in the nature and provides an alternative increase for the economy of coastal communities.

2 MATERIALS AND METHOD

In this research, it will be conducted at the integrated laboratory center of the UIN faculty of science and technology, which will be held in May until October 2018. The macroalgae samples used in this study are Sargassum crassifolium which is transported from water around Pari Island and Big Kotok, Seribu Kepulauan, North Jakarta, Indonesia to the laboratory. Industrial wastewater is provided from hazardous waste processing companies located in Cileungsi, Bogor.

2.1 Preparation of Biosorbent

Before being taken to the laboratory, all samples will be put into a zip plastic bag, then washed with seawater to clean from sediments or small organisms trapped in the macroalgae. henceforth in the laboratory, all samples were washed and rinsed again using distilled water then dried in an oven at 50 C for 24 hours to get a stable weight. Dry samples were grounded with mortars and filtered in sizes 250-500 µm and biosorbents were ready for use. Another 10-50 µm size was prepared at BATAN (National Agency for Nuclear Energy in Indonesia) using a milling device with 12 balls for 1 hour process.

2.2 Adsorption Test

The experimental design used was Completely Randomized Design with two (2) replications. Three variables were tested in this study, including pH, size and weight of biomass. The variety of biomass size was 250-500 µm (sa) and 10-50 µm (sb) whether for biomass dose was 0.1, 0.2, and 0.3 ppm were examined. All samples were tested in pH 7 and 9 and were oscillated for 60 minutes (Putri, 2016). The correlation between size and weight of biomass with adsorption efficiency was analyzed using one-way ANOVA.

Firstly, for the size 250-500 µm, 0.1, 0.2 and 0.3 g of the dried *S. crassifolium* was put into 50 ml wastewater respectively and stirred for 60 minutes using a magnetic stirrer at 200 rpm. The solution pH was adjusted to 7 and 9 with NaOH (0.1 M). Then, the solution were filtered with Whatman paper BF/C code and the filtrate was analyzed using ICP to determine the metals concentration at 543 nm wavelength. The experiment was repeated in the size 10-50 µm.

Metals uptake and removal were calculated as the difference in the metal concentration(s) before and after sorption (Ok et al, 2007), according to Eq. (1).

$$q = (-) \ x \ - \quad (1)$$

$$R = \frac{-}{\ } \ x \ 100\% \quad (2)$$

Where q = metal adsorption (mg/g); M = dry biomass (g); V = volume of the initial lead solution (L); C_i = initial concentration of lead in aquatic solution (mg/L); C_f = final concentration of lead in the aquatic solution (mg/L) at given time (t; min); R = removal percentage (%).

3 RESULTS AND DISCUSSION

3.1 Lead Adsorption

The original strain of Indonesian marine brown algae *Sargassum crassifolium* was examined for lead removal at different variation of size of biomass, 250-500 µm (sa) and 10-50 µm (sb), and also different biomass dose, namely 0.1, 0.2, and 0.3 g. Different pH was also tested which were pH 7 and 9. Most of studies were examined adsorption of lead in aqueous solution (Putri, 2016; Sweetly et al, 2014;

Vimala and Das, 2009) using macroalgae and also mushrooms.

The concentration of hydrogen ions is one of the important parameters in adsorption process which affects the ionization degree of absorbate during the reaction and replacement of positive ion in active sites of cell wall (Sudiarta and Diantariani, 2008). Figure 1 showed that *S. crassifolium* in aqueos solution could remove 98.4% of lead at 60 minutes oscillation. This rapid metal adsorption for *Sargassum* was due to the active binding sites owned by macroalgae such as –COOH, –OH and –NH_2 (Wang and Chen, 2009). This contact time was further used for the study in wastewater solution.

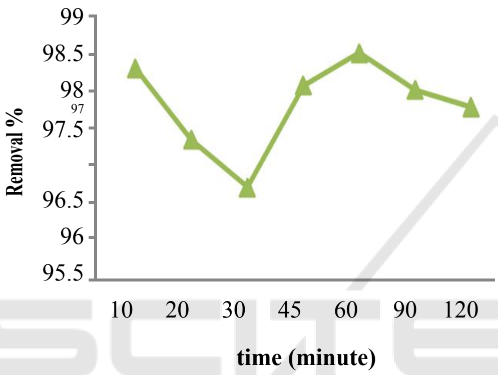

Figure 1: Effect of contact time on the adsorption of lead (Putri, 2016)

Similar findings for adsorption of heavy metals such as chromium, nickel and lead by other adsorbents have been reported by Das and Mondal, 2011; Singh and Singh, 2012 who have shown a balance with achieving 60 minutes. The presence of a fast adsorption rate is likely due to the increasing number of empty sites available for adsorption and is usually controlled by the diffusion process from bulk to surface (Agarry and Ogunleye, 2014). Adsorption after 60 minutes may be a process that is controlled by attachments because the adsorption site is less available in the macroalase cell wall

Figure 2 and 3 shows the observed removal percentage for the assayed Pb ion in the wastewater solution by *S. crassifolium* at various size and weight of biomass and at pH 7 and pH 9. The percentage removal or adsorption efficiency of Pb from the wastewater by dried *S. crassifolium* biomass was found to be 98.11-98.5% (sa) and 99.99% (sb) in various dose of biomass at pH 7, as shown in Fig. 2. At pH 9, the removal percentage almost the same as at pH 7 which was 98.34-98.76 (sa) and 97.71-99.99% (sb) in various biomass dose. This was evidenced by statistical tests that there was no difference in the ability of lead adsorption on both biomass size ($p>0.05$) and also at various dose of biomass ($p>0.05$).

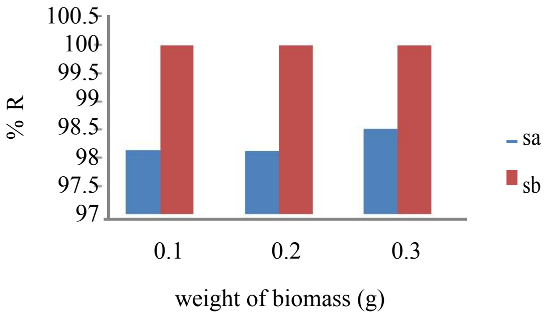

Figure 2: Adsorption capacity on Pb at pH 7

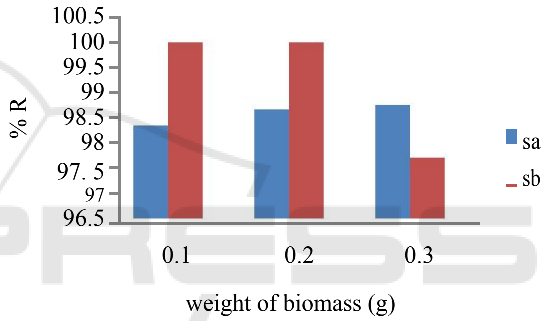

Figure 3: Adsorption capacity on Pb at pH 9

This result was different from the study conducted by Lee and Park (2012) which reported pH 4 was the maximum adsorption of lead in aqueous solution. Similar result was also reported by Vieira et al (2007), Nessim et al (2011), Sweetly et al (2014) and Putri (2016) which was pH 4.5, pH 4-5.5 and pH 5 respectively, showed the optimum lead removal.

Those studies were in aqueous solution which is the heavy metals were adjusted in specific concentration to be tested the capability of adsorption. On contrary to wastewater solution which is used directly without adjustment of the concentration. The heavy metals contained in the wastewater were the mixture of various types of wastes from the various industries. Therefore, it can be presumed that the pH condition was seemly different in aqueous solution and wastewater. There are a lot of types of heavy metals mixed together in a very high concentration and this causes the pH increases. The pH lower than 3.0, the removal of lead was inhibited possibly as result of a competition between lead and hydrogen ions and when the pH increased, the negative charge density on the macroalgae will also increased due to the deprotonation of the metal binding sites, which resulted in increasing the lead adsorption (Vieira et al, 2007; Nessim et al, 2011).

The most important parameters of biosorption is the pH (Dubey el, 2014) and regarding to *Sargassum* sp. which contains many ionizable groups (carboxyl groups), it is liable to be influenced by the pH of the medium which will play a role in binding metallic ions (Sweetly et al, 2014). The higher the pH value, the higher the dissociation if the free sites for the binding process can be produced, and this occurred at pH values over 5.5 (Vieira et al, 2007). That is supported by Ho (2005) which reported pH values in the range of 4.0 to 7.0 were adequate for lead binding. These values are similar to those obtained in the present research, of which was pH 7 the predominance of lead precipitation.

The biomass size, 250-500 µm and 10-50 µm tested in the present study, showed no significant differentiation in adsorption efficiency, nevertheless achieved maximum removal of lead at size 10-50 µm which was higher than at size 250-500 µm. This is supported by the study conducted by Cossich et al (2002) which found the biosorbent size did not influence the capacity and rate of lead removal. However, this is very important for the industry because it is related to the cost of processing waste.

Meanwhile, the biomass dose used in the present study was 0.1, 0.2 and 0.3 g, was not also showed significant different with removal efficiency of lead in wastewater solution. This present study showed that the removal efficiency of lead from wastewater was not improved with the increasing dose of assayed biomass. This result was contrary to Dubey et al (2014) reported that the removal efficiency was improved with the increasing dose of biomass 0.25-1.5 g as more surface area in cell wall of biomass was available for adsorption due to enhance in the active sites. Leusch et al. (1995) also found that larger biomass particles of *Sargassum fluitans* and *Ascophylum nodosum* had higher metal uptake than smaller particles in the case of cadmium, copper, nickel, lead and zinc. However, these can be explained by the study by Jia et al (2003) that was the smaller particles provide a larger surface area for the attachment of chemical reaction and a shorter diffusional path for the substrates which supported the findings of the present study. However, the findings of this study were in accordance with observation made by Sweetly et al (2014) in the uptake of lead by *S. myriocystum* which decreased gradually with increased concentration greater than 2g. Vieira et al (2007) was also found the same results as our findings. Thus, the influence of biosorbent size on metal adsorption apparently is a function of both the type of biomass and the metal ion.

The initial concentration on lead was 13.09 mg/L and after treated by *S. crassifolium* the final concentration was ranged 0.001-9.52 mg/L. The capability of *S. crassifolium* was definitely high. Despite, the final concentration of lead at 0.1 and 0.2 dose and size 10-50 µm was below the permissive level (0.03 mg/L) which is set in the Government Regulation of Republic of Indonesia No. 82/2001 on Water Quality Treatment and Water Pollution Control. The high adsorption ability and achieving safe concentration to be discharged into the waters are the advantages of using macrolgae for industrial wastewater treatment and also environmentally friendly ways.

3.2 Future Trends

A natural environmentally friendly biopolymer recently is definitely found its place among the most important carbohydrates. It is now used effectively in a wastewater treatment. One of them is guar gum silica nano-composites were effectively used in the removal of Cd (II) from aqueous solution at pH 8, contact time 2 hours, temperature 30^{o}C and adsorbent dose 10 mg (Singh and Singh, 2015). Other novel study was hydrogel based on guar gum (Abdel-Halim and Al Deyab, 2011; Khan et al, 2017) economic and ecofriendly biocomposite for removal of hexavalent chromium ion Cr (VI).

Utilization of nanocomposite based on biopolymers is the future developed biosorbent with the environmental and economic considerations on replacing the synthetic polymers. Nanocomposite of biomass is also developed well such as Zhao et al (2011) for chitosan. Our future research targets are to prepare nanocomposite from macroalgae and developed hydrogel based on macroalgae for wastewater treatment, particularly for heavy metals uptake. Therefore, environmental quality could be prevented earlier and the nanocomposite biotechnology can help industries for waste treatment process efficiently.

4 CONCLUSION

The biological method for wastewater treatment has been used as the efficiency on cost and time to adsorb heavy metals, which in addition showed high adsorption capability on heavy metal. The original species of Indonesian marine macroalgae Indonesia *Sargassum crassifolium* exhibited high lead uptake from industrial wastewater reached almost 99.99% in smaller size and dose of biomass at pH 7 and 9 for 60 minutes oscillation. Size and dose of biomass was mentioned and the different pH was analyzed. It was established that smaller size and dose of biomass could alleviate the adsorption capacity of heavy metals in industrial wastewater. This indicated that *S. crassifolium* belonging to *Phaeophyta* division could be chosen as an alternative environmentally-friendly method for wastewater which mostly using chemical methods.

REFERENCES

Abdel-Halem, E.S. & Al-Deyab, S.S., 2011. Hydrogel from crosslinked polyacrilamide/guar gum graft copolymer for sorption hexavalent chromium ion. *Carbohy Poly,* 86, pp. 1306-1312.

Agarry, S.E and Ogunleye, O., 2014. Chemically treated kolanut pod as low cost natural adsorbent for the removal of 2, 4 dinitrophenol from synthetic wastewater: batch equilibrium, kinetic and thermodynamic modelling studies. *Turkish Journal of Engineering and Environmental Science*, 38, pp. 11-40.

Al-Homaidan, A.A., Al-Ghanayem, A.A. and Al-Khalifa, A.H., 2011. Green algae as bioindicator of heavy metal pollution in Wadi Hanifah Stream, Riyadh, Saudi Arabia. *Int. J. Water Resour. Arid Environ*., 1(1), pp. 10-15.

Ashraf, M.A., Mahmood, K. and Wajid, A., 2011. Study of low cost for biosorption of heavy metals. In Proceeding of International Conference on Food Engineering and Biotechnology IPCBEE 9, Singapore, pp. 60-68.

Buhani, Suharso and Sembiring, Z., 2006. Biosorption of Pb (II), Cu (II) and Cd (II) ions on *Sargassum duplicatum* immobilized silica gel matrix. *Indo. J. Chem*., 6 (3), pp. 245-250.

Cossich, E.S., Tavares, C.R.G., and Ravagnani, T.M.K., 2002. Biosorption of chromium(III) by Sargassum sp. biomass. *EJB Electronic Journal of Biotechnology*, Vol.5, No. 2, pp. 133-140.

Das, B. and Mondal, N.K., 2011. Calcareous Soil as a New Adsorbent to Remove Lead from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Study. *Universal Journal of Environmental Research and Technology,* 1(4), pp. 515-530.

Davis, T.A., Volesky, B. and Mucci, A., 2003. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res*., 37, pp. 4311-4330.

Dubey, A., Mishra, A., and Singhal, S., 2014. Application of dried plant biomass as novel low-cost adsorbent for removal of cadmium from aqueous solution. *Int. J. Environ. Sci. Technol*., 11, pp.1043–1050.

Huang, S. and Lin, G., 2015. Biosorption of Hg(II) and Cu(II) by biomass of dried *Sargassum fusiforme* in aquatic Solution. *J. Environ. Health Sci. Eng.,* 13 (21), pp. 1-8.

Hussein H., Ibrahim, S.F., Kandeel, K. and Moawad, H. (2004). Biosorption of Heavy Metals from Wastewater using Pseudomonas sp. *Electronic Journal of Biotechnology,* 7(1), pp.38-46.

Indonesian Government Regulation No. 82 year 2001, The Treatment of Water Quality and Water Pollution Control.

Jia, H., Zhu, G. and Wang, P., 2003. Catalytic behaviors of enzymes attached to nanoparticles; the effect of particle mobility. *Biotechnol. Bioeng*., 84, pp. 406-414.

Khan, T.A., Nazir, M., Ali, I., and Kumar, A., 2017. Removal of chromium (VI) from aqueous solution using guar gum-nano zinc oxide biocomposite adsorbent. *Arab J. Chem.,* Vol 10, Suppl. 2, pp. 2388-2398.

Lee, S.H. and Park. C.H., 2012. Biosorption of heavy metal ions by brown seaweeds from Southern Coast of Korea. *Biotech. and Bioprocess Eng.,* Vol. 17, Issue. 4, pp. 853-861.

Leusch, A., Holah, Z.R. and Volesky, B., 1995. Biosorption of heavy metals (Cd, Cu, Ni, Pb, Zn) by chemically-reinforced biomass of marine algae. *Journal of Chemical and Technology Biotechnology*, Vol. 62, pp. 279-288.

Muhammad, M.N.I. and Nwaedozie, J.M., 2011. Application of Marine Biomass for the Removal of Metals from Industrial Wastewater. *Proceedings* of the First International Technology, Education and Environment Conference African Society for Scientific Research (ASSR).

Nessim, R.B., Bassiouny, A.R., Zaki, H.R., Moawad, M.N. & Kandeel, K.M., 2011. Biosorption of lead and cadmium using marine algae. *Chemistry and Ecology*, 27(6), pp. 579-594.

Ok, Y.S., Yang, J.E., Zhang, Y.S., Kim, S.J. and Chung, D.Y., 2007. Heavy metals adsorption by a formulated zeolit-portland cement mixture. J. Hazard. Mater., 147, pp. 91-96.

Putri, L.S.E., 2016. Biosorption of Lead Using Macroalgae Eucheuma spinosum, Padina minor and Sargassum crassifolium in Aqueous Solution. Asian Journal of Applied Sciences, Volume 4, Issue 2, pp. 520-525.

Putri, L.S.E., Fauziah and Dasumiati, 2015. Biosorption ability of microalgae Scenedesmus dimorphus for Cr (VI) and Cd in aqueous solution. Adv. Sci. Lett., 21, pp. 196-198.

Romera, R., Gonzales, F., Ballester, A., Blazquez , M.L. and Munoz, J.A., 2006. Biosorption with algae: A statistical review. Crit. Rev. Biotechnol., 26, pp. 223-235.

Ronaldo, I.H., Silalahi, N, Wahyuni, 2013. Adsorption of Cu (II) ion using brown algae biomass encapsulated aqua-silica gel. JKK, 2 (3), pp. 148-152.

Singh, S.R. and Singh, A.P., 2012. Adsorption of heavy metals from waste waters on tea waste. Global Journal of Research Engineering, 12 (1), pp. 19-22.

Singh, V. and Singh, S.K., 2015. Cadmium (II) removal from aqueous solution using guar gum-silica nanocomposite. Adv. Mater. Lett., 6, pp. 607-615.

Sudiarta, I.W. and Diantariani, N.P., 20008. Biosorption of Cr (III) on biosorbentof seaweed Euchema spinosum. Indo. J. Chem., 8 (1), pp. 78-82.

Surjani, B.A., 2010. Heavy Metals removal from Industries Wastewater by using Seaweed through Biosorption Process. [Unpublished Thesis]: Faculty of Civil Engineering and Earth Resources, University Malaysia Pahang.

Sweetly, D.J., Sangeetha, K. and Suganthi, B., 2014. Biosorption of heavy metal lead from aqueous solution by non-living biomass Sargassum myriocystum. IJAIEM., 3 (4), pp. 39-45.

Vieira, D.M., Costa, A.C.A.D., Henriques, C.A., 2007. Biosorption of lead by the brown seaweed Sargassum filipendula – batch and continuous pilot studies. Electric journal of Biotechnology, 10(3), pp. 368-375.

Vimala, R. and Das, N., 2009. Biosorption cadmium (II) and lead (II) from aqueous solutions using mushrooms: A comparative study. J. Hazard. Mater., 168, pp. 376-382.

Wang, J. and Chen, C., 2009. Biosorbents for heavy metals removal and their future. Biotechnol. Adv., 27, pp. 195-226.

Zhao, L.M., Shi, L.U., Zhang, Z.L., Chen, J.M., Shi, D.D., Yang, J. and Tang, Z.X., 2011. Preparation and application of chitosan nanoparticles and nanofibers. Brazilian Journal of Chemical Engineering, Vol. 28, No. 3, pp. 353 – 362.