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Biosorption of Lead by Biomass of Dried *Sargassum*

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Abstract: *One of the heavy metal pollutants emerged highly concentration in the watershed of Jakarta city, Indonesia is lead (Pb). Removal of lead using a biological method by using macroalgae is an efficient method from wastewater. Sargassum crassifolium is the original species of macroalgae from Indonesia that was used in this study to analyze the ability of adsorption of lead from aqueous solution and industrial wastewater. Samples collected at Pari and Pramuka Island, Seribu Island, North Jakarta, Indonesia were studied to adsorb lead with a variety of adsorption time of 10, 20, 30, 45, 60, 90 and 120 minutes and a variety of initial concentration of lead, 200, 300, 400,500, 750 and 1000 mg/L, using duplicate assessment at the pH 5. The removal of lead from the industrial wastewater using macroalgae S. crassifolium should further be analyzed. The highest lead removal was 98.4 in the concentration of 1000 mg/L achieved within 60 minutes. The binding of lead by S. crassifolium followed the Freundlich model (R^2=0.976) with the maximum adsorption capacity was 55.56 mg/g. The removal of lead from wastewater was 75% for 60 minutes contact time with the final concentration was 0.01 mg/L under the safe limit for the environment. Thus, S. crassifolium has a high prospect as an adsorbent of heavy metals in industrial wastewater treatment.*

Keywords: *Aqueous solution, biosorption, industrial wastewater, lead, macroalgae*

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I. Introduction

Rapid industrialization has resulted in an increasing amount of heavy metals releasing from industries into the environment[1]. Disposal of heavy to an environment impacts an accumulation of toxic pollutants on a living organism. This refers to the stability and persistence of heavy metals once they are in an environment, thus, it is difficult to degrade them[2].

Indonesia has already had the regulation on water pollution which is the Indonesian Government Regulation No. 82 of 2001[3] on the Treatment of Water Quality and Water Pollution Control, a threshold limit of lead is 0.03 mg/L. Currently, the water quality in Indonesia mostly has decreased due to untreated wastewater discharged directly to the waters and has occurred exceeding the threshold[4,5] and also was found in marine organisms[5,6] with concentration over the permitted level by Indonesian government based on Decision of Environment Ministry of Indonesia Republic No. 51/2004[7]. Many industries use lead in their industrial process, such as in piping manufacturing, batteries, paint manufacturing, and fuel[8]. Lead, the most toxic metal can cause heme-effect, neuro-effect, and renal-effect[8], and also the chronic toxicity resulted in critical damage to DNA, enzymes, proteins, and membrane-based lipids[9].

Biomass has been used widely to reduce heavy metal contamination in water including macroalgae[1,10,11], microalgae[12], mushroom[13], and agriculture waste[14,15,16]. In Indonesia, the study of macroalgae as a biosorbent of heavy metal is limited which reported adsorption of Cu(II) on *Sargassum crassifolium*[17], Cr(III) on *Euchema spinosum*[18], Pb in *Eucheuma spinosum, Padina minor and Sargassum crassifolium*[19], and Pb(II) on *Sargassum duplicatum* [20]. The study of lead adsorption by macroalgae strains, however, has not been researched widely. As a biosorbent, macroalgae have important advantages including low cost, the abundance distribution in water, size, high ability to accumulate metals through its cell wall[14]. This study examined and compared the removal capability of *Sargassum crassifolium* on lead both in the aqueous solution and the industrial wastewater. *Sargassum crassifolium* is one of the brown macroalgae widely found in Indonesian water, but the utilization has not optimal for pollutants adsorbent rather than as raw material for cosmetics and medicine. Therefore, the result is worth for alternative solution for wastewater treatment. The Langmuir and Freundlich model in aqueous solution was also used to analyze an adsorption isotherm of biomass.

II. Material and Methods

This study was carried out in Integrated Laboratory Center of Faculty of Science and Technology, State Islamic University Syarif Hidayatullah Jakarta. The samples of macroalgae used in this study were *Sargassum crassifolium* were taken from the water surrounding Pari and Pramuka Island, Thousand Islands, North Jakarta, Indonesia. The samples of macroalgae used in this study were *Sargassum crassifolium* which were taken from water surrounding Pari and Pramuka Island, Thousand Islands, North Jakarta, Indonesia. The industrial wastewater was provided from a waste treatment company located in Cileungsi, Bogor.

Preparation of Biosorbent

Before transportation to laboratory, all samples were put in the zipped plastic bag after being washed by sea water to clean up from sediments or small organisms which were trapped in the macroalgae. In the laboratory, all samples were washed and rinsed again using distilled water and then dried in oven at 50 ^oC for 24 hours to get stable weight. Dried samples were grounded with a mortar and pestle and sieved to the size 250-500 µm and the biosorbents were ready to use.

Stock Solution of Lead

The lead solution was prepared for diluting 200mg/L of stock solution which was made by dissolving $Pb(NO_3)_2$ in deionized water. The stock solution was stored in the air tight polyethylene bottle at room temperature and ready for use in experiments using as aqueous solution.

Determination of the Optimum Contact Time

Batch experiment which aimed to determine the optimum time of adsorption was carried out in Erlenmeyer flasks, using 25 ml of 200 mg/L of the lead solution and 0.5 g of each biosorbent. The solution in Erlenmeyer flasks was stirred and kept under shaking at 200 rpm for 10, 20, 30, 45, 60, 90 and 120 minutes. Then, the solution was filtered and analyzed by flame Atomic Absorption Spectrometry (AAS) *Perkin Elmer A. Analyst 700*. Each treatment was conducted in triplicate.The optimum time of adsorption was decided from the measurement of AAS which showed the highest concentration of lead adsorbed. This optimum time, moreover, was used to determine the isotherm and capacity of biosorption.

Capacity of Adsorption

Solutions of fixed volume (50 ml) with varying concentration of 200, 300, 400, 500, 750 and 1000 mg/L were placed in Erlenmeyer flasks and thoroughly mixed with 0.5 g of biosorbent dose, and then stirred in a rotary shaker at 200 rpm for an optimum time obtained from the previous experiment. The filtration of solution through filter paper was conducted and the filtrate was analyzed using flame Atomic Absorption Spectrometry (AAS) *Perkin Elmer A. Analyst 700*. Each treatment was also conducted in triplicate.

The experiment using industrial wastewater was continued to come from a waste treatment company located in Cileungsi, Bogor, West Java, Indonesia. It was designed in Completely Randomized Design with two replications. The heavy metals Pb with 5 variations of pH, namely 2, 3, 4, 5, and 9 oscillated for 60 minutes as contact time. The characteristics of Industrial wastewater, pH and initial concentration of heavy metals, was measured using ICP (Inductively Coupled Plasma). Furthermore, 0.5 g of dried *S. crassifolium* was put into 50 mL wastewater and stirred for 60 minutes using a magnetic stirrer at 200 rpm. The solution pH was adjusted to 2, 3, 4, 5, and 9 with HCl (0.1 M) and NaOH (0.1 M). Then, the solution was filtered with Whatman paper BF/C code and the filtrate was analyzed using ICP to determine the concentration of metals at 543 nm wavelength.

Calculation of Metal Uptake

The metal adsorption with *E. spinosum, P. minor* and *S. crassifolium* was calculated by the following formula[21].

$$q = (C_i - C_f) \times \frac{V}{M}$$

$$R = \frac{C_i - C_f}{C_i} \times 100\%$$

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=bioremoval efficiency (%).

Adsorption Isotherm

Adsorption isotherm was represented by Langmuir and Freundlich model through equilibrium condition established between adsorbed metal ion on biosorbent (q) and the unabsorbed metal ion in the solution (C_f). The linear form of Langmuir and Freundlich isotherm was adopted from[22] given as followed:

Langmuir isotherm: $C_f/(q) = 1/ab + 1/a\, C_f$
Freundlich isotherm: $\log(q) = \log k + 1/n \log C_f$
Where C_f=final concentration of lead in the aquatic solution (mg/L); q=amount of adsorbed metal by adsorbent (mg/g); k and a=capacity of maximum adsorption; b=Langmuir's constant; n=intensity of adsorption.
Langmuir Isotherm was determined through calculating q, $C_f/(q)$, log (q), log C_f. The plots of $C_f/(q)$ versus C_f and log (q) versus log C_f were drawn using *IBM SPSS Statistic 20* to test Langmuir and Freundlich adsorption model and coefficient correlation respectively.

III. Results and Discussion

The original strain of Indonesian marine brown algae (*a phylum of Phaeophyta*), *Sargassum crassifolium*, was examined for lead removal at the different varieties of initial concentration that ranged from 200 to 1000 mg/L and variable contact period in pH 5 which was the best value for lead uptake[11,13]. Putri[19] has studied lead in three types of macroalgae including *S. crassifolium*, Sweetly et al[11] examined only *Sargassum* while Vimala and Das[13] studied on mushrooms, and all of these were particularly examined in aqueous solution.

The concentration of hydrogen ions in adsorption is one of the important parameters affecting the ionization degree of absorbate during the reaction and replacement of positive ion in active sites of the cell wall[18]. Figure 1 showed that *S. crassifolium* could remove 98.4% of lead in an aqueous solution at 60 minutes oscillation. This rapid metal adsorption for *Sargassum* was higher than was found by[11] which reached only 89.75% and this was due to the abundant availability of active binding sites on macroalgae such as –COOH, –OH and $–NH_2$ [23]. After 60 minutes, lead adsorption tended to decline as saturation had already occurred. Therefore, it can be assumed that the more amount of biomass the more availability of active sites to bind ions which were proved by Huang and Lin[10] using 3 g/L biomass to get the highest adsorption of metals.

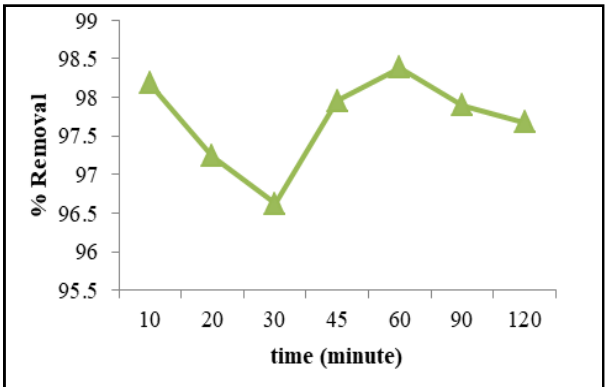

Figure 1: The effect of contact time on the adsorption of lead[17]

The Effect of biomass concentration on lead adsorption by *S. crassifolium* is shown in Figure 2. The trend observed was increasing in lead removal with the increasing concentration of lead. The adsorption of lead showed a rising trend and could still increase the above concentration of 1000 mg/L of lead. It proved that *Phaeophyta* has a high capacity to adsorb heavy metals in solution due to the largest amount of active binding sites.

The study observed that *Phaeophyta* had a higher uptake capacity of heavy metal than *Rhodophyta* (red algae)[24]. Meanwhile, the unsaturated condition had not occurred until the highest initial concentration of lead as the adsorption trend was still increasing on both algae. The upward trend of *S. crassifolium* on lead adsorption was seemed to be superior to red algae which were in line with[25].

The lead removal in aqueous solution by dried biomass of *S. crassifolium* was described using the Langmuir and Freundlich isotherm model. The Langmuir and Freundlich isotherm exhibited linear regression data to predict the maximum adsorption capacity of the adsorbent obtained from the equation (Figure 3 and Figure 4). The calculation of the constants and linear regression results were given in Table 1. *Sargassum crassifolium* showed a better fit to Freundlich isotherm with R^2 values of 0.976. It means that the interaction of ion showed a better fit to Freundlich isotherm with R^2 values of 0.976. It means that the interaction of ion exchange takes place between the metal ion and biosorbent whereby the proton displaces the metal ions from the binding sites, such as alkaline ion, carboxyl, and sulphonic[23].

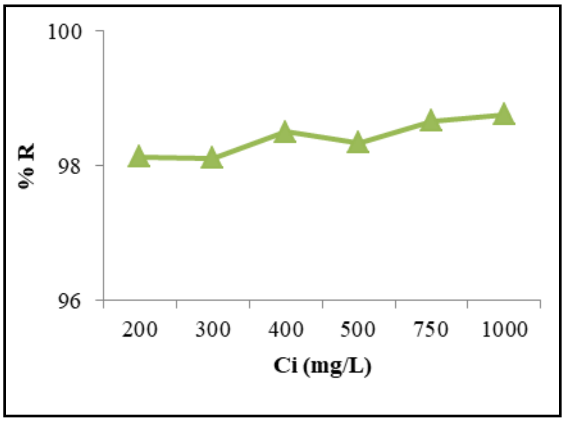

Figure 2: The Effect of biomass concentration on adsorption of lead[19]

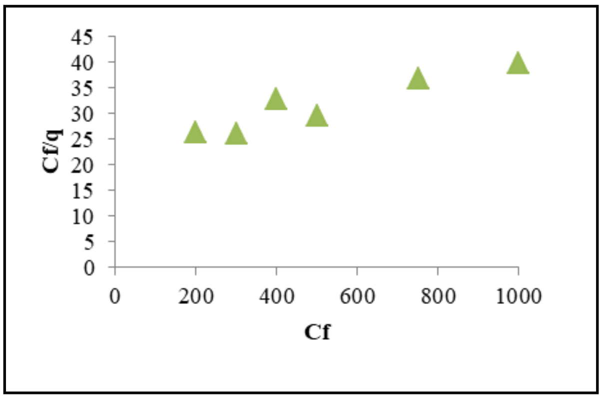

Figure 3: Langmuir equation for adsorption of lead on *S. crassifolium* (Y = 22.635+0.018X) in aqueous solution[19]

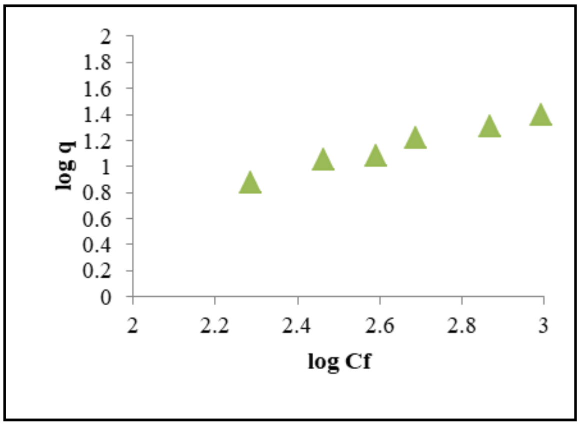

Figure 4: Freundlich equation for adsorption of *S. crassifolium* (Y = - 0.769+0.725X) in aqueous solution[19]

The maximum adsorption capacity of lead by *S. crassifolium* was 55.56 mg/g or 0.27 mmol/g (Table 1). This result was seemly similar to the study of Romera et al[25] which found that brown algae had higher heavy metals removal than red and green algae and mostly lead removal as its high affinity[23]. The result of this study can be elevated through the activation of the acid solution, such as HCl or H_2SO_4[26] which can improve several H^+ ions of the surface acidity which is an important part of the algae to bind heavy metals[27].

Tabel 1: Constant value of Langmuir and Freundlich isotherm for *S. crassifolium*[19]

Langmuir			**Freundlich**		
a	b	R^2	k	n	R^2
55.56	0.0008	0.882	2.453	1.379	0.976

The capability of *S. crassifolium* to adsorb lead in aqueous solution, then, was continued to be examined in the industrial wastewater. The industrial wastewater used was a mixture of wastewater solutions from various industrial companies which contains a lot of toxic heavy metals. The initial concentration was 0.04 mg/L and after the treatment using *S. crassifolium*, the concentrations were below the initial concentration (Table 2) which showed the great adsorption capability of *S. crassifolium,* although the percentage of removal was less. Only at pH 3, the lead could adsorb 75% by *Sargassum* (Figure 5). This study was supported by Davis et al[27] that had got the highest adsorption capacity mostly in acidic pH range. It is was assumed due to the dissolution of some cytoplasmic components or ions, such as carbonates released into the solution and anion types, similar to the study by Sudiarta and Diantariani[18], Susanti[28], and Davis et al[27]. Being compared to the study in aqueous solution, it was less concentration of lead had already in the regulated threshold limit, which was 0.01 mg/L. Thus, it was good to conserve the environment from heavy metals pollution, especially lead.

Table 2: Characterization of the untreated industrial wastewater

Parameter	Initial Conc. (mg/L)	Final Conc. (mg/L)
	0.04	
pH 2		0.033
pH 3		0.01
pH 4		0.026
pH 5		0.031
pH 9		0,046

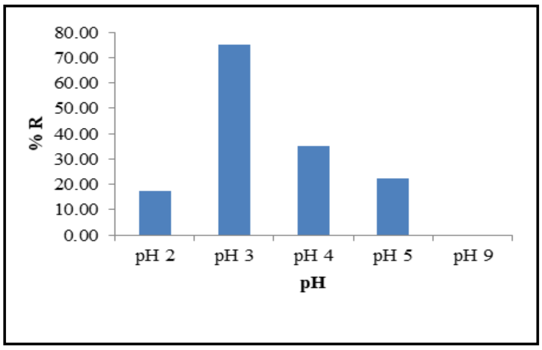

Figure 5: Removal percentage of lead on industrial wastewater

Future Trends

A natural friendly biopolymer recently is found its place among the most important carbohydrates. It is now used effectively in wastewater treatment. One of them is nano-composites of guar gum silica 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[29]. Another novel study was hydrogel based on guar gum[30,31] is one of the economic and eco-friendly bio-composite for removal of hexavalent chromium ion Cr(VI).

Nano-composite based on biopolymers is a future biosorbent that can be developed as a substitute for synthetic polymers. The nano-composite of biomass has already made by Zhao et al[32] study for chitosan. Our future research targets are to prepare nano-composite 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 the waste treatment process efficiently.

Moreover, using the obtained materials (alginate and algae waste biomass) as an adsorbent for the removal of metals is also challenging. In this process, the iron nanoparticles functionalized with alginate in order not to lose soluble alginate, as reported by Lucaci et al[33], which showed over 97% removal of metal, below the maximum permissible limit (0.2 mg/L). In the future, algae are one of the most valuable adsorbents that can be used and developed well through nanotechnology utilization.

IV. Conclusion

The original species of Indonesian marine macroalgae Indonesia *Sargassum crassifolium* has potentially lead adsorption reached 75%-98.4% within 60 minutes both in aqueous solution and industrial wastewater. The highest adsorption capacity was 55.56 mg/g that fit the Freundlich model. The removal of lead by *S. crassifolium* in industrial wastewater was also high reached 75%, although not so high as in an aqueous solution. It indicated that *S. crassifolium* belonging to the phylum of *Phaeophyta* could be claimed as the potential bio-sorbent of lead supported by the stronger form of cell wall predominantly alginic acid or alginate in acidic pH. This biomass could be chosen as an alternative material which is more environmentally friendly instead of the chemical substances in the wastewater treatment.

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