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Biosorption of Lead using Macroalgae *Eucheuma spinosum*, *Padina minor* and *Sargassum crassifolium* in Aqueous Solution

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ABSTRACT--- ***Lead is one of water the pollutants emerged highly concentration in watershed of Jakarta city, Indonesia. Biosorption using macroalgae is the efficient method used to eliminate heavy metals from liquid waste. Eucheuma spinosum, Padina minor and Sargassum crassifolium are the origin species of macroalgae from Indonesia that were used to analyze the ability of adsorption of lead from aqueous solution. Samples collected at Pari and Pramuka Island, Seribu Island, North Jakarta, Indonesia were used to adsorb lead with variety of adsorption time of 10, 20, 30, 45, 60, 90 and 120 minutes and variety of initial concentration of lead, 200, 300, 400,500, 750 and 1000 mg/L, using duplicate assessment at the pH 5. The highest lead removal was 98-99% in the concentration of 750 mg/L for E. spinosum and of 1000 mg/L for P. minor and S. crassifolium which was achieved within 60 minutes. The binding of lead by S. crassifolium followed Freundlich model while Langmuir model fitted better in E. spinosum and P. minor with their R^2 of 0.976, 0.984 and 0.934, respectively. The maximum adsorption capacity of lead was 55.56 mg/g for S. crassifolium, followed by P. minor and E. spinosum was 40.00 and 32.26 mg/g.***

Keywords --- Biosorption, Lead, Macroalgae

1. INRODUCTION

The increase population initiating rapid industrialization resulted in increase amount of heavy metals releasing from industries into the environment [1]. Once heavy metals are disposed to environment, their presence and accumulation have a toxic effect on living organism. Heavy metals are stable and persistent in environmental, so it is difficult to degrade them [2].

Based on Indonesian Government Regulation No. 82 of 2001 on the Treatment of Water Quality and Water Pollution Control [3], a threshold limit of lead is 0.03 mg/L. Currently, a decrease in water quality due to discharge of lead in Indonesian water has occurred exceeding the threshold [4, 5] and had already found in marine organisms with concentration over the permitted level by Indonesian government based on Decision of Environment Ministry of Indonesia Republic No. 51/2004 [5, 6, 7]. Lead is one of heavy metal widely used in piping manufacturing, batteries, paint manufacturing and fuel which has high toxic effects both for the environment and human health [8]. Lead, the most ubiquitous toxic metal, is detectable in practically all phases of the inert environment and in all biologic system which causes heme-effect, neuro-effect and renal-effect [8]. The chronic toxicity of lead resulted in critical damage to DNA, enzymes, proteins and membrane based lipids, then finally the antioxidant defense system was impaired [9].

Biological agent has been used widely to reduce heavy metal pollution in water including macroalgae [1, 10, 11], microalgae [12], mushroom [13], agriculture waste [14]. In Indonesia, study of macroalgae as biosorbent of heavy metal is limited which reported adsorption of Cu(II) on *Sargassum crassifolium* [15], Cr(III) on *Euchema spinosum* [16] and Pb(II) on *Sargassum duplicatum* [17]. However, study of lead adsorption on various Indonesian strains of macroalgae has not been conducted widely. As biosorbent, macroalgae offers several important advantages including low cost, their abundance distribution in water, size, longevity, high ability to accumulate metals and easy to identify [14]. Therefore, this study is the first one to use macroalgae *Euchema spinosum, Padina minor and Sargassum crassifolium* as biosorbent of lead. Those macroalgae are widely found in Indonesian water, but the utilization has not optimal, especially as adsorbent of heavy metals. Therefore, this study was conducted aiming to analyze adsorption ability of *Euchema spinosum, Padina minor and Sargassum crassifolium* for lead. The adsorption isotherm was also analyzed through Langmuir and Freundlich model.

2. MATERIALS AND METHOD

This study was carried out in Integrated Laboratory Center of Faculty of Science and Technology, State Islamic University Syarif Hidayatullah Jakarta from May to November 2015. The samples of macroalgae used in this study were *E. spinosum, P. minor* and *S. crassifolium* which were taken from water surrounding Pari and Pramuka Island, Thousand Islands, North Jakarta, Indonesia.

2.1 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 C for 24 hours to get stable weight. Dried samples were grounded with a mortal and pestle and sieved to the size 250-500 µm and the biosorbents were ready to use.

2.2. 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.

2.3. 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 lead solution and 0.5 g of each biosorbents. The solution in Erlenmeyer flasks were 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.

2.4. Isotherms Determination and 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 Erlenmyer flasks and thoroughly mixed with 0.5 g of biosorbent dose, and then stirred in rotary shaker at 200 rpm for optimum time obtained from 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.

2.5. Calculation of Metal Uptake

The metal adsorption with *E. spinosum, P. minor* and *S. crassifolium* was calculated by the following formula [18].

$$q = (C_i - C_f) \text{ x } \frac{V}{M} \quad ; \quad R = \frac{C_i - C_f}{C_i} \text{ x } 100\%$$

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 (%).

2.6. Adsorption Isotherm

Adsorption isotherm was represented by Langmuir and Freundlich model through equilibrium condition established between adsorbed metal ion on biosorbent (q) and unabsorbed metal ion in the solution (C_f). The linear form of Langmuir and Freundlich isotherm was adopted from Mulyana et.al. [19] 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.

3. RESULTS AND DISCUSSION

Three original strain of Indonesian marine macroalgae *Euchema spinosum, Padina minor* and *Sargassum crassifolium* were examined for lead uptake potential at different variation of initial concentration that ranged from 200 to 1000 mg/L and variable contact period. In this study, different pH effect was not examined but each solution was maintained in pH 5 which was the best value for lead uptake [11, 13]. pH is one of the most important parameters in the experiments on biosorption, it should be examined. Sweetly et al. [11] examined only *Sargassum* while Vimala and Das [13] mushrooms. As known that concentration of hydrogen ions in adsorption is one of the important parameters that affect the ionization degree of absorbate during the reaction and replacement of positive ion in active sites [16].

Figure 1showed that *E. spinosum*, *P. minor* and *S. crassifolium* reached high adsorption capacity of lead at 60 minutes which showed 97-98% of maximum lead removal. This rapid metal adsorption especially for *Sargassum* was higher than reported by Sweetly et al. [11] which reached 89.75% and this was due to the abundant availability of active binding sites on macroalgae such as –COOH, –OH and $–NH_2$ [20]. 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 was proved by Huang and Lin [10] where the highest adsorption was obtained for the biomass content 3 g/L.

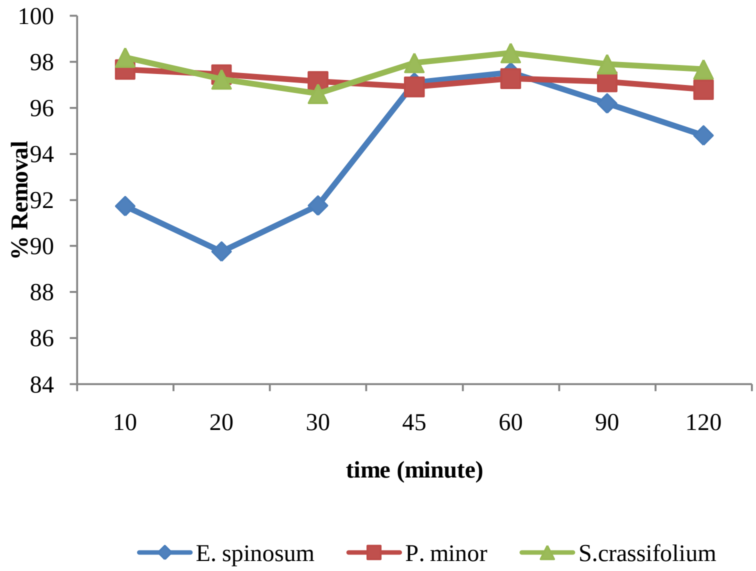

Figure 1: Effect of Contact Time on the Adsorption of Lead by Three Different Macroalgae

Effect of biomass concentration on absorption of lead by macroalgae is exhibited in Figure 2. The trend observed was increasing in lead removal with the increasing concentration of lead. The maximum lead removal by *E. spinosum* achieved 99.9% at initial concentration of lead 750 mg/L, then it decreased slightly to 99.87%. For *P. minor* and *S. crassifolium*, the adsorption of lead apparently showed rising trend and could be still increase above 1000 mg/L of lead concentration. It proved that phylum of brown algae *Phaeophyta* (*P. minor* and *S. crassifolium*) and red algae *Rhodophyta* (*E. spinosum*) are excellent heavy metals biosorbent due to the largest amount of active binding sites. Based on Brinza et al. [21], *Phaeophyta* had higher uptake capacity of heavy metal than *Rhodophyta*, but in this study *E. spinosum* showed high uptake oflead although it was saturated above 750 mg/L. While unsaturated condition had not occurred until highest initial concentration of lead (1000 mg/L) on *P. minor* and *S. crassifolium* because the adsorption trend were still increasing on both algae. The upward trend of lead adsorption by *P. minor* and *S. crassifolium* seemed to be that they offered better sorption than red algae and this condition was similar with Romera et al. [22].

The lead uptake capacity by dried biosorbent was described using Langmuir and Freundlich isotherm model. The Langmuir and Freundlich isotherm exhibited linear regression data to predict maximum adsorption capacity of the adsorbent obtained from the equation (Figure 3 and Figure 4). The calculation of constants and linear regression results were provided

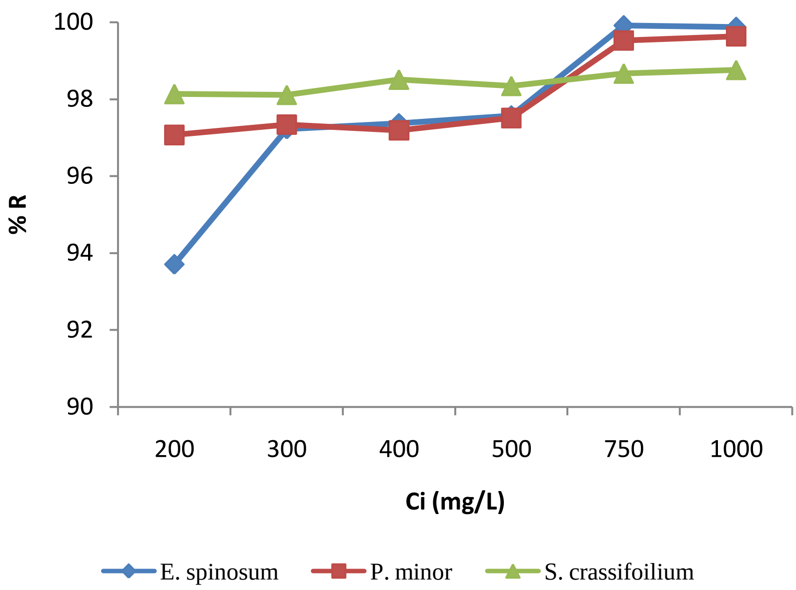

Figure 2: (a) Effect of Biomass Concentration on the Adsorption of Lead by Three Different Macroalgae

in Table 1. *E. spinosum* and *P. minor* were fitted better to Langmuir isotherm in terms of lead adsorption with higher R^2 values of 0.984 and 0.934 respectively. It means that Freundlich isotherm was not able to describe adequately the relationship between the amount of lead adsorbed by *E. spinosum* and *P. minor* and their equilibrium concentrations in solution. In contrary, *S. crassifolium* showed better fit to Freundlich isotherm with R^2 values of 0.976. It is indicated that ion exchange interactions takes place between metal ion and biosorbent whereby the proton displaces the metal ions from the binding sites, such as carboxyl and sulphonic [20].

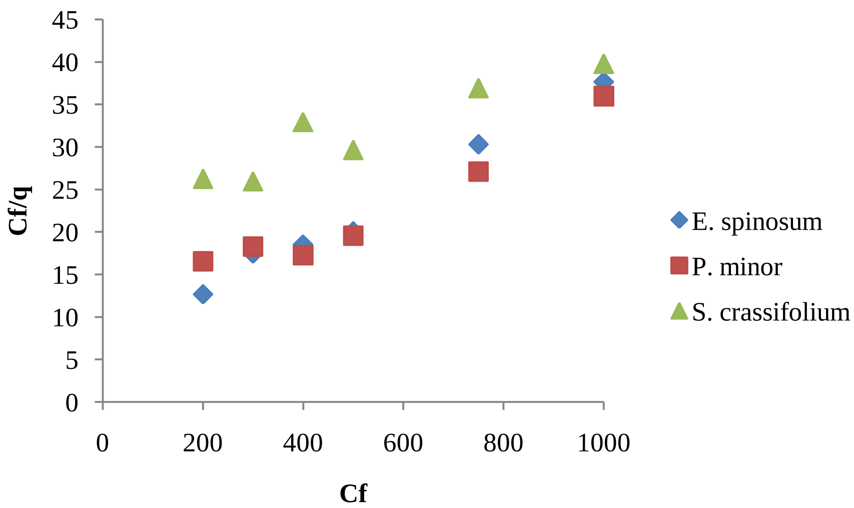

Figure 3: Langmuir Equation for adsorption of Lead on *E. spinosum* (Y = 6.803+0.031X), *P. minor* (Y = 9.669+0.025X) and *S. crassifolium* (Y = 22.635+0.018X)

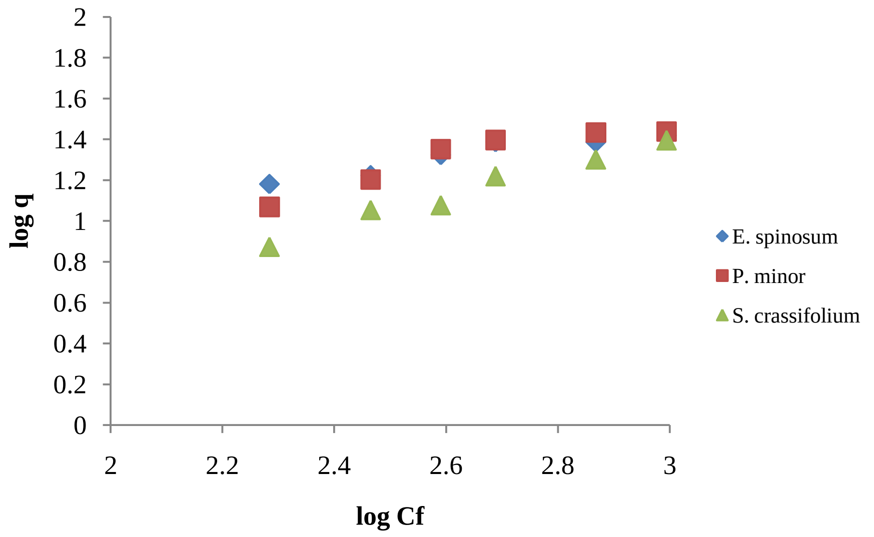

Figure 4: Freundlich Equation for adsorption of Lead on *E. spinosum* (Y = 0.387+0.352X), *P. minor* (Y = -0.094+0.532X) and *S. crassifolium* (Y = -0.769+0.725X)

Based on Langmuir and Freundlich isotherm models provided the maximum adsorption capacity of lead by *E. spinosum*, *P. minor* and *S. crassifolium* were calculated to be 32.26, 40.00 and 55.56 mg/g or 0.16, 0.19 and 0.27 mmol/g respectively (Table 1). *S. crassifolium* and *P. minor* had higher adsorption capacity value than *E. spinosum*. This result was supported by Romera et al. [22] who showed that brown algae had higher heavy metals uptake than red and green algae and the most potential occurred in lead adsorption as its high affinity [20]. Nevertheless, the adsorption capacity of lead by *E. spinosum* and *P. minor* was still not as much as reported by Romera et al. [22] reached 1.239 mmol/g and 0.651 mmol/g. The result of this study can be enhanced through activation using acid solution, such as HCl or H_2SO_4 [23] which can improve the properties of the surface acidity. An increase number of H^+ ions, the more parts ofthe algae to bind heavy metals [24].

Tabel 1: Constant Value of Langmuir dan Freundlich Isotherm

Absorbent	**Langmuir**			**Freundlich**		
	a	**b**	**R^2**	**k**	**n**	**R^2**
E. spinosum	32.26	0.0046	0.984	3.322	2.841	0.892
P. minor	40.00	0.0026	0.934	4.846	1.390	0.862
S. crassifolium	55.56	0.0008	0.882	2.453	1.379	0.976

4. CONCLUSION

Three original species of Indonesian marine macroalgae Indonesia *Euchema spinosum, Padina minor* and *Sargassum crassifolium* have potentially lead adsorption reached 98-99% within 60 minutes at equilibrium adsorption. The highest adsorption capacity was 55.56 mg/g achieved by *S. crassifolium* which fit Freundlich model while *E. spinosum* and *P. minor* followed Langmuir model and their maximum adsorption per unit biomass reached 32.26 and 40.00 mg/g, respectively. *Sargassum crassifolium* belonging to *Phaeophyta* division could be claimed as the most which fit better potential biosorbent of lead which is supported by the stronger form of cell wall predominantly alginic acid or alginate than *E. spinosum (Rhodophyta)*.

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