The capacity of biocharcoal prepared from sawah lettuce plants (*limnocharis flava*) as adsorbent of lead ions

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Abstract. Sawah lettuce plants are commonly regarded as weeds because it grows wildly in the rice fields. The plants can be converted into biocharcoal which in turn be utilized as metal ion adsorbents since it richly contained biomass. This research aims to determine the optimum contact time, weight, and also concentration of biocharcoal adsorption capacity of sawah lettuce plant on lead(II) ions. All the adsorbed ions content on biocharcoal was determined using the AAS method. The optimum contact time was determined among the variation time from 30 to 150 minutes, while char weight variations were from 25 to 125 mg. The lead(II) ions concentrations were varied from 20 to 1000 ppm. The results showed that the optimum biocharcoal of the sawah lettuce plant absorbed lead ions at 120 minutes contact time of 99.95%, the char weight variation of sawah lettuce to lead adsorption showed a gradual increase, with a maximum weight of 125 mg of percentage by 99.76% and the optimum concentration of lead metal was 500 ppm with 99.98% lead ions adsorbed.

1. Introduction

The utilization of biocharcoal produced from different organic raw material in the environmental remediation as adsorbent has been wildly implemented for various metallic ions including Cd(II) [1–3]. The increasing number of industries in developing countries such as Indonesia is assumed to be parallel with the number of waste, whether in the form of solid, liquid or gas, in particular, the heavy metals [4]. The toxicity caused by a heavy metal that can reduce water quality is lead which could destroy an order of aquatic ecosystems [5–8]. In humans, lead can cause serious problems such as damage to the kidneys, liver and reproductive system and can affect the brain [9]. Based on the research by Fujiastuti, et al [10] who have conducted research on the accumulation of lead (Pb) in shrimp (*Mysis* Sp) at the mouth of the Palu river, and also Arsad, et al [11] who examined the accumulation of lead metal (Pb) in mullet fish (*Liza melinoptera*) that live in the estuary waters of the Poboya river, have found that the average value of lead metal content in both samples are above the allowed food limit according to food standards of SNI 01-2729.1-2006 Indonesia in which the Pb level allowed in food is 0.4 mg/kg. This indicates that the rivers in Central Sulawesi have been contaminated by lead ions and therefore it is a necessary precaution to decrease the levels of these heavy metals contamination using alternative materials such as biocharcoal (charcoal).

The study of the application of natural latex as adsorbent by Ali, et al. [12] has established the types of adsorbents which are divided into natural organic and natural inorganic adsorbents, where one of the natural organic adsorbents is sawah lettuce. Sawah lettuce (*Limnocharis flava* (L.) Buch) which can
typically be found in the rice field in the tropical countries, was regarded as weeds and no economic values. However, the plant can be used as a raw material for biocharcoal (char) preparation which is beneficial as an adsorbent. In addition to genetic plants, there have also been many uses of waste generated from other organic wastes. As in research conducted by Sangkota [13] which utilizes water hyacinth charcoal (Eichornia crassipes) as an adsorbent of lead metal and Ningsih, et al [14] have conducted research on the adsorption of lead ions from its solution using adsorbents fabricated from corn cobs. and the use of biocharcoal as an absorbent of the ions in water has been carried out by Napitupulu et al [2] who conducted research on the adsorption of cadmium ions using biocharcoal from durian peels; Pangenda et al. [15] have conducted research on the biocharcoal adsorption capacity of snake skin fruit seeds as an adsorbent for chromium ions as well as Podala, et al [16] conducted research on adsorbing lead metal ions using biocharcoal from cocoa shells (Theobroma cacao L). All the organic material used as raw materials for biocharcoal fabrication have to contained biomass.

Thermodynamics conversion of biomass or cellulose into charcoal can be through the mechanism proposed by Antal and Gronly [17]: $C_6H_{10}O_5 \rightarrow 3.74C + 2.65H_2O + 1.17CO_2 + 1.08CH_4$ where from this mechanism carbon is produced by at 62.4%. This paper presents the results of the the biocharcoal adsorption capacity of a sawah lettuce plant towards the lead ions in solution which will describe the optimum touch time of lead in the solution to the adsorption power of the sawah lettuce plant biocharcoal, determine the optimum weight of the sawah lettuce plant biocharcoal against the adsorption power of lead in the solution and determine the optimum concentration of lead in the solution that can be adsorbed by the sawah lettuce plant biocharcoal.

2. Materials and Methods

The materials used in this study such as Pb stock solution (NO$_3$)$_2$ (Merck), HNO$_3$ (Smart lab), and NH$_4$OH (Merck) are commercially available. The analysis of lead ion in solution was performed on Atomic Absorption Spectrophotometer (SSA) GBC 932AA.

Samples of clean sawah lettuce plants were dried at the oven with a temperature of 60 °C for 24 hour to reduce the water content followed by pulverizing and ultimately converting the refined samples in the furnace at a temperature of 300 °C. This aims to carry out a pyrolysis process where the end result of the process will produce biocharcoal as the final result. Higher temperatures in the carbonization process greatly affect the quality of biocharcoal, including the carbon content produced [18]. Biocharcoal is then washed using distilled water, the purpose of washing the biocharcoal is to remove the remaining impurities. The biocharcoal was then put in the oven at a temperature of 105 °C for ± 1 hour to carry out the drying process and remove the water content that is still contained in biocharcoal. Furthermore, biocharcoal is mashed and sieved using 70 mesh sieve, in order to obtain finer particle size and greater surface area. The size of the adsorbent particles is one of the factors that affect adsorption. In the static method of adsorption (batch), the smaller the size of the adsorbent grain will increase the surface area [19] which in turn will increase the capacity of an adsorbent [20].

2.1 Variation of Biocharcoal Contact Time for Lead Adsorption

80 mg of biocharcoal was mixed with 60.21 ppm 25 mL lead solution at pH 5 into five of 100 mL Erlenmeyer flasks and then were added HNO$_3$ and NH$_4$OH solutions. Each Erlenmeyer flasks was closed with a rubber stopper and shaken using a shaker with a variation of time 30, 60, 90, 120 and 150 minutes and after that, it was allowed to stand for 24 hours to determine the optimum time of the adsorption of biocharcoal of genjer plants. The filtrate and residue are then separated through a screening process. The filtrate obtained then measured its concentration using SSA.
2.2 Variations in Biocharcoal Weight on Lead Adsorption
25, 50, 75, 100 and 125 mg biocharcoal were mixed with 25 mL of 60.21 ppm lead solution at pH 5 to which HNO₃ and NH₄OH solutions were added in a closed 100 mL Erlenmeyer flasks with the optimum time of biocharcoal that has been obtained and allowed to stand for 24 hours to determine the optimum weight of biocharcoal in adsorbing Pb ions. The filtrate and residue are then separated through a filtering process. The filtrate obtained then measured its concentration using SSA.

2.3 Variation of Solution Concentration on Lead Adoption by Biocharcoal
25 mL of 1000 ppm lead solution was diluted into 8 different concentrations of 20, 40, 60, 80, 100, 250, 500, and 750 ppm and 1000 ppm at pH 5 to which 5 HNO₃ and NH₄OH solutions were added. The initial concentration of this solution was measured using SSA. Each lead solution was put into a 100 mL Erlenmeyer flasks and mixed with biocharcoal to achieve the optimum weight with the obtained optimum time and after that all the mixtures were allowed to stand for 24 hours to determine the optimum concentration of lead solution which was adopted by the biocharcoal of the sawah lettuce. The filtrate and residue are then separated through a filtration process. The filtrate obtained then measured its concentration using SSA.

2.4 Data Analysis Techniques
Data obtained from the measurement of lead ions concentration using SSA were calculated according to a mass balance using the equation [21, 22]:

\[ C_b = (C_i - C_{eq}) \]

subsequently

\[ \%Pb = \frac{C_b}{C_i} \times 100 \]

where Cb is the concentration of absorbed Pb (mg/L); Ci is the initial Pb concentration (mg/L); C_eq is the concentration of Pb at equilibrium (mg/L).

3. Results and Discussion
The process of biocharcoal adsorption of sawah lettuce plants through three different conditions, namely the variation of biocharcoal contact time, variation of biocharcoal weight and variation of solution concentration to lead adsorption by biocharcoal. Data on the results of measurements of lead ions content in the variation of the contact time of biocharcoal on the adsorption of lead ions are shown in table 1.

Table 1. The measurement results of the adsorbed Pb concentration on the variation of the biocharcoal contact time

| Contact Time (minute) | C_i (mg/L) | C_eq (mg/L) | C_b (mg/L) | Pb absorbed (%) |
|----------------------|------------|-------------|------------|----------------|
| 30                   | 60.21      | 0.04        | 60.17      | 99.93          |
| 60                   | 60.21      | 0.07        | 60.14      | 99.88          |
| 90                   | 60.21      | 0.27        | 59.94      | 99.55          |
| 120                  | 60.21      | 0.03        | 60.18      | 99.95          |
| 150                  | 60.21      | 0.05        | 60.16      | 99.91          |

Table 1 shows that the most optimum contact time obtained in which the biocharcoal adsorbed the lead ions in imitation solutions is at the 120th minute while the highest percentage of lead ions adsorption by the adsorbent of the biocharcoal among the variation of contact time is 99.95% (at 120 minutes). Lead metal (Pb) adsorptions increase at the initial of contact time 30 minutes then decrease at a contact time of both 60 minutes and 90 minutes, then increase at time 120 minutes, and decrease again at contact time of 150 minutes. The phenomenon can be explained that in the initial minutes the lead ions adsorption capacity increases and takes place very quickly because the interaction between the lead ions and the adsorbent occurs effectively. This is because all the active sites of biocharcoal contained in the genetically adsorbent plant form an electrostatic bond with the lead ions in the solution. This is also due to the availability of active surfaces on the surface of many adsorbents. Rapid absorption is usually
due to the diffusion process that occurs between the adsorbates and the surface of the adsorbents [23]. The contact time between the metal ions and the adsorbent greatly influences the adsorption power. The longer the contact time the adsorption power will also increase until a certain time where it reaches a maximum time. This happens because the lead ions contained in the solution have been completely absorbed by the adsorbent. In addition, the adsorption process is also influenced by the size of the adsorbent used that causes the surface area of interaction is relatively large so that the possibility of very effective interaction between the active site of the adsorbent with metal ions [24]. Based on the description above, it is found that the optimum contact time of the biocharcoal to adsorb lead ions occurs at 120 minutes with a percentage of adsorption of 99.95%.

3.1 Effect of Biocharcoal Weight Variation on Lead Metal Adsorption

Data on the results of measurements of lead ions content in the variation of the weight of the biocharcoal against the adsorption of lead ions are shown in Table 2.

**Table 2.** The results of measurements of Pb concentrations adsorbed on the variation of the weight of the biocharcoal

| Weight (mg) | C_1 (mg/L) | C_{eq} (mg/L) | C_b (mg/L) | Pb absorbed (%) |
|------------|------------|---------------|------------|-----------------|
| 25         | 60.21      | 0.28          | 59.92      | 99.53           |
| 50         | 60.21      | 0.23          | 59.98      | 99.61           |
| 75         | 60.21      | 0.19          | 60.02      | 99.68           |
| 100        | 60.21      | 0.15          | 60.06      | 99.75           |
| 125        | 60.21      | 0.14          | 60.07      | 99.76           |

Table 2 shows that the weight of the adsorbent gradually increased from 25 mg to 125 mg, causing an increase in the percentage of lead ions absorbed and the highest percentage results 99.76% at the biocharcoal weight of 125 mg. One plausible explanation is that the more adsorbents, the higher the adsorption capacity [24]. This happens because of the density of biocharcoal bulks in solution so as to produce a fairly effective interaction between the active center of the bulks wall of biocharcoal with lead ions, the more adsorbing agent, the more the active center of the adsorbent reacts. Therefore, when the amount of biocharcoal is enlarged, the ratio is no longer fulfilled, so that it affects the adsorption of lead metal ions by biocharcoal [25]. The increase in lead metal adsorption is also due to the lead ions present in the solution which have not been fully absorbed by biocharcoal, in other words the lead ions in the solution have not been completely absorbed by biocharcoal. In addition, this also occurs because the surface of biocharcoal is not saturated with lead ions so that the increase in biocharcoal weight increases the adsorption of the ions by biocharcoal [26].

3.2 Variation of Solution Concentration on Lead Metal Adsorption by Biocharcoal

Data on the results of measurements of lead ions content in variations of the solution concentration of the adsorption of lead ions by biocharcoal are shown in table 3.

Table 3 shows that increasing the concentration of lead solutions affects the adsorption capacity of biocharcoal. At concentrations of 20 to 500 ppm an increase in the percentage of metal ions adsorbed continuously and the highest percentage results the capacity of 99.98% in 500 ppm. The continuing increase in lead ions adsorption is caused when the active group of the adsorbent has not been saturated by the film of adsorbate, then the increase of adsorbate concentration will increase the amount of adsorbate adsorbed [27]. It is also likely that the concentration of lead ions continues to increase with an increasing concentration on the lead ion solution. This is possible because there are several adsorption groups that have active groups proportional to the area of the adsorbent [28]. This is consistent with the statement of Fato et. al. [29] that the metal ion concentration correlates with the amount of the active contained on the surface of the adsorbent when the number of active sites is considerably larger than the number of metal ions, the absorption capacity will be higher. The increase in adsorption capacity
indicates the greater amount of lead ions being adsorbed on the active surface. High concentrations will increase the amount of lead in the solution, so the more likely it will be adsorbed [30].

Table 3. The results of measurements of the concentration of lead adsorbed on the variation of the concentration of the solution

| Concentration (ppm) | C_I (mg/L) | C_eq (mg/L) | C_b (mg/L) | Pb absorbed (%) |
|---------------------|------------|-------------|------------|-----------------|
| 20                  | 14.48      | 0.17        | 14.31      | 98.82           |
| 40                  | 24.24      | 0.16        | 24.08      | 99.33           |
| 60                  | 32.62      | 0.15        | 32.47      | 99.54           |
| 80                  | 48.53      | 0.13        | 48.40      | 99.73           |
| 100                 | 60.21      | 0.12        | 60.09      | 99.80           |
| 250                 | 190.85     | 0.09        | 190.76     | 99.95           |
| 500                 | 417.17     | 0.06        | 417.11     | 99.98           |
| 750                 | 632.57     | 0.16        | 576.41     | 91.12           |
| 1000                | 1000       | 101.39      | 898.61     | 89.86           |

Based on the data above shows that there is a decrease in sorption at a concentration of 750 to 1000 ppm and obtained a percentage of sorption in a sequence which is 91.12% and 89.86%. This is due to that in the concentration of 750 to 1000 ppm, the availability of the number of biocharcoal adsorbent particles is smaller than the number of lead ion particles adsorbed, so the adsorption process decreases. In this case, the adsorbent has been saturated with lead ions so that by increasing the concentration of lead ions, the number of adsorbed metal ions will decrease [20, 31, 32].

4. Conclusions
The optimum contact time required for biocharcoal prepared from sawah lettuce plant to adsorb lead ions is 120 minutes with percentage capacity of 99.95%. The variation in weight of the biocharcoal on lead adsorption shows a gradual increase, where at the maximum weight (125 mg) a percentage of sorption is obtained at 99.76%. The optimum concentration required by biocharcoal to absorb lead metal ions occurs at a concentration of 500 ppm with an absorbed percentage of 99.98%.

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