Utilization of red fruit’s peel (*freycinetia arborea gaudich*) as biochar for lead (Pb) adsorption

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Abstract. Red fruit is a plant-like flower pandanus, which can be used as an ingredient in traditional medicine by the people of Papua. Red fruit also can be found in the mountains Petiro Rano surrounds Siuri Lake (a tourism object) in Poso-Indonesia. Peel of red fruit consist of cellulose and lignin so it can be utilized as biochar and used as the adsorbent of heavy metal such as Lead. The use of biochar as adsorbent can reduce pollution and improve soil pH and river containing heavy metals. This study utilized red fruit peel as biochar to adsorb Lead ions in water. The method used in this study was laboratory experiments and the analysis was using a Spectro Direct spectrophotometer. The finding showed that the biochar’s water content was 2.3%, ash content was 8.2% and biomass content was 89.5%, these results showed that the characteristic of biochar of red fruit peel was very good to use as adsorbent. The optimum weight of biochar that adsorbs Lead ions was 40 mg with the percentage of adsorption was 99.04%. While the optimum contact time of adsorption of Lead ion by biochar was 60 minutes with 98.98% percentage of absorption.

1. Introduction
Red Fruit is a kind of traditional medicinal fruit originating from Papua-Indonesia and called Kuansu by the people of Wamena, the indigenous people in the region. Red fruit is a pandanus family plant with a tree resembling pandanus, the scientific name is Pandanus Conoideus. The height of this plant can reach 16 meters and of 5 to 8 meters free branch trunks supported by roots on the lower trunk. Red fruit is commonly found in Papua New Guinea, sporadically began to be planted in several regions such as Maluku, Sulawesi, Kalimantan, Java, and Sumatra. This plant can grow in the lowlands to an altitude of 2,500 m above sea level, with low soil fertility, acid to slightly acidic (pH 4.30-5.30), a shade of 0-15%, and grow in groups around river flow, used by the communities as a flavouring food with high nutritional value because it contains beta-carotene, a natural coloring that does not contain heavy metals and harmful microorganisms. Besides, red fruit is functioned as a supporter of daily staple food, and cures various diseases namely cancer, HIV, malaria, cholesterol, diabetes mellitus, gout and osteoporosis [1]. The habits of the people in Wamena, Timika, and villages in the region often consume red fruit as a worm medicine, blindness disease, and skin disease. They believe that red fruit can make more muscular, improve stamina, and prevent them from degenerative diseases such as hypertension, diabetes, heart disease and cancer [2].
Central Sulawesi red fruit located in Poso Regency surrounding the Siuri lake tourist attraction in the town of Tentena, precisely in the mountains of the West Pamona region "Petiro Rano". Poso Red fruit has the same type of shape as red fruit in Papua. Seeing the shape, size, place to grow and others, the red fruit in Central Sulawesi is likely to include the *Pandanus Bacari* species although the species names are different but are part of the same family [3]. The communities in the region do not know much about the existence of the red fruit. Red fruit peel very much like jackfruit, but red and sharp pointed. The most dominant part of the red fruit is the peel. The existence of the peel is so abundant which becomes waste that pollutes the environment. Then it needs to be utilized as biochar for absorption activities. Biochar can be used as a soil pH balancer if the soil contains heavy metals that have acidic pH [4]. The used of rice husk as an absorber of copper and lead metal ions in wastewater [5], and to improve soil fertility [6] has been known. The benefits of biochar lie in two main properties, namely having a high affinity for nutrients and persistent in the soil. Both of these properties can be used to solve some important agricultural problems, such as soil damage and food security, water pollution by agrochemicals, and climate change [7].

The study of the properties of biochar prepared from red fruit’s peel, and its ability to adsorb lead (Pb) ion was conducted. Using organic waste such as red fruit peel is one of the ways to reduce environmental pollution. Biochar utilized from Red Fruit’s peel will be characterized according to Indonesian National Standard (SNI), then find out its ability as an adsorbent by using the various of biochar weight and the length of contact time in the solution. The optimum weight and contact time of biochar from red fruit’s peel that affects the Lead (Pb) ion adsorption was determined.

2. Research Method

2.1. Preparation of Biochar
Red fruit’s peel was cut into small pieces and then washed using clean water and dried in the sun for ± 5 days. The resulted samples were put into the oven at 105°C for 1 hour, then placed into a furnace at a temperature of 300°C with low oxygen levels for 2 hours. The biochar resulted from red fruit’s peel was cooled in a desiccator. The biochar mashed using mortars and pestle then sieved using a 200-sieve mesh. Biochar from red fruit’s peel is stored in a dry and sealed container.

2.2. Characterization of Biochar

2.2.1 Calculation of water content. Three grams biochar was placed in a flask that has been weighed. The flask then put it into the oven and the temperature was set to 105 °C for 1 hour. After 1 hour the sample was put into desiccator and then weighed. The weight measurement was repeated until a constant weight is obtained. The water content then calculated using the following formula [8].

\[
\text{Water content} = \frac{B - F}{B - G} \times 100\%
\]

Information:
- \(B\) = flask mass with biochar (g)
- \(F\) = mass of the flask with dried biochar (g)
- \(G\) = flask mass (g)

2.2.2 Calculation of Ash content. Three grams of biochar is carefully weighed. Then it was put into the furnace for 1 hour then the temperature set to 500°C. After an hour biochar was cooled in a desiccator and then weighed. The procedure was repeated until a constant weight is obtained. Then the ash content was calculated using the following formula [8].

\[
\text{Ash content} = \frac{F - G}{B - G} \times 100\%
\]
Information:
B = flask mass with biochar (g)
F = flask mass with ash (g)
G = flask mass (g)

2.2.3 Calculation of Biomass level. Biomass content can be found from the analysis of water and ash content [8].

Biomass content = 100% - (Moisture + Ash content)

2.3. Measurement of Lead adsorption based on biochar weight variation
Amount of 20, 40, 60, 80 and 100 mg biochar were placed into 5 flasks then 25 mL of 100 ppm lead solution was added respectively. The pH adjusted to 4 by using buffers solution. The mixture was then shaken for 1 hour, then set aside for 24 hours. After 24 hours, the mixture was filtered then the concentration of the solution in the sample was measured by using the Spectro Direct spectrophotometer.

2.4 Measurement of Lead adsorption based on biochar contact time variation
Amount of 40 mg biochar was mixed with 25 mL of 100 ppm lead solution in five 100 mL flask. Each flask was covered with aluminum foil and tied with rubber and then shake using a shaker with a variation of time 30, 60, 90, 120 and 150 minutes. The resulted mixture then filtered by using filter paper. The concentration of the solution in the sample was measured by using Spectro Direct spectrophotometer.

2.5 Calculation of Lead concentration adsorbed
The concentration of the lead adsorbed calculated by using the equation as follows [9].

\[
\% \text{ Adsorption} = \frac{n(C_i - C_{eq})}{C_i} \times 100\%
\]

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

Cb = Ci - Ceq

Information:
Cb = absorbed Pb concentration (mg/L)
Ci = initial Pb concentration (mg/L)
Ceq = Pb concentration at equilibrium (mg/L)

3. Result and Discussion

3.1 Water, Ash, and Biomass content
The water content calculation aims to determine the hygroscopic nature of the biochar. Biochar water content was obtained at 2.3%. Based on the moisture content of the biochar, it can be seen that the biochar from red fruit peel is hygroscopic and can adsorb gases or other liquids. This is because biochar has large pores or surface area [10]. The smaller the water content, the better the quality of biochar. In general, biochar always contains water even in small amounts, because the bonding structure of the constituent C atoms is difficult to release all of its water [11]. These results are following the requirements of the Indonesian National Standard (SNI) for biochar quality standards, where the moisture content of biochar must be less than 15% (SNI 06-3730-95) [12]. Moisture content from the results of this study is relatively small, this shows that the water content in the sample has evaporated during the carbonization process.

The determination of biochar ash is carried out to determine the metal oxide content in biochar. Red fruit husk biochar produced in this study has ash content of 8.2%. Ash is metal oxides in charcoal which
consist of nonvolatile minerals in the ignition process. The high level of ash produced can affect the adsorption capacity of biochar. The higher the ash content, the weaker the adsorption capacity of biochar. This is due to the presence of excessive ash which can cause clogging of pores in biochar so that the surface area of biological charcoal decreases, thus the blockage occurs because the pores of charcoal are filled with metal minerals such as K, Na, Ca, and Mg [13]. The number of ash obtained are following the requirements of the Indonesian National Standard (SNI) for biochar quality standards, which is less than 10% (SNI 06-3730-95) [14]. The results obtained indicate that the ash content contained in biochar is relatively low, this is indicating that there is no blockage in the pores of biochar. Biomass can be obtained from plants directly or indirectly and utilized as energy or materials in large quantities. The yield of the biomass of 89.5% shows that biochar indicated that the carbon of biochar can be maintained and does not have an effect on greenhouse gas emissions [5].

3.2 Effect of biochar weight variation on lead (Pb) adsorption level

Measurement of lead concentration adsorbed was done using the Direct spectrophotometer. The amount of lead adsorbed (Cb) by biochar was different between the initial lead concentration (Ci) and the lead concentration at equilibrium (Ceq). To obtain the maximum adsorption results, the measurement conducted in the various biochar weight as shown in table 1.

| Biochar weight (mg) | Ci(mg/L) | Ceq (mg/L) | Cb (mg/L) | % Pb adsorbed |
|---------------------|----------|------------|-----------|---------------|
| 20                  | 100      | 2.72       | 97.29     | 97.29         |
| 40                  | 100      | 0.96       | 99.04     | 99.04         |
| 60                  | 100      | 0.99       | 99.01     | 99.01         |
| 80                  | 100      | 1.64       | 98.36     | 98.36         |
| 100                 | 100      | 2.06       | 97.94     | 97.94         |

The adsorbent is a factor that greatly affects the process of adsorption. The weight of biochar indicated the number of adsorbent particles that can adsorb metal ions at certain concentrations. The determination of the optimum weight is carried out in a metal solution at a concentration of 100 ppm shown in Figure 3.1

![Figure 3.1. Curve relationship between the weight of biochar (mg) and % Pb ion absorbed.](image)

Figure 3.1 shows the adsorption of lead ion influenced by the weight of the adsorbent. The curve indicated that the lead ion adsorption increased from 20 mg to 40 mg, but the adsorption decreased from 60 mg to 100 mg. The increasing of the mass of the biochar from 20 mg to 40 mg is proportional to the increase of the number of particles and the surface area of biochar so that it causes an increase in the active adsorption side, and its absorption efficiency also increases with the increase of adsorbent mass [15], thus when an adsorbent mass increases, it causes an increase in the efficiency of adsorption and a
decrease in adsorption capacity. The adsorption process takes place at the surface layer of cells which have opposite charge sites to the metal ion charge so that the interaction is passive and relatively fast. Particles of the adsorbent have a negatively charged active site which interacts with positively charged metal ions [16]. Lead ion adsorbed tends to decrease with the addition of biochar weighing 60 mg to 100 mg. This is because the metal ions contained in the solution have been completely adsorbed by biochar [17], the surface of the adsorbent is already saturated with lead ions so that the increase in the weight of the adsorbent relative no longer affects the increase in absorption of metal ions by the adsorbent [18]. Based on the data above, it can be seen that the optimum weight of biochar to adsorb Lead ion is 40 mg. The percentage for lead is 99.04% and the weight of lead ion adsorbed is 61.9 mg/g.

3.3 Effect of biochar contact time on lead (Pb) adsorption level

Another factor that also affects the adsorption process is contact time. In a certain period of time there will be an equilibrium between the adsorbent (biochar) and adsorbate (metal), where the time needed to reach this equilibrium state is called the optimum time of adsorption (table 2). To achieve the state of equilibrium (maximum adsorption) of metals by adsorbents, a time span is needed. The amount of adsorbed metal increases with time to a point, where all active sites in the biomass are saturated with metals, so the amount of adsorbed metal does not experience significant changes. Determination of optimum contact time on lead ion adsorption by biochar from red fruits’ peel was done in 5 variations of contact time; 30 minutes, 60 minutes, 90 minutes, 120 minutes, and 150 minutes, and the adsorbent weight was 40 mg (Figure 3.2).

Table 2. Lead percentage adsorbed based on the biochar contact time variation

| Biochar weight (mg/L) | time (minute) | Ci (mg/L) | Ceq (mg/L) | Cb (mg/L) | % Pb terjerap |
|----------------------|--------------|-----------|------------|------------|---------------|
| 40                   | 30           | 100       | 2.78       | 97.22      | 97.22         |
| 40                   | 60           | 100       | 1.02       | 98.98      | 98.98         |
| 40                   | 90           | 100       | 1.27       | 98.73      | 98.73         |
| 40                   | 120          | 100       | 3.36       | 96.64      | 96.64         |
| 40                   | 150          | 100       | 3.51       | 96.49      | 96.49         |

Figure 3.2. Curve Relationship between contact time an % Pb ion adsorbed

Based on the data presented in Figure 3.2, it can be explained that lead ion adsorption has increased from 30 minutes to 60 minutes of contact time. However, at 90 minutes and 150 minutes of contact time
usage, the percentage of lead ion adsorbed was decreased. The increase was due to the effective interaction between the biochar lead ions. That is because of all the active sides in biochar bind to the lead ions in the solution. Also, the adsorption process is also influenced by the size of the surface area of the adsorbent so that the possibility of interaction very effective between the active site of the adsorbent with metal ions [9]. The initial increase in the adsorption percentage can be attributed to the increased surface area of the biosorbent and the availability of more adsorption sites. The decrease in the amount of adsorption can be related to the overlap or aggregation of the adsorption location resulting in a decrease in the total adsorbent surface area [17].

The contact time between the metal ions and the adsorbent greatly affects the adsorption capacity. The longer the contact time, the adsorption will also increase until a certain time will reach a maximum, and then it will go down again. Lead ion adsorption decreased at 90 minutes of contact time. The decrease was occurred due to the desorption process. This is a phenomenon in physical adsorption that states that the adsorption process is reversible [19]. This is because the bond between the groups contained in the adsorbent and the metal ions is weak so that eventually it is released back into the solution. Only clusters that bind strongly with adsorbents can still bind because of the length of time of contact [20]. The optimum contact time of biochar from red fruits’ peel to adsorb lead ion was 60 minutes with the percentage of sorption was 98.98%, and the weight of lead ion adsorbed was 61.86 mg/g. The optimum time is reached when the increase of Lead ion adsorbed reached its maximum point so that the addition of contact time will not have a significant effect on reducing the Lead level in the sample.

4. Conclusion
Utilization and Characterisation of biochar from red fruits’ peel has been done, and found the water content was 2.3%, the ash content of biochar was 8.2%, and the biomass content was 89.5%, so that the biochar from red fruits’ peel meets Indonesia's national standard biochar, which is the water content of 15% and ash content of 10%. The optimum weight required for biochar from red fruits’ peel to adsorb lead ions is 40 mg with a percentage of 99.04% sorption, and the weight lead ion adsorbed was 61.9 mg/g. The optimum contact time for the lead ion was 60 minutes with 98.98% sorption percentage and lead ion absorbed was 61.86 mg/g.

Acknowledgments
Authors wishing to acknowledge assistance from students of the chemistry study program, special work by technical staff and Lab assistant at Chemistry Laboratory of Tadulako University

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