Preparation and characterization of jatropha curcas leaves as a biosorbent for Pb(II) and Cd(II) removal in liquid waste

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Abstract. This study aims to determine the capacity of Jatropha leaves to absorb Pb (II), Cd (II) and their mixture in liquid waste. Jatropha leaves were obtained from Durian, Labu Beach, North Sumatra, heated for 4 hours and 24 hours, then characterized by XRD, FTIR, and SEM. XRD and FTIR spectra confirmed there are no structural differences of Jatropha leaf biosorbent with 4 hour and 24-hour pretreatment. SEM images indicate that the surface of the biosorbent prepared for 24 hours is smoother than the 4-hour preparation. The number of Jatropha leaves which absorbed Pb (II) and Cd (II) were measured with AAS and the optimum concentration of 0.5 gram of adsorbent for Pb (II) is 80 ppm (90 minutes) adsorbed up to 95.52%. It is higher than the absorption of Cd(II) which is 76.37% at a concentration of 100 ppm (90 minutes). But the mixture of Pb (II) and Cd (II) induce the opposite result. Cd (II) was absorbed more by 92.48% while Pb (II) was 88.62% at a concentration of 100 ppm for 90 minutes. Although Pb (II) can be absorbed more than Cd (II), when the two heavy metals mixed, Cd (II) is absorbed more than Pb (II).

1. Introduction
The rapid development of industry, environmental problems or environmental pollution have become the main aspects which need attention. Poor waste management causes a lot of waste generated by the industry to be discharged directly to nature which causes damage to the environment polluted by the waste. [1,2] Environmental contamination by heavy metals such as Pb$^{2+}$ and Cd$^{2+}$ induced the waters and the environment pollution that may be harmful to community. Some modern methods such as deposition [3,4], electrochemical [5,6], ion exchange [7,8], and microorganisms [9,10] have been developed to eliminate the heavy metal content in the wastewater. This method shows satisfactory results but it requires fairly expensive operating costs and time-consuming. The adsorption method becomes an alternative choice to remove heavy metal, because of its easy and effective application.

Some of the organic ingredients such as mangosteen rind, algae, water hyacinth and oil palm have previously been used as biosorbent. These natural adsorbents are able to absorb heavy metals from the environment efficiently in their role as biosorbents and heavy metal bioaccumulation. The presence of secondary metabolites such as flavonoids with amino groups, carboxyl, thiol, hydroxyl-carbonyl and phosphate will formed complex compounds with heavy metal ions. [11-15] Biosorbents are made from all natural materials that contain carbon, both organic carbon and inorganic carbon with the condition that the material has a porous structure, like Jatropha curcas leaves [16]. Jatropha leaves have relatively large porous structure and contain some of organics group which induce as a function of biosorbent for the development of water purification contaminated with Pb(II) and Cd (II) metals.
The number of liquid wastes that simultaneously contain both of Pb (II) and Cd (II) metals, and the varying amounts of Pb (II) and Cd (II) that are more absorbed by using some biosorbents, so in this study we developed to make adsorbents with selective adsorption properties between metal Pb (II) and Cd (II) by Jatropha curcas L. leaves as specific biosorbent.

2. Experimental
Jatropha leave taken from Durian Village, Pantai Labu District, Deli Serdang, North Sumatera. Pb(II) and Cd(II) solution were prepared from Pb(NO$_3$)$_2$ and Cd(NO$_3$)$_2$. For biosorbent characterization were used Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX), Fourier Transform Infrared (FTIR). Metal ion contain was measured by Atomic Absorption Spectroscopy (AAS).

2.1. Biosorbent Preparation
10 grams of jatropha leaves (Jatropha curcas L.) was cleaned with distilled water to remove dust from the leaves surface and air-dried for 24 hours. The dried leaves, separate become 2 part and inserted into the oven at 105°C for 4 hours for the first one and applied for 24 hours of the second one. Biosorbent then mashed using an electric blender and sieved with a size of 100 mesh to get a uniform biosorbent size.

2.2. Biosorbent Characterization
Characterization of Jatropha curcas L. leaves biosorbent was carried out by determining the degree of crystallinity using XRD (X-Ray Diffractometry), morphological analysis with SEM (Scanning Electron Microscope), and analysis of functional groups with FTIR (Fourier Transform Infrared).

2.3. Effect of Initial Concentration on Biosorbent Adsorption of Pb(II) dan Cd(II)
0.5 grams of biosorbent was mixed to 30 mL of Pb (II) and Cd (II) ions solution which various concentration of 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 ppm. All solution was stirred at 100 rpm for 30 minutes. The filtered solution was analyzed using AAS.

2.4. Effect of Contact Time on Biosorbent Adsorption of Pb(II) dan Cd(II)
0.5 grams of biosorbent was mixed to 30 mL of Pb (II) and Cd (II) ions solution which optimum concentration as previously obtained. the solution was stirred at 100 rpm with a variation of time 30 minutes, 60 minutes, 90 minutes and 120 minutes. The filtered solution was analyzed using AAS.

2.5. Effect of Initial Concentration on Biosorbent Adsorption of Pb(II) dan Cd(II) Mixture Solution
0.5 grams of biosorbent was mixed to 15 mL of Pb (II) solution and 15 mL Cd (II) solution which various concentration of 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 ppm. All solution was stirred at 100 rpm for 30 minutes. The filtered solution was analyzed using AAS.

2.6. Effect of Contact Time on Biosorbent Adsorption of Pb(II) dan Cd(II) Mixture Solution
0.5 grams of biosorbent was mixed to 15 mL of Pb (II) solution and 15 mL Cd (II) solution which optimum concentration as previously obtained. the solution was stirred at 100 rpm with a variation of time 30 minutes, 60 minutes, 90 minutes and 120 minutes. The filtered solution was analyzed using AAS.
3. Results and Discussion

3.1. XRD Characterization
Changes in the crystallization structure that occur in biosorbent with different preparation time treatments can be identified through XRD pattern (Figure 1)

![XRD pattern](image)

**Figure 1.** XRD pattern of jatropha leaves prepared for 4 hours and 24 hours

Two different biosorbents of jatropha leaves which differen
treatment heating time as 4 hours and 24 hours were induced insignificantly different of XRD pattern. Even though, biosorbent with 4 hours pretreatment time showed sharp peak at 14.96°, 18.10°, 24.34° and 64.27°. In the other hand, Jatropha leaves biosorbent with 24 hour heating preparation has intensity with a high peak value at 14.65°, 17.77°, 24.14° and 64.38°; . Although there is no significant difference between the heating of the jatropha leaves for 4 hours to 24 hours but by using EXPO 2014 also showed a slight difference in the structure of jatropha leaves which were prepared for 4 hours heating formed as a triclinic crystal system while the heating for 24 hours changed the jatropha leaves crystal system to monoclinic.

| Biosorbent Pretreatment | a(Å)  | b(Å)  | c(Å)  | α(°) | β(°)   | γ(°)   | Vol (Å³) | Crystal System |
|------------------------|-------|-------|-------|------|--------|--------|----------|----------------|
| 4 h                    | 8.87  | 15.49 | 12.86 | 115.64 | 109.42 | 38.49 | 991.94   | Triclinic      |
| 24 h                   | 12.05 | 6.11  | 8.331 | 90   | 101.1  | 90     | 602.63   | Monclinic      |

3.2. FTIR Characterization
The spectra analysis showed the presence of some functional groups in the jatropha leaves. The uptake that is believed to be related to the functional groups in leaf biosorbent at a distance of 4 hours is at wave number 3270.52 cm⁻¹. Absorption with broadband in the area of 3000-4000 cm⁻¹ was indicated as a hydroxyl group, which shows OH bonds, although the contribution of hydroxyl groups from hydrated water molecules cannot also be ignored.

In the 4-hour biosorbent there is absorption of the wavenumber 3270.52 cm⁻¹ as the OH group, in absorption with the wave number 2917.98 cm⁻¹ as the CH group, at the peak of the absorption with the wave number 2104.13 cm⁻¹ indicated as CN group and in the absorption with the wavenumber 1049.79
cm$^{-1}$ as a CO group. And even leaf biosorbent heating pretreatment was increased become 24 hours, but no significant change of organic functional group contains as shown in Figure 2. The presence of these organic groups was contributed to enhance heavy metals ion adsorption.

![FTIR spectrum of jatropha leaves prepared for 4 hours and 24 hours](image)

**Figure 2.** FTIR spectrum of jatropha leaves prepared for 4 hours and 24 hours

3.3. **SEM Characterization**

Characterization with SEM images was carried out to compare morphological changes that occur in Jatropha leaves. In this study, Jatropha (Jatropha curcas L.) leaves using different heating preparations aimed to compare the absorption of the biosorbent for absorption of Pb (II) and Cd (II) Metals. Based on the image of SEM characterization results, castor leaf biosorbent with time preparation 4 hours heating looks more coarse and there are many small flakes that are suspected to be impurities that are still present in biosorbents because there are still as presence of many organic compounds, which have the potential to help the absorption of Pb (II) and Cd (II) metals while in 24-hour biosorbents look more smoother and cleaner. Indicate the 24-hour biosorbent heating removes the remains of impurities that are still present in the biosorbent and the presence of damaged structures in the biosorbent, the biosorbent used for this study is a 4-hour heating biosorbent because it is more optimal for the absorption of Pb (II) and Cd (II) metal ions.

![SEM Images of jatropha leaves prepared for 4 hours (A) and 24 hours (B)](image)

**Figure 3.** SEM Images of jatropha leaves prepared for 4 hours (A) and 24 hours (B)
3.4. Effect of adsorbent initial concentration in the adsorption process

The purpose of determining the optimum concentration of adsorbent is to determine the concentration of the adsorbent which suitable for the Pb (II) and Cd(II) to achieve the optimum conditions. Figure 4 showed the optimum initial concentration of Pb(II) adsorption is 80 ppm with % Removal as 59.26% while Cd (II) was absorbed as 51.59% but at a concentration of 100 ppm. The absorption capacity of metal ions was influenced by the initial concentration value of the adsorbate solution. The adsorption capacity will increase with the increasing of an initial concentration and will reach the highest value at the optimum concentration and then the adsorption capacity will decrease with the increase in initial concentration due to the saturated of adsorbent was formed. The properties of the metal Pb (II) which has a greater molecular weight compared to Cd (II) makes the optimum conditions were adsorbed higher than Cd (II). The stronger attraction between Pb (II) ions and the functional groups in Jatropha leaves biosorbents also induces the higher absorption amount of Pb (II) when equilibrium absorption was achieved.

![Figure 4. Initial Concentration effects on Pb(II) and Cd(II) Adsorption](image)

![Figure 5. Initial Concentration effects on Mixture of Pb(II) and Cd(II) Adsorption](image)
In a solution with a mixture of Pb (II) and Cd (II) shows an interesting phenomenon. At initial concentration of 20, 40 and 60 ppm, Pb (II) solution was absorbed higher than Cd (II). When 60 ppm, Pb (II) ions are absorbed by 47.71% while Cd (II) ions are 45.29%. But at concentrations above 60 ppm Cd (II) ions are absorbed higher than Pb(II) and reach optimum conditions at a concentration of 100 ppm as 57.36% and Pb (II) ions are also optimum at 100 ppm but with absorption of 54.95%. The strong interaction between the Pb metal and the functional groups in the biosorbent induce high adsorption of Pb(II) at low concentrations whereas with the increasing of initial concentration of the solution, Cd (II) more adsorbed than Pb (II). It suggests the same Pb(II) have larger molecular weights causing the faster the equilibrium of absorption is achieved.

3.5. Effect of contact time in the adsorption process
Determination of the optimum contact time also performed to determine the time needed by the adsorbent in the adsorption process until the saturation state is achieved at the maximum concentration described above.

![Graph showing adsorption time vs. percent removal for Pb(II) and Cd(II).](image1)

**Figure 6.** Contact Time effects on Pb(II) and Cd(II) Adsorption

![Graph showing adsorption time vs. percent removal for Mixture of Pb(II) and Cd(II).](image2)

**Figure 7.** Contact Time effects on Mixture of Pb(II) and Cd(II) Adsorption
The absorption of Pb (II) ions with an initial concentration of 80 ppm solution reaches an optimum contact time of 90 minutes as 95.52%, and the absorption of Cd (II) ions reaching the saturation point after 90 minutes of the absorption process occurs with an initial concentration of 100 ppm solution with an absorption as 76.39%. The effect of larger molecular weight of Pb (II) compared to Cd (II) also contributes to the absorption of Pb (II), due to the stronger attractive force with functional groups on the biosorbent of jatropha leaves. Whereas in the adsorption of the mixed solution of Pb (II) and Cd (II) ions, it also reached the saturation point after 90 minutes, but Cd (II) ions were absorbed as 92.48%, higher than Pb (II) ions which were only absorbed by 88.62%.

Supporting the assumptions stated on the effect of the initial concentration above, when both of them are in solution, Cd (II) ions can be more absorbed compared to Pb (II) due to smaller molecular weights so that they can more quickly interact with the functional groups involved on biosorbent. Although both of them reach the saturation point of absorption equilibrium after 90 minutes, Cd (II) is absorbed by a higher amount.

4. Conclusion

In this study have prepared Jatropha leaves as a potential biosorbent to remove Pb(II) and Cd(II) as well as their mixture presence in liquid waste. Pb(II) was adsorbed as 95.53% which optimum adsorption when 0.5 gram adsorbent and 100 ppm initial concentration for 90 minutes and Cd(II) was adsorbed as 76.39% in same initial concentration and contact time. Whereas, Cd(II) was adsorbed higher than Pb(II) in mixture of them in solution. Cd(II) adsorbed as 92.48% and Pb(II) as 88.62% at same optimum state with 80 ppm initial concentration and adsorption time 90 minute. Jatropha leaves was released to use as potential adsorbent for heavy metal removal from liquid waste solution.

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