Adsorption selectivity of Jatropha curcas leaves on Pb(II) and Cd(II) mixture contaminant removal in liquid waste

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Abstract
Jatropha leaves from Durian, Labu Beach, North Sumatera was prepared as a biosorbent for the selectivity absorption of Pb$^{2+}$ and Cd$^{2+}$ in their mixture system. Jatropha curcas leaves was prepared by heating at 105 °C for 4h, then characterized by XRD and FTIR. FTIR spectra indicate the content of organic groups as -OH, -CN and -CO groups in their function to reduce of Pb and Cd ions in liquid contaminant. Pb$^{2+}$ and Cd$^{2+}$ were adsorbed in the single system obtained as optimum amount of Pb$^{2+}$ at 100 mgL$^{-1}$ and 60 min contact time is 4.72 mgg$^{-1}$ which higher than Cd$^{2+}$ as 4.42 mgg$^{-1}$ at 100 mgL$^{-1}$ ion solution for 90 min. Interestingly, in the mixture solution of Pb and Cd ions, Cd$^{2+}$ was adsorbed as 2.64 mgg$^{-1}$ which higher than Pb$^{2+}$ adsorption amount as 2.11 mgg$^{-1}$ at 100 ppm solution and adsorption time for 90 min. It indicates the mixture content of Pb and Cd ions in liquid solution shows a preferential adsorption properties compared with their single system adsorption.

1. Introduction
Environmental pollution by heavy metal ions causes serious socio-environmental problems and has a detrimental impact on public health and the population surroundings. Heavy metals like zinc, lead, nickel, cadmium, copper, mercury, and also chromium are most contaminant which pollutes the water due to their large amounts source contaminated in wastewater which released from the industrial activity.

Conventional treatment methods were generated to reduce of heavy metals contents were used like chemical precipitation, reverse osmosis, ion exchange, phytoremediation, electro-chemicals, and ultra-filtration [1-5]. Then, the method by adsorption with use biomaterial or biosorption become new attractive method to reduce heavy metal content in liquid waste because their simple and cheap in preparation and easy in application.

Some of biosorbent were used as heavy metal removal like bio-sorbent from alga [6], peels of banana [7] and water hyacinth [8]. Bio-sorption has a potential process in heavy metals removal contaminants include the micro level of contaminant. The Biosorption mechanism formed as complex processes which comprise the binding between adsorbate material and the bio-sorbent. Many natural ingredients were potential as biosorbents because of the binding of metal ions by chemical sorption
(ion exchange) binding, complexation, reduction, chelation, and precipitation or physical sorption (electrostatic interaction or van der Waals forces) [9,10]. Bio-sorbents is contain of functional (chemicals) groups like amide, amine, carbonyl, carboxyl, sulfonate, imidazole, imine, phenolic, and phosphate groups that can attract metal ions [11-15].

Bio-sorbents are made from all natural materials that contain carbon, both organic carbon and inorganic carbon which has a porous structure, like jatropha curcas leaves (Jatropha curcas L.). The chemical as organic content of jatropha leaves is carbohydrate (45.4 %), fat (3.2 %), protein (28.0 %), ash (23.4 %) [16, 17]. Bio-sorbent from jatropha leaves also have studied to heavy metal ion removal like Cr, Cu and Zn, but no report of jatropha leaves as bio-sorbent to adsorb Pb and Cd ion in contaminant water [18,19]. 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$^{2+}$ and Cd$^{2+}$ [5-8].

The number of liquid wastes that simultaneously contain both of Pb and Cd ions, and the varying amounts of them which are more absorbed by using some bio-sorbents, so in this study we developed to make adsorbents with selective adsorption properties between Pb$^{2+}$ and Cd$^{2+}$ ions by Jatropha curcas L. leaves as specific bio-sorbent.

In this study we prepared Jatropha curcas L. leaves as biosorbent to adsorb Pb and Cd ions in water solution. Because the presence of liquid waste that simultaneously contains both Pb$^{2+}$ and Cd$^{2+}$, and the varying amounts of Pb$^{2+}$ and Cd$^{2+}$ ions which absorbed by using some bio-sorbents, it is necessary to develop adsorption properties with selective between metal Pb$^{2+}$ and Cd$^{2+}$ in mixture system.

2. Materials And Methods
Jatropha leave was taken at Durian Village, Pantai Labu District, Deli Serdang, North Sumatera. Pb and Cd ions solution were prepared from Pb(NO$_3$)$_2$ and Cd(NO$_3$)$_2$. Biosorbent characterization were used X-ray Diffraction (XRD) and Fourier Transform Infra red (FTIR). Pb and Cd ions content of before and after adsorption were measured by Atomic Absorption Spectroscopy (AAS).
2.1. Biosorbent Preparation

10g of jatropha leaves (Jatropha curcas L.) was cleaned with aquadest to remove contaminant from the leaves surface and air dried for 24 h. The dried leaves, inserted into the oven at 105 °C for 4 hours. 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 Diffractometer), and FTIR (Fourier Transform Infra red) to observe organic groups contents.

2.3. Initial Concentration Effect of on Pb\(^{2+}\) dan Cd\(^{2+}\) Adsorption in Single System.

0.5 g of biosorbents was mixed to 30 mL of Pb\(^{2+}\) and Cd\(^{2+}\) ions solution which various concentration of 20 mgL\(^{-1}\), 40 mgL\(^{-1}\), 60 mgL\(^{-1}\), 80 mgL\(^{-1}\), 100 mgL\(^{-1}\) and 120 mgL\(^{-1}\). All solution was stirred at 100 rpm for 30 min. The filtered solutions were analyzed using AAS.

2.4. Adsorption Time Effect of Pb\(^{2+}\) dan Cd\(^{2+}\) Adsorption in Single System

0.5 grams of biosorbent was mixed to 30 mL of Pb\(^{2+}\) and Cd\(^{2+}\) ions solution which optimum concentration as above obtained. The solution was stirred at 100 rpm with a variation of time 30, 60, 90 and 120 minutes. The filtered solutions were analyzed using AAS.

2.5. Initial Concentration Effect of Pb\(^{2+}\) dan Cd\(^{2+}\) in Mixture System.

0.5 grams of biosorbent was mixed to 15 mL of Pb\(^{2+}\) solution and 15 mL Cd\(^{2+}\) solution which various concentration of 20 mgL\(^{-1}\), 40 mgL\(^{-1}\), 60 mgL\(^{-1}\), 80 mgL\(^{-1}\), 100 mgL\(^{-1}\) and 120 mgL\(^{-1}\). All solutions were stirred at 100 rpm for 30 min. The filtered solutions were analyzed using AAS.

2.6. Contact Time Effect of Pb\(^{2+}\) dan Cd\(^{2+}\) Adsorption in Mixture System.

0.5 grams of biosorbent was mixed to 15 mL of Pb\(^{2+}\) solution and 15 mL Cd\(^{2+}\) solution which optimum concentration as previously obtained. The solution was stirred at 100 rpm with a variation of time 30, 60, 90 and 120 minutes. The filtered solutions were analyzed using AAS.
3. Results And Discussion

FTIR spectra (Fig. 1) was obtained of some functional groups in the Jatropha curcas L. leaves bio-
sorbent at 3000 cm\(^{-1}\) to 4500 cm\(^{-1}\) is a typical peak for the stretching vibration of the OH-group, and
the presence of the -OH bond indicates that Jatropha curcas leaves produced tends to be more polar.
Thus the prepared Jatropha curcas leaves can be used as an adsorbent for polar substances such as
solution and gas. Whereas the wavelength of 2917.98 cm\(^{-1}\) shows the CH group vibration and 2104.13
cm\(^{-1}\) shows the vibration strain C = C. Strong uptake at 1616.50 cm\(^{-1}\) indicates a vibrational strain of
C = C (alkenes), and 1049.79 cm\(^{-1}\) indicates a vibration comparable to C-O groups. These functional
groups content can capture the metal ions which involve the interaction of metal ions by chemical
attraction like transfer of binding metal or ion exchange through complexation process as physical
interaction as Van der Waals forces or electrostatic interaction.

Fig 2 observed that the optimum initial concentration of Pb\(^{2+}\) in single system was adsorbed at 80
ppm is 2.85 mgg\(^{-1}\). At the initial concentration of 20 mgL\(^{-1}\), the absorption capacity of Pb\(^{2+}\)metal is
0.89 mgg\(^{-1}\), then gradually increase until 800 ppm. The absorption amount of heavy metals was
influenced by the initial solution amount of their solution. On the other hand, Cd\(^{2+}\) was adsorbed
optimum as 2.16 mgg\(^{-1}\) at 100 ppm initial concentration which lower than Pb\(^{2+}\) adsorption amount. At
the beginning state, the bio-sorbent adsorption amount increased with the increasing of metal ion
amount in solution and then attains as equilibrium state. However, the bio-sorbent capture efficiency
reduces with increase in metal ion concentration. Higher rates of this adsorption effective rate were
produced by ions completion interaction with the suitable binding section at low concentration.

However, the presence of remaining not bonding metal ions in the solution is increase because of the
equilibrium of binding sites state at high concentration.

Interestingly, in mixture system of the mixture Pb\(^{2+}\) and Cd\(^{2+}\) in liquid solution, at initial stage Pb\(^{2+}\)
was adsorbed higher than Cd\(^{2+}\) until reach equilibrium at 60 mgL\(^{-1}\). Then with increasing initial
concentration higher than 60 mgL\(^{-1}\), Cd\(^{2+}\) more adsorbed than Cd\(^{2+}\) even though their optimum
adsorption reach at the same initial concentration is 100 mgL$^{-1}$ which Pb(II) was adsorbed as 1.32 mgg$^{-1}$ and Cd$^{2+}$ as 1.45 mgg$^{-1}$. The higher absorption of Pb$^{2+}$ than Cd$^{2+}$ due to the interaction of the two metal ions with the content of organic groups in the Jatropha curcas leaves. The negative charge of the functional groups in these adsorbents induce a function as a lewis base which makes it easier to bind with hard acids such as Pb$^{2+}$ compared to Cd$^{2+}$ which are soft acids [20].

Whereas the highest adsorption amount of Cd$^{2+}$ was adsorbed in Jatropha curcas leaves higher than Pb$^{2+}$ in mixture system because of ionic radius differences of Pb$^{2+}$ and Cd$^{2+}$. Cd$^{2+}$ ions with small ionic radius will be more quickly attracted and / or adsorbed while Pb$^{2+}$ ions which have larger ionic radii even though at initially, they have higher adsorbed but saturation will occur more quickly. This is also supported by the steric effects that occur and will cause a decrease in the amount of adsorbent contact with the adsorbent site [6]. In mixture system, the optimum amount of lead is reduce by increasing in the concentration of solution while it reaches maximum adsorption in single solution. The time which needed to reach the highest adsorption was influenced by the characteristic of heavy metal, Jatropha curcas leaves, and also both of effect as shown in Fig. 3. In single system, Pb$^{2+}$ was adsorbed maximum after 60 min as 4.72 mgg$^{-1}$ but Cd$^{2+}$ reach saturated adsorption amount after 90 min as 4.42 mgg$^{-1}$. Within an hour, the rate of biosorption rapid was caused by the vacancy of all the Jatropha curcas leaves active sites and suitable to adsorb metal ion almost 90% of the metal binding. But, by the time, the remaining metal ion in the solution increase the percentage of saturation so that decrease the rate of biosorption [21]. Supporting of the initial concentration effects in binary system, Cd$^{2+}$ was continuously increase adsorbed higher than Pb$^{2+}$ by increasing the contact time. Cd$^{2+}$ was adsorbed as 2.64 mgg$^{-1}$ and Pb$^{2+}$ as 2.11 mgg$^{-1}$. It confirm that molecular weight and ionic radius were give the high contribution to increase Cd$^{2+}$ adsorption amount compare than Pb$^{2+}$.

To confirm Jatropha curcas leaves stability as Jatropha curcas leaves of heavy metals adsorption, XRD analysis also perform both of before and after adsorption stage (Figure 4). It indicate not significant different each, even stronger peak shows around 25 and 65 degree suggest as containing Pb and Cd.
due to the adsorption process. It confirms that these adsorption process not disturbed their Jatropha curcas leaves structure.

4. Conclusions

Jatropha curcas leaves shows preferential adsorption properties because of the existence of Pb\(^{2+}\) and Cd\(^{2+}\) in liquid waste. Pb\(^{2+}\) ions was adsorbed higher than Cd\(^{2+}\) in single system due to Pb\(^{2+}\) as hard acid have stronger interaction with functional groups in jatropha curcas leaves. Pb\(^{2+}\) reached saturated value with lower initial concentration of solution and also faster contact time needed to get the higher adsorption amount compare than Cd\(^{2+}\). However, the opposite phenomena found in binary system of mixture Pb\(^{2+}\) and Cd\(^{2+}\) solution. Even in initially stage, Pb\(^{2+}\) adsorbed higher than Cd\(^{2+}\), but by increasing initial concentration and contact time Cd\(^{2+}\) adsorption amount exceed Pb\(^{2+}\) which indicate Pb\(^{2+}\) ion radius which higher than Cd\(^{2+}\) give a negative effect when their existence together in the same solution. It can be new propose of Pb\(^{2+}\) and Cd\(^{2+}\) removal in liquid solution with their concurrent existence in liquid waste.

Declarations

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests of this research

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Authors' contributions

Moondra Zubir: Setup for all experiment reagent, procedure and laboratory permit.
Zainuddin Muchtar: Prepare and Data Analysis of FTIR characterization of adsorbent
Mahmud Mahmud: Prepare and Data Analysis of XRD characterization including for computation analysis
Hafni Indriati Nasution: Setting for Adsorption Analysis of Single System
Ricky Andi Syahputra: Setting for Adsorption Analysis of Mixture System
Siti Rahmah: Prepare for AAS Analysis dan Data analysis to declare heave metal adsorption amount.
Esly Gusti Kristanti: Doing the experiment of Pb(II) for single and mixture system
Wan Musta Khairul Akma: Doing the experiment of Cd (II) for single and mixture system

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Figure 1

FTIR spectrum of jatropha leaves prepared at 105 oC for 4h.
Initial concentration effects on Pb2+ and Cd2+ adsorption in Single and Mixture System.
Figure 3

Contact Time effects on Pb2+ and Cd2+ adsorption in Single and Mixture System.

Figure 3

Contact Time effects on Pb2+ and Cd2+ adsorption in Single and Mixture System.
Figure 4

XRD patterns of jatropha leaves before adsorption and after adsorption.