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# The Effect of Contact Time of Javabark Adsorbent *(Lannea coromandelica ( Houtt.)Merr)* on CD (II) Adsorption Capacity

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**Abstract.** According to Indonesian Minister of Health Regulation No. 2 of 2023, the maximum limit for cadmium in bottled water is 0.003 mg/L. In this study, tannin biosorbents were used from the extraction of Javanese bark. Javanese bark contains tannin compounds that have the potential to bind heavy metals. This study aims to determine the effect of varying contact times of Java wood bark biosorbent on the adsorption capacity of Cd (II). The method used is an experiment to study the effect of contact time of Java wood bark biosorbent on the adsorbate. The contact times used for the Java wood bark biosorbent were 20, 40, 60, 80, 100, 120, 140, and 160 minutes. The residual Cd (II) concentration in the solution was determined using a UV-Vis spectrophotometer. The adsorption capacity of Cd (II) at contact times of 20, 40, 60, 80, 100, 120, 140, and 160 minutes was 0.073; 0.075; 0.078; 0.079; 0.116; 0.060, 0.052; 0.035 mg/g. From the results of the study, it can be concluded that the longer the contact time of the biosorbent in the adsorption of Cd (II) metal, the adsorption capacity will increase until it reaches the optimal contact time. After reaching the optimal contact time, adsorption decreases due to the desorption process. In this study, the optimal contact time for Java wood bark biosorbent was obtained at 100 minutes with an adsorption capacity of 0.116 mg/g.

## Introduction

Water used for drinking must meet various requirements in accordance with SNI 01 3553 2006, namely physical, chemical, and microbiological requirements. One of the chemical requirement parameters states that water for consumption must not contain metal elements that exceed the threshold limit. The increase in metal elements in the processing of bottled drinking water can be influenced by the processing method. In studies conducted by (Amelia & Rahmi (2017) and Kesumaningrum et al. (2019)) on the analysis of heavy metals Cd (II) in bottled drinking water, results exceeding the threshold limits were obtained, ranging from 0.0065 to 0.0098 and 0.0083 mg/L. According to Indonesian Ministry of Health Regulation No. 2 of 2023, the maximum cadmium limit in bottled drinking water is 0.003 mg/L.

Therefore, more effective and efficient methods are needed to reduce heavy metals in bottled drinking water (AMDK) available on the market. One method that can be employed is the adsorption process.The adsorption process was chosen because of its simple technique and operation, wide availability of adsorbents, high efficiency, good reversibility, and affordable cost (Nthwane et al., 2024). In the adsorption process, an adsorbent is required to absorb the adsorbate. In this study, an innovation in biosorbents was developed by utilizing the bark of the Java wood tree as a biosorbent. The use of natural materials in the adsorption of heavy metals has several advantages, namely, being environmentally friendly, not requiring high costs, and being easy to implement (Rahmi & Sajidah, 2017). The bark of the Java wood tree contains tannins, which have numerous hydroxyl groups (-OH) that can be used to bind heavy metals. Based on research conducted (Iriany et al., 2017), the use of tannins from acacia leaf biomass biosorbents for Pb (II) metal achieved an

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efficiency of 80.35% with an adsorption capacity of 0.950 mg/g. Tannins are compounds that are easily soluble in water, which can reduce adsorption effectiveness. Therefore, in its application, modification into a more stable matrix is necessary. The modification that can be performed is through polymerization. The purpose of polymerization is to ensure that conjugated double bonds formed become increasingly numerous and stable, thereby enhancing adsorption. This is supported by research conducted (Budiraharjo et al., 2015) on the use of broken glass leaf biomass as an adsorbent. The highest adsorption percentage was obtained in the adsorbent polymerized with formaldehyde, namely 99.12%, with an adsorption capacity of 5.947 mg/g. In the adsorption process using biosorbents, several factors can influence the process, one of which is contact time. Contact time is a parameter related to the reaction rate, expressed as a change in concentration over time. The longer the contact time, the greater the amount of adsorbed ions. Determining the contact time is used to determine the optimal time for the biosorbent in the adsorption process up to the maximum limit (Zian et al., 2016). In this study, variations in contact time were used, namely 20, 40, 60, 80, 100, 120, 140, and 160 minutes. In this study, a UV-Vis spectrophotometer was used, with complexation performed using ditizon to form ditizonate metal.

## Experimental

### Material and Methods

The materials used for this study were Java wood bark, CdSO4.H2O crystals (Pro Analyze) (Merck), distilled water, 37% formaldehyde solution (Pro Analyze) (Merck), H2SO4 solution (Pro Analyze) (Merck), Ditizon crystals (Pro Analyze) (Merck), chloroform solution (Pro Analyze) (Merck), NaOH crystals (Pro Analyze) (Merck), and plastic wrapping.

### Procedures

### Biosorbent

The bark of the Java wood tree was collected, cleaned, and cut into small pieces. The pieces of bark were dried at a temperature of 60°C. After the drying process was complete, the bark was ground into a powder using a grinder. The ground powder is sieved using a 200-mesh sieve. It is then mixed with 37% formaldehyde in a 1:4 (g/ml) . This mixture is added to 100 ml of 0.5 N $H_2SO_4$. The mixture is heated using a hotplate at 60°C for 3 hours. The mixture is cooled, filtered, and washed with distilled water. The biosorbent is dried at 60°C in an oven until a constant weight is achieved.

### Standard Curve

Standard cadmium solutions of 1, 2, 3, 4, and 5 ppm were prepared in 20 mL volumes and added to a beaker. NaOH 1% solution was added dropwise until the pH reached 9. Each solution was then mixed with 5 mL of a 0.0015% ditizon solution until a pink complex formed. The pink-colored organic phase is separated and measured using a UV-Vis spectrophotometer at a wavelength of 518 nm.

### Variation of Contact Time

0.5 grams of polymerized biosorbent was added to an Erlenmeyer flask containing 20 mL of 5 ppm cadmium solution. The mixture was stirred using a shaker for 20, 40, 60, 80, 100, 120, 140, and 160 minutes. The filtrate was separated and adjusted to pH 9. The solution was then added with 5 mL of 0.0015% thizone solution and stirred until a pink-colored complex was obtained. The pink-colored organic phase was collected and analyzed using a UV-Vis spectrophotometer at a wavelength of 518 nm.

## Result and Discussion

### Preparation of Biosorbents from Java Tree Bark

In this study, biosorbents from Java tree bark were used because Java tree bark contains tannin compounds. These compounds have many hydroxyl (-OH) groups that can interact with adsorbate components. According to (Yantri., 1998) in (Achmadi., et al., 2017), biosorbents with hydroxyl (-OH) and carboxylate groups can be utilized for the adsorption of heavy metal ions. This statement is supported by several studies that have been conducted, namely (Pratini, 2017) and (Iriany et al., 2017) on the use of tannin compounds as biosorbents in the adsorption process of Cd (II) heavy metals. The adsorption capacities obtained were 5.27 mg/g and 3.81 mg/g, respectively. In the study, Java wood bark with a 200 mesh was used because the smaller the biosorbent particle size, the larger the surface area, allowing for more optimal adsorption of the adsorbate. This is because smaller particles have greater intermolecular forces, resulting in better adsorption (Fika et al., 2021).

Tannins have polar properties and are easily soluble in water, and can form precipitates when interacting with heavy metals (Achmadi et al., 2017). In the use of tannins as biosorbents, these properties can reduce their effectiveness. Therefore, modification into a more stable matrix form is necessary. This modification can be done through a polymerization process. The purpose of polymerization is to strengthen the structure of tannin as a biosorbent so that it does not easily dissolve in water (Desniorita et al., 2022). Through the polymerization process, the hydroxyl groups in tannin will bond to form a stronger structure that is resistant to solvents and produce a more stable number of active groups. Tannin polymerization can be carried out using formaldehyde as a cross-linking agent, and the addition of $H_2SO_4$, which functions as an acid catalyst, can accelerate the reaction. The reaction that occurs is as follows (Beltrán-Heredia et al., 2012):

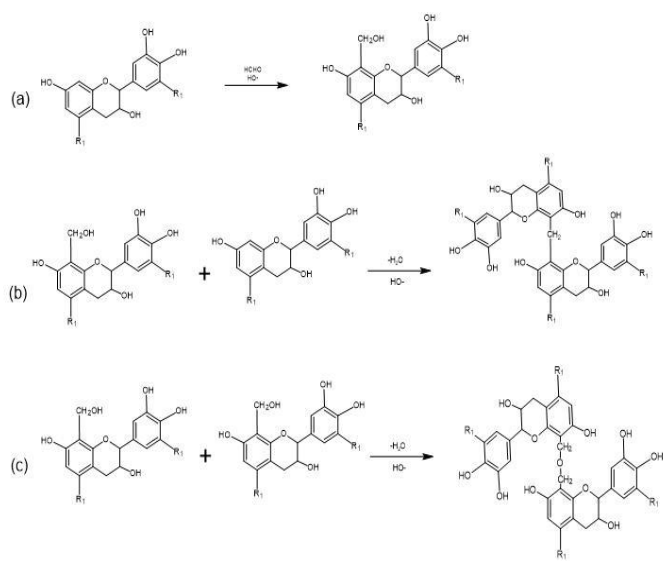


**Figure 1.** The mechanism of tannin compound polymerization reaction (Beltran-Heredia et al., 2012).

When formaldehyde is added to tannins, a nucleophilic addition reaction occurs between the hydroxyl group (-OH) on the aromatic ring of flavonoids and the carbon of formaldehyde. This reaction results in the formation of a methyl hydroxy group (-$CH_2OH$) bound to the tannin structure. Subsequently, the reaction product undergoes a condensation reaction, where the previously formed hydroxymethyl group (-$CH_2OH$) reacts further with another hydroxyl group (-OH) from the tannin molecule. This reaction produces a methylene bridge (-$CH_2$-). As shown in part (b) of the figure, two flavonoid molecules bonded through the methylene group (-$CH_2$) form a polymer. In figure (c), the hydroxymethyl groups from two flavonoid molecules form a methylene ether bridge (-$CH_2$–O–$CH_2$-), resulting in a branched structure (Beltrán-Heredia et al., 2012).

## Standard Curve

The results of the concentration-absorbance relationship curve for the Cd (II) standard solution show a linear relationship, indicating that as the concentration increases, the absorbance value also increases. Based on the absorbance results above, the linear regression equation y = 0.00986x + 0.4722 was obtained, with a correlation coefficient (R) of 0.997 and a coefficient of determination ($R^2$) of 0.995. The correlation coefficient value approaching 1 indicates that the regression equation is linear, meaning that absorbance is directly proportional to concentration and has a strong correlation consistent with the Lambert-Beer law. The allowed regression value is close to 1 and meets the requirements specified by SNI 6989.84:2019, which states that the allowed linear regression correlation coefficient value is r ≥ 0.995.

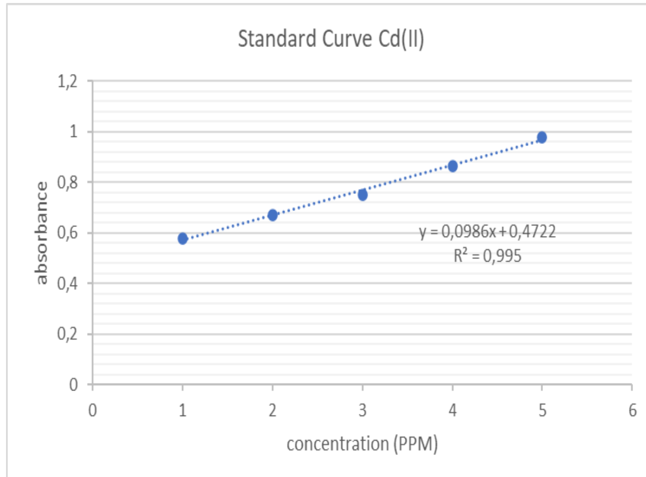


**Figure 2.** Standart Curve Cd(II).

## Determination of Adsorption Capacity

The adsorption process of Cd (II) heavy metals by Java wood bark biosorbents is influenced by chemical and physical factors. One of the chemical factors that plays a role is the presence of tannin compounds in biosorbents. Tannins have hydroxyl (-OH) functional groups that are polar in nature (Langi et al., 2022). This allows interaction with Cd (II) ions, which are also polar. As a result, attractive forces between molecules occur. This interaction involves Van der Waals forces, leading to electrostatic interactions when Cd (II) is in close proximity to the active groups of the biosorbent (Liu et al., 2015). Based on the adsorption difference curve at contact times of 20, 40, 60, and 80 minutes, no significant differences were observed, with average adsorption percentages of 29.09%, 29.90%, 30.77%, and 31.33%, respectively, and adsorption capacities of 0.073, 0.075; 0.078; and 0.079 mg/g. Although the increase is relatively small, the results indicate that the number of adsorbate molecules interacting with the active groups on the biosorbent continues to increase with increasing contact time. At this stage, the adsorption process is still effective because the active groups on the biosorbent surface are not yet completely filled.

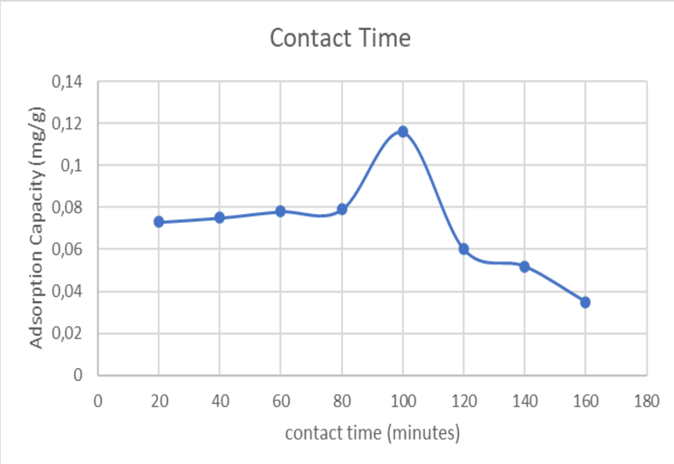


**Figure 3.** Curve Capacity Adsorption.

At a contact time of 100 minutes, the highest adsorption percentage of 45.93% was obtained with an adsorption capacity of 0.116 mg/g. This indicates that under these conditions, the active groups on the biosorbent are still available in sufficient quantities to bind with the adsorbate molecules, allowing the adsorption process to proceed optimally. However, after 100 minutes of contact time, at 120, 140, and 160 minutes, a decrease in adsorption (%) of 23.75%, 20.66%, and 14.25% was obtained, with adsorption capacities of 0.060, 0.052, and 0.035 mg/g, respectively. The decrease in adsorption percentage indicates that desorption occurs during the contact time. Where Increasing the contact time is no longer effective. This is because the biosorbent has reached saturation point. Most of the active groups on the biosorbent have been filled with adsorbate molecules, so that the remaining adsorbate molecules have no place to bind. In addition, there is a process of releasing adsorbate molecules that were previously weakly bound to the biosorbent. This is reversible physical adsorption.

## Conclusion

Based on the research conducted on the analysis of the effect of contact time variation of the biosorbent bark of the Java Wood tree (Lannea coromandelica (Houtt.) Merr.) on the adsorption capacity of Cd (II) metal, it can be concluded that the longer the contact time of the Java Wood bark biosorbent used in the adsorption of Cd (II) metal, the adsorption capacity will also increase. Once the optimal contact time is reached, desorption occurs, as the biosorbent has reached saturation in Cd(II) metal adsorption. The optimal contact time was found to be 100 minutes, with an adsorption capacity of 0.116 mg/g and an adsorption percentage of 45.93%.

## Conflict of Interest

The authors declare that there is no conflict of interest.

## Acknowledgements

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