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Exploring The Potential of Mango Seed as A Bioadsorbent for Pb(II) Removal in Aqueous Solution

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Abstract

Various industrial activities produce heavy metals as by-products or wastes. Lead is a metal trace element from sewage disposal, vehicle fumes, and atmospheric emissions from industrial activities. Mango seeds are composed of cellulose, lignin, and hemicellulose, which have many potential binding groups. Mango seeds, which are often considered waste, can be utilized as a low-cost biosorbent due to their various functional groups, such as hydroxyl, carboxyl, carbonyl, alcohol, amide, and aromatic groups. Mango seed are organic waste with potential as low-cost biosorbent for heavy metals removal. The purposes of the study are: (1) to explore the optimum condition of biosorbent in absorbing heavy metal species (Pb (II)), and (2) to analyze the adsorption model of synthetic waste containing Pb(II). Mango seeds have a considerable potential to be used as a biosorbent to absorb heavy metal ions. The optimum conditions for Pb^{2+} ion adsorption is at pH 6 with contact time 70 minutes, and concentration of biosorbent 2.0 g/L. Adsorbate adsorption follows the Freundlich model, and adsorption occurs only in a few surface layers. The kinetic parameters of adsorbent satisfied pseudo-second-order reaction. The optimum adsorption capacity (qm) of mango seed biosorbent in absorbing Pb ions is 43.86 mg/g.

Keywords: Adsorption; biosorbent; heavy metal; lead; mango seed.

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1. INTRODUCTION

Environmental pollution by heavy metals is a serious problem lately because it can damage environmental ecosystems. Various industrial activities, such as metallurgy, fertilizers, pesticides, textiles, leather, batteries, photography, and electroplating, produce heavy metals as by-products or wastes. All heavy metals, in a particular concentration, are toxic and could be harmful to an organism. Heavy metals dissolved in the aquatic environment could enter the food chain, magnify, and affect the ecosystem. Some examples of heavy metals are Hg, Cr, Co, Ni, Cu, Zn, Ag, Au, Pb, Cd, and Sn (J. Wang & Chen, 2009). Lead is a metal trace element that spread to the environment through human activities such as sewage disposal, vehicle fumes, and atmospheric emissions from industrial activities.

Studies in wastewater treatment to remove metal ions are exciting objects, with numerous known methods such as particle deposition, oxidation-reduction reaction, adsorption, ion exchange, or any other methods. One of the methods that emerged for the absorption of heavy metal ions is by using a biosorbent. Biosorption is a method used to remove heavy metals through passive binding to plant biomass or microorganisms. The biosorption process requires a solid phase (sorbent or biosorbent) in a liquid phase (solvent, generally water). The biosorption method has advantages such as simplicity, low cost, high efficiency, and regenerative ability (Das et al., 2008).

Numerous biosorbents have been examined for their capacity to eliminate heavy metals. For instance, *Sansevieria trifasciata* has been studied for lead (Yuningsih et al., 2014), and langsat fruit skin has been studied for lead (II) and Zn (II) (Furqoni et al., 2015). Additionally, *Nypa fruticans Merr* has been examined for Cu(II), Pb(II), and Cd(II) (Rumiati et al., 2015). Activated silica/lignin has been studied for iron (Noviyanti et al.,

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2022), while modified shrimp shell and combination of rice husk and zeolite has been studied for metanil dyes and Pb(II) respectively (Saputro et al., 2021; Zein et al., 2022). Biosorption technology is a method that employs plant biomass to absorb metal ions in large volumes of water with low metal concentrations.

Mango is one of most planted trees in Indonesia and from various variety of those mango, Indramayu mango considered a very popular mango. Mango seeds, which are often considered waste from the fruit, can be utilized as a low-cost biosorbent due to their various functional groups, such as hydroxyl, carboxyl, carbonyl, alcohol, amide, and aromatic groups (Malekbala et al., 2012). Studies conducted by (Wang et al., 2022) have demonstrated the high adsorption capacity and fast uptake of Pb(II) and Cd(II) by mango seed biosorbent, indicating its potential as a biosorbent for heavy metals removal.

This research aims to optimize the adsorption capacity and kinetics model of Indramayu mango seed biosorbent for Pb and to determine whether the adsorption process follows a monolayer or bilayer model. The study investigates the optimum conditions of pH, contact time, and adsorbent dosage, as well as the adsorption model of synthetic waste containing Pb, using a completely randomized design.

2. MATERIALS AND METHODS

Materials

Materials needed in this research are solvent, standard solution, synthetic sample, and dried mango seed. Mango seeds obtained from Indramayu mango seeds that have been dried. For sample and standard preparation, we used H_2SO_4 (p.a. Merck) and NaOH (p.a. Merck) for pH conditioning, and HNO_3 (p.a. Merck) for sample preparation. Standard solution and synthetic sample were made from $Pb(NO_3)_2$ salt (p.a. Merck).

Instrumentation

We were using atomic absorption spectrophotometer (AAS) Simadzu AA-6600 for Pb analysis. For biosorbent characterization, we were using Quantax EDXS scanning electron microscopy (SEM). We also using Micromeritrics TriStar II 3020 for BET surface area and porosity analysis.

Procedure

The research was conducted at the Instrumentation Laboratory, AKA Bogor Polytechnic, from April - July 2019, and it has three stages: biosorbent preparation, determining the optimum conditions for the adsorption experiment, and determining the optimum adsorption capacity of biosorbent in trapping Pb metal ions. In the first stage is making biosorbent from mango seeds. The mango seeds were cleaned, dried, crushed, sieved on mesh 40 to mesh 80, and dried in oven (105 ºC for 3 hours).

In the second stage, we determined the optimum experimental conditions by varying the conditions of biosorbent concentration, contact time, and pH. We added 25 mg/L Pb solution (pH 2) to a series of prepared biosorbent (0.05; 0.10; 0.15; 0.20; 0.30 g) in 100 ml erlenmeyer, before shaked in agitator apparatus for 30 minutes. The filtered samples then added with HNO_3 for AAS measurement and optimum concentration determination. We used the obtained optimum concentration, with the same procedure, to determine the optimum contact time and optimum pH. In the third stage, we used the data to figure out the isothermal adsorption and optimum adsorption capacity (Zakaria et al., 2017). We conducted test with varied Pb concentration (1, 5, 10, 25, 50, 100, 150, and 200 mg/l) and all optimum condition (biosorbent concentration, contact time, and pH).

Isothermal adsorption is adsorption that occurs at constant temperature conditions, where the adsorption and adsorption rates are relatively the same, resulting in an equilibrium state. The isotherm equation usually describes the adsorption equilibrium, the parameters of which indicate the surface properties and affinity of the adsorbent under constant temperature and pH conditions. Previous studies have investigated the adsorption isotherm of heavy metal ions and their relationship to pH, adsorbent amount, allied ion concentration, contact time, and temperature (Barkhordar & Ghiasseddin, 2004; Gupta & Bhattacharyya, 2008). Two widely used adsorption isotherm equation are Langmuir's and Freundlich's isotherms (Gupta & Bhattacharyya, 2008), which are obtained with straight-line equation curves by plotting Ce/qe vs Ce and log qe vs log Ce, respectively.

$$\frac{C_e}{q_e} = {}^{1}/_{(b\, q_m)} + \left(\frac{1}{q_m}\right) C_e \qquad \text{............(1)}$$

$$q_e = K_f C_e^{1/n} \qquad \text{............(2)}$$

$$R = \frac{1}{1 + K_f C_e} \qquad \text{............(3)}$$

where:

Ce = concentration of adsorbate at equilibrium in the liquid phase (mg/L)
qe = concentration of adsorbate in the solid phase / adsorbent (mg/g)
1/qm = slope or sensitivity
qm = optimum adsorption capacity (mg/g)
1/bqm = Intercept
b qm = equilibrium constant
Kf = Adsorption capacity mg/g
n = adsorption intensity

The optimum adsorption capacity of the adsorbent against the adsorbate can be estimated using Equation (1) and Equation (2), and the Langmuir equation can be used to obtain an R-value that describes the dimensions of the equilibrium parameter or the separation factor. The Langmuir equation indicates monolayer adsorption, while the Freundlich model indicates bilayer adsorption. The adsorption efficiency obtained from the experiment can be calculated using Equation (4) and Equation (5), where qe is obtained from converting the value of Ce. To determine whether this adsorption follows the Langmuir model equation, a Ce/qe versus Ce graph is plotted, and the correlation coefficient and linear regression equation are calculated.

$$\%\ \text{adsorption} = \frac{(C_0\text{-}C_e)}{C_0} \times 100\% \qquad \text{...(4)}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad \text{....(5)}$$

Where:

qe = number of metal ions adsorbed (mg/g)
Co = initial concentration of metal ions in solution (mg/L)
Ce = concentration of metal ions in solution at equilibrium (mg/L)
V = volume of solution (L), m = mass of the adsorbent (g).

3. RESULTS AND DISCUSSION

Biosorbent Characterization

Powdered mango seed with size <850 µm were tested for water content. Adsorbent water content from the three tests ranged from 1.4 to 1.5% w/w which is relatively small that it can prevent agglomeration between biosorbent particles. In **Figure 1**, the mango seed biosorbent product is shown in the form of cutted and powdered. Using Fourier Transform Infra-Red (FTIR), characterization identified hydroxyl and carbonyl groups at the absorption peak of 2158 and 2020 cm^{-1}. The content of functional groups in biosorbent is a great potential to be used as heavy metal adsorbents.

The surface morphology of the mango seed biosorbent was examined using SEM before and after the adsorption process. Prior to adsorption, **Figure 2a** reveals a significant presence of large pores and some smooth granular shapes in the prepared biosorbent. However, after adsorption, a dark layer covered the surface, indicating a change in shape and pore structure of the biosorbent (**Figure 2b**). This suggests that Pb was accumulated on the biosorbent surface.

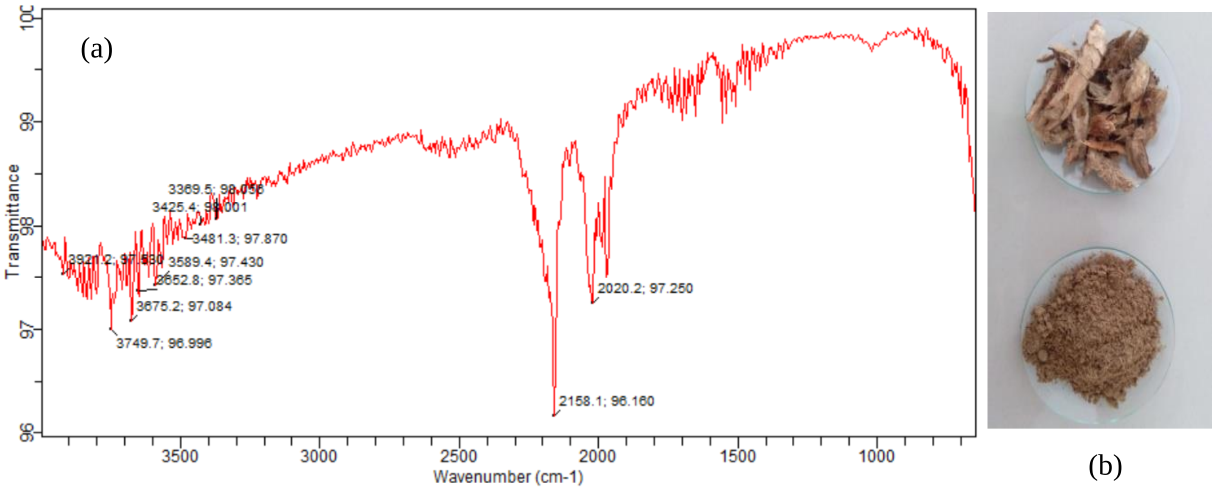

Figure 1. Mango seed biosorbent: (a) FTIR spectra, and (b) raw material

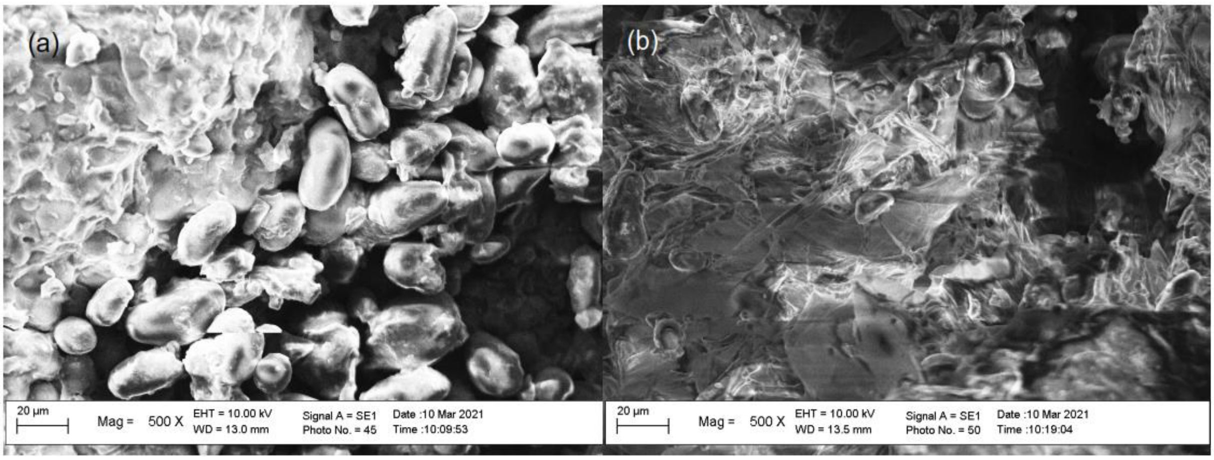

Figure 2. Biosorbent SEM image (a) before and (b) after adsorption

Optimum pH and Dosage

The optimum adsorption conditions were determined to maximize the adsorption capacity, considering experimental parameters such as pH, biosorbent concentration, and contact time. The pH of the adsorbate solution was varied from 2 to 6 to investigate the effect on the adsorbent's ability to absorb Pb heavy metal ions, while keeping the Pb concentration, biosorbent concentration and contact time constant.

Acidic conditions favor heavy metal adsorption, with Ni(II) adsorbing best at pH 4 and Pb(II) at pH 4 (Kristianto et al., 2019; Shofiyani & Gusrizal, 2010), primarily due to electrostatic interactions. **Figure 3a** demonstrates a significant increase in adsorption capacity and efficiency from pH 3 to 4, followed by a slight increase up to pH 6. These findings align with previous studies (Çelebi et al., 2020; Lo et al., 2012; Ucarli et al., 2020), where the optimal pH range for adsorption ranged from 5 to 7. The presence of H^+ ions in the acidic solution competes with Pb^{2+} ions for adsorption on the biosorbent's functional groups, reducing its ability to absorb Pb ions. The optimum adsorption capacity was achieved at pH 6, with an adsorption efficiency ranging from 34% to 81%. The experiments utilized an initial Pb adsorbate concentration of 100 mg/l, a contact time of 30 minutes, and a biosorbent concentration of 4 g/l.

The biosorbent concentration depends on the amount of biosorbent and the volume of the solution used in the experiment. In this study, biosorbent concentrations of 2, 4, 8, 12, and 16 g/l were examined. **Figure 3b** illustrates that the lowest biosorbent concentration of 2 g/l resulted in the highest adsorption capacity. This suggests that the initial estimation of the required biosorbent dosage may have been inaccurate, indicating the potential for using a small amount of biosorbent as a low-cost option for Pb(II) removal. Compared to other studies (Wang et al., 2022; Çelebi et al., 2020; Lo et al., 2012; Beidokhti et al., 2019), which utilized higher biosorbent concentrations (10 g/L or more), the effective utilization of 1-2 g/L of mango seed biosorbent demonstrates its efficiency. Additionally, it should be noted that the adsorption kinetics may have influenced the decreasing adsorption observed. The contact time used in determining the biosorbent concentration was consistently set at 30 minutes, while the equilibrium time ranged from 70 to 120 minutes, as shown in **Figure 3c**.

Contact Time and Kinetic Model

The adsorbate adsorption process by the adsorbent is an equilibrium process. To find out how much influence time has on the adsorption process, we conducted a variation of contact time tests. In **Figure 3c**, it can be seen the effect of contact time on the adsorption capacity. The equilibrium of the Pb ion adsorption process by the biosorbent requires a relatively short time. The adsorption equilibrium has been reached from 70 to 120 minutes where the adsorption capacity value tends to be stable due to saturated active site and adsorption process depend on metal ion migration in liquid phase to the surface of adsobent-adsorbate complex (Yu et al., 2000).

The kinetic models were done by plotting time (t) vs log of adsoption capacity (qe) and time vs t/qe as Lagergren equation. In addition, the adsorption rate constant (k), optimum adsorption capacity (qe) and determination coefficient have also been calculated. Based on data as seen on **Table 1**, determination coefficient for the first-order reaction was smaller than the pseudo second-order reaction, predictive value of adsorption capacity was compared to the experimental value of the optimum adsorption capacity had a different 69.1%. This suggest that first-order reaction was less suitable to be applied as a model for the adsorption kinetics of mango seed biosorbent and pseudo second-order reaction, with the determination coefficient (R^2) > 0.99 was more suitable, with the error of 1.28%. The kinetic parameters of adsorbent satisfied pseudo-second-order reaction because it had a high degree of accuracy in predicting the optimum adsorption capacity. The pseudo second-order model contains the external liquid film diffusion, intraparticle diffusion, and adsorption on the surface of the adsorbent; this model provides a more comprehensive and accurate description of the adsorption mechanism between adsorbat and adsorben (Zhang et al., 2017).

Adsorption Capacity and Type

The optimum adsorption capacity is obtained by conducting experimental treatment based on optimum condition in previous experiments. The adsorption experiment was carried out using varied Pb initial concentration with a biosorbent concentration of 2 g/L, a contact time of 70 minutes, and adsorbate pH 6. As shown in **Figure 4**, adsorption capacity tended to stagnant in biosorbent concentration of more than 150 mg/l due to filled active site. Based on calculation, optimum adsorption capacity of Indramayu mango seed was 43.86 mg/g. This value obtained from Pb(II) initial concentration of 150 mg/L and the remaining of 61.05 mg/l in equilibrium state.

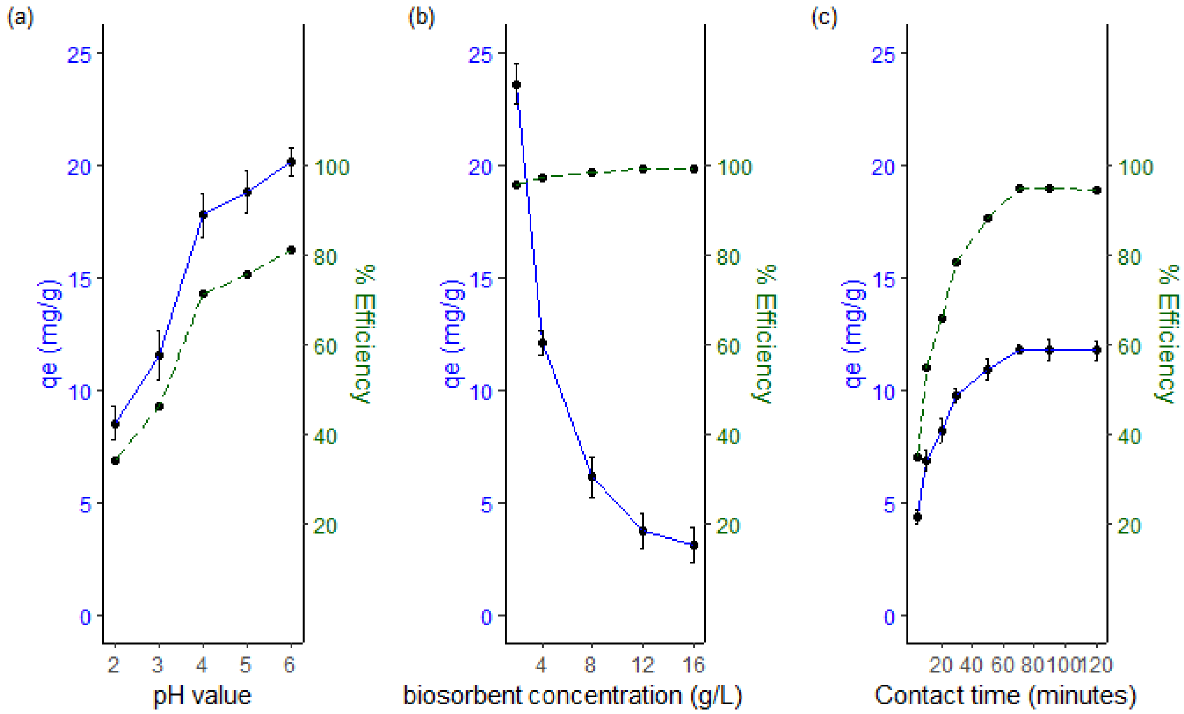

Figure 3. Biosorption optimal condition: (a) pH, (b) initial concentration, and (c) contact time. Blue and dashed-green line each represent qe in mg/g and efficiency in % respectively.

Table 1. Comparison of first order and pseudo second-order reaction

Pb initial concentration	qe (experiment)	First-order reaction				Pseudo second-order reaction			
		K_1 (min^{-1})	qe (cal)	% different	R^2	K_2 (g/mg min)	qe (cal)	% different	R^2
50 mg/L	9.37	0.026	2.90	69.1	0.964	0.025	9.49	1.28	0.998

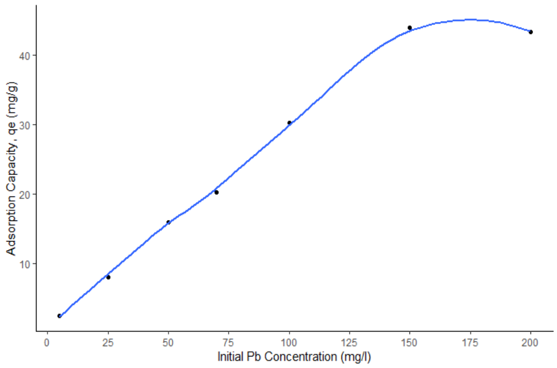

Figure 4. Optimum adsorption capacity of indramayu mango seed biosorbent

Pb(II) isothermal adsorption were analyzed using two-equation models, Langmuir (Ce/qe vs Ce) and Freundlich (log (qe) vs log (Ce)) models. These equations were used to determine the type of adsorption process that occurs, whether physical or chemical adsorption between the biosorbent and the adsorbate. It shows in **Figure 5** that the results obtained tend to follow the Freundlich equation because the resulting coefficient of determination (R^2) is greater than the Langmuir equation. This value shows that the biosorbent is multilayer, so that the interaction of the biosorbent with the adsorbate forms several layers; or in other words, the adsorption dominated by physical adsorption.

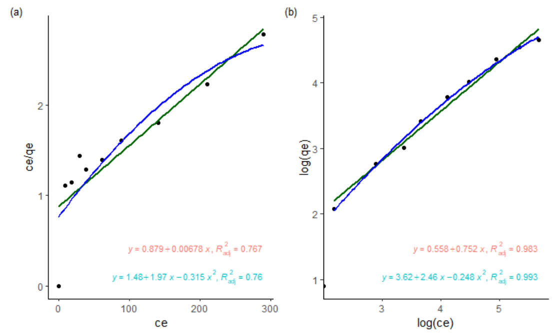

Figure 5. Adsorption isotherm: (a) Langmuir, (b) Freundlich

Overall, the study provides valuable information on the potential use of powdered mango seed biosorbent for heavy metal adsorption. The study shows that the biosorbent has good adsorption capacity and can be optimized for better performance. The characterization of the biosorbent using FTIR and SEM provides important information on the structure and surface morphology of the biosorbent, which can aid in the optimization of the biosorbent's performance. The study's findings can contribute to the development of more efficient and effective heavy metal adsorption processes using natural and sustainable materials like powdered mango seed biosorbent.

4. CONCLUSION

The optimum conditions for Pb^{2+} ion adsorption is at pH 6; contact time is 70 minutes, and the biosorbent concentration is 50 mg/25 mL or 2000 mg/L. Adsorbate adsorption by biosorbent follows the Freundlich model and only in a few surface layers. The optimum adsorption capacity (qm) of mango seed biosorbent in absorbing Pb ions is 43.86 mg/g. In conclusion, the study suggests that mango seeds can be an effective and low-cost biosorbent for removing heavy metal ions, specifically Pb^{2+} ions, from wastewater. The study also provides valuable information on the optimum conditions for the maximum adsorption capacity of the mango seed biosorbent, which can be helpful in designing and optimizing the adsorption process for practical applications. Further research can explore the potential of mango seeds for removing other heavy metal ions and evaluating their performance in real wastewater treatment systems. Overall, the findings of this study highlight the importance of using natural and sustainable materials for environmental remediation.

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