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Comparison of Chromium and Zinc Biosorption Utilizing Leaves of *Psidium Guajava*

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ABSTRACT

This study explores the effectiveness of *Psidium guajava* (guava) leaves are used for biosorbent to remove zinc (Zn) and chromium (Cr) from aqueous solutions. Adsorption tests have been conducted, and the Langmuir, the Freundlich, and the Temkin isotherm models are utilized to evaluate the equilibrium data. The results indicate that *Psidium guajava* demonstrates distinct adsorption patterns and a significant affinity for Zn and Cr. The Freundlich model provided the best description for Zn adsorption, while the Temkin model offered an excellent fit for Cr adsorption. The removal efficiencies for Cr and Zn were 82.5% and 74.4%, respectively, with adsorption capacities of 3.20 mg/g for Cr and 5.20 mg/g for Zn. Outcomes establish that *Psidium guajava* leaves are an economical and environmentally friendly biosorbent for removing heavy metals, offering an effective solution for environmental remediation and wastewater treatment.

Keywords: Psidium guajava, Zinc, Chromium, Adsorption Isotherm

1. Introduction

Pollution from heavy metals is a significant issue due to industrial as well as human activities, as it releases harmful compounds into the environment. The industrial sector primarily contributes to this pollution, emitting hazardous substances into wastewater through various processes, including metallurgy, electroplating, metal processing, tanneries, mining, pharmaceuticals, pesticides, chemical manufacturing, and the production of rubber and plastics. [1]. Over the past few decades, many conventional methods of treatment have been utilized for removing heavy metals that exist in wastewater. To remove highly concentrated levels of each potentially toxic metal from wastewater, a variety of chemical and physical technological techniques have been developed and utilized, including cation surfactants, reverse osmosis, photocatalysis, oxidation/reduction, ultrafiltration, ion exchangers, and electrochemical techniques [2]. Adsorption is widely used in industrial applications since it can be found in most natural physical, chemical, and biological systems. Applications of adsorption include the production of activated charcoal, synthetic polymers, and water filtration [3]. Biosorption is the term used to describe the capacity of biological substances to absorb heavy metals in wastewater using physicochemical or metabolically controlled processes. This complex process is influenced by several factors, including cell physiology, physicochemical elements such as pH, ionic strength, temperature, and metal concentration, as well as the composition of the cell walls of microorganisms [4]. In this context, lignocellulosic agricultural by-products have attracted significant attention as effective biosorbents due to their structural and chemical characteristics that facilitate metal binding. In metal biosorption, cellulose-rich agricultural products showed promising potential. Along with various functional groups, the main constituents of agricultural biomass waste—hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water, hydrocarbons, and starch—play a crucial part in metal binding and assist in the removal of heavy metals [5, 6]. The unique chemical composition, global availability, renewability, and low cost of agricultural waste make it an environmentally friendly and effective alternative for heavy metal remediation [7].

Hexavalent Cr(VI) in liquid waste poses a greater threat compared to trivalent Cr(III) and is also more challenging to remove. It is recognized globally as a carcinogenic heavy metal with severe health impacts, including skin allergies and pulmonary and liver damage [8, 9]. A maximum discharge limit of 0.05 mg/L for Cr(VI) in industrial effluents has been defined by the World Health Organization (WHO) [10]. Similarly, Zn(II), while less toxic than Cr(VI), can accumulate in the environment at elevated concentrations, posing risks to aquatic life and human health. It is a common pollutant in effluents from the drainage of acid mines, galvanizing plants, the processing of natural ore, and the treatment of wastewater from municipal facilities. Being non-biodegradable, zinc bioaccumulates in the food chain and becomes toxic to humans at intake levels of 100–500 mg/day [11]. For the purpose of ensuring that zinc is effectively removed from drinking water, the WHO recommends a maximum concentration of 5.0 mg/L [12]. Numerous studies have explored its removal from aqueous solutions, with adsorption being a widely applied technique. However, chemical adsorbents often raise environmental concerns due to their non-biodegradable nature. These environmental and health concerns show a growing demand for sustainable, eco-friendly alternatives to chemical adsorbents. In these circumstances, biosorbents provide an appropriate means to eliminate heavy metals consisting of Zn(II) and Cr(VI). Among plant-based options, guava

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(*Psidium guajava*), native to tropical and subtropical regions, has attracted attention for its potential in metal ion removal. Its raw leaves contain approximately 6% fixed oils, 0.365% volatile oils, 3.15% resin, 8.5% tannins, and various other stable compounds [13]. Studies have illustrated the effectiveness of guava-derived waste materials such as leaves [14], peels [15], seeds [16], and bark [17] as cost-effective and efficient biosorbents for eliminating pollutants from aqueous environments. S. K. Das et al. [18] reported that guava leaves can be effectively utilized in a continuous column technique to remove hazardous Cr(VI) ions, demonstrating that they can be used as a sustainable absorbent. S. Kartohardjono et al. [19] obtained higher than 99% chromium removal efficiency, with guava leaves and fruits revealing sorption capacities of 4.2 and 2.9 mmol/g, respectively. Mariana et al. [20] have reconfirmed that guava leaves can adsorb Cr(VI) from water. In a separate study, L. P. Y. Foo et al. [21] investigated cadmium (Cd^{2+}) biosorption using various plant-based materials, and they found that guava peels outperformed those of *Ananas comosus* and *Parkia speciosa*, with an adsorption capacity of up to 39.68 mg/g. Similarly, O. Abdelwahab et al. validated the effectiveness of guava leaves as biosorbents by evaluating their ability to remove Cd^{2+} using both raw and activated leaves. O. Abdelwahab et al. [22] confirmed the effectiveness of guava leaves as biosorbents by studying their ability to remove Cd^{2+} ions using both raw and activated leaves. Additionally, another study focused on optimizing activated carbon derived from guava waste for the adsorption of methylene blue dye [23]. Moreover, S. Kamsonlian et al. [24] demonstrated the potential of guava leaf biomass for removing arsenic (As^{3+} and As^{5+}) by showcasing absorption capacities of 1.06 mg/g and 2.39 mg/g, respectively. Guava leaves are potential efficient biosorbents for purifying wastewater contaminated with heavy metals, as demonstrated by multiple studies highlighting their capacity to adsorb various toxic metals effectively [25].

Psidium guajava is a widespread plant throughout Bangladesh. Its leaves are abundant and readily available, making them easy to use when needed. This study investigates the effectiveness of *Psidium guajava* leaves as a biosorbent for eliminating ions of zinc and chromium from aqueous solutions. Additionally, Zinc and chromium adsorption onto the leaves of *Psidium guajava* has been analyzed using isotherm models.

2. Method and Material

2.1 Preparation of the Bio-sorbent

Psidium guajava leaves were cleansed using water from the tap and then rinsed with double-deionized water that has been distilled. Six days were spent drying them in the sun until their weight remained constant. After drying for 48 hours at 50ºC, the leaves were crushed and then sifted through a sieve with 0.25 mm pores.

2.2 Metal Solution Preparation

To achieve a concentration of 1000 mg/L in each flask, specific amounts of zinc chloride ($ZnCl_2$) and potassium dichromate ($K_2Cr_2O_7$) were dissolved in distilled water to prepare solutions containing Zn^{2+} and Cr^{6+} ions. The stock solution (1000 mg/L) was then diluted according to requirements to create standard solutions with concentrations ranging from 5 to 13 mg/L.

2.3 Metal Solution Preparation

Batch biosorption experiments were conducted by mixing the biomass with metal ions at room temperature (25±0.1°C) in a glass tube. In conical flasks, 0.5 g of *Psidium guajava* leaves was mixed with 100 mL of aqueous metal solutions containing zinc and chromium to evaluate how the initial ion concentration impacts Zn(II) and Cr(VI) ion biosorption, within a concentration range of 5–13 mg/L. The mixtures were stirred continuously with a magnetic stirrer at a uniform rotational speed with a hot plate for 180 min. A UV–VIS spectrophotometer (DR-6000) was used to measure the equilibrium metal concentrations in the filtrates after the solutions had been stirred and filtered. All experiments involving toxic Cr(VI) were conducted using appropriate personal protective equipment (PPE). After adsorption with guava leaf powder, all solid waste and liquid effluent containing chromium and zinc were collected in clearly labeled hazardous waste containers. This waste was then transferred to the laboratory's hazardous waste system for final neutralization and disposal.

The collected data was used to calculate the percentage removal and adsorption capacity of *Psidium guajava* using Eq. (1) and (2).

$$Percentage\ Removal = \frac{c_o - c_e}{c_o} \times 100 \tag{1}$$

$$Adsorption\ Capacity = \frac{(c_o - c_e) \times V}{m} \tag{2}$$

Where c_o and c_e represent the initial and final metal concentrations (mg/L) in the liquid phase, respectively, adsorbent weight is denoted by m, and the liquid phase volume is denoted by V(L) [26].

2.4 Modeling

The equilibrium adsorption isotherm is crucial for figuring out the biosorption mechanism, particularly the distribution of adsorbed ions between the solid and liquid states of the adsorbent. Zn (II) and Cr (VI) ion biosorption by *Psidium guajava* leaves has been investigated in this study using the isotherms of Langmuir, the Freundlich, and the Temkin.

2.4.1 Langmuir Isotherm

Langmuir adsorption is used to measure and compare the adsorptive capacities of various adsorbents, which is usually used to explain the adsorption of gas-solid phases. A well-known model, the Langmuir isotherm, predicts a decrease in accessible interaction sites as the metal ion concentration rises. According to this hypothesis, biosorption takes place on a homogeneous surface by monolayer sorption, in which there is no interaction between the molecules that have been adsorbed. Eq. (3) is the expression for the Langmuir equation.

$$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m} \tag{3}$$

Where c_e is the equilibrium concentration of adsorbate (mg/L), the quantity of metal ions adsorbed on the biosorbent (mg/g) at equilibrium time is denoted by q_e, the adsorption capacity (mg/g) is associated with the Langmuir constant, k_L, and the monolayer capacity of the biosorbent is denoted by q_m [27].

2.4.2 Freundlich Isotherm

It is possible to explain adsorption processes carried out on heterogeneous surfaces by employing the Freundlich isotherm. Eq. (4) provides the Freundlich isotherm in its linear form.

$$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m} \quad (4)$$

Where the adsorption intensity is represented by 1/n, the adsorption capacity (L/mg) is denoted by k_f [27].

2.4.3 Temkin Isotherm

Use of the Temkin isotherm is limited to ion concentrations in the middle part of the spectrum. The linear form of the Temkin isotherm model is given by Eq. (5) [27].

$$q_e = \frac{Rt}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (5)$$

Where K_T stands for the Temkin Isotherm constant(L/g), and the Temkin constant (J/mol), denoted by b, is associated with the heat of sorption.

3. Result and Discussion

The investigation regarding the biosorption of Zinc (Zn) and Chromium (Cr) using Psidium guajava leaves indicates distinct adsorption characteristics and capacities, providing insights into their potential for heavy metal removal from aqueous solutions. Utilizing isotherm models of the Langmuir, the Freundlich, and the Temkin, the research meticulously reviewed data on equilibrium and evaluated how initial metal ion concentration influences adsorption capacity and removal efficiency. The parameters from the batch adsorption methods for Zn (II) and Cr (VI) are provided in Table 1 and 2, respectively.

Table 1 Initial and equilibrium concentration of chromium

Sample	Initial conc. C_0 (mg/L)	Equilibrium Conc. C_e (mg/L)	% Removal	Adsorption q_e (mg/g)
1	05	0.87	82.5	0.41
2	07	1.25	82.2	0.58
3	09	1.73	80.8	0.73
4	11	2.59	76.4	0.84
5	13	3.48	73.3	0.95

Table 2 Initial and equilibrium concentration of zinc

Sample	Initial conc. C_0 (mg/L)	Equilibrium Conc. C_e (mg/L)	% Removal	Adsorption q_e (mg/g)
1	05	1.28	74.4	0.37
2	07	2.05	70.7	0.49
3	09	2.73	69.7	0.63
4	11	3.40	69.1	0.76
5	13	4.10	68.5	0.89

3.1 Effect of initial Cr (VI) and Zn (II) ion concentration

The investigation into the effect of initial metal ion concentration presents crucial insights into the performance and efficiency of the biosorbent under different load conditions. The impact of varying initial metal ion concentrations (5–13 mg/L) is demonstrated in Figs. 1 and 2. A consistent trend was observed for both Zn(II) and Cr(VI): the adsorption capacity increased with rising initial metal ion concentration, whereas removal efficiency declined. For Cr(VI), the removal efficiency decreased from 82.5% to 73.3% as the initial concentration varied from 5 to 13 mg/L, while the adsorption capacity ranged between 0.41 and 0.95 mg/g. This inverse relationship occurs because, although a higher initial concentration enhances the driving force for mass transfer and promotes greater absolute metal uptake, the finite number of adsorption sites becomes saturated, reducing the proportion of ions removed relative to the total present.

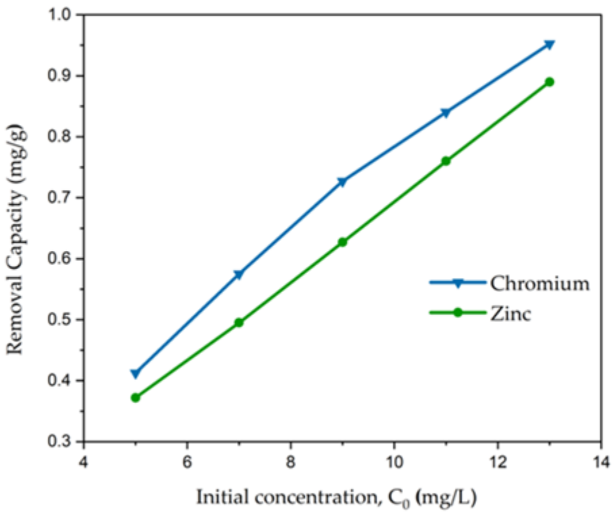

Fig. 1 Removal Capacity of Zn and Cr

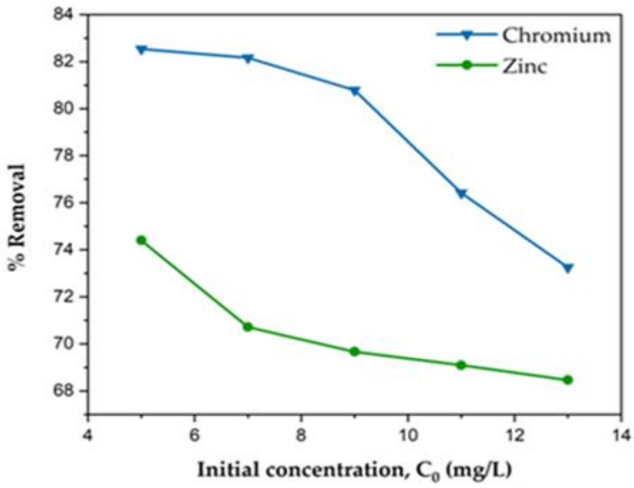

Fig. 2 Percentage Removal of Zn and Cr

A similar pattern was recorded for Zn(II), with the removal efficiency declining from 74.4% to 68.5% over the same concentration range, while the capacity of adsorption increased from 0.37 to 0.89 mg/g. Across all concentrations, Cr(VI) consistently achieved higher removal efficiencies than Zn(II), indicating a stronger affinity or more effective binding mechanism of Psidium guajava leaves for chromium ions. A vital comparison between Cr and Zn discloses that Chromium consistently demonstrated a higher removal efficiency than Zinc across all evaluated initial concentrations. This indicates that even at higher starting concentrations, A higher percentage of the chromium ions is removed from the solution using the Psidium guajava biosorbent simply because of its stronger affinity or more efficient binding mechanisms for these ions under these experimental conditions. In comparison to other natural adsorbents that have been previously reported, the adsorption capacity values found in this study are quite significant, as shown in Table 3.

Table 3 Comparison of adsorption capacities

Adsorbent	Adsorbate	q_e mg/g
Rice husk ash	Zn	9.588
Phragmites australis shoot	Zn	5.75
Activated sludge	Zn	5.71
Natural rice husks (RH)	Zn	0.905
Calcined rice husks (RHA)	Zn	1.1
Guava leaf biomass	As (III)	1.06
Guava leaf biomass	As(V)	2.39
Peanut shell	Cr(VI)	0.0222
Cactus leaves	Cr (VI)	7.082
Coconut tree sawdust	Cr (VI)	3.6

3.2 Adsorption Isotherms

Analysis of adsorption isotherms reveals the specific adsorption behavior of each metal. Fig. 3, 4, and 5 exhibit the corresponding graphs for the Langmuir, the Freundlich, and the Temkin equations, respectively. Table 4 provides an overview of the model characteristics

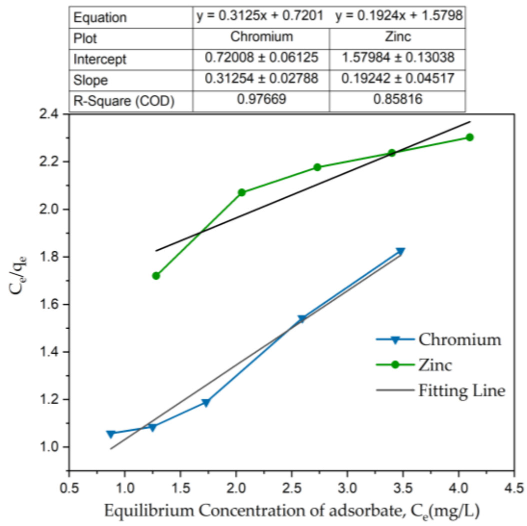

Fig. 3 Langmuir Isotherm

For Zn(II) and Cr(VI), the adsorption capacities (q_m) of Psidium guajava leaves were calculated to be 5.19701 mg/g and 3.19956 mg/g, respectively, indicating a stronger affinity of the biosorbent for Zn(II). This difference in uptake capacity can be attributed to variations in the physicochemical characteristics of the biosorbent surface and the specific interaction tendencies of each metal ion toward the available binding sites. The Langmuir isotherm model, which presupposes monolayer adsorption on a uniformly adsorbent surface, highlighted distinct differences in the adsorption behaviors of Cr(VI) and Zn(II) on *Psidium guajava* leaves. For Cr(VI), the model demonstrated a strong correlation, with a maximal capacity of 3.19956 mg/g for monolayer adsorption. In contrast, Zn(II) displayed a lower correlation but showed a significantly higher value of 5.19701 mg/g, indicating that *Psidium guajava* leaves can theoretically bind more zinc ions per unit mass.

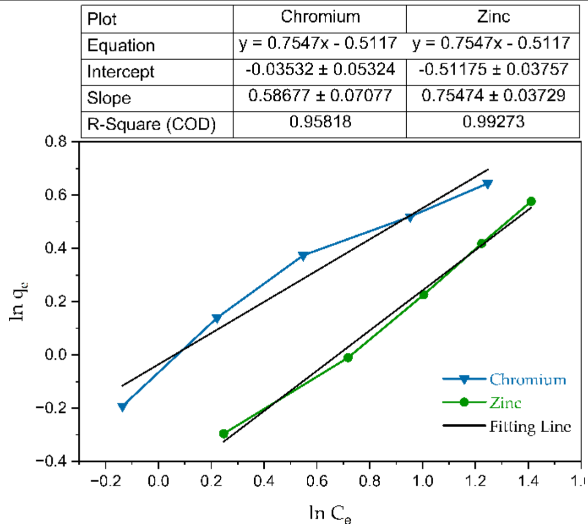

Fig. 4 Freundlich Isotherm

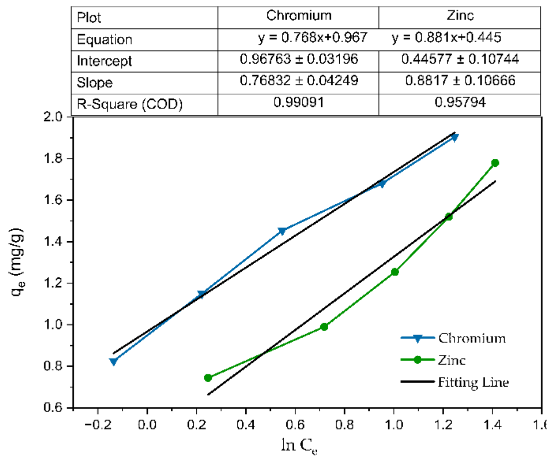

Fig. 5 Temkin Isotherm

These differences suggest that, although the statistical fit is somewhat weaker for Zn(II), the biosorbent has a substantially greater theoretical binding capacity and affinity for Zn(II) compared to Cr(VI) under the Langmuir model assumptions. The higher value for Zn(II) implies a stronger interaction between the metal and the biosorbent, which may result from variations in ionic radius, electronegativity, or coordination chemistry between the two metal ions. These findings suggest that while the Langmuir model aligns more closely with Cr(VI) adsorption behavior, Zn(II) exhibits greater binding potential and interaction strength with the biosorbent.

Table 4 Isotherm Parameters

Isotherm Model	Parameter	Chromium	Zinc
Langmuir Isotherm	q_{max} (mg/g)	3.19956	5.19701
	K_l (L/mg)	2.30394	8.21043
	R^2	0.97669	0.85816
Freundlich Isotherm	n	1.70425	1.32496
	K_f (L/mg)	0.96529	0.59945
	R^2	0.95818	0.99273
Temkin Isotherm	b (J/mol)	0.76832	0.88170
	K_T (L/mol)	3.52337	1.65796
	R^2	0.99091	0.95794

The Freundlich model describes adsorption occurring on heterogeneous surfaces and allows for the formation of multilayers, revealing distinct behaviors for Cr(VI) and Zn(II). This model fit the adsorption data for Zn(II) exceptionally well, outperforming its fit for Cr(VI). Specifically, for Cr(VI), the model produced an R^2 value of 0.95818 and an n value of 1.70425. In contrast, Zn(II) achieved an exceptionally high 0.99273 R^2 value and a value of 1.32496 for n. Both n values fall between 1 and 10, indicating favorable adsorption; however, the higher correlation for Zn(II) suggests that heterogeneous, multilayer adsorption mechanisms better represent its uptake. This stronger fit implies that a broader range of active sites, possibly differing in energy and binding strength, contributes to the adsorption of Zn(II). In comparison, Cr(VI) adsorption appears less dependent on surface heterogeneity.

The Temkin model, which considers the interactions between adsorbates and adsorbents, assumes that as the coverage of the surface increases, the heat of adsorption reduces linearly. This model demonstrated a stronger correlation with Cr(VI) adsorption than Zn(II), indicating that variations in adsorption energy are more significant for Cr(VI) binding. This suggests that Cr adsorption may follow a mechanism where surface energy changes with coverage, reflecting an actively heterogeneous biosorbent surface. The strong fit of the Temkin model for Cr thus provides valuable theoretical insight that adsorption onto *Psidium guajava* leaves is influenced by heterogeneous surface energies and dynamic adsorbate–adsorbent interactions.

The best fit of the Freundlich model for Zn(II) indicates the presence of surface heterogeneity. This suggests that multiple types of binding sites contribute to the uptake of zinc ions. In contrast, the excellent fit of the Temkin model for Cr(VI) emphasizes the influence of variable adsorption energies during the binding process. This implies that the surface of the biosorbent exhibits a range of interaction strengths towards chromium ions. Consequently, these findings reveal that heterogeneous multilayer interactions primarily govern the adsorption of Zn(II). In contrast, the uptake of Cr(VI) is more affected by variations in binding energy. This underscores the different adsorption mechanisms at work for each metal, demonstrating the distinctive ways each heavy metal interacts with the *Psidium guajava* biosorbent and verifying its effectiveness as a cost-effective, eco-friendly technique for removing heavy metals from aqueous solutions.

4. Conclusion

Three adsorption models have been utilized to evaluate the adsorption equilibrium, demonstrating a good fit for zinc and chromium removal. The Temkin model has shown the best fit for chromium removal, whereas the Freundlich model indicated the most appropriate for removing zinc. The removal efficiencies are 82.5% for chromium and 74.4% for zinc, with corresponding adsorption capacities of 3.19956 mg/g and 5.19701 mg/g. *Psidium guajava* leaves appear to effectively remove Zn (II) and Cr (VI) from aqueous solutions, highlighting their potential as a cost-effective alternative adsorbent for wastewater treatment. Due to the abundance, low cost, and significant biosorption capacity, *Psidium guajava* leaves present a promising option for heavy metal removal. Future studies could focus on chemically modifying *Psidium guajava* leaves to optimize their adsorption capabilities and test their effectiveness in absorbing other heavy metals, such as cadmium, mercury, and lead. Additionally, investigations into adsorption kinetics, thermodynamics, SEM-EDS, BET surface area analysis, and XPS atomic percentages should be conducted more thoroughly to gain a better understanding of the adsorption process and the characteristics of this biosorbent.

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NOMENCLATURE

Symbol	Meaning	Unit
c_0	Initial Concentration	(mg/L)
c_e	Equilibrium Concentration	(mg/L)
q_e	Adsorption Capacity	(mg/g)
q_{max}	Maximum Adsorption Capacity	(mg/g)
K	Equilibrium Adsorption Constant	(L/mg)
K_l	Langmuir Constant	(L/mg)
K_f	Freundlich Constant	(L/mg)
K_T	Temkin Isotherm Constant	(L/mol)
b	Temkin Constant	(J/mol)
R^2	Relative Correlation Value	
n	Freundlich Constant of the Biosorption	