GSC Biological and Pharmaceutical Sciences

eISSN: 2581-3250 CODEN (USA): GBPSC2

Cross Ref DOI: 10.30574/gscbps

Journal homepage: https://gsconlinepress.com/journals/gscbps/

(RESEARCH ARTICLE)

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Efficient biosorption of mercury (Hg) using *Carica papaya* stem waste as biosorbent

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GSC Biological and Pharmaceutical Sciences, 2026, 34(03), 168-178

Publication history: Received on 11 February 2026; revised on 17 March 2026; accepted on 20 March 2026

Article DOI: https://doi.org/10.30574/gscbps.2026.34.3.0108

Abstract

A Molecule shifts from a fluid bulk to a solid surface through a surface process known as adsorption. The presence of heavy metals in water represents a major environmental challenge, posing significant risks to human health and ecosystems. Traditional methods of removal are often inefficient and costly, creating a need for more effective and sustainable alternatives. Biosorption, which uses living or non-living biomass to adsorb pollutants, offers a promising solution. This study explores the use of agro waste of *Carica papaya*(stem) for the removal of mercury ions from water. The mercury concentration and the functional groups involved in biosorption were analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Fourier-Transform Infrared Spectroscopy (FTIR). The results show that *Carica papaya* achieved an adsorption efficiency of 87.99% at a mercury concentration of 600 ppm, pH 4, and after a 24-hour contact period. These findings highlight the potential of *Carica papaya*(stem) as an eco-friendly and effective approach for water purification and environmental conservation.

Keywords: Biomass; Bio-sorption; *Carica papaya*; Heavy metal; Wastewater

1. Introduction

The presence of heavy metal pollutants in water poses serious environmental and public health threats. Conventional techniques for eliminating these pollutants, like ion exchange, chemical precipitation, and filtration, frequently have drawbacks because of their high expense, inefficiency, and negative effects on the environment. Consequently, there is an increasing demand for more economical and sustainable alternatives[1]. Biosorption, a technique that uses living or non-living biological materials, such plant biomass, to absorb and eliminate contaminants from water, is one such substitute. This approach is thought to be energy-efficient, environmentally benign, and able to handle substantial amounts of contaminated water [2].

Biosorption is the ability of biological materials to take up heavy metals from wastewater through physico-chemical or metabolically driven pathways. [3].

The potential of *Carica papaya* (papaya stem) powder for removing mercury ions from aqueous solutions is the main topic of this study[4]. Removing mercury from water is crucial since it is a very toxic heavy metal that provides serious environmental risks even at low quantities [5]. By examining the uptake of mercury ions at a concentration of 600 ppm, pH 4, and during a 24-hour contact period, the biosorption ability of *Carica papaya* stem was evaluated. The concentration of mercury in the solution before and after biosorption was measured using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), and the functional groups on the *Carica papaya* (stem) biomass involved in the biosorption process were identified using Fourier-Transform Infrared Spectroscopy (FTIR). The findings showed that *Carica papaya* (stem) has a remarkable adsorption effectiveness of 87.99%, suggesting that it could be a useful biosorbent for removing mercury.

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High level of adsorption capacity suggests that *Carica papaya* could serve as a promising, low-cost, and sustainable method for mercury removal from water, with broader implications for water purification and environmental conservation. The study highlights the feasibility of using natural, readily available materials for the remediation of contaminated water, offering an innovative approach to addressing the growing concern of heavy metal pollution.

2. Materials and Methods

2.1. Reagents

Sigma-Aldrich Chemical Co., USA, provided all analytical-grade chemicals used in this investigation. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used to measure the amounts of heavy metal ions in the treated solutions. A Shimadzu spectrophotometer was used to acquire the samples' Fourier-Transform Infrared (FTIR) spectra.

2.2. Metal Ion Solution Preparation

1.35 grams of mercury sulfate were dissolved in 1000 milliliters of deionized water to create a standard stock solution of mercury (Hg) at a concentration of 1000 parts per million. The stock solution was then serially diluted with deionized water to produce mercury solutions with concentrations ranging from 200 ppm to 1000 ppm.

2.3. *Carica papaya* as Adsorbent

The *Carica papaya* plant material used in this study came from the Institute of Science's college garden in Mumbai District, India. The obtained plant material (stem) was carefully washed with both tap and deionized water to get rid of any impurities. For the trials, the material was cleaned, dried thoroughly in the sun for seven days, and then ground into a fine powder.

2.4. Characterization

The functional groups in the adsorbent within the 4000-400 cm^{-1} range were identified using FTIR analysis. Samples of biomass with and without metals were analysed. ICP-AES was used to determine the concentration of mercury ions in the solution both before and after treatment, enabling the assessment of mercury removal effectiveness.

2.5. Batch Adsorption Studies

The efficiency of *Carica papaya* as an adsorbent for removing mercury from aqueous solutions was assessed using batch adsorption equilibrium studies. In these tests, different amounts of 25 grams of the adsorbent were applied to 1000 millilitres of mercury solution. At room temperature, the mixture was constantly stirred at 120 rpm in 250 mL conical flasks. ICP-AES was used to measure the concentration of mercury ions in the solution both prior to and during the adsorption process. The following formulas were used to determine the % adsorption and the adsorption capacity at equilibrium (qe) in mg/g:

$$qe = \frac{(Co - Ce)\ \mathrm{V}}{X}$$

$$\%\ \text{of adsorption} \ = \frac{(Co - Ce)}{Co}\ X\ 100$$

Where:
Co = initial concentration of mercury ions in the solution (mg/L)
Ce = equilibrium concentration of mercury ions in the solution (mg/L)
V = volume of the solution (L)
X = weight of the adsorbent used (g) [6].

2.5.1. Effect of Initial pH

Using 0.1M HCl and 0.1M NaOH, the pH of the mercury solution was adjusted between 2.0 and 10.0 to investigate the impact of initial pH on mercury uptake. These different pH levels were used in batch biosorption tests.

2.5.2. Effect of Contact Time

Experiments were carried out over a period of 30 minutes to 72 hours in order to assess the impact of contact time on mercury elimination. The ideal duration for optimum mercury uptake was determined by evaluating the biosorption effectiveness at various contact times.

2.5.3. Effect of Temperature

By varying the mercury solution's temperature between 25 °C and 45 °C, the impact of temperature on the biosorption process was investigated. To find out how temperature affects mercury removal effectiveness, batch biosorption studies were carried out at different temperatures.

2.5.4. Effect of Adsorbent Dose

By changing the amounts of *Carica papaya* (stem) adsorbent, the impact of adsorbent dose on the effectiveness of mercury removal was investigated. A 1000 mL solution of 100 mg/L Hg (II) was mixed with various doses (1.0 g, 2.0 g, 3.0 g, 4.0 g, and 5.0 g). To find the ideal adsorbent dose for efficient mercury removal, the experiments were conducted with constant shaking at 120 rpm.

3. Results and Discussion

3.1. Biosorption experiment

The objective of this study was to identify the optimal mercury concentration (ppm) at which *Carica papaya* oven-dried powder achieves maximum adsorption. The highest adsorption efficiency was observed at a 600-ppm concentration, as indicated by the initial results. In the following experiments, this 600-ppm concentration was chosen to examine the effects of pH, contact time, adsorbent dose, and temperature on the biomass's adsorption capacity. The optimization of mercury adsorption at various concentrations (before and after treatment) is presented in Table 1 and Figure 1.

Table 1 Optimum Hg adsorption report

Sample No	Before Treatment	After Treatment	% Biosorption
1.	200 ppm	79.023	60.48
2.	400 ppm	97.24	83.79
3.	600 ppm	57.68	87.99
4.	800 ppm	245.67	69.29
5.	1000 ppm	419.019	58.09

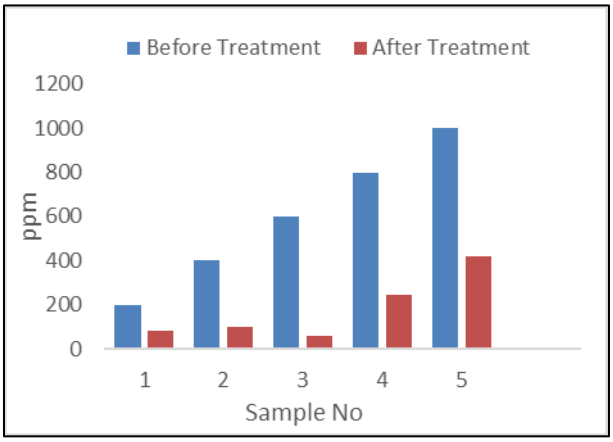

Figure 1 Reduction of Hg

3.2. Effect of pH

Mercury biosorption was greatly impacted by the pH of the solution. After a 24-hour incubation period and an initial mercury concentration of 600 ppm, maximum metal uptake was reached at pH 4. Protonation of functional groups on the biomass surface, which restricts the availability of negatively charged binding sites, is the cause of reduced biosorption at lower pH values. Higher pH levels encourage active site deprotonation, which strengthens the biosorbent's electrostatic attraction to metal ions [7]. The ideal pH found is in line with earlier research on *Eichhornia crassipes* and *Pistia stratiotes L.* [8]. However, the type of biosorbent and the particular characteristics of the target metal ion determine how much pH affects biosorption effectiveness [6]. The variation in biosorption capacity with pH is presented in Table 2 and Figure 2.

Table 2 Effect of pH on biosorption capacity

SN	pH	Reduction (ppm)
1.	2	331.68
2.	4	49.39
3.	6	268.1
4.	7	63.01
5.	8	89.46
6.	10	312

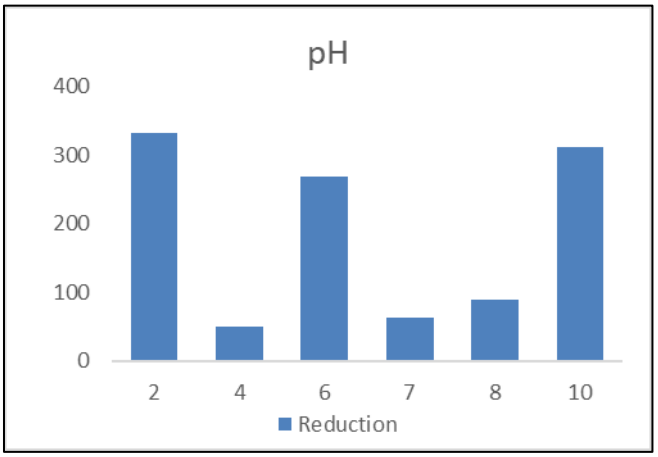

Figure 1 Effect of pH on biosorption

3.3. Effect of contact time

At an initial concentration of 600 ppm, the impact of contact time on metal ion biosorption was examined across time intervals of 30 minutes, 1 hour, 3 hours, 24 hours, 48 hours, and up to 72 hours. As contact time increased, biosorption capacity rose and peaked at 24 hours. Furthermore, the efficiency of metal removal was greatly improved by increasing the dosage of biomass. Because there were more active biosorption sites available, the maximum clearance was obtained with 3 g of fungal biomass and a 24-hour contact duration. Table 3 and Figure 3 provide an overview of how contact time affects biosorption performance [9]. The findings show that the quantity of accessible binding sites and, hence, the degree of metal uptake are directly controlled by the dosage of the biosorbent. These findings are consistent with earlier research [10].

Table 3 Effect of contact time on Biosorption capacity

SN	Time	Reduction
1.	30 min	201.85
2.	1 hr	160.52
3.	3 hrs	130.121
4.	24hrs	48.02
5.	48hrs	88.019
6.	72hrs	149.11

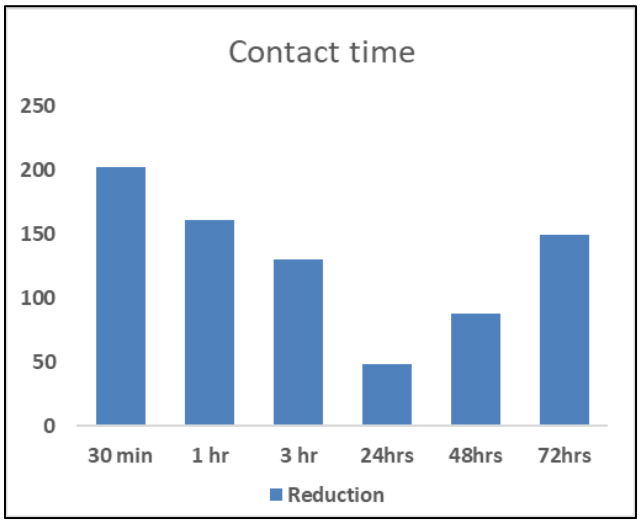

Figure 2 Effect of contact time on biosorption

3.4. Effect of Dosage

At an initial metal concentration of 600 ppm, the impact of biomass dosage on metal biosorption was examined throughout a range of 1–5 g. The effectiveness of metal removal increased in proportion to an increase in biomass dosage. Because there were more active biosorption sites available, the removal effectiveness was best when 3 g of *Carica papaya* (stem) biomass was used with a 24-hour contact time [11]. Table 4 and Figure 4 show how biomass concentration affects biosorption capability. These results show that the number of binding sites accessible for metal absorption is directly controlled by the amount of biosorbent, which in turn controls the overall biosorption performance. The findings align with research that has already been published [5].

Table 4 Effect of biomass concentration on biosorption capacity

SN	Dose (gm)	Reduction
1.	1	210.25
2.	2	160.62
3.	3	48.02
4.	4	133.01
5.	5	139.02

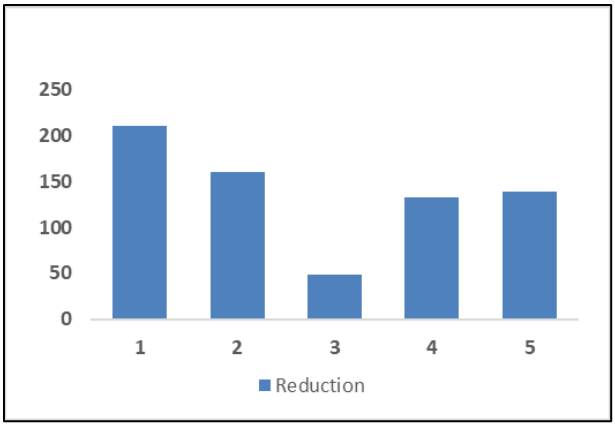

Figure 3 Eeffect of dosage on biosorption

3.5. Effect of temperature

At an initial metal concentration of 600 ppm, the impact of temperature on biosorption was examined throughout a range of 25 °C to 45 °C. At 30 ± 1 °C, the maximum adsorption efficiency of 87.99% was recorded. Beyond this optimal temperature, a drop in biosorption capacity was observed, reaching 59.95% at 35 °C and then 38.07% at 45 °C. These findings show that the biosorption process is temperature-dependent, with maximum adsorption taking place at lower temperatures and a notable decrease in capacity at temperatures above 40°C. The weaker connections between the metal ions and the dried *Carica papaya* biomass, as well as potential structural alterations in the biosorbent, might be the cause of the decreased biosorption effectiveness at higher temperatures. Table 5 and Figure 5 show how temperature affects biosorption capability. These results are in line with earlier research on the biomasses of neem, java palm, guava, sapota, custard apple, and mango leaves [12].

Table 5 Effect of temperature on biosorption capacity

SN	Temp	Reduction
1.	25	208.29
2.	30	48.02
3.	35	160.2
4.	40	247.69
5.	45	310.17

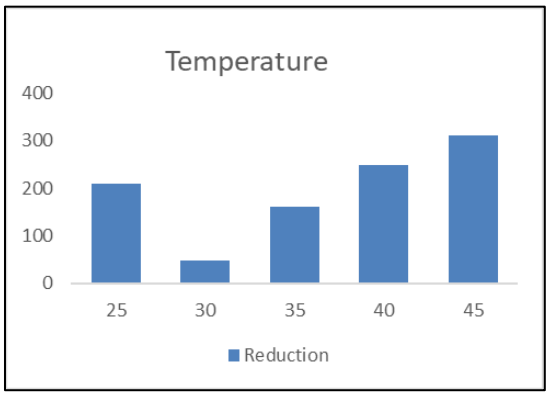

Figure 5 Effect of temperature on biosorption

3.6. Evidence of Hg adsorption in *Carica papaya* through FTIR Analysis

Functional group changes related to the treatment procedure are clearly visible in the FTIR spectra of papaya biomass before and after treatment. The stretching vibrations of the –OH group are represented by the absorption bands at 3381 cm^{-1} and 3356 cm^{-1}, which show that the biomass contains hydroxyl moieties. Following treatment, these peaks significantly decreased and vanished, indicating that hydroxyl groups were involved in chemical interactions [13].

The stretching vibration of the C=O group or the bending of adsorbed water molecules are responsible for the band at 1630 cm^{-1}. This peak's decreased strength after treatment suggests that carbonyl groups may interact with reactive species. Similarly, peaks at 1400 and 1382 cm^{-1}, which are attributed to the C–H bending vibrations of methyl/methylene groups, were shown to exist following treatment, indicating that the biomass's aliphatic structures were substantially undamaged [14].

Strong absorption bands at 1130 and 1122 cm^{-1} are indicative of ether or ester bonds' C–O stretching vibrations. Following treatment, these peaks decreased or vanished, indicating their involvement in binding or chemical alteration processes. Bands at 693, 490, and 479 cm^{-1} in the lower wavenumber area represent skeletal vibrations that may be related to metal–oxygen stretching or aromatic substitutions. Molecular structural changes are also supported by changes in these bands.

3.6.1. Disappearance of Peaks

Following treatment, distinctive peaks such as 3381 and 3356 cm^{-1} (–OH stretching) and 1130 and 1122 cm^{-1} (C–O stretching) vanish, indicating their active participation in the interaction process. Chemical interactions are also indicated by the weakening of the 1630 cm^{-1} (C=O stretching) band, which is probably the result of carbonyl group alteration or binding.

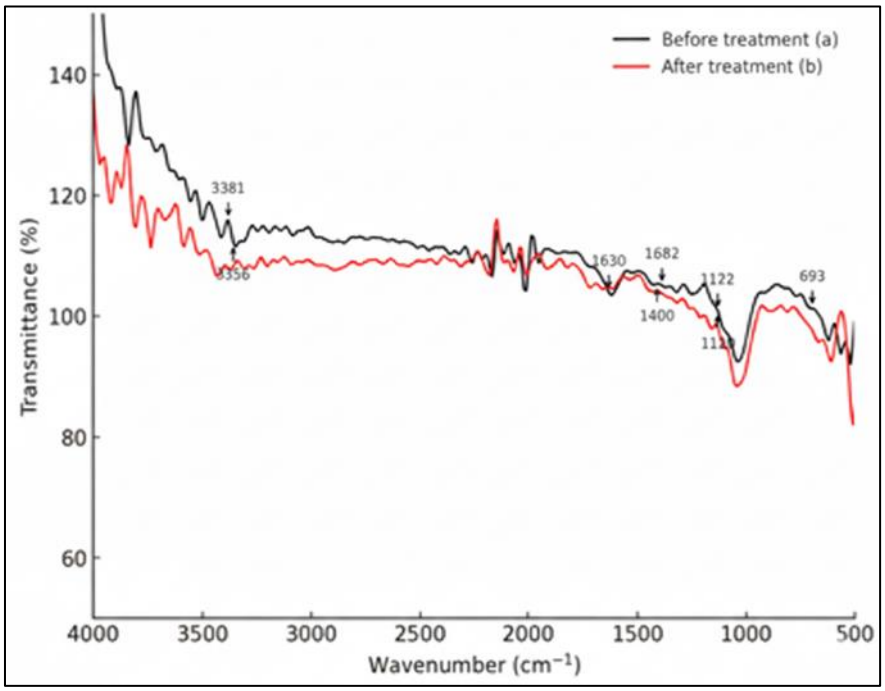

Figure 6 FTIR report of before and after treatment of Hg on *Carica papaya*

3.6.2. Langmuir Adsorption Model

Adsorption isotherms were used in batch tests to assess the adsorption properties. For the description of metal ion biosorption by *Carica papaya* biomass, the Langmuir model worked well. It might be stated as:

$$\frac{q_e}{q_{max}} = \frac{K_L C_e}{1 + K_L C_e}$$

Where:
(q_e) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g).
(q_m) is the maximum adsorption capacity of the adsorbent (mg/g).
(C_e) is the equilibrium concentration of the adsorbate in the solution (mg/L).
(K_L) is the Langmuir adsorption constant related to the affinity between the adsorbent and adsorbate (L/mg) [15].

A link between the concentration of metal ions in a solution and the amount adsorbed onto the solid phase at equilibrium is provided by an adsorption isotherm, which is used to investigate the interaction between metal ions and adsorbents. The Langmuir adsorption model states that adsorption takes place at a limited number of distinct locations on the adsorbent, each of which may hold a single molecule. It is presumed that these locations have the same energy and are far enough apart to prevent molecules adsorbed at nearby sites from interacting [16]. The adsorption process may be examined using kinetics, statics, and dynamics equations. Kinetics uses the equations for the migration of the adsorbate outside the adsorbent particle and the saturation of the adsorbent particles[17].

So, the results obtained according to the Langmuir adsorption model are as below:

- **pH:**

Maximum Adsorption Capacity (q_m) = 909.09 mg/g

Langmuir Constant (K_L) = 826446.281 L/mg

The slope and intercept values are derived from fitting the experimental data to the Langmuir equation. The slope (0.0011) indicates the rate at which adsorption increases with increasing concentration of metal ions in solution. The intercept (4.00E-05) reflects the starting value when the concentration of metal ions approaches zero.

The qmax value of 909.0909091 mg/g indicates that, under the pH conditions used, the maximum adsorption capacity is relatively high, suggesting that the adsorbent can accommodate a large amount of metal ions at equilibrium. However, the **k** value of 826446.281 L/mg suggests that the affinity between the adsorbent and metal ions is moderate, meaning that adsorption is not excessively strong under these conditions but still significant.

- **Dosage**

Maximum Adsorption Capacity (q_m)= 2500 mg/g

Langmuir Constant (K_L) = 6250000 L/mg

When the adsorbent dosage is varied, the qmax increases significantly to 2500 mg/g, indicating a higher maximum adsorption capacity. This higher capacity means that with more adsorbent available, the system can adsorb more metal ions, which could be attributed to the increased number of available adsorption sites.

Additionally, the k value of 6250000 L/mg is much higher than that for pH, which implies a much stronger affinity between the adsorbent and metal ions at higher dosages. This suggests that increasing the adsorbent dosage enhances the efficiency and effectiveness of metal ion biosorption, likely due to more binding sites becoming available for adsorption.

- **Temperature**

Maximum Adsorption Capacity (q_m)_ = 3333.3 mg/g

Langmuir Constant (K_L) = 11111111.11 L/mg

With temperature variation, the qmax value is 3333.3 mg/g, which is also relatively high. This indicates that, at higher temperatures, the adsorbent can adsorb a considerable amount of metal ions, suggesting that the adsorption process is thermodynamically favourable at these conditions.

The k value of 11111111.11 L/mg is the highest among the factors, indicating a very strong affinity between the adsorbent and the metal ions at higher temperatures. This might suggest that temperature positively influences the

adsorption efficiency, potentially due to enhanced molecular movement and better interaction between the metal ions and the adsorbent surface.

- **Contact Time**

Maximum Adsorption Capacity (q_m)= 2500 mg/g

Langmuir Constant (K_L) = 6250000 L/mg

The contact time has a qmax of 2500 mg/g, similar to the dosage, suggesting that the maximum capacity for adsorption is the same at both conditions. This implies that the duration of exposure may not significantly affect the adsorption potential once equilibrium is reached, as the adsorbent has already achieved its adsorption capacity.

The k value for contact time is the same as for dosage (6250000 L/mg), indicating that the affinity between metal ions and the adsorbent is comparable. However, contact time might affect the rate at which adsorption occurs, as longer contact times usually allow more ions to be adsorbed, even though the maximum capacity remains the same

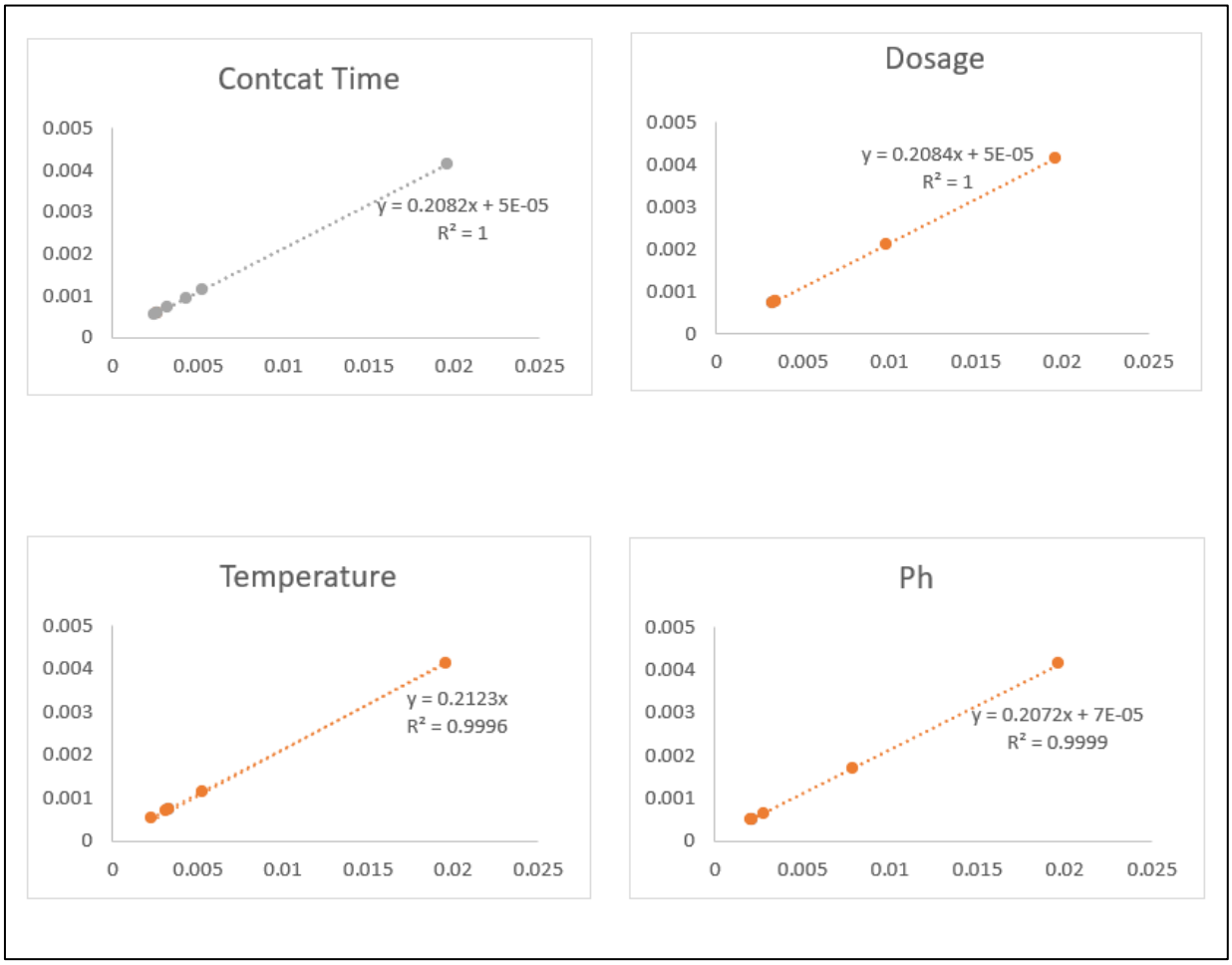

Figure 7 Langmuir adsorption isotherm plot for Hg (II) biosorption by *Carica papaya* biomass. contact time, Dosage, Temperature, pH

4. Conclusion

The potential of *Carica papaya* agro-waste, particularly papaya stem, as an efficient biosorbent for mercury (Hg) absorption was investigated in this work. The biosorption tests showed that 4.0 was the ideal solution pH for Hg(II) adsorption using fully developed *Carica papaya* stems. With a 3 gm adsorbent dose and a 24-hour agitation period, the optimal starting Hg(II) concentration in the solution for the adsorbent was determined to be 600 mg/L.

The surface functional groups promoting metal ion biosorption were shown by the FTIR analysis. Papaya stem waste is a promising low-cost biosorbent because of its high capacity and metal affinity for Hg(II) removal, as demonstrated by the experimental findings. Papaya stems may be chemically modified in the future to improve their ability to remove metals. Overall, the study indicates that *Carica papaya* agro-waste may be a viable and effective way to reduce mercury contamination in water sources.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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