Biosorption potential of Lantana camara leaves’ biosorbent to remove Zn (II) ions from synthetic aqueous solution

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Research Article

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Biosorption potential of *Lantana camara* leaves’ biosorbent to remove Zn (II) ions from synthetic aqueous solution

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Abstract

Inorganic metal pollution is becoming more prevalent as industrialization progresses. Despite being an essential element, Zn (II) can be detrimental if consumed in excess. In this study, the possibility of using *Lantana camara* leaves to prepare a biosorbent that can eliminate Zn (II) ions from contaminated wastewater solutions was investigated. BET surface area, FTIR and SEM analysis were carried out to characterize the prepared *Lantana camara* leaves biosorbent (LCLB). It was reported that increasing biosorbent dosage and contact duration improves Zn (II) ion removal while it decreases with rising initial concentrations of Zn (II) ions and temperature. At pH 6, 5 g adsorbent dosage, and 45 minutes contact time, excellent removal capabilities (85.06%) were reported. The pseudo-second-order rate model fit the kinetics of Zn (II) adsorption well ($R^2 > 0.998$), and the predicted adsorption capacity of the model agreed well with the experimental outcomes. The Langmuir isotherm ($R^2 > 0.996$) was the best suited isotherm model for Zn (II) adsorption onto LCLB, implying monolayer adsorption. Thermodynamic experiments revealed that Zn (II) adsorption on the biosorbent’s surface was spontaneous and exothermic. Desorption studies implied that the biosorbent can be recycled effectively up to two cycles. An investigation of the maximum adsorption capabilities of different untreated biomaterial-based residues found that LCLB is an effective, inexpensive, and environmentally acceptable biosorbent for use in the removal of contaminants from polluted aqueous media.

Keywords


Introduction
Rapid industrialization in neoteric years has caused the emission of enormous quantities of contaminated wastewater and undeniably is an utmost contributor to environmental deterioration. These wastewaters contain various inorganic and organic contaminants which include heavy metals, dyes, chlorine compounds (e.g., inorganic chloramines), and pharmaceutical-products waste mainly. The emergence of toxic heavy metals in the aqueous media is a principal source of concern considering their severe toxicity and proclivity of persistence in the food cycle even in trace amounts (Kumar et al., 2006). In the human body, heavy metals can enter via water, food, and air. Biological functions are disrupted when these hazardous metals attach to the cellular structures of organisms (Arora & Chauhan, 2021). Zinc (II) is a vital heavy metal that functions in numerous enzymes as a cofactor e.g., carboxypeptidase, carbonic anhydrase, etc., and thus pertinent for a human body (Kirova et al., 2015), but Zn (II) also becomes harmful because of over-accumulation in the human body when its concentration is over a permissible amount (Hajahmadi et al., 2015). Zn (II) is discharged into the environment because of discharged effluents of galvanizing plants, municipal sewage treatment plants, acid mine drained water plants, and natural ores also (Agarwal et al., 2004; Hajahmadi et al., 2015). Pertained to the World Health Organization (WHO), the permissible quantity of Zn (II) is 5mg/L. Over a daily permissible limit, Zn (II) can cause vomiting, anemia, stomach cramps, skin irritations, nausea, coughing, dehydration, volume and frequency of ventilation, increase in breathing rate, gastrointestinal, renal, depression, neurological disturbances (Borbely & Nagy, 2009; Mishra et al., 2010). It is therefore necessary to remove Zn (II) ions from the water sources. Numerous ways are utilized to eliminate the heavy metals from contaminated wastewater including physical (sedimentation, flotation, filtration), chemical (ion exchange, chemical precipitation, adsorption, dechlorination), and biological (activated sludge process, nutrient removal) procedures (Ahmaruzzaman, 2008). But, all these have some drawbacks such as high investment and maintenance costs, enormous energy efficiency, inadequate selectivity, less effectiveness (El-Araby et al., 2017). Biosorption is a potentially cost-effective alternative to these traditional methods with high efficiency; minimization of chemical sludges; biosorbent recycling and the prospect of metal recovery (Ahmaruzzaman, 2008; Borbely et al., 2009). Various plants, fungus, bacteria, etc have previously been used as biosorbents e.g., Paecilomyces sp. fungus (Rodriguez et al., 2013), Streptomyces fradiae biomass (Kirova et al., 2015), sesame husk leaves (El-Araby et al., 2017), leaves of Urtica dioica (Tiwari et al., 2017), Eupatorium Adinoforum and Acer Oblongum leaves (Vishwakarma et al., 2018), Pyras pashia leaves (Sharma et al., 2020), macrofungus Ganoderma lobatum (Yang et
Lantana camara is an evergreen shrub of Verbenaceae family, abundant in tropical and sub-tropical regions. It is widely found in India, Pakistan, Sri Lanka, Afghanistan, Myanmar, North and South America. The research aims to identify the viability of an adsorbent prepared with Lantana camara leaves to remove Zn (II) ions from wastewater, for which the five parameters pH, temperature, metal ion concentration, contact time, and biosorbent dose were altered to perform batch experiments. After statistical analysis of the batch experiment findings, isotherm models (e.g., Langmuir, Freundlich, and Temkin isotherms) and kinetic models (e.g., pseudo-first-order and pseudo-second-order kinetic studies) were applied to the experimental data. For thermodynamic characterization of the sorption process, the standard Gibbs free energy change, standard enthalpy change, and standard entropy change were also determined. The Lantana camara plant is infamous for suppressing the growth of other plants in its vicinity. Its use as a biosorbent might help in controlling its unrestrained and destructive growth. In this way, this research supports the concept of environmental sustainability by demonstrating the viability of employing Lantana camara as a cost-effective, natural bio-waste material for Zn (II) sorption.

Materials and methods

Biosorbent preparation

Lantana camara leaves were garnered from the immediate vicinity of Khatyari, Almora, Uttarakhand, India (29°35'43"N 79°38'55" E). These leaves were extensively washed with double distilled water to eradicate dirt particles and soluble pollutants and then dried in a hot air oven for 48 hours (Popular Traders S.N.-1680) at 333 K. They were then smashed and ground in a grinder to obtain the powdered form. The crushed biomass was activated for up to 24 hours at room temperature in 0.1 N HNO₃, then filtered and rinsed with double distilled water. The activated biomass was dried in a hot air oven at 333 K for 48 hours. It was passed through 63-micron sieves (240 BSS). The sieved biomass was then placed in an airtight bottle.

Preparation of adsorbate
A 1000 mg/L stock solution of Zn (II) ions was prepared by dissolving 4.376 g of ZnSO$_4$.7H$_2$O in 1000 mL of double-distilled water. 0.1 N HCl and 0.1 N NaOH were used to alter the pH of the working solutions. The pH of working solutions was found out using the Systronic 361 model of an electronic pH meter.

**Determination of pH$_{PZC}$ (Point of Zero Charge)**

The biosorbent LCLB’s point of zero charge, or pH$_{PZC}$, was determined using a sequence of 6 beakers, each 100 mL in volume, each containing a suspension of 1 g of biosorbent in 100 mL of double-distilled water, the pH of which had been initially adjusted using either 0.1 N HCl or 0.1 N NaOH to range from 2 to 7. These solutions were stirred in a rotatory flask shaker (Zexter S.N. -1685) for 48 h and the final pH of these solutions was determined using pH meter (Systronic 361 model). Lastly, a graph was drawn to depict the results as ΔpH v/s pH$_i$.

**Surface area and pore size analysis**

The surface area of the LCLB was obtained by using Brunauer, Emmett and Teller (BET) textural analysis. A prominent and well-known technique for figuring out the surface area, pore size distribution, and total pore volume of the adsorbent using BET is nitrogen adsorption. Using a nitrogen adsorption equipment, the LCLB’s nitrogen adsorption isotherms were estimated at 77.35 K (Quantachrome instruments version 5.21). The analyzed sample weighed around 0.03 g.

**Biosorption experiments**

pH, temperature, biosorbent dose, time of contact, and adsorbate concentration were all investigated in batch studies to examine how they affected metal ion removal. By adjusting the parameter under study while leaving the others constant, the ideal condition of each parameter was discovered. The experiments were carried out in conical flasks with a capacity of 250 mL and a working solution of 100 mL with a concentration of 10 mg/L. The filtered solution was digested with concentrated HNO$_3$ after being filtered using Whatman no. 42 filter paper. The whole biosorption process is depicted in Fig.1.
Fig. 1: A representative diagram of biosorption process for removal of Zn (II) ions using LCLB

An atomic absorption spectrophotometer was used to determine the final quantity in the digested solution (AAS, Thermo Scientific, U.S., Model: FLASH 2000) using equation (1):

\[ \text{Removal} \% = \frac{C_i - C_e}{C_i} \times 100 \]  

Where \( C_i \) is the starting metal ion concentration (mg/L) and \( C_e \) is the metal ion concentration (mg/L) at equilibrium.

The adsorption capacity/metal uptake is calculated using equation (2):

\[ Q_e = (C_i - C_e) \frac{V}{m} \]  

Where, \( C_i \) and \( C_e \) are the initial and final concentration of metal ions, \( V \) is the volume of solution in litre and \( m \) is the mass of biosorbent in gram.
Biosorption kinetics

Pseudo-first-order kinetic model

The linear form of this kinetic model is demonstrated in the form of equation (3) (Lagergren, 1898):

\[ \ln \left( Q_e - Q_t \right) = \ln Q_e - K_1 t \]  

Where \( Q_e \) is the concentration of metal ions adsorbed at equilibrium in mg/L while \( Q_t \) is at any time \( t \). \( K_1 \) indicates the rate constant of the pseudo-first-order kinetic model (min\(^{-1}\)).

Pseudo-second-order kinetic model

The straight line equation for this model can be expressed in the following way as in Eq. (4) (Ho and McKay 1999):

\[ t = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \]  

Where \( K_2 \) implies the rate constant for the pseudo-second-order kinetic model (g/mg/min) and all other terms have the previously stated meanings.

Biosorption isotherms

Langmuir adsorption model

This model is premised on a presumption that solutes are adsorbed in a monolayer onto the adsorbent’s surface with a definite number of identical binding sites and uniform adsorption energy (Langmuir, 1916). Langmuir adsorption model is expressed as follows:

\[ \frac{C_e}{Q_e} = \frac{C_e}{Q_{\text{max}}} + \frac{1}{K_L Q_{\text{max}}} \]  

Where \( C_e \) is the metal ion concentration at equilibrium (mg/L), \( Q_e \) is the number of metal ions removed (mg/g), \( K_L \) is Langmuir isotherm constant (L/mg) and \( Q_{\text{max}} \) is the maximum adsorption capacity (mg/g).

The interaction between metal ions and the adsorbent surface is further calculated by dimensionless constant i.e., separation factor (\( R_L \)). \( R_L \) is expressed as follows:

\[ R_L = \frac{1}{1 + K_L C_o} \]
Where $C_0$ is the initial amount of adsorbate (mg/L) and $K_L$ is the Langmuir constant (L/mg). The isotherm is favorable if $0 < R_L < 1$, unfavorable if $R_L > 1$, irreversible if $R_L = 0$ and linear if $R_L = 1$.

**Freundlich adsorption model**

This isotherm model consists of an empirical equation that proposes multilayer adsorption on the heterogeneous surface (Freundlich, 1907). It is expressed mathematically as follows:

$$\log Q_e = \frac{1}{n} \log C_e + \log K_F$$

Where, $K_F$ is the Freundlich isotherm constant for the adsorbent's adsorption capacity, while $n$ is an empirical value. If $1/n$ is between 0 and 1, the adsorption process is likely to be favorable.

**Temkin adsorption model**

The basis of Temkin isotherm relates with an assumption that due to adsorbent-adsorbate interactions, adsorption energy reduces linearly with surface coverage (Temkin and Pyzhev, 1940). It can be represented in linear form as follows:

$$Q_e = B_T \ln A + B_T \ln C_e$$

Where $A$ is the equilibrium binding constant (L/g), and $B_T$ is the Temkin constant associated with the heat of adsorption ($B_T = RT/b$, where $R = 8.314$ J/mol/K, $T$ is the absolute temperature, and $B_T$ is the heat of adsorption in J/mol).

**Thermodynamic study of adsorption**

Thermodynamic parameters i.e., a change in Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$), and entropy ($\Delta S^\circ$) were determined using the underneath equations:

$$\Delta G^\circ = -RT \ln K_c$$

$$K_c = \frac{Q_e}{C_e}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$
Where, \( R \) is the universal gas constant (8.314 J/mol/K), \( T \) is the temperature (K), \( Q_e \) is the concentration of adsorbed metal ions (mg/L), \( C_e \) is the metal ion concentration in solution (mg/L) and \( K_c \) is equilibrium constant.

**Desorption studies**

This research project also looked into desorption of Zn (II) ions from loaded LCLB. Three different chemical reagents including double distilled water, 0.1M HCl and 0.1M NaOH were assessed as eluents. The biosorption-desorption process was recycled four times in a row using the most efficacious effluent. Desorption experimentation was handled out using 100 mL conical flasks having 50 mL of eluent solution. The 1g of loaded biosorbent was suspended in the flask containing 50 mL eluent solution. The mixture was stirred at 170 rpm at 298±1.5K for 45 min. The biosorbent was separated by filtering the solution using Whatman 42 filter paper. The concentration levels of Zn (II) ions in the desorption solution were determined by Atomic Absorption Spectroscopy (AAS).

**Desorption capacity**

The desorption capacity of loaded biosorbent for desorption of adsorbed Zn (II) ions \( (Q_{e,\text{desorption}} \text{ (mg/g)}) \) is calculated by using the following equation (12):

\[
Q_{e,\text{desorption}} = \frac{V_d \times C_d}{m_d}
\]  

(12)

Where \( C_d \) is the Zn (II) ions concentration in a desorption solution (mg/L), \( V_d \) is the volume of desorption solution (L) and \( m_d \) is the mass of metal-loaded adsorbent (g).

**Desorption efficiency**

The percentage of Zn (II) desorbed from the loaded material is calculated as follows:

\[
\text{Desorption} \% = \frac{Q_{e,\text{desorption}}}{Q_{e,\text{adsorption}}} \times 100
\]  

(13)

Where \( Q_{e,\text{adsorption}} \) is the Zn (II) ions concentration loaded on the biosorbent before desorption calculated by equation (2).

**Statistical analysis**

The mean and standard error of data from at least three different experiments are displayed. The mean and standard error of data from at least three separate experiments is displayed. The adsorption results of using LCLB were analyzed by t-test (\( P<0.05 \)) comparing with the findings of controlled experiments. The experimental data were subjected to a single-factor analysis (One Way ANOVA) at a 5% of significance level to compare the
treatment means. The correlation coefficient ($R^2$) was used to assess the applicability of linear equations of isotherm and kinetic models using Microsoft Excel 2007 statistical tools (version Office XP, Microsoft Corporation, USA).

**Results and discussions**

**BET textural analysis**

The nitrogen adsorption experiments at liquid nitrogen temperature, 77.35 K, and the BET method of surface texture characterization were used to evaluate the surface area of the adsorbent. By multiplying the value of $V_m$ by the molecular surface area of $N_2$, the BET surface area was computed after the monolayer adsorption capacities were calculated using the BET equation (0.162 nm$^2$). The LCLB has average pore diameter and total pore volume of 15.48 and 0.052 cm$^3$ g$^{-1}$, respectively. It was determined that the adsorbent had a surface area of 35.327 m$^2$ g$^{-1}$.

**FT-IR spectroscopic characterization**

A Fourier transform infrared (FT-IR) spectrometer (Perkin Elmer, USA, Model: Spectrum 400) was used to identify and characterize the functional groups on the LCLB in the range 400-4000 cm$^{-1}$. The alteration in functional groups on the LCLB surface prior and afterward the sorption of Zn (II) ions is depicted in Fig. 2. Before adsorption, the peak at 3412.311 cm$^{-1}$ suggests the existence of the hydroxyl (-OH) group, 2928.043 cm$^{-1}$ indicates the existence of asymmetric alkyl –CH$_2$ and –CH stretching vibrations, 1642.681 cm$^{-1}$ indicates carbonyl (–HC=O) stretching vibrations, 1427.633 cm$^{-1}$ indicates ketonic (R$_2$C=O) group, 1067.305 cm$^{-1}$ represents C-O stretching of alcohols or even carboxylic acids and 643.775 cm$^{-1}$ aromatic amino acids (-NH$_2$ group). After adsorption, these peaks shift to 3404.103, 2930.506, 1645.143, 1430.916, 1062.380 and 638.030 cm$^{-1}$ respectively. The shifts in functional groups imply that these functional groups were involved in binding Zn (II) ions onto LCLB. The cell walls of the biomass are mainly made up of cellulose, hemicelluloses, and lignin which contain these functional groups that cause binding of the positively charged metal ions (Panneerselvam et al., 2011; Moghazy et al., 2019).
Fig. 2: FT-IR spectra of LCLB (a) before and (b) after adsorption of Zn (II) ions respectively

SEM analysis

Fig. 3 shows the surface morphological pattern of the biosorbent surface prior and post Zn (II) ions adsorption using a scanning electron microscope (SEM) (JEOL, Japan, Model: JSM 6100). The considered SEM images are of 100X magnification and it is visible that the Before the biosorption process, the biosorbent surface seems to have a number of distinct and asymmetrical vacant pores and craters; following the biosorption process, these vacant apertures get filled. It can be said that there is a significant affinity between Zn (II) ions and porous or rough biosorbent surface.
Fig. 3: SEM images of LCLB surface (a) before and (b) after adsorption of Zn (II) ions respectively

From the physicochemical properties analysis for the three adsorbents, it is observed that the adsorbents possess most of the desirable characteristics of an adsorbent.

**Effect of physico-chemical parameters on metal ion removal**

The parameters under study affect the removal of metal ions in different ways, the outcome of the study was analyzed by single-factor analysis as shown in Table 1. The critical differences (i.e., CD values) were found to be significant enough (more than 5% of significance level), which implied that the considered parameters had a significant effect on % removal efficiency of the biosorbent.
Table 1: Effect of various parameters on Zn (II) ions removal using LCLB (Single-factor analysis or One-way ANOVA)

<table>
<thead>
<tr>
<th>pH</th>
<th>$C_e$ (mg/L)</th>
<th>T (min)</th>
<th>$C_e$ (mg/L)</th>
<th>Dose (g)</th>
<th>$C_e$ (mg/L)</th>
<th>$C_i$ (mg/L)</th>
<th>$C_e$ (mg/L)</th>
<th>T(K)</th>
<th>$C_e$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>7.75±0.07</td>
<td>20</td>
<td>4.67±0.07</td>
<td>1</td>
<td>2.89±0.04</td>
<td>10</td>
<td>3.080±0.05</td>
<td>298</td>
<td>2.75±0.05</td>
</tr>
<tr>
<td>3</td>
<td>6.8±0.03</td>
<td>40</td>
<td>3.51±0.03</td>
<td>2</td>
<td>2.26±0.06</td>
<td>20</td>
<td>8.047±0.07</td>
<td>308</td>
<td>2.98±0.04</td>
</tr>
<tr>
<td>4</td>
<td>5.15±0.07</td>
<td>60</td>
<td>2.75±0.02</td>
<td>3</td>
<td>1.86±0.04</td>
<td>30</td>
<td>13.57±0.02</td>
<td>318</td>
<td>3.54±0.08</td>
</tr>
<tr>
<td>5</td>
<td>4.55±0.04</td>
<td>80</td>
<td>2.16±0.04</td>
<td>4</td>
<td>1.66±0.02</td>
<td>40</td>
<td>21.34±0.07</td>
<td>328</td>
<td>3.83±0.08</td>
</tr>
<tr>
<td>6</td>
<td>2.74±0.05</td>
<td>100</td>
<td>1.85±0.02</td>
<td>5</td>
<td>1.49±0.02</td>
<td>50</td>
<td>29.05±0.08</td>
<td>338</td>
<td>4.33±0.10</td>
</tr>
<tr>
<td>7</td>
<td>3.84±0.04</td>
<td>120</td>
<td>1.85±0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CD</td>
<td>0.173</td>
<td>0.133</td>
<td>0.140</td>
<td>0.208</td>
<td>0.241</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SE (m)</td>
<td>0.056</td>
<td>0.043</td>
<td>0.044</td>
<td>0.065</td>
<td>0.075</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

±Standard Error, SE (m) Standard Error Mean, CD Critical Difference

Also, t-test was performed between the experimental and controlled groups and the t-stat values were significantly greater than that of the P-values (Table 2), implying that using the biosorbents provided significant results in removal of heavy metals and the experimental work was on the right track.
Table 2: t-test values for the comparison between controlled and experimental groups using LCLB for biosorption of Zn (II) ions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>pH</th>
<th>Contact time</th>
<th>Biosorbent dose</th>
<th>Metal ion concentration</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-stat value</td>
<td>38.98</td>
<td>123.52</td>
<td>-</td>
<td>96.506</td>
<td>58.342</td>
</tr>
<tr>
<td>P-value</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
<td>-</td>
<td>&lt;0.0005</td>
<td>&lt;0.0005</td>
</tr>
</tbody>
</table>

Note: Since control experiments are those performed without using the biosorbent and compared with those performed with the biosorbent, therefore there are no t-test values in case of biosorbent dose as a parameter.

The experimental results in Table 1, showed that the LCLB provided the best results for biosorbent dose of 5 g when optimum pH was 6, the contact time was 45 minutes, initial adsorbate concentration was 10 mg/L at temperature 298±1.5 K. The experimental results of contact time variation are rationalized with the appropriate kinetic models. Similarly, the results of variation in initial metal ion concentration are relatable with biosorption isotherms while the results of temperature variation are relatable with the evaluation of thermodynamic parameters.
Fig. 4: Effect of (a) pH, (b) contact time, (c) biosorbent dose and (d) initial metal ion concentration on the Zn (II) ions % removal efficiency of LCLB

Effect of pH and pH_{PZC}

By varying the pH from 2 to 7, for a contact time of 45 min, initial metal ion concentration of 10 mg/L using 1 g of biosorbent dose at 298±1.5 K temperature and 170 rpm of stirring speed; the effect of pH on the percent removal of Zn (II) ions by LCLB was investigated (Table 1). The percent removal efficiency of Zn (II) increased from pH 2-6 (from 22.43% to 72.6%) and subsequently decreased from pH 6 to pH 7 (Fig. 4 (a)). It is owing to the high abundance of H^+ ions at lower pH values, which have better mobility than heavy metal ions and connect to biosorbent active sites before metal ions. However, as pH is raised, the probability of creating metal hydroxide complexes increases, reducing the number of free-moving metal ions (Redha 2020). Thus, there is always an
optimum pH value (pH 6 in present case) at which the % removal is the maximum. Therefore, all other batch experiments were performed at an optimum pH value of 6. (Ahmady-Asbchin et al., 2014) also found pH 6 as an optimum pH while using a living bacteria *Pseudomonas aeruginosa* as a biosorbent for the removal of Zn (II) from wastewater.

![Fig. 5: Determination of point of zero charge (pH\textsubscript{PZC})](image)

It was ascertained that pH\textsubscript{PZC}, or pH at point of zero charge, is a significant characteristic to show the biosorption ability on the surface of the biosorbent and designates the interaction between the sorbent and the sorbate. A substrate's ability to adsorb positively charged heavy metals depends on this factor. At pH < pH\textsubscript{PZC}, the surface of the biosorbent is positively charged and at pH > pH\textsubscript{PZC}, the surface of the biosorbent is negatively charged. In this study, the pH\textsubscript{PZC} was found to be 3.0 (Fig. 5) and it is noteworthy that LCLB has a significant % removal efficiency beyond pH 3, which is caused by the biosorbent surface's substantial negative charge for pH > 3, which draws the positively charged metal ions.

**Effect of biosorbent dose**

The percentage of adsorbed Zn (II) ions increased from 71.06% to 85.06 % (at optimum conditions of pH 6, contact time of 45 min, initial metal ion concentration of 10 mg/L, the temperature of 298±1.5 K ) when the biosorbent dose was increased from 1 g to 5 g (Fig. 4 (c) and Table 1). This is relatable because increasing the biosorbent dose increases the number of functional sites for metal ions to chelate with (Redha et al., 2020; Giri et al., 2021). Negi et al. (2021) also found the similar results while using *Tectona grandis* leaves as a biosorbent for removing Zn (II) ions from wastewater. It is worth noting, however, that large biosorbent doses cause aggregation of
active binding sites on the biosorbent surface, which could explain the smaller increment in the removal percentage in the later phase (El-Araby et al., 2017).

**Effect of contact time and biosorption kinetics**

Extending the contact time from 20 min to 80 min resulted in a significant rise in the percent removal (53.3 % to 81.5 %); however, it was monotonous on increasing the contact time from 100 min to 120 min with 79% of optimum removal efficiency (Fig. 4 (b)). The other parameters were fixed at optimum pH of 6, biosorbent dose of 1 g, initial metal ion concentration of 10 mg/L, 298±1.5 K temperature, and 170 rpm of stirring speed (Table 1). Thus, the adsorption process attained equilibrium after 100 min on using LCLB as a biosorbent. (Ahmady-Asbchin et al., 2014) also found similar pattern and the biosorption process attained the equilibrium at 90 min of the contact time while using *Pseudomonas aeruginosa* as a biosorbent. Typically, contact time refers to the duration allotted for the biosorption process to occur (Redha 2020). The results suggested that the active sites were rapidly filled in the early phase, while there were fewer active sites available for subsequent adsorption on the biosorbent surface and eventually, the biosorbent surface gets saturated (Prasad et al., 2013; Sharma et al., 2020; Giri et al., 2021).

Analysis of biosorption kinetics was performed by withdrawing samples at selected time intervals ranging from 20, 40, 60, 80, 100 and 120 min and the results were examined with pseudo-first-order and pseudo-second-order kinetic models as shown in Fig. 6 and Table 3. The correlation coefficient ($R^2$) value for the pseudo-first-order kinetic model (0.970) was lesser than that of the pseudo-second-order kinetic model (0.998). In the same way, the calculated value of $Q_e$ (9.345 mg/g) and the experimental value of $Q_e$ (8.15 mg/g) were close to each other for the pseudo-second-order kinetic model while there was a significant difference between the two in case of the pseudo-first-order kinetic model because the $Q_e$ (experimental) was 6.520 mg/g while $Q_e$ (calculated) was 9.345 mg/g. Therefore, pseudo-second-order kinetic model was found to be the suitable one with the experimental data of contact time variation.
**Fig. 6:** (a) Pseudo-first-order and (b) Pseudo-second-order kinetic models for removal of Zn (II) ion using LCLB.

**Table 3:** Kinetic parameters for biosorption of Zn (II) on LCLB (pH: 6.0; contact time: 20-120 min; biosorbent dose: 1 g; concentration: 10 mg/L; temperature: 298 ± 1.5 K, stirring rate: 170 rpm)

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_e$ (mg/g)</td>
<td>$K_1$ (min$^{-1}$)</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>6.520</td>
<td>0.036</td>
</tr>
</tbody>
</table>
Several studies suggested the better applicability of pseudo-second-order kinetic model e.g., Zn (II) biosorption using waste *Streptomyces fradiae* biomass also followed the pseudo-second-order kinetics (Kirova et al., 2015).

**Effect of initial metal ion concentration and biosorption isotherms**

The % removal decreased from 69.2% to 41.89% on increasing the metal ion concentration from 10 mg/L to 50 mg/L (Fig. 4 (c) and (Table 1). All the variable parameters were in their respective optimum values. As the metal ion concentration rises, all of the active sites eventually fill, leaving no room for the remaining metal ions to fill at higher metal ion concentrations, resulting in a fall in overall percent removal (El-Araby et al., 2017).

The linear plots of Langmuir, Freundlich and Temkin adsorption isotherms are given in Fig. 7(a). The Langmuir isotherm constants $K_L$ and $Q_{max}$ were calculated from the intercept and slope of the linear equation (5). The maximum adsorption capacity ($Q_{max}$) was 2.778 mg/g (Table 4). The $R_L$ values corresponding to the Langmuir isotherm were 0.497, 0.331, 0.248, 0.198, 0.165 for initial metal ion concentrations of 10, 20, 30, 40, 50 mg/L respectively i.e., between 0 and 1, which implied favorable adsorption of Zn (II) ions (Tiwari et al., 2017; Giri et al., 2021).
Fig. 7: (a) Langmuir, (b) Freundlich and (c) Temkin adsorption isotherms for Zn (II) adsorption on LCLB

Table 4: Langmuir, Freundlich and Temkin isotherm parameters for Zn (II) ions biosorption on LCLB

<table>
<thead>
<tr>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
<th>Temkin Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_L (L/mg)</td>
<td>Q_max (mg/g)</td>
<td>R^2</td>
</tr>
<tr>
<td>R^2</td>
<td>K_F (mg/g)</td>
<td>1/n</td>
</tr>
<tr>
<td></td>
<td>B_T (J/mol)</td>
<td>A (L/g)</td>
</tr>
<tr>
<td>0.1017</td>
<td>2.778</td>
<td>0.996</td>
</tr>
<tr>
<td>0.412</td>
<td>0.498</td>
<td>0.984</td>
</tr>
<tr>
<td>0.630</td>
<td>0.929</td>
<td>0.993</td>
</tr>
</tbody>
</table>
Similarly, Fig. 7(b) represents the plot for Freundlich isotherm for which the constants $K_F$ and $n$ were calculated from the intercept and slope of the plot drawn considering Eq. (7). The value of $1/n$ lies between 0 and 1 (0.498), favoring the biosorption. For Temkin isotherm, the constants $B_T$ and $A$ were calculated from the straight-line graph of $Q_e$ versus $\ln C_e$ plotted considering Eq. (8). Since, $B_T = -\Delta H$ (corresponds to the heat of adsorption), which consequently indicates that the higher the value of $B_T$, the more exothermic the process will be (Zinicovscaia et al., 2020). In the current study, $B_T = 0.630$ J/mol, therefore, the biosorption involves an exothermic process. Although both models Langmuir and Temkin isotherms appear to be a good fit for the experimental outcomes, as shown in Table 3, Langmuir provides the best fit with a correlation coefficient of 0.9962. This implies a monolayer adsorption of Zn (II) ions on the LCLB surface. A comparative study of the maximum adsorption capacities ($Q_{\text{max}}$) of various biosorbents was done for Zn (II) ions adsorption and LCLB was found to be significant. Table 5 represents a comparison of adsorption capacities of Zn (II) using other biosorbents.

**Table 5:** Zn (II) ions adsorption capacity of various biosorbents

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>Maximum adsorption capacity (mg/g)</th>
<th>Isotherm model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Artocarpus altilis</em> seed husk</td>
<td>90.91</td>
<td>Freundlich</td>
<td>(Godfrey et al., 2018)</td>
</tr>
<tr>
<td><em>Streptomyces fradiae</em> biomass</td>
<td>61.09</td>
<td>Langmuir</td>
<td>(Kirova et al., 2015)</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em> (living bacteria)</td>
<td>46.1</td>
<td>Freundlich</td>
<td>(Ahmady-Asbchin et al., 2014)</td>
</tr>
<tr>
<td>Sea nodule residue</td>
<td>21.09</td>
<td>Langmuir</td>
<td>(Agrawal et al., 2004)</td>
</tr>
<tr>
<td><em>Tectona grandis</em> leaves</td>
<td>16.42</td>
<td>Langmuir</td>
<td>(Kumar et al., 2006)</td>
</tr>
<tr>
<td>Untreated rice husk</td>
<td>12.41</td>
<td>Langmuir</td>
<td>(Zhang et al., 2013)</td>
</tr>
<tr>
<td><em>Tectona grandis</em> leaves</td>
<td>4.31</td>
<td>Langmuir</td>
<td>(Negi et al., 2022)</td>
</tr>
</tbody>
</table>
Effect of temperature and evaluation of thermodynamic parameters

The effect of temperature on % removal was examined at temperatures 298 K, 308 K, 318 K, 328 K, 338 K. It continuously decreased from 72.46% to 56.66% on increasing the temperature (Fig. 8 (a) and Table 1). During these experiments the optimum pH value was 6, the contact time was 45 minutes with a biosorbent dose of 1 g, initial metal ion concentration of 10 mg/L at a stirring speed of 170 rpm.

**Fig. 8:** (a) Effect of temperature on % removal of Zn (II) on LCLB and (b) Plot of ln $K_c$ versus 1/T for thermodynamic parameters
Depending on the process, temperature can have a positive or negative impact on biosorption (Redha, 2020). The decline in % removal efficiency with the temperature rise suggests that probably the biosorptive interactions between the metal ions and the biosorbent surface weakened due to increasing temperature and therefore, the process should be exothermic (Sharma et al., 2021). The negative value of $\Delta H^\circ$ (-14.782 KJ/mol) also supported this fact (Fig. 8 (b) and Table 6). If the standard enthalpy change of biosorption ranges between 2.1 and 20.9 KJ/mol, then the process corresponds to physisorption, whereas it is considered as chemisorption if enthalpy change ranges between 20.9 and 418 KJ/mol (Prasad et al., 2013). Therefore, the biosorption of Zn (II) ions on LCLB surface can be demonstrated as physical adsorption. The negative $\Delta G^\circ$ outcomes demonstrate that the sorption process occurred spontaneously (Table 6).

Table 6: Thermodynamic parameters for Zn (II) ions biosorption on LCLB

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>T(K)</th>
<th>ln Kc</th>
<th>$\Delta G^\circ$ (KJ/mol)</th>
<th>$\Delta H^\circ$ (KJ/mol)</th>
<th>$\Delta S^\circ$ (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>0.964</td>
<td>-2.389</td>
<td>-14.782</td>
<td>-41.320</td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>0.856</td>
<td>-2.194</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>0.601</td>
<td>-1.590</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>328</td>
<td>0.476</td>
<td>-1.300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>338</td>
<td>0.269</td>
<td>-0.0757</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notably, the standard Gibbs free energy change decreases on increasing the temperature, which defines that the biosorption process becomes less spontaneous at higher temperatures. The negative value of $\Delta S^\circ$ (-41.320 J/mol/K) indicates that biosorption of Zn (II) ions followed an associative mechanism at the metal ion-biosorbent interface and therefore the standard entropy decreased on the LCLB surface (El-Araby et al., 2017).

Probable mechanism of biosorption process
Typically, the biosorption process moves forward in three different ways: 1) intracellular accumulation, 2) precipitation on cell’s surface and 3) extracellular precipitation. Any one of these three sorption paths, or all three at once, can be followed by a specific biosorption process. Microorganisms exhibit intracellular accumulation, whereas biosorption, which utilizes dead biomass as an adsorbent, takes place at cell surfaces using a variety of mechanisms, including ion exchange, complexation, chelation, physisorption, micro-precipitation, and chemical adsorption (Vilvanathan and Shanthakumar 2018; Freitas et al. 2019). Actually, cellulose, hemicelluloses, and lignin are the key components of such biomaterials; these substances contain a variety of functional groups that promote ion-exchange and the formation of complexes with metal ions (Anastopoulos et al., 2019). Cell walls of microbial biomass provide evidence of this mechanism, referred to as surface sorption, in process. When microorganisms create chemicals that facilitate deposition in the presence of hazardous metals, cellular metabolism-dependent precipitation occurs (de Freitas et al. 2019). In contrast, precipitation that is independent of metabolism takes place following a chemical reaction between the metal and the cell surface.

From FT-IR spectra, it is obvious that the various functional groups were involved in the adsorption process, indicating the involvement of various chemical mechanisms such as ion exchange, complexation or chelation (Fig. 9). However, the thermodynamic outcomes indicate that the biosorption process involved physical interactions (Vander Waal’s and strong electrostatic interactions majorly as the value of $\Delta H = -14.782$ kJ/mol) (Hernández-Francisco et al., 2020). The applicability of pseudo-second-order kinetic model indicates the probability of chemisorption as a major biosorption mechanism. Overall, we can say that biosorption process might involve precipitation on cell’s surface and extracellular precipitation involving both physical and chemical interactions between metal ions and biosorbent (El-Araby et al., 2017; de Freitas et al., 2019; Negi et al., 2021).
Fig. 9: Probable mechanisms for adsorption of Zn (II) ions on LCLB

Desorption Studies

From the desorption studies using distilled water, 0.1M NaOH and 0.1M HCl as eluents, it was observed that both distilled water and sodium hydroxide have a weak potential to desorb the adsorbed Zn (II) ions from both the biosorbents. The 0.1M hydrochloric acid (HCl) was the most appropriate eluent for the removal of Zn (II) ions among all three eluents as shown in Table 7.

Table 7: Desorption % of LCLB for desorption of Pb (II) ions using different eluents
<table>
<thead>
<tr>
<th>Eluents</th>
<th>Desorption efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double-Distilled water (H₂O)</td>
<td>6.33±0.82</td>
</tr>
<tr>
<td>Sodium hydroxide (NaOH)</td>
<td>4.08±0.39</td>
</tr>
<tr>
<td>Hydrochloric acid (HCl)</td>
<td>89.05±0.79</td>
</tr>
</tbody>
</table>

Fig. 10: Desorption % of LCLB using 0.1 M HCl to elute Zn (II) ions

The reusability of LCLB was further investigated by four consecutive cycles of adsorption-desorption processes using 0.1M HCl as an eluent. (Embaby et al., 2022) also found HCl as a better eluent compared to other eluents such as H₂SO₄, HNO₃, NaCl or NaOH. For LCLB, % desorption was 89.05% for first cycle, 79.74% for second cycle, 58.87% for third cycle and 47.83% for the fourth cycle (Fig. 10). It may be deduced that LCLB can be utilized effectively for up to 2 cycles with a lesser drop in desorbing capability between the first and second cycles as compared to a significant drop between second and third cycles. The decreased desorption % can be attributable to a number of factors, including the material destruction brought on by low pH levels and distended biosorbent due to presence of 0.1 M HCl in subsequent cycles.
Conclusion

The present study revealed that LCLB has large surface area value, micro porous structure, and various functional groups which are indicative of its excellent properties, highlighting its underlying adsorption capability. The outcomes of batch adsorption experiments showed how each variable had a significant impact on the uptake of metal ions. The optimum value of pH was found to be 6 for maximum % removal. The optimum capacity for monolayer adsorption was 2.778 mg/g. The best-fitting isotherm and kinetic models with experimental findings were the Langmuir isotherm model and pseudo-second-order kinetic model respectively. The process of biosorption was affirmed to be spontaneous (\(\Delta G^\circ = (-)\text{ve}\)), exothermic (\(\Delta H^\circ = -14.782 \text{ KJ/mol}\)) and followed an associative mechanism (\(\Delta S^\circ = -41.320 \text{ J/mo/K}\)). Participation of functional groups (FT-IR spectroscopic analysis), suitability of pseudo-second-order kinetic model, value of standard enthalpy change and decrease in % removal efficiency with increasing temperature during the biosorption process, implied the involvement of both the chemical and physical adsorption mechanisms. Also, LCLB was found to be recyclable enough for two cycles using hydrochloric acid as an eluent. Since *Lantana camara* is an undesirable weed, using it to produce biosorbent to treat wastewater can also be a prime illustration of waste management.

Declarations

Ethics approval and consent to participate

This article does not contain any research with human participants nor animals performed by any of the authors which violate ethical standards.

Consent for publication

All authors listed in this manuscript agree to be published.

Availability of data and materials

Although the manuscript contains data representation itself, additional data will be made available on reasonable request.

Competing interests

The authors declare no competing interests.

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Authors’ contributions

A. N. conceptualized, investigated, curated the data, wrote the original draft and edited the manuscript. S.K.J. supervised and validated the work and N.S.B. did supervision, validation and visualization.

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