Central Composite Design for Adsorption of Pb(II) and Zn(II) Metals on PKM-2 *Moringa oleifera* Leaves

Neethu Jayan, Laxmi Deepak Bhatlu M,* and Saufishan Thalikassery Akbar

**ABSTRACT:** Biosorption is a very effective technique to eliminate the heavy metals present in the wastewater that utilize nongrowing biomass. The adsorption ability of the Periyakulam-2 (PKM-2) variety of *Moringa Oleifera* leaves (MOLs) to eliminate Pb(II) and Zn(II) ions from an aqueous solution was examined in this work. Fourier transform infrared (FTIR) spectroscopy, field-emission scanning electron microscopy, energy-dispersive X-ray (EDX) analysis, X-ray powder diffraction, and Brunauer–Emmett–Teller methods were used to characterize the PKM-2 variety of MOLs. The set of variables consists of the metal ion initial concentration, a dosage of the adsorbent, and pH were optimized with the help of the response surface methodology to get maximum metal removal efficiency of lead and zinc metals using the PKM-2 MOL biosorbent. A maximum Pb(II) removal of 95.6% was obtained under the condition of initial concentration of metal ions 38 mg/L, a dosage of the adsorbent 1.5 g, and pH 4.7, and a maximum zinc removal of 89.35% was obtained under the condition of initial concentration of metal ions 70 mg/L, a dosage of the adsorbent 0.6 g, and pH 3.2. The presence of lead and zinc ions on the biosorbent surface and the functional groups involved in the adsorption process were revealed using EDX and FTIR analysis, respectively. The adsorption data were evaluated by employing different isotherm and kinetic models. Among the isotherm models, Langmuir’s isotherm showed the best fit and maximum adsorption capacities are 51.71 and 38.50 mg/g for lead and zinc, respectively. Kinetic studies showed accordance with the pseudo-second-order model to lead and zinc metal adsorption. Thermodynamic parameters confirmed (ΔG° < 0, ΔH° < 0, and ΔS° > 0) that the sorption mechanism is physisorption, exothermic, spontaneous, and favorable for adsorption. The results from this study show that the MOL of the PKM-2 type is a promising alternative for an ecofriendly, low-cost biosorbent that can effectively remove lead and zinc metals from aqueous solutions.

1. **INTRODUCTION**

Discharges from industries consisting of organic and inorganic pollutants are the main source of environmental pollution. These substances are harmful to people, animals and their habitats, and the environment.¹ Heavy metals are one of these pollutants which are poisonous and hazardous to humans and other living species.² These heavy metals are nondegradable and bioaccumulate through the food chain, resulting in alteration of their metabolism.³ The World Health Organization (WHO) categorized nickel (Ni), mercury (Hg), lead (Pb), arsenic (As), chromium (Cr), zinc (Zn), cadmium (Cd), and copper (Cu) under metals that have formidable concern.⁴ Many of these heavy metals are dangerous, making it necessary to monitor and maintain their existence under the permissible limit.⁵ Zinc is a fundamental micronutrient, but excess consumption through ingesting zinc-contained food and water and inhaling zinc vapors results in system dysfunction, pancreatic issues, high-density cholesterol, and anemia. It is reported that the Bureau of Indian Standards suggested that 5 mg/L is the permissible level of zinc in drinking water.⁶ Neural toxicity, dizziness, depression are some significant effects of lead in human beings. The WHO has restricted its maximum concentration in drinking water to 0.01 mg/L as lead toxicity also results in kidney-, liver-, and brain-related issues.⁷ To mitigate the discharge of lead from industrial effluents, which is the primary source of lead, the Environmental Regulatory Authority of India has limited lead concentration in effluents as 1.0 mg/L before disposal.⁸ The legal constraints on the disposal of effluents from industries and of environmental concerns require economically viable heavy-metal removal methods apart from the uneconomical conventional methods. The conventional methods, including ion exchange, precipitation, ultrafiltration, reverse osmosis, evaporation, electro-

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plating, and membrane processes, are economically not viable due to toxic waste generation, incomplete removal of heavy metals, high energy, and treatment cost. Alternatively, biosorption attained attention due to the low cost and no additional energy requirement, minimal chemical and biological sludge generation, regeneration of the biosorbent, and high efficiency in heavy metal removal.

Biosorption is a method that uses nongrowing biomass with a high quantity of lignin and cellulose, such as leaves, flowers, pods, and barks, as a biosorbent to bind and concentrate selected ions or other molecules from aqueous solutions. Recent studies focus on employing biomass to eliminate heavy metals effectively from effluents. Various biosorbents that have previously been shown to be effective for heavy metal removal are *Urtica dioica* leaves, *Curcuma longa* leaf powder, brewed tea waste, *Laurus nobilis* leaves, *Citrus grandis* (pomelo) leaves, tamarind fruit shells, lemon, bean and artichoke shells, banana biochar, *Moringa oleifera* seeds, leaves of *Corchorus olitorius*, *Saccharum bengalense*, durian peels, rose biomass, cellulose metallothionein, *Peganum harmala* seeds, *M. oleifera* pods, eggshells, coconut tree sawdust (CTS), and sugarcane bagasse. These sorbents have a good affinity toward positively charged heavy metals. *M. oleifera* is a drought-resistant tropical nutritionally rich plant with high antiviral, anti-inflammatory, and antifungal properties. *M. oleifera* tree, also known as the miraculous tree, is easily available in most places and has many medical applications. The significant properties of *M. oleifera* biomass for water treatment are analyzed and utilized for the heavy metal remediation using the adsorption process.

The ability of *M. oleifera* to eliminate heavy metals has already been reported in many studies. Sajidu et al. reported 92% removal of lead, whereas Ab Aziz et al. reported 81% lead removal using unmodified *M. oleifera* seeds. Bhatti et al. reported 90% removal of zinc using *M. oleifera* biomass. Tavares et al. determined the biosorbent potential of *M. oleifera* parts such as husk, seeds, and pods for removing lead from contaminated water and reported efficiencies of 98.3, 99.4, and 96.6%, respectively, in the literature. Reddy et al. utilized chemically modified *M. oleifera* leaves for lead removal, which produced 91% efficiency. Imran et al. used unmodified *M. oleifera* leaves to remove lead from contaminated water, which has reported 98.6% lead removal efficiency obtained at a high lead concentration (160 ppm).

Periyakulam-2 variety of *M. oleifera*, abbreviated as PKM-2, is an improved annual *Moringa* variety released by the Horticultural College and Research Institute of Tamil Nadu Agricultural University, India, by breeding programs. In this study, we assessed the ability of the PKM-2 variety of unmodified *M. oleifera* leaves, which avoid the extra cost and effort required for the modification of the biosorbent, to remove lead and zinc at a lower concentration, less than 100 ppm, from aqueous solution. To the best of our knowledge, the unmodified *M. oleifera* leaves of the PKM-2 variety have not been utilized to remove heavy metals from aqueous solutions so far.

Response surface methodology (RSM) is a statistical method for extracting and modeling the influencing parameters, getting optimum conditions, and validating those parameters. A quadratic model was designed using the Design-Expert software (version 13) to determine the optimum values of influencing parameters. We employed central composite design (CCD) under RSM to explore the influence of the three factors: initial concentration of metal ions, a dosage of the biosorbent, and pH on the response and obtained the optimum condition of the biosorption process. Field-emission scanning electron microscopy—energy-dispersive X-ray (FESEM-EDX) spectroscopy, XRD, Fourier transform infrared (FTIR) spectroscopy, and Brunauer–Emmett–Teller (BET) analysis were used to analyze the structure of the biosorbent and confirm the adsorption of heavy metals understudy on the surface of the biosorbent. Equilibrium, kinetic, and thermodynamic studies for the adsorption of lead and zinc on the biosorbent from aqueous solution was also conducted in this study.

### 2. RESULTS AND DISCUSSION

#### 2.1. PKM-2 *M. oleifera* Leaves: Characteristics.

##### 2.1.1. Powder X-ray Diffraction Analysis

Figure 1. XRD pattern of PKM-2 *Moringa oleifera* leaves (before adsorption and after adsorption).
Figure 1 showed weak and unresolved peaks, indicating the predominance of amorphous nature. The biosorption process benefited from this amorphous nature of the biosorbent, which helps the metal to penetrate the surface quickly. According to Reddy et al., a high amount of lignin, cellulose, and tannin provides an amorphous nature to the biosorbent.35 The XRD patterns after the adsorption of Pb(II) ions and Zn(II) ions on the PKM-2 *M. oleifera* leaves are shown in Figure 1. There is a notable difference between the XRD patterns of PKM-2 *M. oleifera* leaves and PKM-2 *M. oleifera* leaves after the adsorption of Pb(II) ions and Zn(II) ions, respectively. The XRD patterns showed an increase in the peak intensity after the Pb(II) and Zn(II) ion adsorption, which may be due to the deposition of heavy metals or due to the specific interactions that have taken place.40 Pb(II) ions adsorbed on the biosorbent produced new peaks at 35° and 38°. After the adsorption of Zn(II) ions, there was the disappearance of peaks at 2θ = 30, 37, 39, 47, and 59°, and some new peaks appeared at 2θ = 35, 38, and 52°. This variation in the peak intensity occurred due to the metal ions changing the cellulose structure through linking functional groups on the biosorbent.41 Similar peaks showed around 2θ = 14, 21, 24, 29, and 43° for PKM-2 *M. oleifera* leaves and the biosorbent loaded with lead and zinc ions, probably associated with the presence of proteins and cellulose.42 The average size of the biosorbent before and after adsorption was determined using Scherer’s eq 1

\[ d = \frac{0.89\lambda}{\beta \cos \theta} \]  

(1)

where \( \lambda \) (1.54 Å) is the X-ray wavelength, \( \beta \) is the diffraction line full width at half-maximum, and \( \theta \) is the diffraction angle. The average size of the PKM-2 *M. oleifera* leaf powder was determined, and it was 33.6 nm.43 The average size of the biosorbent after adsorption showed a considerable increase in size. The average size of *M. oleifera* leaves after the adsorption of lead was found to be 42.8 nm and after the adsorption of zinc was 52.9 nm.

**2.1.2. FESEM Analysis.** The surface morphology and elemental composition of PKM-2 *M. oleifera* leaves before and after the adsorption of lead and zinc were analyzed by FESEM and EDX analysis. FESEM images showed the surface of PKM-2 *M. oleifera* leaves before adsorption to be rough and irregular in shape, with broken edges displayed in Figure 2a. Bangaraiah et al. reported that these irregular surface structures provide a good surface for heavy metal adsorption.44 After the adsorption of lead and zinc on the biosorbent, FESEM images in Figure 2b,c showed some changes on the biosorbent surface, which signifies the adsorption of these heavy metals. Flake-like deposits formed on the biosorbent surface after contact with Pb(II) ions and...
interactions with the Zn(II) ions made the biosorbent surface smooth. After the adsorption of Pb(II) and Zn(II), the surface of the biosorbent became bright and smooth likely due to the physicochemical interaction between the target metals and functional groups on the biosorbent surface. The elemental composition of PKM-2 M. oleifera leaves before and after adsorption process to identify the mechanism. FTIR analysis was done for PKM-2 Zn(II) ions are important to understand the possible sorption mechanism. The elemental composition of PKM-2 M. oleifera leaves was identified using EDX analysis. Figure 2g–i shows the elemental composition of PKM-2 M. oleifera leaves and after the adsorption of Pb(II) and Zn(II) ions. Elemental composition for PKM-2 M. oleifera leaves displayed by the EDX spectrum (Figure 2g) consists of carbon and oxygen as major elements and potassium, calcium, and magnesium as minor elements. The EDX spectrum recorded after Pb(II) and Zn(II) ions in the EDX pattern for the lead- and zinc-loaded PKM-2 M. oleifera leaves MOL, respectively. The EDX spectrum recorded after lead and zinc adsorption did not show the presence of potassium and calcium elements while showing the reduction in the weight percentage of magnesium. This result signifies the ion exchange mechanism of these metals present in the PKM-2 MOL with the target metals. The EDX spectrum recorded after adsorption of lead and zinc showed the characteristic peaks for Pb(II) approximately at 0.2, oxygen at 0.5, and magnesium at 1.2 keV. This confirmed Pb(II) and Zn(II) binding to the surface of PKM-2 M. oleifera leaves.

2.1.3. FTIR Analysis. The functional groups on the surface of PKM-2 M. oleifera leaves and interactions with Pb(II) and Zn(II) ions are important to understand the possible sorption mechanism. FTIR analysis was done for PKM-2 M. oleifera leaves before and after the adsorption process to identify the characteristic functional groups and shown in Figure 3. Ali et al. reported that the leaves, seeds, flowers, pods, and barks contain large lignin, and cellulose has a great affinity toward positively charged heavy metals. The bands observed around 3085–2980 cm⁻¹ indicate hydroxyl groups and –NH groups, which signify protein and fatty acids in the biosorbent. The absorbance peak at 2871 cm⁻¹ indicates C–H bonds that characterize the lignocellulosic materials and protein present in the biomass. The absorbance peak at 1701 cm⁻¹ was identified as the carboxyl group, and the bands that appeared around 1697–1030 cm⁻¹ were assigned to the N–H stretching band of amino groups, and carboxylic acid characterized proteins present in the Moringa samples. Peaks observed at 1246 cm⁻¹ indicate C–N stretching of amino groups. The absorbance peaks at 636 cm⁻¹ show the presence of C–O vibrations, which are the characteristics of the lignin structure of PKM-2 M. oleifera leaves. The peak observed at 3734 cm⁻¹ and the bands observed around 3085 cm⁻¹ indicate the presence of hydroxyl groups and the –NH group. These functional groups are present in the protein and fatty acid structure in the PKM-2 M. oleifera leaves. The absorbance peak at 2871 cm⁻¹ indicates C–H bonds that characterize the lignocellulosic materials and protein present in the biomass. The absorbance peaks observed between 2400 and 1697 cm⁻¹ were identified as the carboxyl group and the N–H stretching band of amino groups, and carboxylic acid characterizes proteins present in the Moringa leaves. Peaks observed at 1246 cm⁻¹ indicate C–N stretching of amino groups. The absorbance peaks at 552 cm⁻¹ show the presence of C–O vibrations, which are the characteristics of the lignin structure of PKM-2 M. oleifera leaves. The data obtained from the FTIR spectrum showed differences in the absorbance peaks of PKM-2 M. oleifera leaves after adsorption of Pb(II) and Zn(II) ions. After the lead adsorption, the peaks expected for the biosorbent shifted to –OH and –NH (3697–3071 cm⁻¹), C–H (2846 cm⁻¹), carbonyl group (1757 cm⁻¹), C–N (1254 cm⁻¹), and C–O (589 cm⁻¹). The biosorbent loaded with zinc showed a shift in the expected peaks OH and –NH (3699–3067 cm⁻¹), C–H (2833 cm⁻¹), C–N (1260 cm⁻¹), and C–O (504 cm⁻¹). Absorbance peaks observed between 2400 and 1697 cm⁻¹ were less intensified, and some peaks disappeared after the adsorption of metal ions, implying the role of the carboxyl group, carboxylic acid, and the N–H stretching band of amino groups in the adsorption process. The interaction between functional groups present in PKM-2 M. oleifera leaves and the heavy metals.
under study causes variation in peak values.  

From the above results, it is evident that the functional groups that played an essential role in the adsorption of lead and zinc using PKM-2  

M. oleifera leaves are NH, −OH, C−H, −O−C, and −C═O.

2.1.4. BET Analysis. To measure the BET surface area and pore volume distribution, the BET method was used. The leaves of PKM-2 M. oleifera have a specific surface area of 12.289 m² g⁻¹ and a pore volume of 0.1879 cm³ g⁻¹. The average pore diameter was determined using the density functional theory (DFT) technique and was found to be 1.37 nm, as shown in Figure 4a. Based on the International Union of Pure and Applied Chemistry isotherms, the N₂ adsorption−desorption isotherm (shown in Figure 4b) for the sample followed type IV isotherms and was characterized as a mesoporous structure of the adsorbent.

2.2. Optimization of Process Parameters Using RSM. The interactive outcome of three independent variables, such as initial metal concentration, biosorbent dosage, and pH for removing Pb(II) ions and Zn(II) ions, was studied based on the 20 experiments performed. CCD had developed a quadratic model that connects adsorption efficiency and independent variables. A second-order polynomial equation assessed the interaction between variables and response. The empirical model describing the relationship between adsorption efficiency and independent variables is presented in eqs 2 and 3.

\[
R \% \text{ of Pb(II)} = 77.08 + 0.227A + 7.713B + 3.618C \\
- 0.028AB - 0.0117AC - 0.0074BC \\
- 0.0017A^2 - 2.265B^2 - 0.333C^2
\] (2)

\[
R \% \text{ of Zn(II)} = 78.35 + 0.1905A + 11.665B - 1.349C \\
- 0.292AB + 0.00312AC - 0.0342BC \\
+ 0.00128A^2 - 1.905B^2 + 0.0732C^2
\] (3)
where $R$ = the removal efficiency, $A$ = concentration (ppm), $B$ = dosage (g), and $C$ = pH. The observed and predicted values for the metal removal efficiencies are shown in Table 1, and the analysis of variance (ANOVA) for lead and zinc ions removal is provided in Table 2. The statistical significance of the quadratic model was assessed using the $F$-value and $p$-value. The model

| run | concentration (ppm) | dosage (g) | pH | Pb(II) removal efficiency (%) | Zn(II) removal efficiency (%) |
|-----|---------------------|------------|----|-----------------------------|-----------------------------|
|     |                     |            |    | experimental | predicted |                      | experimental | predicted |
| 1   | 45                  | 1.05       | 5  | 97.12          | 95.21        | 81.24          | 81.65         |
| 2   | 45                  | 1.05       | 5  | 95.68          | 95.21        | 79.5           | 81.65         |
| 3   | 45                  | 0.01       | 5  | 90.65          | 91.04        | 86.37          | 85.49         |
| 4   | 45                  | 2.64       | 5  | 91.86          | 92.08        | 66.5           | 67.72         |
| 5   | 10                  | 2          | 8  | 91.71          | 91.55        | 85.71          | 83.89         |
| 6   | 10                  | 0.1        | 8  | 86.59          | 86.58        | 74.98          | 75.4          |
| 7   | 5                   | 1.05       | 5  | 92.98          | 93.06        | 81.45          | 82.96         |
| 8   | 103.8               | 1.05       | 5  | 88.16          | 88.51        | 87             | 87.15         |
| 9   | 10                  | 0.1        | 2  | 85.73          | 85.58        | 79.58          | 78.94         |
| 10  | 80                  | 2          | 2  | 90.51          | 90.25        | 70             | 68.98         |
| 11  | 45                  | 1.05       | 5  | 93.88          | 95.21        | 85.07          | 81.65         |
| 12  | 45                  | 1.05       | 5  | 95.41          | 92.08        | 82.51          | 81.65         |
| 13  | 80                  | 0.1        | 2  | 89.04          | 89.43        | 97.8           | 99.03         |
| 14  | 80                  | 2          | 8  | 86.34          | 86.22        | 66.32          | 66.36         |
| 15  | 80                  | 0.1        | 8  | 85.29          | 84.99        | 97.5           | 96.8          |
| 16  | 45                  | 1.05       | 1  | 90.66          | 90.89        | 85             | 84.87         |
| 17  | 45                  | 1.05       | 5  | 94.15          | 95.21        | 84             | 81.65         |
| 18  | 10                  | 2          | 2  | 90.6           | 90.63        | 87.71          | 87.81         |
| 19  | 45                  | 1.05       | 5  | 95.47          | 95.21        | 82.54          | 81.65         |
| 20  | 45                  | 1.05       | 10 | 85.22          | 85.46        | 80             | 80.93         |

Table 2. Response Surface Quadratic Model for Removing Pb(II) and Zn(II): ANOVA Results

| source          | sum of squares | df | mean square | $F$-value | $p$-value |
|-----------------|----------------|----|-------------|-----------|-----------|
| Pb(II) model    | 261.69         | 9  | 29.08       | 38.58     | <0.0001   | significant |
| $A$-concentration | 2.72          | 1  | 2.72        | 3.61      | 0.0865    |
| $B$-dosage of the adsorbent | 27.22         | 1  | 27.22       | 36.13     | 0.0001    |
| $C$-pH          | 6.95           | 1  | 6.95        | 9.22      | 0.0125    |
| $AB$            | 6.98           | 1  | 6.98        | 9.26      | 0.0124    |
| $AC$            | 12.23          | 1  | 12.23       | 16.22     | 0.0024    |
| $BC$            | 0.0036         | 1  | 0.0036      | 0.0048    | 0.9462    |
| $A^2$           | 41.18          | 1  | 41.18       | 54.64     | <0.0001   |
| $B^2$           | 38.85          | 1  | 38.85       | 51.55     | <0.0001   |
| $C^2$           | 96.95          | 1  | 96.95       | 128.65    | <0.0001   |
| residual        | 7.54           | 10 | 0.7536      |           |           |
| lack of fit     | 0.7006         | 5  | 0.1401      | 0.1025    | 0.9871    | not significant |
| pure error      | 6.84           | 5  | 1.37        |           |           |
| cor total       | 269.23         | 19 |             |           |           |

| Zn(II) model    | 1266.26        | 9  | 140.7       | 55.04     | <0.0001   | significant |
| $A$-concentration | 4.6           | 1  | 4.6         | 1.8       | 0.2095    |
| $B$-dosage of the adsorbent | 320.17        | 1  | 320.17      | 125.26    | <0.0001   |
| $C$-pH          | 28.79          | 1  | 28.79       | 11.26     | 0.0073    |
| $AB$            | 757.38         | 1  | 757.38      | 296.31    | <0.0001   |
| $AC$            | 0.8581         | 1  | 0.8581      | 0.3357    | 0.5751    |
| $BC$            | 0.0761         | 1  | 0.0761      | 0.0298    | 0.8665    |
| $A^2$           | 23.29          | 1  | 23.29       | 9.11      | 0.0129    |
| $B^2$           | 27.48          | 1  | 27.48       | 10.75     | 0.0083    |
| $C^2$           | 4.68           | 1  | 4.68        | 1.83      | 0.2058    |
| residual        | 25.56          | 10 | 2.56        |           |           |
| lack of fit     | 12.42          | 5  | 2.48        | 0.945     | 0.524     | not significant |
| pure error      | 13.14          | 5  | 2.63        |           |           |
| cor total       | 1291.82        | 19 |             |           |           |
terms are significant if the p-values (prob > F) are less than 0.05. However, p-values (prob > F) more than 0.05 indicate that the model terms are insignificant.\textsuperscript{56} From Table 2 (ANOVA analysis) for Pb(II) removal, it is clear that the linear effects of the coefficients B (dosage of the biosorbent) and C (pH) and interactive effects of coefficients AB and AC, and the quadratic effects of coefficients A\textsuperscript{2}, B\textsuperscript{2}, and C\textsuperscript{2} are significant since the p-values of all these terms are less than 0.05, whereas the effect of A (initial Pb ion concentration) and BC are insignificant. Similarly, for Zn(II) removal, the linear effects of the coefficients B and C, interactive effects of coefficients AB, and the quadratic effects of coefficients A\textsuperscript{2} and B\textsuperscript{2} have p-values less than 0.05, which indicate these terms are significant terms and A, BC, AC, and C\textsuperscript{2} have no significant influence on the sorption process. The results are shown in Table 2; the F value is found to be 38.58 for Pb(II) and 55.04 for Zn(II) removal. The p-value of the removal of both heavy metals is less than 0.0001. These F and p-values indicated that model terms are significant for the biosorption of heavy metals under study.

The value of the regression coefficient can be utilized to check the fitting of these models. From Table 3, it is clear that both heavy metal removal values show a high regression coefficient. The adjusted regression coefficient value for Pb(II) removal is 0.972 and that for Zn(II) removal is 0.9624. The coeﬃcients of variation for Pb(II) and Zn(II) removal are 0.9555 and 1.95, respectively. The higher adjusted regression coefficient value and lower coefficient variation value support the reliability of the experiments. The accordance-adjusted R\textsuperscript{2} value validate the acceptability of the selected quadratic model.\textsuperscript{57}

Table 4 shows the results of lack-of-fit testing. When the p-value was more than 0.05, the lack of fit was not significant. The values of 0.9871 for Pb(II) adsorption and 0.524 for Zn(II) adsorption indicated that the lack of fit was not statistically significant.\textsuperscript{58} This established that the quadratic model is valid for the biosorption of both heavy metals by the PKM-2 M. oleifera leaf biosorbent.

Analytical statics were performed to verify and confirm that the model is satisfactory to meet the assumptions of the analysis. The variation of normal percentage probability against internally studentized residuals of Pb(II) and Zn(II) using PKM-2 M. oleifera leaves is shown in Figure 5a, following a straight line, indicating that the error terms are normally distributed.\textsuperscript{53–59} This confirmed the goodness of fit of the model predictions.

Figure 5b shows that the residuals of the predicted values of Pb(II) and Zn(II) biosorption are randomly scattered on both sides of the centerline with no specific patterns. This normal behavior of the residuals indicates that the observed and predicted values be logically consistent with each other for both lead and zinc adsorption.\textsuperscript{60}

The conventional Box–Cox plot is determined to reconfirm the normal distribution of the data and determine the power transformation amount required to put into the response data for normal distribution if the data is not normally distributed. The Box–Cox plot (Figure 6a) for Pb(II) removal reported that lower confidence levels at 95% confidences were obtained for a lambda value of −3 and upper value of 1. Lingamdinnea et al. reported similar results in the literature.\textsuperscript{60} For Zn(II) removal, the best λ was 2.02, which lies between the confidence interval (CI) low value of −0.690 and high value of 4.36, whereas the current lambda (λ) was equal to 1.0. No power transformation was suggested for both Pb(II) and Zn(II) removal, and the ANOVA test can be performed on the experimental data.\textsuperscript{61}

Figure 6b shows the predicted versus actual Pb(II) and Zn(II) removal efficiency graphs. The graph (Figure 6b) indicates that the values for both scenarios lie around the straight line, indicating that the actual values and predicted values are almost identical. It clearly indicates that the observed and predicted values were in good harmony.\textsuperscript{62}

The influence of the independent variables on the adsorption process is presented in Figure 7a,b. Each process variable is perturbed around its reference point of the initial concentration of 45 ppm, dosage of adsorbent 1.05 g, and pH 5, and the perturbation effect of each process factor on the elimination of lead and zinc is determined. The results obtained using the Design-Expert software shown in Figure 7a,b signify that each process variable performs unlike for the overall Pb(II) and Zn(II) removal. The interactive effect of process variables on the process characteristics may attribute to such variations. The effects of each independent variable for lead and zinc adsorption.

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### Table 3. Pb(II) and Zn(II) Ion Adsorption: Standard Fit Statistics

| Source   | Pb(II) | Zn(II) |
|----------|--------|--------|
| Std. dev. | 0.8681 | 1.6    |
| Mean     | 90.85  | 81.81  |
| C.V. %   | 0.9555 | 1.95   |
| R\textsuperscript{2} | 0.972  | 0.9802 |
| Adeq precision | 16.6578 | 28.8939 |

### Table 4. Pb(II) and Zn(II) Ion Adsorption: Lack-of-Fit Statistics

| Source   | Sum of squares (df) | F-value | p-value |
|----------|---------------------|---------|---------|
| Linear   | 217.91 (11)         | 14.49   | 0.0042  |
| 2FI      | 198.7 (8)           | 18.17   | 0.0027  |
| Quadratic| 0.7006 (5)          | 0.1025  | 0.9871  |
| Cubic    | 0 (0)               |         |         |
| Pure error| 6.84 (5)         | 1.37    |         |

For Zn(II) removal, the values of 74.71 for Pb(II) removal are 28.42 for Pb(II) removal and 0.0009 for Zn(II) removal. The interactive effect of process variables on the process characteristics may attribute to such variations. The effects of each independent variable for lead and zinc adsorption.

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are shown in Figure 7a,b, respectively. The independent variables' positive and negative effects can be understood by observing the slope of each graph. From Table 2, it can be inferred that the second potential for all the variables for the lead adsorption and the variables such as concentration and dosage of the adsorbent for zinc adsorption are significant.

2.3. Effect of Parameters on Adsorption. The study of interactive effects of the independent parameters and evaluation of the sustainability of the RSM model for predicting adsorption of lead and zinc using *M. oleifera* leaves were done using 2D contour and 3D surface plots (Figures 8 and 9). The effect of each parameter on the adsorption capacity of *M. oleifera* leaves for lead and zinc removal was found by evaluating the pairs of pH–concentration, concentration–dosage of the biosorbent, and pH–dosage of the biosorbent.

The pH of the medium plays an important role in the sorption process as the hydrogen ion itself acts as the adsorbate, and it affects the solution–metal chemistry. The functional groups on the surface of the biosorbent and the species distribution of metal ions in the aqueous solution influence metal adsorption on pH. The results showed (Figures 8 and 9) that when pH was increased from 2, the adsorption of metals under study on PKM-2 *M. oleifera* leaves was also augmented. The lead removal on PKM-2 *M. oleifera* leaves was attained at pH 4.7, whereas the maximum zinc removal using PKM-2 *M. oleifera* leaves was observed at pH 3.2. The biosorbent's zero point-of-charge (pHzpc) term, which regulates the limits of pH of a solution, could give a possible explanation for the reduction in metal removal at a very low pH value. When the pH of a solution was greater than the pHzpc value, the biosorbent surface attained a negative charge, which promoted cationic adsorption. When pH was less than the pHzpc value, the surface became positively charged due to the presence of more H⁺ ions in the solution, which is more attractive to metal anions.

The pHzpc value for PKM-2 *M. oleifera* leaves was found to be around 5.6 (Figure 10). Azad et al. reported similar results in the literature. The pH of the solution for both Pb(II) and Zn (II) ions is less than the pHzpc value (pH < pHzpc). As a result, the
surface of the biosorbent would get protonated. This creates competition between the H\(^+\) ions and the metal ions [Pb(II) and Zn(II)] for available sites. When the pH value increases at the initial stage, the hydrogen ion concentration reduces, and the sorption of Pb(II) and Zn(II) ions on biosorbent also increases. After reaching the optimum value, the removal efficiency decreases upon increase of the pH value. Pb(II) and Zn(II) removal using crab-shell particles similarly showed maximum removal efficiency at a low pH.\(^{66}\) The very low adsorption at high pH might be because the Pb(II) and Zn(II) ions underwent hydrolysis and precipitated as metal hydroxides.\(^{67}\)

Dosage of the biosorbent influences the metal adsorption on the surface of the biosorbent since the adsorption process is related to the mass transfer phenomena. Dependency of the PKM-2 \textit{M. oleifera} leaf biosorbent on the adsorption of Pb(II) and Zn(II) ions was examined in the range of 0.1−2 g of the biosorbent; the results obtained are shown in Figures 8 and 9. The results indicate that increasing the dose of the biosorbent enhanced the biosorption of Pb(II) and Zn(II). The optimal dose of the biosorbent for Pb(II) ion adsorption was found to be 1.5 g and for Zn(II) ion adsorption to be 0.6 g, based on the results of the experiments. These results are similar to those of removal of these heavy metals using \textit{Tamarindus indica} as the biosorbent.\(^{56}\) The increase in the dosage of the biosorbent increases the removal efficiency, which may be ascribed to the more active sites of adsorption and biosorbent functional groups that may bind to these heavy metals.\(^{69}\) At high biosorbent dosage, equilibrium is attained, and the saturation of active sites results in a low adsorption rate.\(^{70}\) When the dosage of adsorbent further increases, it causes aggregation of biosorbent particles to form larger particles, resulting in the reduction of adsorption ability and the surface area.\(^{67}\)

The influence of the initial concentration of metal ions on the adsorption process was investigated, and the results are shown in Figures 8 and 9. The experiments were carried out on PKM-2 \textit{M. oleifera} leaves with Pb(II) and Zn(II) concentrations ranging from 10 to 80 mg/L. The adsorption efficiency was raised by raising the initial concentration of metal from 10 to 80 mg/L. The maximum adsorption efficiency (95.6%) was attained at 38 mg/L for Pb(II), and the maximum adsorption efficiency (89.35%) was attained at 70 mg/L for Zn(II). Similar findings were reported for the removal of Pb(II) utilizing biomass waste from \textit{Streptoverticillium cinnamomeum} and for the removal of Zn(II) using \textit{M. oleifera} Lam.\(^{71}\) The increasing removal
efficiency with the increase of the initial concentration of metal ions is because the driving force increases as the metal ion concentration rises, accelerating the transfer of metal ions from the solution to the biosorbent surface. The decline in metal...
absorption by the biosorbent at higher concentrations might be due to the salt cation electrostatic attraction, leaving the biosorbent surface unfavorable to the target ions. When metal ion concentrations are high, the adsorption sites on the biosorbent become saturated, resulting in a lack of accessible active sites on the biosorbent surface. In contrast, at lower concentrations, however, an appropriate number of active sites are present for the metal ions to bind on the biosorbent surface.67

Figure 8. 3D surface and 2D contour plots for percentage removal of lead using the PKM-2 variety of M. oleifera leaves vs (a) concentration and dosage of the adsorbate, (b) concentration and pH, and (c) dosage of the adsorbate and pH.
2.4. Model Confirmation and Validation. Figure 11 shows the optimal points of each independent variable along with the maximum and minimum values for the adsorption of lead and zinc, respectively. Optimizing a process with numerous variable interactions is done under various conditions that help to maximize response for all runs. The conditions selected for maximum removal efficiency of Pb(II) and Zn(II) are initial metal ion concentration (in range), dosage (in range), and pH.
The optimized condition for Pb(II) (Figure 11a), which results in the maximum removal efficiency of 95.6%, is an initial concentration of metal ions of 38 mg/L, pH of 4.7, and adsorbent dosage of 1.5 g, whereas for Zn(II) (Figure 11b), the optimized condition is an initial concentration of metal ions of 70 mg/L, pH of 3.2, and adsorbent dosage of 0.6 g, which results in the maximum efficiency of 89.35%.

2.5. Equilibrium Studies on PKM-2 M. oleifera Leaves.

To determine the adsorption capacity of PKM-2 M. oleifera leaves, adsorption equilibrium studies were conducted, which describe the equilibrium relationship between the quantity of Pb(II) and Zn(II) metal ions adsorbed on PKM-2 M. oleifera leaves ($q_e$) and the metal ion concentration in solution.

Figure 12a shows the equilibrium data for lead and zinc ion adsorption. We selected two-parameter equilibrium isotherm models such as Freundlich, Langmuir, and Dubinin–Radushkevich isotherms to correlate our equilibrium results.

Irving Langmuir developed the basic isotherm model that considered the homogeneous surface of the adsorbent, and the model equation’s linear form is given below:

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m}$$  \hspace{1cm} (4)

where $q_e$: adsorbate amount picked up by the biosorbent at equilibrium (mg g$^{-1}$), $C_e$: equilibrium concentration of the adsorbate (mg L$^{-1}$), $q_m$: the adsorbent’s sorption capacity (mg g$^{-1}$), and $K_L$: the Langmuir isothermal constant (L mg$^{-1}$).

The Freundlich adsorption model is an empirical model that is often used to represent equilibrium data. Equation 5 provides
the linear form of the isotherm, which assumes that sorption is multilayer and that surface attributes are heterogeneous.

\[
\ln(q_e) = \frac{1}{n} \ln(C_v) + \ln(K_F)
\]

(5)

where \( \ln(K_F) \) (mg g\(^{-1}\)) and \( n \) are Freundlich isotherm constants. The Polanyi potential theory of adsorption provides the basis for the Dubinin–Radushkevich isotherm. It is given by eq 6 and is used to describe the adsorption process type:

\[
q_e = q_D \exp(B_D \varepsilon_d^2)
\]

(6)

where \( q_D \): Dubinin–Radushkevich isotherm constant (mg g\(^{-1}\)) and \( \varepsilon_d \): Polanyi potential (kJ mol\(^{-1}\)), associated with \( (C_v) \) and given in eq 7.

\[
\varepsilon_d = R T \ln \left( 1 + \frac{1}{C_v} \right)
\]

(7)

where \( R \): gas constant and \( T \): temperature (K). The following eq 8 relates the term \( B_D \) (mol\(^2\) kJ\(^{-2}\)) and the mean free energy of sorption \( E \) (kJ mol\(^{-1}\)).

\[
E = \frac{1}{\sqrt{2B_D}}
\]

(8)

Chemisorption is the sorption mechanism when \( E \) is 8–16 kJ mol\(^{-1}\), whereas physisorption is when \( E \) is less than 8 kJ mol\(^{-1}\).

Model fitting relies on the model’s regression coefficient \( (R^2) \) value. Figure 12b–d shows the equilibrium data predicted by all three models, and Table 5 lists the parameters. The data were tested for the goodness of fit and significance using the chi-square test. The adequacy of the models was tested in the current study, and the governing equation was accepted when the calculated \( \chi^2 \) value was less than the critical \( \chi^2 \) value, at a significance level (\( \alpha \)) of 0.05, otherwise rejected. Furthermore, \( p \)-values less than 0.05 showed a statistically significant difference (SD) between the experimental and predicted sets, and \( p \)-values more than 0.05 showed a statistically insignificant difference (NSD).

From Table 6, it was found that the calculated \( \chi^2 \) values are lower than the respective critical \( \chi^2 \) values, and \( p \)-values are greater than 0.05 for both Langmuir and Freundlich isotherms. From Tables 5 and 6, the regression coefficient \( (R^2) \) values are higher and calculated \( \chi^2 \) values are lower for the Langmuir model of adsorption equilibrium isotherms of (a) experimental data, (b) Langmuir, (c) Freundlich, and (d) Dubinin–Radushkevich for both metal ions.

Figure 12. Adsorption equilibrium isotherms of (a) experimental data, (b) Langmuir, (c) Freundlich, and (d) Dubinin–Radushkevich for both metal ions.

| Metal | Temp (K) | \( q_m \) | \( K_L \) | \( R^2 \) | \( K_D \) | \( N \) | \( R^2 \) | \( q_D \) | \( B_D \) | \( E \) | \( R^2 \) |
|-------|----------|-----------|---------|---------|---------|-------|---------|---------|-------|-------|---------|
| Lead  | 300      | 51.71     | 0.0029  | 0.995   | 0.337   | 1.301 | 0.991   | 18.78   | 439.5 | 0.033 | 0.848   |
| Zinc  | 300      | 38.50     | 0.0038  | 0.995   | 0.404   | 1.418 | 0.992   | 16.96   | 468.3 | 0.032 | 0.867   |
Table 5 shows the computed Dubinin to be greater than 1 for both the heavy metals, indicating the constants are shown in Table 5. The values of \( n \) are observed drawn using experimental data and illustrated in Figure 12c, and Di (Table 7), Pb(II) and Zn(II) metals had the highest adsorption capacity \( M. oleifera \) owing to Pb(II) ions capacity to adsorb Pb(II) ions is larger than that of Zn(II) ions.

Hence, the adsorption mechanism in the Langmuir model suggested that the adsorption sites on the adsorbent (PKM-2 \( M. oleifera \) leaves) are homogeneous, and no interaction between leaves. It was also observed that the regression coefficient \( R^2 \) values of Dubinin–Radushkevich are less [i.e., 0.867 and 0.848 for Pb(II) and Zn(II), respectively] in comparison with Langmuir and Freundlich isotherms. As a result, the Dubinin–Radushkevich isotherm does not adequately describe the experimental data.

### 2.6. Kinetic Studies on PKM-2 \( M. oleifera \) Leaves

Adsorption kinetic experiments determined the rate equation of the kinetics. Pseudo-first-order, pseudo-second-order, and intraparticle diffusion (IPD) equations were used to examine the kinetic data in this work. The pseudo-first-order rate equation has been commonly used to describe the rate of the kinetics of adsorption.

\[
\ln(q_t - q_e) = \ln(q_e) - k_1 t
\]

where \( q_e \): sorption capacity at equilibrium (mg g\(^{-1}\)), \( q_t \): sorption capacity at time \( t \) (mg g\(^{-1}\)), and \( k_1 \): rate constant for the pseudo-first-order rate equation (s\(^{-1}\)).

The pseudo-second-order rate equation is proposed by Ho and McKay and is a commonly used model to predict adsorption kinetics of metal ions on biosorbents.

\[
\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \( k_2 \): pseudo-second-order rate constant (g mg\(^{-1}\) s\(^{-1}\)).

Weber and Morris proposed the IPD to study the kinetic adsorption mechanism, which is represented in eq 11.

\[
q_t = k_3 d^{1/2} + I
\]

where \( k_3 \): IPD rate (mg g\(^{-1}\) s\(^{-1/2}\)) and I: adsorption boundary layer thickness.

Transfer of adsorbent particles to the adsorbent surface happens in several steps during adsorption. The process can be governed by (i) external surface or film diffusion, (ii) pore diffusion, (iii) surface diffusion and pore surface adsorption, or (iv) a combination of one or more steps.

The plots and parameters of three model equations for both Pb(II) and Zn(II) are shown in Figure 13 and Table 8. The amounts of both heavy metals adsorbed by the PKM-2 \( M. oleifera \) leaves estimated and experimentally found were highly similar for the pseudo-second-order kinetic model. The data were tested for significance and goodness of fit using the chisquare test and are presented in Table 9. It was observed that the experimental and calculated \( q_e \) values for the pseudo-second-order rate equation do not differ significantly (NSD). In contrast, the experimental and calculated \( q_e \) values for the pseudo-first-order rate equation differ significantly (SD), and also, the regression coefficient \( R^2 \) values are near 1 for the pseudo-second-order rate equation. Hence, the kinetics of Pb(II) and Zn(II) adsorption of PKM-2 \( M. oleifera \) leaves followed the pseudo-second-order rate equation. Other researchers reported similar findings when the pseudo-second-order model suited well for metal biosorption.

The IPD kinetic equation was used to analyze the adsorption kinetic data for both lead and zinc adsorption. The plots of \( q_t \) and adsorption capacity \( q_e \) of 51.71 and 38.50 mg/g, respectively, with PKM-2 \( M. oleifera \) leaves. It was also observed that the adsorbed adsorbent capacity to adsorb Pb(II) ions is larger than that of Zn(II) ions owing to Pb(II) ions’ smaller hydration enthalpy (1485) and greater electronegativity (1.87).

The Freundlich isotherm model plots \( \ln(q_e) vs \ln(C_e) \) are drawn using experimental data and illustrated in Figure 12c, and the constants are shown in Table S. The values of \( n \) are observed to be greater than 1 for both the heavy metals, indicating favorable adsorption, and the sorption process is physical adsorption.

### Table 6. Statistical Analysis for Predicted and Experimental Values of \( q_e \) (Isotherms)

| model               | metal | p-value | \( \chi^2 \)-Crit | \( \chi^2 \)-Cal | inference |
|---------------------|-------|---------|------------------|-----------------|-----------|
| Langmuir            | lead  | 0.999   | 14.067           | 0.238           | NSD       |
|                     | zinc  | 0.999   | 14.067           | 0.188           | NSD       |
| Freundlich          | lead  | 0.999   | 14.067           | 0.257           | NSD       |
|                     | zinc  | 0.999   | 14.067           | 0.192           | NSD       |
| Dubinin–Radushkevich| lead  | 0.875   | 14.067           | 3.104           | NSD       |
|                     | zinc  | 0.875   | 14.067           | 0.090           | NSD       |

**NSD—no significance difference, SD—significance difference.**
versus $t^{1/2}$ are represented in Figure 13c, and the parameters are listed in Table 8. Figure 13c showed that the lines do not intersect at the origin, and multilinear plots reveal the presence of two or more rate-limiting steps in the adsorption process for the heavy metals under research. The initial part of the curve indicates the surface diffusion, and the linear part of the curve indicates IPD. The nonzero intercept ($I$) implies surface diffusion (Table 8), which is the rate-limiting step in both lead and zinc adsorption.21

2.7. Thermodynamic Studies. In the present study, thermodynamic parameters ($\Delta H^\circ$, $\Delta G^\circ$, and $\Delta S^\circ$) can be

Table 8. Adsorption Kinetic Model Parameters

| metal | run | $q_e$ (exp) | $k_f \times 10^{-4}$ | $q_e$ (cal) | $R^2$ | $k_s \times 10^{-5}$ | $q_e$ (cal) | $R^2$ | $I$ | $k_d$ | $R^2$ |
|-------|-----|-------------|----------------------|-------------|------|----------------------|-------------|------|-----|-------|------|
| lead  | 1   | 20.25       | 2.287                | 13.51       | 0.907| 2.064                | 22.91       | 0.993| 3.62| 0.148| 0.819|
|       | 2   | 28.12       | 2.228                | 18.65       | 0.968| 2.056                | 30.54       | 0.998| 6.98| 0.185| 0.874|
|       | 3   | 37.12       | 2.435                | 26.23       | 0.981| 1.568                | 40.41       | 0.998| 9.09| 0.246| 0.894|
| zinc  | 1   | 15.97       | 1.955                | 11.41       | 0.930| 2.848                | 17.48       | 0.993| 3.27| 0.830| 0.891|
|       | 2   | 22.95       | 2.491                | 16.42       | 0.922| 2.424                | 25.06       | 0.997| 5.40| 1.195| 0.860|
|       | 3   | 31.50       | 2.385                | 18.03       | 0.921| 2.442                | 33.65       | 0.998| 9.62| 1.523| 0.812|

Table 9. Statistical Analysis for Predicted and Experimental Values of $q_e$ (Kinetics)$^a$

| model         | metal | $p$-value | $\chi^2$-Cri | $\chi^2$-Cal | inference |
|---------------|-------|-----------|---------------|---------------|-----------|
| pseudo-first-order | lead  | 0.0017    | 5.991         | 12.679        | SD        |
|                | zinc  | 0.00072   | 5.991         | 14.470        | SD        |
| pseudo-second-order | lead  | 0.680     | 5.991         | 0.769         | NSD       |
|                | zinc  | 0.799     | 5.991         | 0.447         | NSD       |

$^a$NSD—no significance difference, SD—significance difference.
used for calculating the spontaneity of a process through the following thermodynamic \[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \] where the factor 55.5 is the number of moles of pure water per liter and MW is the molecular weight of the adsorbate.

The equilibrium studies were conducted at three distinct temperatures, 303, 313, and 323 K, in conical flasks with 50 and 100 mL solutions of concentration 300 mg L\(^{-1}\) at 200 rpm in a mechanical shaker at a contact time of 4 h to determine thermodynamic parameters, and data are presented in Figure 14a,b. From Figure 14a,b, it is observed that the amount of Pb(II) and Zn(II) removal decreases with a rise in temperature since the sorption process involves physisorption, and van der Waals forces diminish with higher temperature. Langmuir model is more fit for the determination of the thermodynamic studies of lead and zinc. The van’t Hoff plots of ln\( (K_d) \) versus 1/\( T \) for Pb(II) and Zn(II) are illustrated in Figure 14c. The intercept and the slope of the van’t Hoff plot are used to compute the \( \Delta H^\circ \) and \( \Delta S^\circ \) values. Table 10 shows the thermodynamic parameters of the three operating temperatures for adsorption of Pb(II) and Zn(II) on PKM-2 M. oleifera leaves. The negative values of \( \Delta H^\circ \) supported the exothermic character of the adsorption process for both metal ions. Therefore, the adsorption process is spontaneous since both \( \Delta H^\circ \) and \( \Delta G^\circ \) are negative, and the temperatures involved are low. The lower free-energy values also imply that the adsorption process is feasible.

The change in entropy \( \Delta S^\circ \) values that are positive suggests that the sorption process is entropy-governed rather than enthalpy-governed. The positive values of \( \Delta S^\circ \) indicate a rise in randomness and disorder at the solid/solution interface during the adsorption of both metal ions on PKM-2 MOL.

\[ \ln(MW \times 1000 \times 55.5 \times K_d) = \frac{\Delta S^\circ}{R} - \left( \frac{\Delta H^\circ}{R} \right) \frac{1}{T} \]
adsorption enthalpy less than 12 kJ/mol indicates an occurrence of the physical adsorption process.73

**2.8. Adsorption Mechanism.** The electrostatic characteristics between the biosorbent and heavy metals influence the biosorption process, which is the integrated effect of pH of the solution and functional groups on the biosorbent surface.86 pH is an important factor influencing the adsorption process, which compares with the zero-point charge of the biosorbent and determines the distribution of charge on the biosorbent surface.57 The pH of the solution for both Pb(II) and Zn (II) ions is less than the pHzpc value (pH < pHzpc). As a result, the surface of the biosorbent would get protonated. This creates competition between the H⁺ ions and the metal ions [Pb(II) and Zn(II)] for available sites. Iqbal et al. reported in the literature that the ion-exchange mechanism occurs between the targeted heavy metals and the protons and/or the light metals present in the biomass.87

The EDX results confirmed the lead and zinc removal by the ion exchange mechanism with Ca, Mg, and K present in the PKM-2 *M. oleifera* leaves. It is evident from the FTIR analysis that the shifts observed in positions of peaks recommended that amine, carboxylic, hydroxyl, and carbonyl groups are predominant contributors in heavy-metal ion adsorption.88 Maina et al. reported that these functional groups which are present on the PKM-2 *M. oleifera* leaves surface can form anionic sites for metal adsorption on the biosorbent.51 The hydroxyl group and carboxyl groups may involve in the complexation of highly bound cations. Ozer et al. reported that the amino groups and carboxyl foster the reaction with positively charged metal ions.89 Amines can reduce the H⁺ ions, which helps form anionic sites for the metal adsorption on the biosorbent.90 Structural changes shown in the XRD analysis results occurred after the adsorption of Pb(II) and Zn(II) ions, which also signified the electrostatic interaction mechanism between the Pb(II) and Zn(II) ions and the functional groups on the surface of the biosorbent. It can be speculated that the possible adsorption mechanism could be the combined effect of electrostatic interactions between the carboxyl, hydroxyl, or amine group reacting with metal ions and the ion exchange process involving the light metals present in the biosorbent and H⁺ protons with the heavy metals.

**2.9. Industrial Water Analysis for the Removal of Lead and Zinc Using PKM-2 *M. oleifera* Leaves.** A wastewater sample collected from an industry at Coimbatore (Tamil Nadu) was used to evaluate the potential of PKM-2 *M. oleifera* leaves for lead and zinc removal. The collected industrial wastewater sample was used for the experiments without further treatment. The pH of the wastewater sample was found to be 6.1. The total lead and zinc concentration in the sample was determined using atomic emission spectroscopy (AES), and it was found that the concentration of both metals were less than 100 mg/L. A total of 1.5 g of the PKM-2 *M. oleifera* leaf powder was added to 50 mL of sample wastewater and shaken for 4 h at 200 rpm in a mechanical shaker at 27 ± 2 °C. After the AES analysis, the metal removal efficiency obtained for lead and zinc was 92 and 83%. Even though the results showed considerable lead and zinc removal efficiency, these values were less than the adsorption percentage achieved with an aqueous solution. The presence of other metals in the water sample may influence the lead and zinc removal. At pH 6.1 (pH > pHzpc), the surface of the biosorbent was positively charged and favorable for electrostatic interaction between cations and the adsorbent, which results in the high competition between the target heavy metals and other positively charged metals available in the sample.

**3. CONCLUSIONS**

In this study, the adsorption ability of the PKM-2 variety of *M. oleifera* leaves for the removal of lead and zinc metals has been investigated. Characterization of the biosorbent by SEM and XRD analysis reported that the surface of the biosorbent was rough and irregular in shape with broken edges and predominance of amorphous nature. RSM aided in determining the conditions under which maximum lead and zinc metal adsorption on biosorbent occur. The initial concentration of metal ions of 38 mg/L, dosage of 1.5 g, and pH of 4.7 were the optimum operating conditions, which resulted in maximum Pb(II) removal with an efficiency of 95.6% and maximum Zn(II) removal efficiency of 89.35% obtained under the optimum operating condition of the initial concentration of metal ions of 70 mg/L, dosage of 0.6 g, and pH of 3.2. The EDX results confirmed the lead and zinc adsorption by the biosorbent and also showed that the light metals in the biosorbent were replaced with the target metals, signifying the role of the ion exchange mechanism, whereas the FTIR results reported that the NH, −OH, C=H, −O=C, and −C≡O were involved in the sorption process. The equilibrium isotherms for both Pb(II) and Zn(II) adsorption best fit the Langmuir model with adsorption capacities of 51.71 and 26.96 mg/g, respectively. The pseudo-second-order model showed a good fit for the kinetic study. Thermodynamic studies revealed that the sorption process is exothermic, favorable, and physical adsorption. The results have corroborated that the unmodified PKM-2 variety of *M. oleifera* leaves are worthy alternatives for low-cost, ecofriendly, highly efficient biosorbents to remove lead and zinc for concentrations less than 100 ppm.

**4. MATERIALS AND METHODS**

**4.1. Materials.** Lead nitrate Pb(NO₃)₂ and zinc sulphate (ZnSO₄) were purchased from Sisco Research Laboratories Pvt. Ltd, India. pH adjustments were made using hydrochloric acid (HCl) and sodium hydroxide (NaOH), which had been purchased from Merck Specialties Pvt. Ltd. India. All the solutions and reagents were prepared using double-distilled water.

**4.2. Preparation of the Biosorbent.** The PKM-2 variety of *M. oleifera* leaves was collected from local *M. oleifera* trees in Coimbatore, Tamil Nadu, India, from February to March 2021. Using tap water, the collected *M. oleifera* leaves were washed and dried under the sun for about 4−5 days. Then, the dried leaves were ground and sieved in a sieve shaker. The fine powder, which was retained on 180 mesh size, was used for our experiments.

**4.3. Adsorption Studies.** Adsorption batch equilibrium and kinetic studies were performed to evaluate the adsorbent.
adsorption capacity and mechanism of adsorption. The adsorption equilibrium experiments were performed in conical flasks with 50 and 100 mL solutions of concentration 300 mg L\(^{-1}\) at 200 rpm in a mechanical shaker at 27 °C for a contact time of 4 h for both lead and zinc adsorption. For the experiments, the optimal pH values were chosen.

The batch kinetic study was carried out in three-necked conical flasks fitted with a stirrer. Standard 250 mg L\(^{-1}\) lead and zinc solution (450 mL) was transferred to the flask, and the known amounts of the adsorbent (2, 4, and 6 g) were added to it. Metal ion solutions were collected at various time intervals to know the changes in metal ion concentration with time. Inductively coupled plasma AES (ICP-AES) was used to analyze the metal ion concentrations of Pb(II) and Zn(II) in the solutions. Equations 16 and 17 were used to compute the removal efficiency of metal ions and the adsorbing capacity of the adsorbent.15,25

\[
\% \text{ of lead removal} = \% R = \left( \frac{C_i - C_f}{C_o} \right) \times 100 \quad (16)
\]

\[
\text{Adsorption capacity} \quad q_e = \frac{V(C_o - C_f)}{w} \quad (17)
\]

where \(q_e\) is the sorption capacity of the biosorbent (mg g\(^{-1}\)), \(V\): the volume of lead/zinc solution (L), \(C_o\) and \(C_f\): the initial and final concentrations of lead/zinc in solution (mg L\(^{-1}\)), and \(w\): dosage of M. oleifera leaves (g).

### 4.4.1. Determination of pH\(_{\text{Pzpc}}\)

The pH\(_{\text{Pzpc}}\) value of PKM-2 M. oleifera leaves was determined by adding 0.1 g of PKM-2 M. oleifera leaf powder into 25 mL of 0.01 M NaCl. The initial pH of the solution was adjusted between 1 and 12 using diluted 0.1 N NaOH and 0.1 N HCl. After adjusting the pH values, the following suspensions were shaken in a shaker for 24 h at 25 °C. The final pH values were noted, and the graph was plotted using the initial pH values against the difference between the final and initial pH values. The intersection of these two points provides the pH\(_{\text{Pzpc}}\).

### 4.4.2. Optimization of Biosorption Conditions

Many factors affect the sorption of heavy metal ions on the biosorbent surface, and the influence of these factors should be measured correctly. When more than one factor is involved in the process, deliberately changing one or more factors to check the changes on the other variables makes a large number of repetitive experiments. This would be impractical when considering the cost as well as time. The design of experiments is an efficient method that determines the best parameter settings that give an optimum value of the response and fit a model based on the data obtained.26,27 Identifying the factors that influence the experiment and optimizing these parameters for the experiment are the two main applications of the experimental design. CCD under RSM was employed to check the influence of variables on the response and to optimize the biosorption process.91 To decide the optimum conditions, three independent process variables were considered: \(A\): initial metal concentration, \(B\): a dosage of biosorbent, and \(C\): pH. The experimental ranges of the considered variables for both metal adsorption are shown in Table 11. A quadratic polynomial equation was designed using RSM to simulate the response corresponding to the interaction between the variables given below; see eq 18.

\[
R = a_o + \sum a_iX_i + \sum a_{ii}X_i^2 + \sum a_{ij}X_iX_j \quad (18)
\]

### Table 11. Levels of the Sorption Process: PKM 2 M. oleifera Leaves

| description | variable | unit | level |
|-------------|----------|------|-------|
| initial metal concentration | \(A\) | ppm | 10 75 150 |
| dosage of biosorbent | \(B\) | g | 0.1 1 2 |
| pH | \(C\) | | 2 5 8 |

where \(R\) is the predicted response, \(a_o\), \(a_i\), \(a_{ii}\), and \(a_{ij}\) are constant regression coefficients of the model, and \(X_i\) and \(X_j\) represent the independent variables represented by coded values (it is assumed that \(i = 1 \rightarrow 3; j = 1 \rightarrow 3; i \neq j\)).

### 4.4.3. Characterization of the Adsorbent

To know the physical and chemical characteristics, the adsorbent PKM-2 M. oleifera leaves were characterized. The functional groups present in the biosorbent (before and after metal adsorption) were identified with the help of a FTIR spectrophotometer (Shimadzu, IRSpirit). The chemical composition and surface morphology of the PKM-2 M. oleifera leaves were investigated using energy-dispersive X-ray spectroscopy combined with field emission-scanning electron microscopy (FE-SEM) (Carl Zeiss, Gemini 300). The X-ray diffraction of the adsorbent was conducted using third-generation Empyrean, Malvern PAN-Alytical. A single-point N\(_2\)-BET technique was used to measure the specific surface of the biosorbant.

#### AUTHOR INFORMATION

**Corresponding Author**

Laxmi Deepak Bhatlu M — Department of Chemical Engineering, Faculty of Engineering, Karugamam Academy of Higher Education, Coimbatore 641021 Tamil Nadu, India;  orcid:0000-0002-7965-3279; Email: dbhatlu.rs.che@itbhu.ac.in

**Authors**

Neethu Jayan — Department of Chemical Engineering, Faculty of Engineering, Karugamam Academy of Higher Education, Coimbatore 641021 Tamil Nadu, India

Saufshan Thalikassery Akbar — Department of Chemical Engineering, Faculty of Engineering, Karugamam Academy of Higher Education, Coimbatore 641021 Tamil Nadu, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c03069

**Notes**

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