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21 June 2026

CITE THIS ARTICLE

Wahab, E.M.A., Shartooch, S.M. and Alsmadi, M.M., 2027.
Utilization of date pits for the sustainable biosorption of
heavy metals from municipal wastewater in Ramadi city.
Nature Environment and Pollution Technology, 26(1), D1958.
<https://doi.org/10.46488/NEPT.2027.v26i01.D1958>

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PUBLICATION STATUS

PEER REVIEW
Completed

ONLINE VERSION
Prepublished

FINAL ISSUE
March 2027

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Utilization of date pits for the sustainable biosorption of heavy metals from municipal wastewater in Ramadi city

Ethar Munther Abdul Wahab¹, Sufyan Mohammed Shartoo^{2†} and Mo'tasem M. Alsmadi^{3,4}

¹ Department of Biology, College of Education for Women, University of Anbar, Ramadi, Iraq

² Department of Biology, College of Science, University of Anbar, Ramadi, Iraq

³ Department of Pharmaceutical Technology, Faculty of Pharmacy, Jordan University of Science and Technology, Irbid, Jordan

⁴ Nanotechnology Institute, Jordan University of Science and Technology, Irbid, Jordan

† Corresponding author: Sufyan Mohammed Shartoo; dralwaisi@uoanbar.edu.iq

ORCID ID: <https://orcid.org/0000-0001-5227-9072>

Abstract: Heavy-metal contamination of municipal wastewater poses serious risks to aquatic ecosystems and human health. This study evaluated the potential of *Phoenix dactylifera* seed biomass as a low-cost and sustainable biosorbent for removing lead (Pb), copper (Cu), zinc (Zn), and cadmium (Cd) ions from wastewater. Batch biosorption experiments were conducted to optimize the effects of solution pH, temperature, contact time, biosorbent dosage, and particle size. The maximum biosorption efficiencies at a biosorbent dosage of 5 g.L⁻¹ and a particle size of 0.5 mm were achieved at pH 6, 40°C, and a 60-min retention time. Pb showed the highest removal efficiency, reaching 97.83%, followed by Cd, Zn, and Cu. Fourier-transform infrared spectroscopy indicated the involvement of hydroxyl and carboxyl functional groups in metal binding, while scanning electron microscopy revealed changes in the biosorbent surface following adsorption. The equilibrium data fitted both the Langmuir and Freundlich isotherm models, indicating favorable adsorption onto the DSP surface. Application of DSP to municipal wastewater substantially reduced the concentrations of the investigated heavy metals. These findings demonstrate the potential effectiveness and environmental suitability of *P. dactylifera* seed powder as a biosorbent for the tertiary treatment of metal-contaminated municipal wastewater.

Keywords: *Phoenix dactylifera*, Biosorption, Lead, pH zero charge, Isotherm models, FTIR, SEM, Sustainability

1. INTRODUCTION

Heavy metal contamination is one of the most serious environmental problems associated with industrialization, urbanization, and population growth. Metal ions of toxic heavy metals such as Pb²⁺, Cd²⁺, Cu²⁺, and Zn²⁺ are continuously released into water bodies through industrial effluents, mining operations, agricultural runoff, and domestic sewage. Unlike many organic pollutants, heavy metals are non-biodegradable and can accumulate in living organisms and food chains, causing severe ecological and human health problems like neurological disorders, kidney damage, carcinogenic effects, and metabolic disturbances (Nangeelil et al. 2024; Scimeca et al. 2024).

Conventional technologies for heavy metal removal such as chemical precipitation, ion exchange, reverse osmosis, and activated carbon adsorption are associated with high operational costs, energy consumption, and secondary sludge generation (Sharma & Devi 2024; Shofia et al. 2025). Over the years, this has led to increased interest in biosorption as a sustainable and low-cost alternative for wastewater treatment (Khalaf et al. 2025). Biosorption is defined as the passive binding of metal ions to biological materials through functional groups present on the surface of biomass, such as hydroxyl, carboxyl, amino, and carbonyl groups (Wang & Guo 2020; Magdum & Itankar 2026).

Agricultural residues are of great interest as biosorbents due to their availability, biodegradability, and lignocellulosic composition (Khalfaoui et al. 2024). Among these materials, *Phoenix dactylifera* seeds, commonly known as date pits, have shown remarkable potential for the adsorption of heavy metals. Cellulose, hemicellulose, and lignin, which constitute the major components of date seeds, provide numerous active sites that can interact with metal ions through electrostatic attraction, ion exchange, and surface complexation mechanisms. The adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+} ions is mainly due to the presence of functional groups such as hydroxyl and carboxyl groups (Elkhaleefa et al. 2020).

Previous studies have demonstrated that date seed-based biosorbents show high efficiency of adsorption as well as favorable kinetics of adsorption for the removal of heavy metals (Rahman et al. 2025). FTIR analyses have confirmed that hydroxyl, carboxyl, and carbonyl groups take part in the process of binding the metals, while the adsorption behavior is commonly described by Langmuir and Freundlich isotherm models. The adsorption efficiency is greatly influenced by the operational parameters such as pH, contact time, temperature, adsorbent dosage, and initial metal concentration (Hu et al. 2023).

Recent advancements in biosorption technology have mainly focused on enhancing the stability and reusability of biosorbents through immobilization techniques such as calcium alginate and nanoparticle composites (Torres 2020). These modifications improve adsorption capacity and mechanical strength and, therefore, may enhance the suitability of date seed biomass for continuous wastewater treatment.

In Iraq and other date-growing regions, using the seeds of *Phoenix dactylifera* as biosorbents is an environmentally friendly and economically viable way of removing heavy metals. The huge amount of waste from date seeds, together with the increasing water pollution problem, emphasizes the need for locally available biosorbents for sustainable wastewater treatment and environmental protection.

Therefore, this study evaluated the biosorption efficiency of *P. dactylifera* seed biomass for removing Pb, Cd, Cu, and Zn from aqueous solutions and municipal wastewater. The effects of biosorbent form, pH, contact time, temperature, dosage, and particle size were examined, and the equilibrium behaviour was assessed using the Langmuir and Freundlich isotherm models.

2. MATERIALS AND METHODS

2.1. Preparation of biosorbents

Phoenix dactylifera seeds were obtained from the local markets of Ramadi City, Iraq. The seeds were washed with double-distilled water to make them free from any impurity and to remove any adhering residues. After cleaning, the seeds were prepared by two different methods. In the first method, they were dried thoroughly and then used either whole or cut into pieces of different sizes; these samples were designated as dried date seeds (DS). In the second method, the dried seeds were ground to a fine powder and sieved using stainless steel sieves having pore sizes between 0.061 mm and 2 mm to obtain dried date seed powder (DSP). Fig. 1 illustrates the prepared biosorbents. The biosorbent was kept in clean, dry containers to prevent moisture absorption and was used in adsorption experiments for studies on the removal of metal ions.

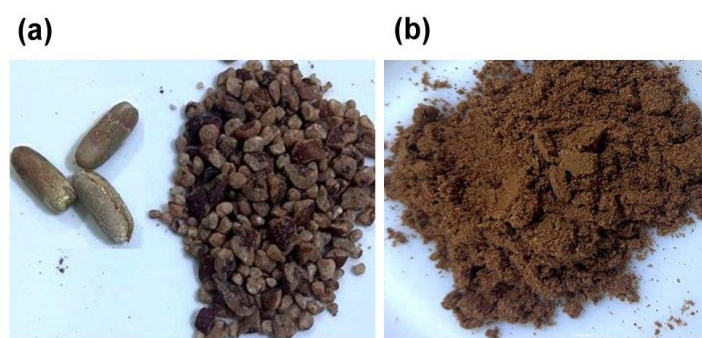


Fig. 1: Prepared biosorbents: (a) dried date seeds (DS) and (b) dried date seed powder (DSP).

2.2. Determination of the Point of Zero Charge, SEM, and FTIR analysis

The point of zero charge (pH_{pzc}) of the *Phoenix dactylifera* DSP biosorbent was determined by the pH drift method. A series of 0.1 M NaCl solutions was prepared in 100 mL conical flasks. The initial pH (pH_i) of each solution was adjusted to values ranging from 2–12 using 0.1 M HCl or NaOH and measured by a pH meter (Thermo Scientific, Orion Star A211, Indonesia). The final volume of each solution was adjusted to 25 mL. Subsequently, 0.5 g of *Phoenix dactylifera* DSP was added to each flask, and then allowed to equilibrate by shaking at 120 rpm for 24 hours. The final

pH (pH_f) was recorded. The difference between initial and final pH values ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$) was plotted against pH_i. The pH_{pzc} was determined at the point where $\Delta\text{pH} = 0$ on the x-axis.

The surface morphology of raw and metal-loaded DSP biosorbent was examined using scanning electron microscopy (SEM) (Tescan–Vega III, Czech Republic). For the adsorption experiment, a multi-metal solution containing 100 mg.L⁻¹ of each ion of lead (Pb), copper (Cu), zinc (Zn), and cadmium (Cd) was prepared. One gram of *Phoenix dactylifera* powder (DSP) was added to the solution and allowed to equilibrate for 2 hours prior to SEM analysis.

The functional groups involved in metal binding were identified using Fourier Transform Infrared (FTIR) spectroscopy (ABB Spectrolab, MB3000, UK). The biosorbent samples were dried first and then mixed with potassium bromide (KBr) (Fluka, Switzerland) at a ratio of 1:10. The mixture was finely ground and pressed into pellets. The spectra were recorded after background correction using pure KBr, and all results were presented on a uniform absorbance scale.

2.3. Batch Biosorption Experiments

The biosorption performance of DSP biomass was evaluated through batch adsorption experiments conducted under controlled laboratory conditions. A multi-metal aqueous solution (100 mL working volume) was prepared with Pb²⁺, Zn²⁺, Cu²⁺, and Cd²⁺ ions –Fluka, Switzerland- each at initial concentration of 100 mg.L⁻¹ for each metal, and then the solution was transferred into 250 mL volumetric flasks for further processing.

Biosorption conditions were optimized through preliminary experiments. These experiments included the evaluation of the biosorbent form and physical characteristics of *Phoenix dactylifera*, using dried seeds and powdered biomass. In each experiment, 0.5 g of the biosorbent was added to 100 mL of metal solution. The flasks were then placed in a shaking incubator at 120 rpm and 30°C for 60 min at neutral pH. The solution was then adjusted to the desired pH using 0.1 M NaOH or 0.1 M HCl.

Additional optimization of biosorption parameters was carried out by studying the operational variables, namely initial pH (3–8), temperature (30°C as control and 10–60°C for thermal studies), contact time (1–120 min), biosorbent dosage (1–20 g.L⁻¹), and particle size range (0.061–2 mm). During the particle-size experiments, the biosorbent dosage was maintained at 10 g L⁻¹ to ensure comparability among treatments. The value of optimum pH obtained from these sets of experiments was used in the subsequent adsorption studies.

A blank control solution that contains the same metal ions without DSP biosorbent was prepared under the same experimental conditions to serve as a reference for the evaluation of adsorption efficiency. After the biosorption process, all samples were centrifuged at 3000 rpm for 40 min at room temperature. Then, they were subjected to filtration through a 0.45 µm membrane filter to remove suspended particles. The residual concentrations of heavy metal ions in the aqueous phase were determined by Flame Atomic Absorption Spectrophotometry (FAAS) (AA-7000, Shimadzu, Japan), under the following calibration data of specific limit of detection (LOD), limit of quantification (LOQ), and wavelength:

- Pb, LOD 0.003 mg/l, LOQ 0.021 mg/l, 217 nm.
- Zn, LOD 0.003 mg/l, LOQ 0.021 mg/l, 213.9 nm.
- Cu, LOD 0.004 mg/l, LOQ 0.021 mg/l, 324.8 nm.
- Cd, LOD 0.002 mg/l, LOQ 0.014 mg/l, 228.8 nm.

All experimental processes were conducted in a similar and repeatable manner to ensure the validity of the results and establish the best conditions for maximum biosorption efficiency of *Phoenix dactylifera* DSP biomass. The overall removal efficiency was calculated by the standard adsorption efficiency equation. These procedures were used in all the subsequent experiments to find the best efficient biosorption process. The overall efficiency of the biosorption process was measured using Equation 1 and the quantity adsorbed at equilibrium. (q_e) in mg.g^{-1} Equation 2:

$$\text{Biosorption efficiency \%} = \frac{C_i - C_f}{C_i} \times 100 \dots \dots (1)$$

$$q_e = (C_i - C_f) \times \frac{V}{W} \dots \dots (2)$$

Where (C_i) and (C_f) are the initial and final concentrations of metal, respectively. V (L) represents the volume of the heavy metal solution, while W (g) represents the weight of the DSP. All measurements were performed in triplicate, and the mean values were reported.

2.4. Biosorption Isotherms

The Langmuir and Freundlich isotherm models were used to describe the interaction between adsorbate species and the biosorbent surface in fitting the experimental equilibrium data and to provide insight into the adsorption mechanism. The above analysis was carried out to evaluate the equilibrium behavior of heavy metal ion adsorption onto *Phoenix dactylifera* biosorbent.

Langmuir defined gas adsorption on a solid interface as being analogous to gas-phase condensation on a liquid surface, wherein inelastic collisions result in a "lag" or residence time at the point of impact. The model assumed equal-

energy monolayer sites with no interaction between adsorbed molecules. Further, the model examined only low to high pressures. These assumptions might not hold due to increasing pressure and heterogeneity in the rock fabric of hydrocarbon deposits. Therefore, the Langmuir model's prediction accuracy might decrease. Experimental data are usually plotted to help indicate the nature of adsorbate-adsorbent interaction at constant temperature (Ofomaja 2017).

The following is the linearized form of the Langmuir equation 3:

$$\frac{1}{qe} = \frac{1}{KL q_{max}} \times \frac{1}{Ce} + \frac{1}{q_{max}} \dots \dots \dots (3)$$

Where K_L and q_{max} are the Langmuir constants for adsorption energy and maximum adsorption capacity, respectively. Ce and qe denote the equilibrium concentration (mg.L^{-1}) and amount adsorbed at equilibrium time (mg.g^{-1}), respectively (Tran 2022). The Langmuir isotherm model may be used to explain adsorption equilibrium conditions and provide parameters (q_{max} and K_L) for quantitatively evaluating adsorption behaviours in various adsorbate-adsorbent systems (Abazli et al. 2022). The values of K_L and q_{max} may be computed by graphing $1/(qe)$ against $1/(Ce)$ (Obaid 2020). The Langmuir adsorption isotherm can alternatively be represented by the equilibrium parameter, RL , a dimensionless constant separation factor, as shown in equation 4 below:

$$RL = \frac{1}{1 + KL \times Ci} \dots \dots \dots (4)$$

where K_L is the Langmuir constant and Ci is the initial concentration in mg.L^{-1} .

The empirical isotherm of the Freundlich is a suitable isotherm for adsorption from solution. The most suitable isotherm for describing π - π interaction, H-bonding, and electrostatic attraction is the Freundlich isotherm (Pereira et al. 2023). The logarithmic form can be conveniently written as the following equation 5:

$$\ln qe = \ln Kf + \frac{1}{n} \times \ln Ce \dots \dots \dots (5)$$

where kf and n stand for the adsorption capacity and intensity, respectively. The intercept and slope of the plot of $\ln qe$ vs $\ln ce$ may be used to get the constants Kf and n .

2.5. Municipal wastewater samples

Wastewater samples were collected from three local drains in the city of Ramadi (Table 1). These drains were selected from a densely populated area where nearby houses discharge large quantities of untreated wastewater directly into the river. This wastewater contains various pollutants and is discharged without prior treatment. Wastewater samples were collected from the center and sides of the waterway using 500 mL pre-sterilized, dark-colored glass

containers with tight-fitting lids. The collected samples were taken to the laboratory for chemical analysis, including the measurement of heavy metal concentrations under optimal biosorption conditions.

Table 1: Sampling sites of Ramadi City drainages.

Site number	GPS	
	Latitude	Longitude
S 1	33.464930	43.245072
S 2	33.463824	43.340273
S 3	33.435416	43.266315

2.6. Statistical Analysis

A one-way analysis of variance (ANOVA) was employed to evaluate the significance of differences among the experimental data obtained under various operating conditions. Statistical analyses were performed using IBM SPSS Statistics (2022 version). In addition, all nonlinear regression analyses, parameter estimations, and graphical representations of the Langmuir and the Freundlich isotherm models were performed using OriginLab-Origin software (Version 8). Statistical significance was assessed at $p < 0.05$.

3. RESULTS AND DISCUSSION

The present study investigated the effects of temperature, pH, contact time, particle size, and biosorbent dosage on the biosorption efficiency of *Phoenix dactylifera* seed biomass for the removal of heavy metal ions. An initial concentration of 100 mg.L^{-1} was used to determine the optimum operating conditions for maximum metal removal.

3.1. Biosorption Performance of DS and DSP

Both *P. dactylifera* DS and DSP have the potential to perform biosorption for pollutant removal, but their efficiency and mechanism differ due to differences in composition and structure (Nehhal et al. 2025). The pH was maintained at 7 throughout the preliminary experiment to promote a negatively charged biosorbent surface and enhance electrostatic attraction toward positively charged metal ions. Higher pH values were avoided because metal precipitation may interfere with the adsorption process.

Preliminary results indicated an overall increase in the efficiency of the biosorption process when using DSP compared to DS. Statistical analysis of the results showed significant differences in biosorption efficiency between the two biomass forms for the investigated heavy metals ($p < 0.001$). The LSD value of 2.469 further indicated that DSP performed better than DS. DSP is also readily available as a waste material from local date-processing and pastry industries. The mean removal efficiencies obtained using DSP were 88.7 ± 2.4 , 66.8 ± 2.1 , 59.4 ± 0.9 , $49.9 \pm 0.6\%$ for Pb, Cd, Zn,

and Cu, respectively. These values were higher than those obtained using DS, which were $68.2 \pm 1.7\%$ for Pb, $39.4 \pm 0.6\%$ for Cd, $32.8 \pm 0.7\%$ for Zn, and $26.7 \pm 0.3\%$ for Cu, as shown in Fig. 2.

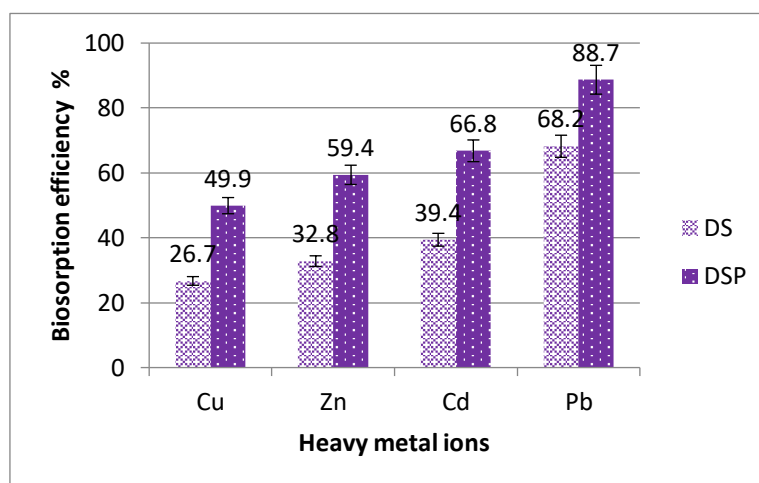


Fig. 2: Comparison between DS and DSP biosorption efficiency.

The biosorption efficiencies obtained using DSP indicated different binding affinities for the investigated metals. However, to increase the efficiency of the biosorption process, DS may need some modifications by activating with sulfuric acid, which increases the formation of effective functional groups of $-\text{SO}_3\text{H}$, and other modifications that enhance the efficiency of the treatment process (Ghanim 2023). In contrast, DSP consists of a high percentage of cellulosic fibers, carbohydrates, and various proteins, where all of these materials are rich in active carboxyl and hydroxyl groups that can bind heavy metal ions easily, quickly, and effectively through the electrostatic attraction mechanism (Akasha 2014). Therefore, DSP do not require any modifications that may be economically unfeasible, and can be used directly in the treatment process. Thus, DSP was selected for the subsequent biosorption experiments in this study.

3.2. Determination the Point of Zero Charge (pH_{pzc})

The point of zero charge (pH_{pzc}) is a key physicochemical parameter that defines the surface charge behavior of a biosorbent and plays a crucial role in controlling its interaction with metal ions during the adsorption process (Sen et al. 2026). In this study, the pH_{pzc} of *Phoenix dactylifera* (DSP biomass) was determined to be 6.5 (Fig. 3).

This value indicates that the surface of the biosorbent is positively charged at pH values below 6.5, which favors the attraction of anionic species, while at pH values above 6.5, the surface becomes negatively charged due to deprotonation of functional groups. Under these conditions, the biosorbent exhibits enhanced electrostatic attraction toward positively charged metal ions, thereby improving adsorption efficiency in alkaline media where negatively

charged active sites are more available. These findings confirm that solution pH strongly influences the biosorption process.

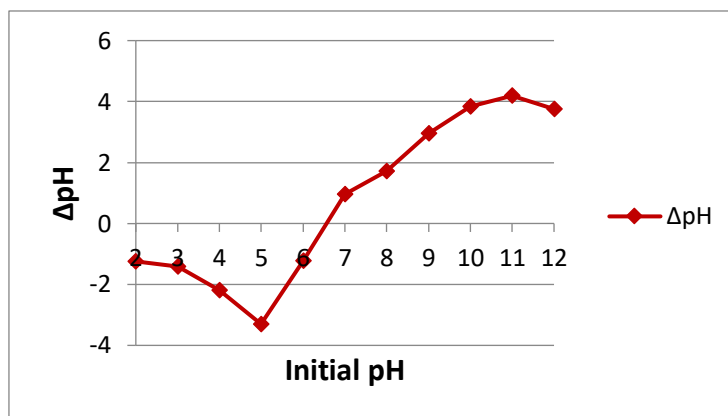


Fig. 3: Point of zero charge (pH_{pzc}) curve of DSP at 30 C°, an agitation speed of 120 rpm, a biosorbent dose of 10 g.L⁻¹, and a pH range of 2–12.

3.3. Biosorption characteristics optimization

3.3.1. Effect of pH

The effect of solution pH on the biosorption performance of *Phoenix dactylifera* biomass was found to be a critical controlling factor governing the uptake of heavy metal ions. The results clearly indicated that pH significantly influenced the adsorption efficiency of all investigated metals (Pb, Zn, Cu, and Cd). The highest overall biosorption efficiencies were observed at pH 6, where Pb exhibited the maximum removal percentage of $88.32 \pm 6.3\%$, followed by Zn ($84.91 \pm 7.2\%$), Cu ($82.87 \pm 7.8\%$), and Cd ($79.85 \pm 6.2\%$) (Fig. 4).

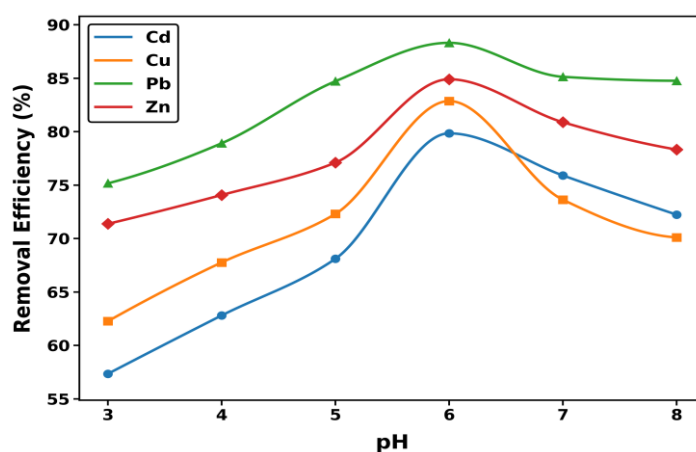


Fig. 4: Effect of solution pH on the removal efficiency of heavy metals by date seed powder.

Under strongly acidic conditions (pH 3–5), the biosorption efficiency was relatively low for all metals, with values ranging from $57.35 \pm 5.7\%$ for Cd at pH 3 to $84.72 \pm 5.7\%$ for Pb at pH 5. This reduction can be attributed to the

excessive competition between hydrogen ions (H^+) and metal cations for the available active binding sites on the biosorbent surface. As the pH increased toward neutral conditions, a progressive improvement in metal removal was observed due to reduced proton competition and increased availability of negatively charged functional groups on the biosorbent surface, which enhanced electrostatic attraction with metal ions (Sahmoune et al. 2024).

Beyond pH 6, a slight decrease in biosorption efficiency was recorded, with values ranging from $70.11 \pm 5.5\%$ for Cu at pH 8 to $85.14 \pm 5.9\%$ for Pb at pH 7. This decline may be associated with the possible formation of metal hydroxide complexes and reduced availability of free metal ions in solution.

The present results agree with previous studies identifying solution pH as an important parameter in the biosorption of heavy metals using plant-based biosorbents, including *Phoenix dactylifera*. The highest removal efficiency observed at slightly acidic pH (pH = 6) is consistent with the findings of Rambabu et al. (Rambabu et al. 2021), who reported that date seed-based biosorbents exhibit enhanced adsorption performance under neutral conditions due to increased deprotonation of surface functional groups such as hydroxyl and carboxyl groups, leading to a higher density of negatively charged active sites.

Similarly, Hu et al. (2023) reported that increasing pH promotes electrostatic attraction between positively charged metal ions and negatively charged biosorbent surfaces. Furthermore, the observed order of metal removal efficiency ($Pb > Zn > Cu > Cd$) is in agreement with Elkhaleefa et al. (2020), who attributed such variation to differences in ionic properties, including hydrated ionic radius and charge density, which influence the affinity of metal ions toward binding sites on biosorbent surfaces (Ayawei et al. 2017; Kasalkar & Wagh 2022).

However, slight discrepancies exist when compared with some studies reporting optimal biosorption of *Phoenix dactylifera* at slightly higher pH values ($\cong 7$) (Çetintaş & Bingol 2018), where such differences may be attributed to variations in biosorbent preparation methods, particle size, and surface activation treatments, all of which can significantly influence the degree of ionization of functional groups and the availability of active adsorption sites (Foo & Hameed 2010).

Statistical analysis using one-way ANOVA confirmed that the effect of pH on biosorption efficiency was highly significant ($P \leq 0.01$) for all tested metals. Moreover, significant differences were observed among the biosorption efficiencies of the different metals, as supported by the least significant difference (LSD) value of 2.058%, indicating clear variability in metal affinity toward the biosorbent under different pH conditions.

Overall, the present study confirms that pH is the dominant factor controlling the biosorption process using *Phoenix dactylifera* DSP, as it directly governs surface charge development, metal ion speciation, and the strength of electrostatic and complexation interactions responsible for heavy metal removal from aqueous solutions.

3.3.2. Effect of Contact Time

Contact time is considered one of the most influential operational parameters affecting the biosorption efficiency of heavy metal ions onto *Phoenix dactylifera* biomass, as it directly controls the interaction period between metal ions and the available active binding sites on the biosorbent surface. The obtained results demonstrated a significant increase in biosorption efficiency with increasing contact time up to the optimum equilibrium period.

At shorter contact times, particularly during the initial adsorption stages, relatively low biosorption percentages were observed for all investigated metals. The recorded values ranged from $41.22 \pm 4.9\%$ for Zn at 1 min contact time to $91.78 \pm 6.84\%$ for Pb at 60 min (Fig. 5).

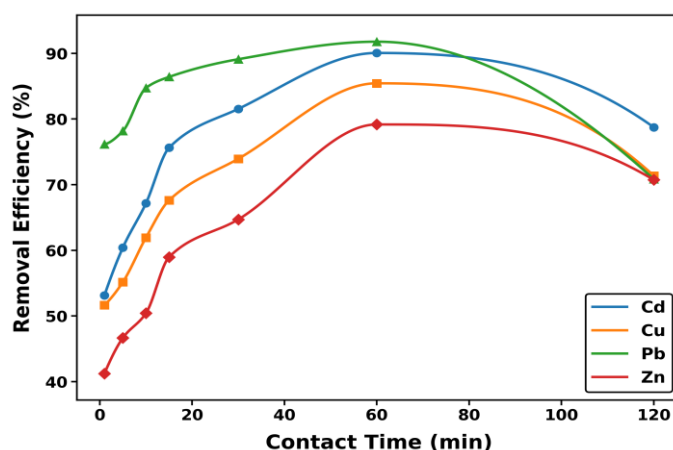


Fig. 5: Effect of contact time on removal efficiency of heavy metals using date seed powder.

The gradual increase in adsorption efficiency with time can be attributed to the progressive occupation of abundant vacant active sites present on the surface of *Phoenix dactylifera* biomass of DSP (Dada et al. 2021; Rambabu et al. 2021). During the initial stage of adsorption, the concentration gradient between the aqueous phase and the biosorbent surface is high, leading to rapid diffusion and attachment of metal ions onto the available functional groups (Tran et al. 2017).

The maximum biosorption efficiency for all examined heavy metals was achieved at 60 min contact time, indicating that equilibrium conditions were reached at this stage. The highest removal percentage was observed for Pb with a value of $91.78 \pm 6.84\%$, followed by Cd ($90.06 \pm 7.06\%$), Cu ($85.44 \pm 5.86\%$), and Zn ($79.17 \pm 6.24\%$). This enhanced adsorption performance may be associated with the increased interaction between metal ions and the oxygen-containing

functional groups naturally present in *Phoenix dactylifera* biomass, such as hydroxyl and carboxyl groups, which facilitate ion exchange and complexation mechanisms (Reta et al. 2023).

However, extending the contact time beyond 60 min resulted in a noticeable decline in biosorption efficiency. At 120 min, the adsorption percentages decreased significantly, ranging from $70.73 \pm 5.3\%$ for Zn to $78.74 \pm 4.18\%$ for Cd. This reduction may be attributed to the saturation of adsorption sites and the possible onset of desorption phenomena caused by prolonged agitation and equilibrium redistribution between the biosorbent surface and the aqueous solution (Wang & Guo 2020).

The observed decrease in biosorption efficiency beyond the optimum contact time (60 min) is in agreement with several previous studies reporting that prolonged agitation can lead to partial site saturation and adsorption–desorption equilibrium shifts on biosorbent surfaces. Similar behavior was reported by Rambabu et al. (Rambabu et al. 2021), who found that adsorption using *Phoenix dactylifera*-based biosorbents reaches equilibrium rapidly, followed by a decline or stabilization due to occupation of active sites. Likewise, Elkhaleefa et al. (Elkhaleefa et al. 2020), confirmed that extended contact time may reduce adsorption efficiency as a result of desorption and redistribution of metal ions between the solid and liquid phases. However, some agricultural biosorbents show a continuous increase or plateau at longer contact times because of stronger binding interactions and slower desorption rates (Dehmani et al. 2026).

Statistical analysis using one-way ANOVA confirmed that contact time had a highly significant effect ($P \leq 0.01$) on the biosorption percentages of all investigated heavy metals. Furthermore, the significant differences among the mean adsorption values were supported by the least significant difference (LSD) value of 14.479, indicating that adsorption efficiency is strongly dependent on equilibrium time. These findings emphasize the importance of optimizing contact time to maximize the biosorption capacity of *Phoenix dactylifera* biomass toward heavy metal removal from aqueous environments.

3.3.3. Effect of Temperature

Temperature is an important environmental factor influencing the biosorption performance of *Phoenix dactylifera* biomass, as it affects metal ion mobility, diffusion rate, and the activity of functional groups located on the biosorbent surface. The effect of solution temperature on the removal efficiency of Cd, Cu, Pb, and Zn ions by DSP is presented in Fig. 6.

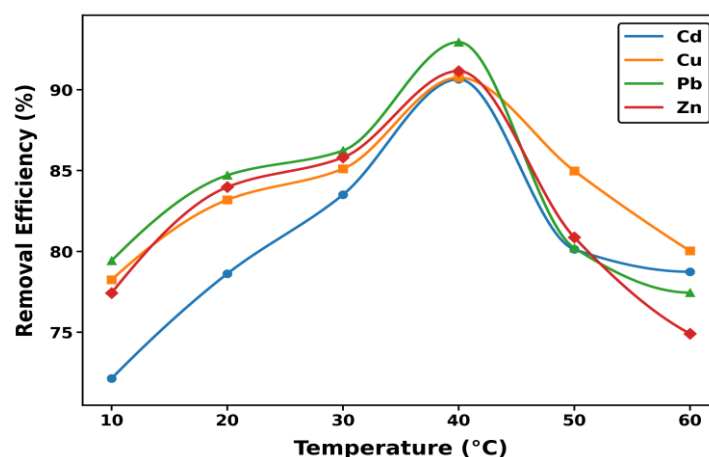


Fig. 6: Effect of temperature on removal efficiency of heavy metals using date seed powder.

The obtained results demonstrated that the biosorption efficiency increased progressively with increasing temperature up to 40°C, at which the highest adsorption percentages for all investigated heavy metals were recorded. At this optimum temperature, Pb exhibited the maximum biosorption efficiency ($92.95 \pm 7.09\%$), followed by Zn ($91.16 \pm 6.94\%$), Cu ($90.76 \pm 6.26\%$), and Cd ($90.65 \pm 6.93\%$).

The enhanced adsorption behavior at moderate temperatures may be attributed to the increased kinetic energy of metal ions, which promotes faster diffusion from the bulk solution toward the active binding sites on the DSP surface. In addition, moderate heating may improve the accessibility of adsorption sites by increasing surface activity and promoting interactions between metal ions and oxygen-containing functional groups such as hydroxyl and carboxyl groups (Abazli et al. 2022).

At lower temperatures, particularly at 10°C, the biosorption efficiency was significantly reduced, with removal values ranging from $72.14 \pm 5.05\%$ for Cd to $79.43 \pm 6.18\%$ for Pb. This decline can be explained by the reduced mobility of metal ions and slower diffusion rates under low thermal conditions, limiting effective interaction with the biosorbent surface (Khalfaoui et al. 2024).

However, when the temperature exceeded 40°C, a noticeable decrease in biosorption efficiency was observed. At 60°C, the adsorption percentages declined and ranged between $74.91 \pm 5.47\%$ and $80.03 \pm 5.07\%$ for Cu and Zn, respectively. This reduction may be associated with partial disruption of weak intermolecular interactions between metal ions and the biosorbent surface, as well as possible structural alteration of surface functional groups at elevated temperatures (Sharma & Devi 2024).

Such behavior suggests that the biosorption process using *Phoenix dactylifera* DSP biomass is more favorable under moderate thermal conditions. Overall, the present study confirms that *Phoenix dactylifera* DSP biomass exhibits optimal

biosorption performance at moderate temperatures, while higher temperatures negatively affect adsorption efficiency due to the weakening of surface interactions.

Statistical analysis confirmed that solution temperature had a highly significant effect ($P \leq 0.01$) on the biosorption efficiency of all examined heavy metals. Furthermore, significant differences among adsorption percentages were observed, as supported by the least significant difference (LSD) value of 2.179%, indicating that temperature plays a critical role in controlling the adsorption capacity and stability of DSP biomass during heavy metal removal processes.

3.3.4. Effect of Biosorbent Dosage

Biosorbent dosage is an important operational parameter influencing the efficiency of heavy metal removal by *Phoenix dactylifera* DSP biomass, as it directly determines the availability of active adsorption sites and the total surface area accessible for metal ion binding. The effect of biosorbent weight on the removal efficiency of Cd, Cu, Pb, and Zn is shown in Fig. 7.

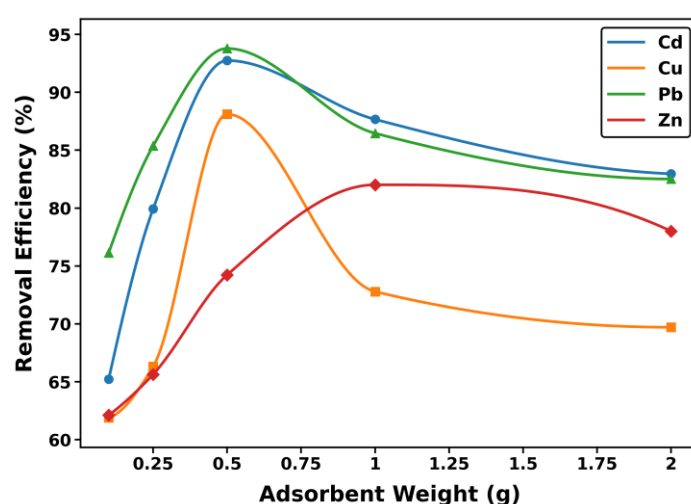


Fig. 7: Effect of adsorbent weight on removal efficiency of heavy metals using date seed powder.

The experimental results revealed that a biosorbent weight of 0.5 g achieved the highest biosorption efficiency for all investigated heavy metals except for Zn. Among the tested metals, Pb exhibited the maximum removal percentage with a value of $93.78 \pm 6.94\%$, followed by Cd ($92.74 \pm 7.06\%$) and Cu ($88.11 \pm 4.77\%$), whereas Zn recorded the lowest adsorption efficiency at $74.23 \pm 6.29\%$.

The higher adsorption efficiency observed at 0.5 g may be attributed to the optimal balance between the number of available active binding sites and the effective dispersion of DSP particles within the solution, which enhances metal ion accessibility and surface interaction. At lower biosorbent dosages (0.1 and 0.25 g), the biosorption efficiencies were

significantly lower for all tested metals. This reduction can be explained by the insufficient number of adsorption sites available to accommodate the metal ions present in solution, resulting in incomplete removal (Torres 2020).

Conversely, increasing the biosorbent weight beyond the optimum level (1 and 2 g) also resulted in a decline in adsorption efficiency. This behavior may be associated with particle aggregation and overlapping of adsorption sites at higher biomass concentrations, which reduces the effective surface area and limits the accessibility of active functional groups responsible for metal binding (Ayawei et al. 2017).

The adsorption behavior observed in this study highlights the important role of the heterogeneous surface structure of DSP and its functional groups, including hydroxyl and carboxyl groups, in controlling metal ion uptake. An optimum biosorbent dosage is therefore essential to maximize adsorption efficiency while maintaining effective utilization of the biosorbent material (Çetintaş & Bingöl 2018).

Statistical analysis using one-way ANOVA demonstrated that biosorbent weight had a highly significant effect ($P \leq 0.01$) on the biosorption percentages of all examined heavy metals. Moreover, significant differences among the mean adsorption values were confirmed by the least significant difference (LSD) value of 1.539, indicating that biosorbent dosage is a critical parameter governing the adsorption performance of *Phoenix dactylifera* DSP biomass.

3.3.5. Effect of Particle Size

Particle size is considered a significant physical parameter affecting the biosorption efficiency of *Phoenix dactylifera* biomass (DSP), as it directly influences the available surface area, accessibility of active adsorption sites, and diffusion behavior of metal ions toward the biosorbent surface. The mean biosorption percentages of Cd, Cu, Pb, and Zn adsorbed by DSP at different particle sizes are presented in Fig. 8.

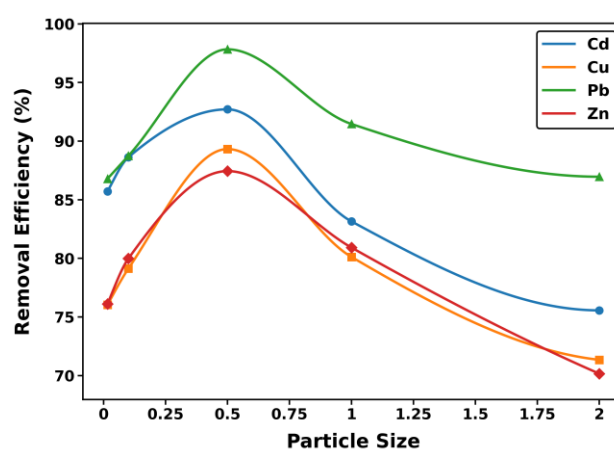


Fig. 8: Effect of particle size on removal efficiency of heavy metals using date seed powder.

The obtained results revealed that a particle size of 0.5 mm achieved the highest biosorption efficiency for all investigated heavy metals. The maximum adsorption percentages recorded at this particle size were $95.83 \pm 7.03\%$ for Pb, $92.71 \pm 6.37\%$ for Cd, $89.32 \pm 6.04\%$ for Cu, and $87.44 \pm 5.66\%$ for Zn. The superior adsorption performance observed at this intermediate particle size may be attributed to the optimal balance between surface area availability and particle stability, which enhances the accessibility of functional groups and facilitates efficient metal ion diffusion and binding (Khalaf et al. 2025).

At the smallest particle size (0.061 mm), the lowest biosorption efficiencies were observed for all examined metals. Although smaller particles generally provide a larger surface area, excessively fine particles may lead to particle agglomeration and reduced pore accessibility, thereby limiting effective interaction between metal ions and adsorption sites. As the particle size increased to 0.1 mm, the biosorption efficiency improved noticeably due to better dispersion and greater exposure of active surface sites.

However, further increases in particle size to 1 and 2 mm resulted in a gradual decline in adsorption efficiency. At the largest particle sizes, the recorded biosorption percentages decreased to $70.16 \pm 4.14\%$ for Zn, $71.34 \pm 6.02\%$ for Cu, $75.56 \pm 5.02\%$ for Cd, and $86.96 \pm 5.18\%$ for Pb. This reduction may be attributed to the decrease in total surface area and limited diffusion of metal ions into the internal adsorption sites of larger particles, which restricts the overall biosorption capacity (Wang & Guo 2020; Kasalkar & Wagh 2022).

The results of this study are consistent with Bhatnagar & Sillanpää (Bhatnagar & Sillanpää 2010), who reported that heavy metal adsorption strongly depends on the surface properties of biosorbents, particularly the presence of functional groups such as hydroxyl and carboxyl groups involved in ion exchange, electrostatic attraction, and complexation mechanisms (Raji et al. 2023).

Statistical analysis using one-way ANOVA demonstrated that particle size had a highly significant effect ($P \leq 0.01$) on the biosorption percentages of all investigated heavy metals. Moreover, significant differences among the mean adsorption values were confirmed by the least significant difference (LSD) value of 1.539, indicating that particle size is a key factor controlling the adsorption efficiency of *Phoenix dactylifera* DSP.

3.4. Biosorption Equilibrium Isotherms

3.4.1. Langmuir isotherm

The Langmuir isotherm model was used to explain adsorption equilibrium conditions and estimate the maximum adsorption capacity ($q_{\max}$) and Langmuir constant (K_L) for the investigated adsorbate–adsorbent systems (Khazaal et

al. 2022). The values of K_L and $q_{\max}$ were calculated by plotting $1/(qe)$ against $1/(Ce)$ (Obaid 2020). The correlation coefficients (R^2) for the adsorption of all metal ions were greater than 0.95, indicating a good fit to the Langmuir model (Fig. 9).

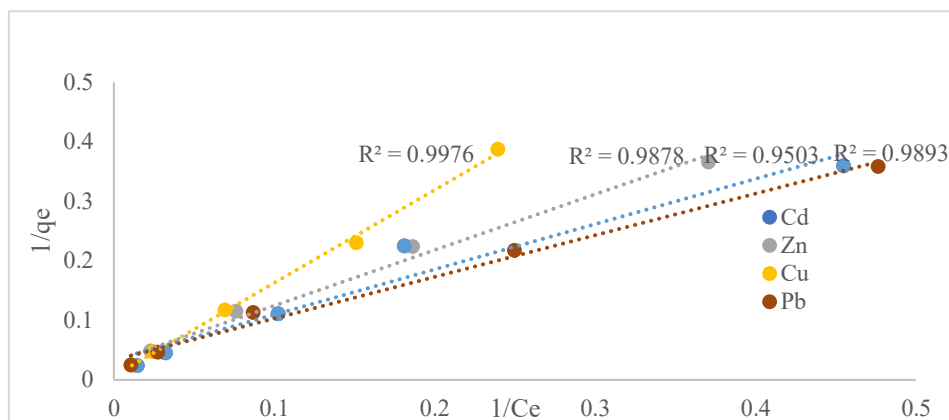


Fig. 9: Langmuir isotherm plots for the adsorption of metal ions onto DSP.

As shown in Table 2, the amount of metal ions needed to form a monolayer on the biosorbent surface ($q_{\max}$ in mg.g^{-1}) was computed from $(1/\text{intercept})$, and the constant affinity of the adsorption sites (K_L in L.mg^{-1}) was computed from $1/(\text{slope } q_{\max})$. The data presented in Table 2 indicate that the $q_{\max}$ values varied with the charge density and ionic radius of the metal ions. The order of $q_{\max}$ was $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$. Although Cd^{2+} had the lowest adsorption capacity, its relatively high Langmuir constant indicated considerable affinity for the adsorption sites. However, it has the lowest adsorption capacity ($q_{\max}$) of the investigated ions. Cd^{2+} may therefore bind strongly to a limited number of high-affinity sites. Copper (Cu^{2+}) has the highest adsorption capacity, indicating a large number of accessible sites for adsorption, despite a lower affinity per site (K_L) (Musah et al. 2022).

Table 2: The values of $q_{\max}$ and K_L for metal-ion adsorption onto DSP.

Date seed powder (DSP)			
Metal	$q_{\max}$	K_L	R^2
Cd^{2+}	29.82	0.03	0.95
Cu^{2+}	148.28	0.003	0.99
Pb^{2+}	30.15	0.04	0.98
Zn^{2+}	32.13	0.0074	0.98

The Langmuir adsorption isotherm can alternatively be represented by the equilibrium parameter, R_L (Khazaaal et al. 2022; Musah et al. 2022). Table 3 displays the R_L values that were computed for each concentration and metal ion.

Table 3: The R_L values at various concentrations and different metal ions.

Date seed powder (DSP)				
Conc.	Cd	Cu	Pb	Zn
30	0.495	0.918	0.469	0.817
50	0.370	0.870	0.347	0.729

100	0.227	0.770	0.210	0.573
250	0.105	0.573	0.096	0.349
500	0.055	0.401	0.050	0.212

According to Table 4, the parameter R_L indicates the type of isotherm. Because all R_L values were within the range $0 < R_L < 1$, adsorption was favourable for all metal ions and initial concentrations (Maharjan & Jha 2022). Consequently, the experimental data showed a good fit to the Langmuir isotherm, with favourable R_L values and correlation coefficients greater than 0.95, as shown in Fig. 9.

Table 4: The interpretation of R_L values.

Type of isotherm	R_L value
Unfavorable	$R_L > 1$
Linear	$R_L = 1$
Favorable	$0 < R_L < 1$
Irreversible	$R_L = 0$

3.4.2. Freundlich isotherm

The Freundlich isotherm is an empirical model suitable for adsorption from solution. It is commonly used to describe interactions involving hydrogen bonding and electrostatic attraction (Pereira et al. 2023). A strong linear relationship between $\ln q_e$ and $\ln C_e$ was observed, with R^2 values greater than 0.88, as shown in Fig. 10. Table 5 presents the evaluated constants.

The fact that every metal ion adsorption had n values greater than one, as shown in Table 5, suggests that the adsorption process is physical and highly heterogeneous (Jasper et al. 2020; Abazli et al. 2022). A high adsorption capacity, represented by K_F , did not necessarily correspond to a high adsorption intensity, represented by n . The K_F value may be influenced by particle characteristics, including size distribution, specific surface area, and surface functional groups. As shown in Fig. 10, the adsorption data for all metal ions fitted the Freundlich model, with correlation coefficients greater than 0.88 and n values greater than 1 (Sharafinia et al. 2021; Abazli et al. 2022).

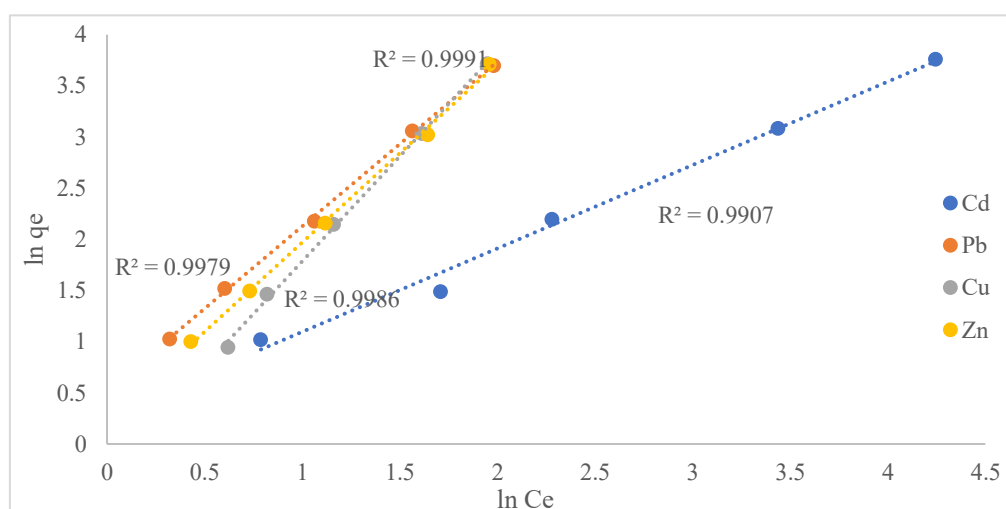


Fig. 10: Freundlich isotherm plots for removing metal ions from aqueous solutions by DSP.**Table 5:** The values of n and K_F for metal-ion adsorption onto DSP.

Metal	Date seed powder (DSP)		
	K_F	n	R_2
Cd^{2+}	1.28	1.21	0.99
Cu^{2+}	1.49	1.46	0.99
Pb^{2+}	2.55	1.74	0.99
Zn^{2+}	1.71	1.5	0.99

The adsorption behavior observed in this study may be attributed to the complex surface composition of *Phoenix dactylifera* DSP biomass, which contains multiple oxygen-containing functional groups such as hydroxyl, carboxyl, and phenolic groups capable of interacting with heavy metal ions through electrostatic attraction and ion exchange mechanisms. The relatively high correlation coefficients obtained from the Freundlich model further support the heterogeneous nature of the biosorbent surface and indicate the possibility of multilayer adsorption during the biosorption process (Jasper et al. 2020; Obaid 2020). Overall, the Freundlich isotherm findings confirm that *Phoenix dactylifera* DSP biomass possesses a heterogeneous surface structure with energetically diverse adsorption sites, making it an effective biosorbent for the removal of heavy metal ions from aqueous solutions.

3.5. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of raw date powder and metal-loaded samples (Cd-date, Cu-date, Zn-date, and Pb-date) shown in Fig. 11 reveal significant differences, indicating an interaction between functional groups of the date matrix and adsorbed metal ions. The raw date spectrum reveals a broad and strong absorption band at about 3400 cm^{-1} , which is due to O-H and N-H stretching vibrations of hydroxyl, phenolic, and amino groups (Sadia et al. 2021). The peak at approximately 2920 cm^{-1} indicates aliphatic C-H stretching (Volkov et al. 2021), whereas the bands around $1650\text{--}1600\text{ cm}^{-1}$ are attributed to C=O and amide I vibrations of proteins and carbonyl compounds (Anastasiadis 2025).

Additional peaks at 1400 cm^{-1} and 1050 cm^{-1} represent the symmetric stretching of carboxylate groups and C-O stretching of polysaccharides, respectively (Gieroba et al. 2023). The FTIR spectra reveal distinct new absorption bands in the low-frequency region following metal adsorption, demonstrating the establishment of metal-oxygen bonds on the date surface. The fitted M-O band centres were Zn-O near 539 cm^{-1} (Vidhya et al. 2022), Cd-O near 508 cm^{-1} (Kannan et al. 2022), Pb-O near 485 cm^{-1} (Yousef et al. 2025), and Cu-O near 655 cm^{-1} (Huang et al. 2022); these bands were absent from the raw date spectrum.

The emergence of these bands, together with modest changes in the O-H, C=O, and COO^- bands, shows that hydroxyl, carbonyl, and carboxylate groups engage in coordination. The higher frequency for Cu-O (655 cm^{-1}) is

compatible with a stronger/shorter Cu–O contact (and the typically larger covalent nature of Cu coordination), whereas the lower frequency for Pb–O near 485 cm^{-1} is consistent with a heavier metal and weaker Pb–O stretching.

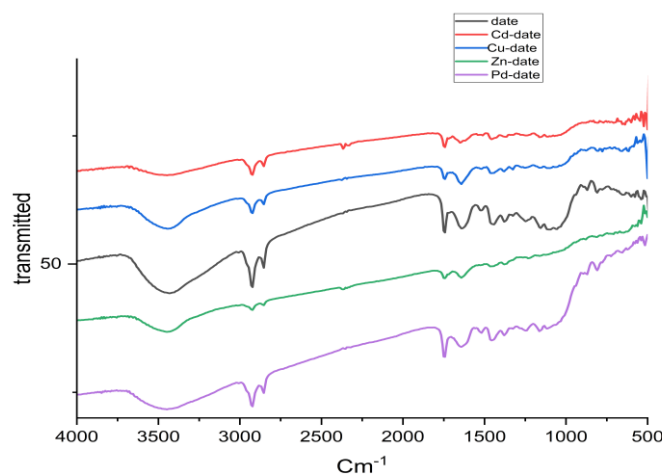


Fig. 11: FTIR spectra for DSP with heavy metal ions

The FTIR analysis confirms that *Phoenix dactylifera* DSP biomass contains multiple oxygen- and nitrogen-containing functional groups that play a crucial role in the effective binding and removal of heavy metal ions from aqueous solutions.

3.6. SEM Morphological Analysis of *Phoenix dactylifera* DSP Biomass

The morphology of non-treated and heavy metal mixture treated with date seed biomass was investigated using SEM. Fig. 12A shows date seed biomass (DSP) before biosorption at magnifications of 1.00 kx and 5.00 kx, whereas Fig. 12B shows date seed biomass (DSP) after biosorption of the studied heavy metals at the same magnifications.

The initial observation of Fig. 12A at 1.00 k $\times$ reveals the presence of completely aggregated and clumped particles with colors of varying intensity that tend to be pale. In general, these particles are characterized by relatively smooth surfaces, free of fine aggregates and crusty structures, and with sizes of approximately 10 microns. In contrast, Fig. 12B at 1.00 k $\times$ indicates the existence of small brilliant, randomly distributed, more intensely darker colored aggregates with rough surfaces, granular scale-like structures, and less uniform distribution between small and large particles, as observed more clearly at 5.00 k $\times$ magnification.

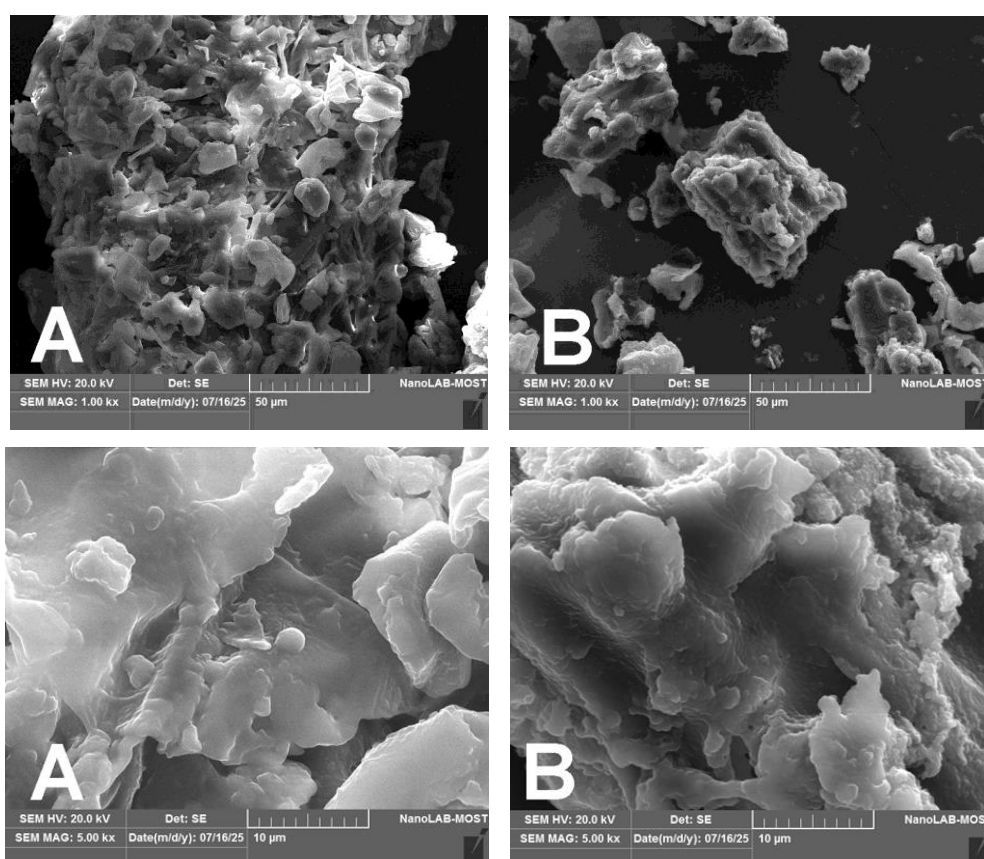


Fig. 12: SEM images of DSP (a) before biosorption, (b) after heavy metal biosorption at magnifications of 1.00 kx and 5.00 kx.

Such observed changes in the biomass morphology may be due to the deposition of heavy metal ions onto the surface of the dried biomass (Kaleem et al. 2023). However, the changes in the morphology of the biomass may be attributed to the cross-linking of functional groups and metal ions (Arief et al. 2008).

3.7. Municipal drainage analysis

Municipal drainage water is loaded with large and varied quantities of inorganic and organic pollutants coming from homes, hospitals, food, textile, paint and tanning factories, various mechanical and electronic industries, heavy industries, and other various municipal and industrial sources that contribute significantly to increasing the pollution load in such waters.

The results of the present study revealed the presence of heavy metal concentrations (lead, zinc, copper, and cadmium) that exceed the permissible limits in the effluent water of drainages. The highest recorded concentrations were 2.69 mg L^{-1} for Pb and 0.03 mg L^{-1} for Cd. The results also indicate the presence of slight differences in the values of these concentrations when examining the water discharged from such drainages. However, all of these concentrations disappeared upon treatment using DSP. Table 6 presents the concentrations of heavy metals before treatment at the

under-study drainages of Ramadi city, and after treatment using DSP, with the permissible limits for heavy metals in the effluent waters according to the World Health Organization (WHO 2013).

Table 6: Heavy metal concentrations in drainage water before and after treatment with DSP

Sites	HMs concentration in Drainage raw water (mg.L ⁻¹)				HMs concentration after DSP treatment				WHO permissible limits (mg.L ⁻¹)			
	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd
S1	2.69±0.7	1.32±0.3	0.59±0.08	0.03±0.0	Not detected				0.01	5	1	<0.1
S2	1.89±0.4	0.94±0.1	0.77±0.06	0.01±0.0	Not detected							
S3	2.01±0.6	1.11±0.3	1.26±0.1	0.02±0.0	Not detected							

The discharge of untreated municipal drainage water may contribute to increased heavy metal concentrations in the Euphrates River. These findings confirm the need for tertiary treatment to reduce heavy metal concentrations to permissible levels before the wastewater is discharged into the river.

4. CONCLUSIONS

The current study evaluated the potential of *Phoenix dactylifera* seed biomass as a biosorbent for removing heavy metal ions from aqueous solutions and municipal wastewater collected from selected local drainages of Ramadi city. *Phoenix dactylifera* seed biomass was selected for its local abundance and low cost, as well as its ability to adsorb metal ions from the surrounding environment. The cellular structure of such seeds and their content of cellulose fibers rich in active binding groups make them suitable for adsorbing heavy metal ions from polluted water, thereby reducing their concentration and hazardous effects.

The biosorption experiment was conducted under practical experimental conditions with low application costs, such as neutral pH, moderate temperature, and a retention time not exceeding 60 min. The adsorption mechanism and behavior were described using Langmuir and Freundlich isotherm models. Date seed powder demonstrated great efficiency material for biosorption of heavy metal ions from municipal wastewater. Analysis of drainage wastewater samples revealed that they contained unacceptable concentrations of some heavy metals. However, from a scientific point of view, future research and studies should target other biosorbents for improving the adsorption process, and coordinate with relevant authorities to design a treatment system that can be integrated into existing municipal water treatment projects in the country, thus preserving a healthy and sustainable aquatic environment.

Authors Contributions: Conceptualization, methodology, software, validation, formal analysis, and investigation by E.M. and S.M., writing, reviewing and editing, by S.M. and M.M. The authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

Acknowledgments: The authors thank the scientific staff working in the Biology Department, College of Science, University of Anbar, Iraq, for their valuable assistance in completing this work.

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