



Optimized Zn(II) Biosorption using Lignocellulosic Biomass from *Vitis Vinifera*: Kinetics, Isotherms, and Life Cycle Assessment Overview

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Received: 15 April 2025 / Accepted: 17 August 2025 / Published online: 3 October 2025
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Abstract This research investigates the optimized biosorption of zinc ions using lignocellulosic materials derived from *Vitis vinifera*, specifically grape stems and vine shoots. The study aims to address heavy metal pollution by utilizing agricultural waste for sustainable and cost-effective zinc ion removal from wastewater. The biosorbents were prepared and characterized, and key parameters such as initial zinc ion concentration, pH, biosorbent dose, and stirring time were optimized using Response Surface Methodology with Box-Behnken Design. The kinetics of adsorption were represented by pseudo-first-order and pseudo-second-order models, while the equilibrium isotherms were characterized using Langmuir and Freundlich models. The research achieved zinc ion removal efficiencies of up to 99.41% for grape stems and 91.93% for vine shoots. The optimal conditions for biosorption were found to be a pH of 7, a biosorbent dose of 2.1 g for grape stems and 2.5 g for vine shoots, and a stirring time of 25 min for grape stems and 18 min for vine shoots. Functional groups and alterations in the surface morphology of the biosorbents were verified through Fourier-transform infrared spectroscopy and scanning electron microscopy combined with energy-dispersive X-ray spectroscopy. Life

Cycle Assessment provided insights into the environmental impacts of zinc biosorption.

Keywords Zn(II) biosorption · Lignocellulosic biosorbents · Life cycle assessment · Adsorption isotherms and kinetics · Wine industry waste valorization

1 Introduction

Human activities, such as industrial discharges and improper agricultural practices, are the primary contributors to heavy metal pollution in water bodies, resulting in significant health and environmental hazards (Rouibah et al., 2023). Once released, heavy metals persist in the environment, are non-biodegradable, and accumulate in living organisms. This leads to their entry into the food chain, posing severe threats to aquatic ecosystems and human health (Çelebi et al., 2020). These pollutants are particularly harmful due to their toxicity and long-term environmental impact. Among heavy metals, zinc (Zn(II)) is a common contaminant in wastewater generated by industries such as galvanization, mining, fertilizer, metallurgy, battery manufacturing, and agriculture (Tokay & Akpınar, 2021). Zn(II) plays a vital role in human metabolism in trace amounts. However, excessive exposure can lead to a range of health issues, including nausea, vomiting, abdominal cramps, anemia, pancreatitis, and neurological disorders (Elleuch

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et al., 2021). Furthermore, Zn(II) accumulation in sediments increases exposure for benthic organisms, disrupting aquatic ecosystems (Anjum et al., 2024). Given these threats, finding sustainable and cost-effective solutions for Zn(II) removal has become essential. Traditional wastewater treatment methods, such as chemical precipitation, reverse osmosis, and ion exchange, are often expensive, energy-intensive, and produce secondary waste that requires additional management (Fouda-Mbanga et al., 2021; Saravanan et al., 2020). In this context, biosorption has emerged as a promising method for reducing heavy metals from wastewater. This process, which uses low-cost biological materials like agricultural waste, microbial biomass, and other renewable natural resources, offers several advantages over conventional methods (Ali Redha, 2020). It is cost-effective due to the use of waste materials, highly efficient in removing metal ions even at low concentrations, and sustainable since it generates minimal secondary waste (Ali Redha, 2020; Syeda et al., 2022). Moreover, biosorption systems are relatively easy to operate and maintain, making them suitable for use in developing regions or remote areas. The biosorbents can also be regenerated and reused, further reducing operational costs and minimizing waste.

Lignocellulosic materials are widely regarded as promising biosorbents due to their abundance, cost-effectiveness, and capacity to adsorb various contaminants, including heavy metals (Maia et al., 2021). These materials are primarily composed of lignin, hemicellulose, and cellulose, creating a complex structure rich in functional groups that facilitate strong interactions with metal ions (Abdolali et al., 2014). Agricultural residues, in particular, offer a readily available and economical source of lignocellulosic material for biosorption applications (Kainth et al., 2024). However, these residues are often discarded or burned, contributing to environmental pollution. Repurposing them as biosorbents aligns with circular economy principles, enhancing the value of waste while mitigating its environmental impact. The wine industry, a key economic sector in Spain and La Rioja, generates significant quantities of lignocellulosic waste, including vine shoots (pruned woody branches) and grape stems (grape cluster skeletons). In 2023, Spain cultivated over 961,000 ha of vineyards, yielding approximately 36.4 million hl of

wine (Federación Española del Vino, 2024). La Rioja accounted for 47,189 hectares of vineyards, producing over 2 million hectoliters annually, representing 5.5% of the national production (Ministerio de Agricultura, Pesca y Alimentación, 2024). This thriving sector produces between 2 and 3 million tons of waste annually across Spain, with vine shoots contributing 1.70–3.05 tons per hectare depending on vineyard management practices. Additionally, grape stems account for approximately 4% of the total processed grape weight. These lignocellulosic residues represent a valuable, yet underutilized, resource for biosorption. Using these materials as biosorbents not only promotes sustainable waste management but also offers an economical approach to addressing water treatment issues, especially in the removal of Zn(II) and other heavy metals from polluted water.

In addition to addressing the removal of heavy metals through biosorption, this research incorporates a life cycle assessment (LCA) to evaluate the environmental impacts associated with Zn(II) biosorption processes. While biosorption has demonstrated significant potential as an eco-friendly water treatment technology, assessing its sustainability through LCA is essential. LCA is a methodology used to assess the environmental impacts associated with all stages of a product's or process's life cycle, starting from the extraction of raw materials, through manufacturing and use, to its final disposal (Osman et al., 2024). In the context of biosorption, LCA provides a comprehensive assessment of sustainability by considering adsorption efficiency, energy consumption, resource use, emissions, and waste generation (Pundlik et al., 2021). It enables the comparison of different biosorbents to identify the most environmentally sustainable options and helps determine whether biosorption is an environmentally preferable alternative to conventional water treatment methods (Filote et al., 2021). Several research have shown that biosorbents derived from agricultural waste generally have a lower environmental footprint compared to synthetic adsorbents, such as activated carbon (Habibi et al., 2023). However, a comprehensive analysis of all life cycle stages is crucial for obtaining accurate and complete results. Despite its importance, LCA studies in biosorption remain limited, particularly in terms of comparing different materials and evaluating their performance in industrial-scale applications.

The efficiency of Zn(II) removal from wastewater using vine shoots and grape stems as biosorbents is evaluated and compared in this study, employing RSM with a BBD to optimize key process parameters. Recent studies have demonstrated the potential of agricultural waste, including winery by-products, in heavy metal biosorption, such as grape pomace for Cu(II) and Pb(II) removal (Haydar et al., 2020), and grape stems for Cu(II) and Ni(II) adsorption (Villaescusa et al., 2004). However, comparative analyses of biosorbents from the same industrial sector remain limited. Furthermore, the integration of LCA to evaluate not only the efficiency but also the environmental sustainability of biosorption processes remains underexplored. By valorizing vine shoots and grape stems, this study contributes to the circular economy while addressing the dual issues of managing agricultural waste and mitigating water pollution. The novelty of this work lies in combining process optimization with environmental impact assessment, offering a comprehensive approach to advancing sustainable wastewater treatment.

2 Materials and Methods

2.1 Preparation and Characterization of Lignocellulosic Biosorbents

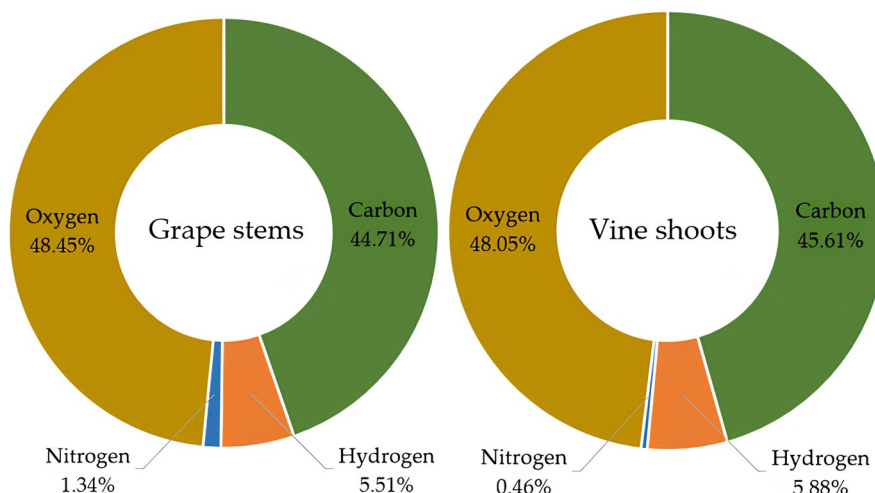
Vitis vinifera vine shoots and grape stems, agricultural residues generated during vineyard maintenance and winemaking, were collected and prepared as biosorbents. Vine shoots, woody branches pruned from grapevines during annual pruning in late winter or early spring, were gathered directly from vineyards. Grape stems, by-products of the destemming process in wineries, are the structural remains of grape clusters left after the separation of berries during winemaking. These residues are widely available and often regarded as waste, making their repurposing for biosorption both cost-effective and environmentally beneficial. To prepare these materials for biosorption, they were washed three times with deionized water to remove impurities, including residual pesticides, dust, and other organic matter. This step is crucial, as surface contaminants can interfere with metal ion adsorption and affect experimental reproducibility. The cleaned residues were then sun-dried for 72 h under ambient conditions to reduce moisture

content while preserving their structural integrity. Once dried, the residues were ground and sieved to obtain a uniform particle size of less than or equal to 320 μm , making them suitable for biosorption applications. A uniform particle size enhances surface area availability, improving metal ion binding efficiency and adsorption kinetics (Xu et al., 2022).

The elemental composition of carbon, hydrogen, nitrogen, and oxygen in the biosorbents was analyzed using a LECO Truspec Micro CHN analyzer. To ensure accuracy and consistency, all experiments were performed in triplicate, maintaining a relative deviation within $\pm 0.13\%$. The average results, consistent with typical lignocellulosic materials, are presented in Fig. 1. The high carbon content observed in both biosorbents suggests a well-developed lignocellulosic structure, which plays a key role in adsorption performance. To confirm the high lignin content characteristic of lignocellulosic biosorbents, the Klason TAPPI T222 om-6 method was applied. Lignin content was measured in triplicate to ensure reliability, yielding values of 37.3% for vine shoots and 48.6% for grape stems, further supporting their suitability as biosorbents. These values align with previous studies, which report lignin contents of approximately 30% for vine shoots, as found by Pereira et al., (2023), and around 45% in the research of Dávila et al., (2019). The lignin content obtained for grape stems is consistent with the findings of Cassoni et al., (2022), who reported similar values for raw grape stem waste.

2.1.1 FTIR Analysis of Lignocellulosic Biosorbents

Fourier-transform infrared (FTIR) spectroscopy was employed to identify the functional groups present in the lignocellulosic biosorbents and to investigate their potential involvement in Zn(II) biosorption. The spectra of grape stems and vine shoots, before and after Zn(II) uptake, were acquired using a PerkinElmer Spectrum Two FTIR spectrometer equipped with a single-reflection diamond crystal for attenuated total reflectance (ATR) measurements. This method requires no sample preparation and allows direct analysis of solid samples. Approximately 2–3 mg of finely ground biosorbent was placed on the diamond crystal using a microspatula and gently pressed to ensure optimal contact. This setup facilitates efficient interaction between the infrared radiation and

Fig. 1 Elemental composition of the biosorbents

the sample, allowing penetration a few microns deep. The reflected IR signal is then directed to a mercury cadmium telluride (MCT) detector through the instrument's optical pathway.

Spectral data were recorded in the mid-infrared region ranging from 4000 to 450 cm^{-1} , using a resolution of 4 cm^{-1} , an aperture of 8.94 mm , and averaging 20 scans per spectrum to enhance the signal-to-noise ratio. The resulting spectra were analyzed to identify the characteristic absorption bands of lignocellulosic components such as cellulose, hemicellulose, and lignin. Additionally, shifts in peak positions and changes in band intensities after Zn(II) biosorption were evaluated to elucidate the involvement of specific functional groups in the metal binding mechanisms.

2.1.2 SEM–EDX Analysis of Lignocellulosic Biosorbents

The surface morphology and elemental composition of the lignocellulosic biosorbents (grape stems and vine shoots) were analyzed before and after the Zn(II) biosorption process using scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX). The samples were prepared by placing them onto carbon adhesive tapes previously attached to standard SEM stubs. Subsequently, they were sputter-coated with a 12 nm Au layer using a Quorum Q150T-S sputter coater to enhance conductivity and improve imaging resolution.

SEM imaging was conducted with a Hitachi S–3000N scanning electron microscope, operating under high vacuum conditions with an accelerating voltage of 20 keV and a working distance of 15.0 mm . The morphological characteristics of the biosorbents were examined at different magnifications to assess surface texture, porosity, and structural changes induced by Zn(II) biosorption.

For elemental composition analysis, EDX spectra were acquired using a Bruker QUANTAX EDS system equipped with an XFlash® 6130 detector. Semi-quantitative chemical composition was determined using internal standard quantitative analyses. The EDX results provided insights into the elemental distribution on the biosorbent surfaces, allowing for the identification of Zn(II) binding and potential modifications in surface composition after the biosorption process.

2.2 Experimental Design by Response Surface Methodology

Biosorption, which involves interactions at the liquid solid interface, is influenced by several factors, including pH, metal ion concentration, or biosorbent dose (Jaafari & Yaghmaeian, 2019). These parameters require careful optimization to maximize the efficiency and reproducibility of the process, particularly for large-scale applications. Response Surface Methodology (RSM) is a powerful tool for this purpose, as it uses statistical and mathematical models to identify optimal values for the parameters involved.

This approach helps in understanding the biosorption mechanisms more comprehensively (Kowalczyk et al., 2021) and is widely applied to model processes that are influenced by multiple variables (Ba Mohammed et al., 2020). In this research, optimization was carried out using the Box-Behnken Design (BBD), a three-level optimization design within RSM methodology. The BBD enables the investigation of both linear and interaction effects of the variables on the response. This factorial design does not require all possible combinations of variable levels, reducing the number of experiments compared to other designs. As a multivariate statistical tool, RSM is commonly employed in biosorption studies to optimize conditions and validate mathematical models fitted to experimental data (Isam et al., 2019). Statistical analysis of experimental results, through response surface plots, was used to determine the optimal settings that maximize biosorption efficiency while minimizing the number of experiments and associated costs. The removal efficiency of Zn(II) was considered the dependent response, and analysis of variance (ANOVA) was used to assess the adequacy of the model.

The quadratic model was fitted to the experimental data using Design-Expert v.23.1.0 software to identify the optimal parameters for maximizing the response. A total of 25 experiments were conducted, considering the following input parameters: (1) initial Zn(II) concentration (Zn_0), (2) initial pH of the solution (pH), (3) stirring time during biosorption (Tim), and (4) biosorbent dose from vine shoots or grape stems (Bio_D). Stirring speed was maintained consistently at 200 rpm, as this value has been identified as optimal in previous studies. Zarei et al., (2024) reported 150 rpm as the optimal stirring speed for Zn(II), Cd(II), and Pb(II) biosorption using a fungal biosorbent in industrial wastewater, while Joshi et al., (2023) found that 200 rpm maximized Zn(II) removal efficiency during biosorption onto eucalyptus leaf powder. Table 1 presents the specific ranges

and values of the input parameters used in the experiments. The outputs are the Zn(II) removal percentage using grape stems (% R_GS) or vine shoots (% R_VS).

2.3 Biosorption Experiments

To assess Zn(II) biosorption without interference of other heavy metals, synthetic solutions were prepared by dissolving zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) in distilled water. This methodology ensured that only Zn(II) ions were present in the solution, maintaining a controlled environment to study the biosorption process. By using synthetic solutions, it was possible to achieve high reproducibility and maintain consistent experimental conditions, which are critical for accurate measurements and comparisons across different test conditions. Zinc concentration was measured using a PinAAcle 500 spectrophotometer, employing flame atomic absorption spectroscopy (FAAS) to determine Zn(II) levels. The method followed the standard operating procedures for FAAS analysis to ensure high accuracy and sensitivity in detecting metal ions.

To adjust the pH of the synthetic solutions within the range of 2.0 to 7.0, hydrochloric acid (HCl) was used. The pH of the distilled water was initially around 7.0, and to lower it, small amounts of HCl were added dropwise. pH changes were monitored in real time using an XS PH50 Violab DHS pH meter until the desired pH value was achieved. This precise adjustment ensured that the pH remained within the required range for optimal biosorption conditions. All chemicals used in this study were of analytical grade and sourced from Merck & Company.

2.4 Life Cycle Assessment (LCA)

Life cycle assessment (LCA) is a systematic approach to measure the environmental impacts of a product or process from the extraction of raw materials to its final

Table 1 Range and levels of input parameters for the Zn(II) biosorption experiments

Input parameter	Notation	Magnitude	Range and levels		
			−1	0	1
Initial Zn(II) concentration	Zn_0	mg/L	10	55	100
Initial pH of the solution	pH	-	2	5	7
Stirring time during biosorption	Tim	minute	10	95	180
Lignocellulosic biosorbent dose	Bio_D	g	0.1	1.6	3

disposal (Flores et al., 2019). Natural biosorbents are generally more eco-friendly and cost-effective than traditional chemical adsorbents (Rai, 2022). In this study, LCA was applied to evaluate two optimizations for Zn(II) removal from wastewater using vine shoots and grape stems as biosorbents. The first optimization aims to maximize Zn(II) removal efficiency while optimizing resource and energy consumption, thereby reflecting a balance between performance and sustainability. The second optimization prioritizes maximum removal efficiency regardless of available resources. By comparing these scenarios, this study identified trade-offs and opportunities to enhance the overall sustainability of the biosorption process. The international standards ISO 14040 and ISO 14044 ensure systematic and consistent evaluation (Rashid et al., 2023). ISO 14040:2006 establishes the fundamental principles and framework for conducting LCA, whereas ISO 14044:2006/2018 specifies methodological requirements, as shown in Fig. 2.

2.4.1 Goal and Scope

The first step in LCA is to define the goal and scope, which determines the direction and boundaries of the study. The objective of this research was to evaluate and compare the environmental impacts associated with the two optimization scenarios considered for each biosorbent (vine shoots and grape stems). This assessment aims to identify the most sustainable alternative based on Zn(II) removal efficiency, and resource and energy consumption (Aghili & Golzary,

2023). This study follows a "gate-to-gate" approach, considering the stages from biosorbent preparation to its application in contaminated water treatment. It does not include the generation of agricultural waste or final disposal of spent biosorbents. The functional unit, which serves as the reference for impact comparisons, is defined as the treatment of 1 L of water with a specific Zn(II) concentration.

2.4.2 Life Cycle Inventory (LCI)

This phase involves collecting and quantifying the input and output flows for each optimization scenario (Maity et al., 2024). The inputs include the initial Zn(II) concentration in the water, the biosorbent dosage, energy consumption by the magnetic stirrer during biosorption, and the volume of contaminated water treated. The outputs include emissions to water, specifically the amount of Zn(II) remaining after the biosorption process. agricultural waste-based biosorbents are used, no emissions to the air are generated. The spent biosorbent is sent to an authorized waste management facility, and thus, it is not considered an output. The life cycle inventory (LCI) is based on experimental data and supplemented with information from the Ecoinvent database to ensure accuracy and reliability.

2.4.3 Life Cycle Impact Assessment (LCIA)

The Life Cycle Impact Assessment (LCIA) step quantifies the environmental impacts associated with each optimization based on the inventory data (Corominas et al., 2020). This study employed the CML-IA baseline methodology, which is a widely used midpoint approach for wastewater treatment systems. The midpoint indicators focus on the early stages of the causal chain, providing a clear, standardized, and easily understandable impact evaluation (Khanali et al., 2022). Impact assessment was conducted using SimaPro v.9.2.0.2. The impact categories included global warming potential, acidification, eutrophication, and human and ecological toxicity, among others. Each category reflected a specific environmental issue. For instance, Zn(II) emissions to water contribute to aquatic ecotoxicity, while energy consumption affects GWP due to CO₂ emissions from electricity generation.

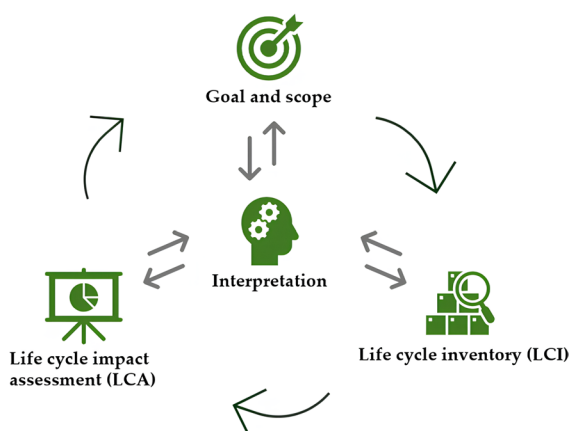


Fig. 2 Key steps for LCA methodology

2.5 Adsorption Kinetics

The adsorption kinetics of Zn(II) onto lignocellulosic biosorbents (vine shoots and grape stems) were analyzed to determine the adsorption rate and underlying mechanisms. Batch experiments were conducted by mixing 0.1 g of the biosorbent (*Bio_D*) with Zn(II) solutions at initial concentrations (*Zn_0*) of 25, 50, 70, and 100 mg/L. The solution pH (*pH*) was maintained at 7, with a stirring speed of 300 rpm at room temperature (21 °C).

At specific time intervals (10, 44, 78, 110, 146, and 180 min), samples were collected and analyzed for residual Zn(II) concentration. The amount of Zn(II) adsorbed at equilibrium and at different time points (Q_t) was calculated using Eq. (1) (Tokay & Akpınar, 2021):

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 and C_t (mg/L) are the initial and residual Zn(II) concentrations at time t (min), respectively, V (L) is the solution volume, and m (g) is the mass of the biosorbent.

To describe the adsorption kinetics, the experimental data were fitted to the pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order model is given by Eq. (2) (Revellame et al., 2020).

$$\ln(Q_e - Q_t) = \ln(Q_e - k_1 t) \quad (2)$$

where Q_e (mg/g) is the equilibrium adsorption capacity, k_1 (min^{-1}) is the rate constant of the pseudo-first-order model, and t (min) is the stirring time.

The pseudo-second-order model is represented by Eq. (3) (Vareda, 2023).

$$\frac{1}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \quad (3)$$

where k_2 (g/mg·min) is the rate constant of the pseudo-second-order model.

2.6 Adsorption Isotherms

The equilibrium sorption isotherms were analyzed to describe the uptake capacity of the vine shoots and grape stems as biosorbents for Zn(II) ions. The experiments were conducted at *pH* 7, using *Zn_0* ranging from 10 to 100 mg/L, a *Bio_D* of 0.45 g, and a *Tim* of

180 min. Among the different models available, the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherms are the most applied for characterizing metal biosorption.

The Langmuir isotherm assumes monolayer adsorption onto a surface with a finite number of identical and energetically equivalent sites (Gaikwad et al., 2024). It also postulates that once a site is occupied, no further adsorption can occur at that site, and there is no interaction between adsorbed molecules. The linear form of the Langmuir model is expressed in Eq. (4) (Chen, 2015):

$$\frac{1}{Q_e} = \frac{1}{k_L Q_m} \frac{1}{C_e} + \frac{1}{Q_m} \quad (4)$$

where Q_m (mg/g) is the maximum adsorption capacity, C_e (mg/L) is the equilibrium metal ion concentration, and k_L (L/mg) is the Langmuir adsorption equilibrium constant. The feasibility of the adsorption process can be assessed using the dimensionless separation factor (R_L), defined in Eq. (5):

$$R_L = \frac{1}{1 + k_L Zn_0} \quad (5)$$

The value of R_L indicates the favorability of biosorption: $R_L > 1$ suggests an unfavorable process, $R_L = 1$ corresponds to linear adsorption, $0 < R_L < 1$ indicates a favorable process, and $R_L = 0$ represents irreversible adsorption (Guerrero-Fajardo et al., 2020).

In contrast, the Freundlich isotherm describes adsorption on heterogeneous surfaces and assumes multilayer adsorption (Kainth et al., 2024). It is an empirical model that provides insights into the adsorption intensity and capacity. The linear form of the Freundlich equation is given as Eq. (6) (Vigdorowitsch et al., 2021):

$$\ln Q_e = \ln k_F + \frac{1}{n} C_e \quad (6)$$

where k_F (mg/g)(L/mg) is the Freundlich adsorption capacity constant, and n is a constant related to adsorption intensity. The value of $1/n$ provides information about the adsorption intensity and the surface heterogeneity of the adsorbent (Cardoso et al., 2020).

In addition to the Langmuir and Freundlich models, the Dubinin–Radushkevich (D–R) isotherm was applied to further characterize the Zn(II) biosorption process. This model is commonly used to describe adsorption on

heterogeneous and microporous surfaces and is particularly useful for distinguishing between physical and chemical adsorption mechanisms by estimating the mean adsorption energy (E) (Kutluay, 2021). The linear form of the D–R model is expressed as Eq. (7):

$$\ln Q_e = \ln Q_m - \beta \varepsilon^2 \quad (7)$$

where Q_e (mg/g) is the amount of adsorbate at equilibrium, Q_m (mg/g) is the maximum adsorption capacity, β (mol^2/J^2) is a constant related to the adsorption energy, and ε is the Polanyi potential, calculated as Eq. (8) (Kutluay & Temel, 2021):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

where R is the universal gas constant ($8.314 \text{ J/mol}\cdot\text{K}$), T is the absolute temperature (K), and C_e (mg/L) is the equilibrium concentration of Zn(II).

From the β value, the mean adsorption energy (E) (kJ/mol) can be calculated using the following equation (Eq. (9)):

$$E = \frac{1}{\sqrt{2\beta}} \quad (9)$$

The value of E provides insight into the adsorption mechanism. If $E < 8 \text{ kJ/mol}$, the process is predominantly physisorption, involving weak van der Waals forces. If $8 < E < 16 \text{ kJ/mol}$, the process is

considered chemisorption, involving stronger chemical interactions. Values of $E > 16 \text{ kJ/mol}$ suggest more complex processes such as ion exchange or structural rearrangement (Adedeji & Jahan, 2023).

The D–R model thus offers additional understanding of the interaction forces between Zn(II) ions and the biosorbent surface.

3 Results and Discussion

3.1 Experimental Findings and Analysis

Table 2 presents the input parameters and their output results. The output variable examined was the percentage of Zn(II) ions removed from water during the biosorption process. This process used either grape stems (% R_{GS}) or vine shoots (% R_{VS}) as biosorbents.

3.2 Analysis of Variance

The experimental results obtained from the BBD were used to develop a mathematical model, typically a quadratic regression model, to describe the relationship between the independent variables and Zn(II) removal efficiency (Ighalo & Eletta, 2020). The second-order polynomial equations derived for Zn(II) removal using grape stems (% R_{GS}) and vine shoots (% R_{VS}) are presented in Eqs. (10) and (11), respectively:

$$\begin{aligned} \%R_{GS} = & 32.04406 + 0.46577Zn_0 + 12.08488pH + 58.72456Bio_D + 0.10010Tim - \\ & 0.00431Zn_0pH + 0.06782Zn_0Bio_D - 0.00085Zn_0Tim - 3.42378pHBio_D - \\ & 0.00497pHTim - 0.01386Bio_DTim - 0.00498(Zn_0)^2 - 0.9728pH^2 - 8.56881Bio_D^2 + \\ & 0.00008Tim^2 \end{aligned} \quad (10)$$

$$\begin{aligned} \%R_{VS} = & 13.33565 + 0.906406Zn_0 - 16.04079pH + 38.14660Bio_D - 0.057641Tim - \\ & 0.007716Zn_0pH - 0.079316Zn_0Bio_D - 0.000465Zn_0Tim - 1.63929pHBio_D + \\ & 0.001544pHTim + 0.020406Bio_DTim - 0.006073Zn_0^2 + 2.57644pH^2 \\ & 5.35969Bio_D^2 + 0.000534Tim^2 \end{aligned} \quad (11)$$

Table 2 Experimental results of Zn(II) biosorption

	<i>Zn_0</i> mg/L	<i>pH</i> -	<i>Bio_D</i> g	<i>Tim</i> min	% <i>R_GS</i> %	% <i>R_VS</i> %
1	10	2	1.6	95	56.82	25.05
2	100	7	1.6	95	78.93	70.63
3	55	2	3.0	95	84.94	81.36
4	55	5	3.0	10	88.19	44.53
5	10	5	1.6	10	82.41	44.56
6	100	5	0.1	95	22.72	38.96
7	55	7	1.6	180	97.15	96.87
8	55	5	0.1	180	42.03	29.67
9	10	7	1.6	95	88.41	66.85
10	55	2	0.1	95	15.62	14.1
11	10	5	0.1	95	36.57	20.75
12	55	2	1.6	10	77.09	66.71
13	55	7	3.0	95	92.69	90.38
14	55	7	1.6	10	89.06	71.36
15	100	2	1.6	95	49.88	31.44
16	10	5	1.6	180	85.96	51.51
17	55	2	1.6	180	87.38	85.9
18	55	5	3.0	180	90.31	53.2
19	100	5	1.6	10	81.25	43.45
20	55	5	0.1	10	33.19	30.65
21	100	5	1.6	180	71.72	43.28
22	55	7	0.1	95	77.87	36.69
23	55	5	1.6	95	87.23	54.87
24	10	5	3.0	95	90.76	49.05
25	100	5	3.0	95	94.77	46.91

The analysis of variance (ANOVA) for Zn(II) removal using grape stems (%*R_GS*) as a biosorbent is presented in Table 3. The model exhibited a high coefficient of correlation ($R^2=0.9220$), indicating that 92.20% of the variability in the response is explained by the model, suggesting a strong fit with the experimental data. The model's F-value of 8.45 with a p-value of 0.0009 confirms its statistical significance at a 95% confidence level. Among the inputs, *Bio_D* had the strongest influence (F-value=68.52, p-value<0.0001), followed by *pH* (p-value=0.0126). Additionally, the interaction between *pH* and *Bio_D* was significant, highlighting the importance of their combined effect on the biosorption process. The quadratic term for *Bio_D* also showed significance, suggesting a non-linear relationship.

For vine shoots, the ANOVA results (Table 4) show a lower coefficient of correlation ($R^2=0.7507$), meaning the model explains 75.07% of the variability

in %*R_VS*, indicating a weaker fit compared to grape stems. Among the inputs, *pH* (p-value=0.0308) and *Bio_D* (p-value=0.0101) were identified as statistically significant, with *Bio_D* exerting the greatest effect (F-value=10.01). Comparing the ANOVA results for both biosorbents, the model for grape stems demonstrated a stronger correlation with the experimental data than vine shoots, highlighting its better predictive capability. In both cases, *Bio_D* and *pH* were the most significant factors, confirming their crucial role in the Zn(II) biosorption process.

3.3 Influence of Input Parameters

3.3.1 Influence of Initial Zn(II) Concentration (*Zn_0*) and *pH* (*pH*) on Zn(II) Removal

The response surface plots in Fig. 3(a) (for grape stems) and Fig. 3(b) (for vine shoots) illustrate the

Table 3 ANOVA results for grape stems

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	13100.66	14	935.76	8.45	0.0009
A-Zn ₀	153.78	1	153.78	1.39	0.2659
B-pH	1018.21	1	1018.21	9.19	0.0126
C-Bio_D	7589.23	1	7589.23	68.52	<0.0001
D-Tim	43.40	1	43.40	0.3919	0.5453
AB	0.9669	1	0.9669	0.0087	0.9274
AC	78.40	1	78.40	0.7079	0.4198
AD	42.77	1	42.77	0.3862	0.5482
BC	633.08	1	633.08	5.72	0.0379
BD	4.57	1	4.57	0.0413	0.8430
CD	11.68	1	11.68	0.1055	0.7520
A ²	287.61	1	287.61	2.60	0.1382
B ²	0.9529	1	0.9529	0.0086	0.9279
C ²	914.01	1	914.01	8.25	0.0166
D ²	1.02	1	1.02	0.0092	0.9256
Residual	1107.58	10	110.76		
Cor Total	14,208.24	24			

Table 4 ANOVA results for vine shoots

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	8915.68	14	636.83	2.15	0.1136
A-Zn ₀	25.54	1	25.54	0.0862	0.7750
B-pH	1869.32	1	1869.32	6.31	0.0308
C-Bio_D	2965.30	1	2965.30	10.01	0.0101
D-Tim	283.40	1	283.40	0.9570	0.3510
AB	3.09	1	3.09	0.0105	0.9206
AC	107.22	1	107.22	0.3621	0.5607
AD	12.67	1	12.67	0.0428	0.8403
BC	145.13	1	145.13	0.4901	0.4998
BD	0.4423	1	0.4423	0.0015	0.9699
CD	25.32	1	25.32	0.0855	0.7759
A ²	427.01	1	427.01	1.44	0.2575
B ²	668.45	1	668.45	2.26	0.1639
C ²	357.59	1	357.59	1.21	0.2976
D ²	42.04	1	42.04	0.1420	0.7142
Residual	2961.29	10	296.13		
Cor Total	11,876.97	24			

combined effect of Zn₀ and pH on Zn(II) removal efficiency.

pH is a crucial parameter influencing Zn(II) biosorption, as it affects both the speciation of zinc

in solution and the biosorbent's surface properties (Kayranli et al., 2021). Biosorption mechanisms like ion exchange and surface complexation are highly dependent on pH, which regulates the availability of functional groups on the biosorbent (Maia et al., 2021; Torres, 2020). At lower pH values, an excess of hydrogen ions (H⁺ or H₃O⁺) leads to the protonation of the active sites, reducing the number of available binding sites for Zn(II) ions due to electrostatic repulsion (Dang et al., 2021; Kajeiou et al., 2020). Consequently, Zn(II) removal efficiency is lower under acidic conditions due to competition between Zn(II) and H⁺ for sorption sites (Dias et al., 2023). The experimental results obtained in this study align with these theoretical considerations. As shown in Fig. 3, for both biosorbents, Zn(II) removal efficiency increased with pH. %R_{VS} increased from approximately 51% at pH 3 to around 55% at pH 5 and reached approximately 80% at pH 7. Similarly, %R_{GS} increased from around 70% at pH 3 to approximately 86% at pH 5 and peaked at 95% at pH 7. These trends are consistent with previous research that have documented an increase in Zn(II) biosorption with pH up to a range of 7.0–8.0 (Liu et al., 2019). For instance, Joshi et al., (2023) achieved 80% Zn(II) removal at pH 7.0–7.5 using lyophilized *Pseudomonas putida* biomass, while Tiwari et al., (2022) found that *Dalbergia sissoo* sawdust exhibited maximum biosorption at pH 7. Furthermore, studies on lignocellulosic biosorbents indicate that optimal metal removal occurs within the pH range of 4–7 (Madeła & Skuza, 2021).

Zn₀ also plays a significant role in biosorption efficiency. At low Zn₀ values, a higher proportion of the Zn(II) ions can be adsorbed due to the abundance of available active sites on the biosorbent surface. However, at higher Zn₀, these sites become saturated, reducing removal efficiency (Karnwal, 2024). In this study, for vine shoots, %R_{VS} increased from approximately 40% at Zn₀=10 mg/L to around 55% at Zn₀=55 mg/L, followed by a decline to approximately 43% at Zn₀=100 mg/L. A similar trend was observed for grape stems, where %R_{GS} increased from about 79% at Zn₀=10 mg/L to 87% at Zn₀=55 mg/L, before decreasing to approximately 72% at Zn₀=100 mg/L. These results align with previous studies, which report that biosorption efficiency generally increases with Zn(II) concentration until reaching a saturation plateau, beyond which

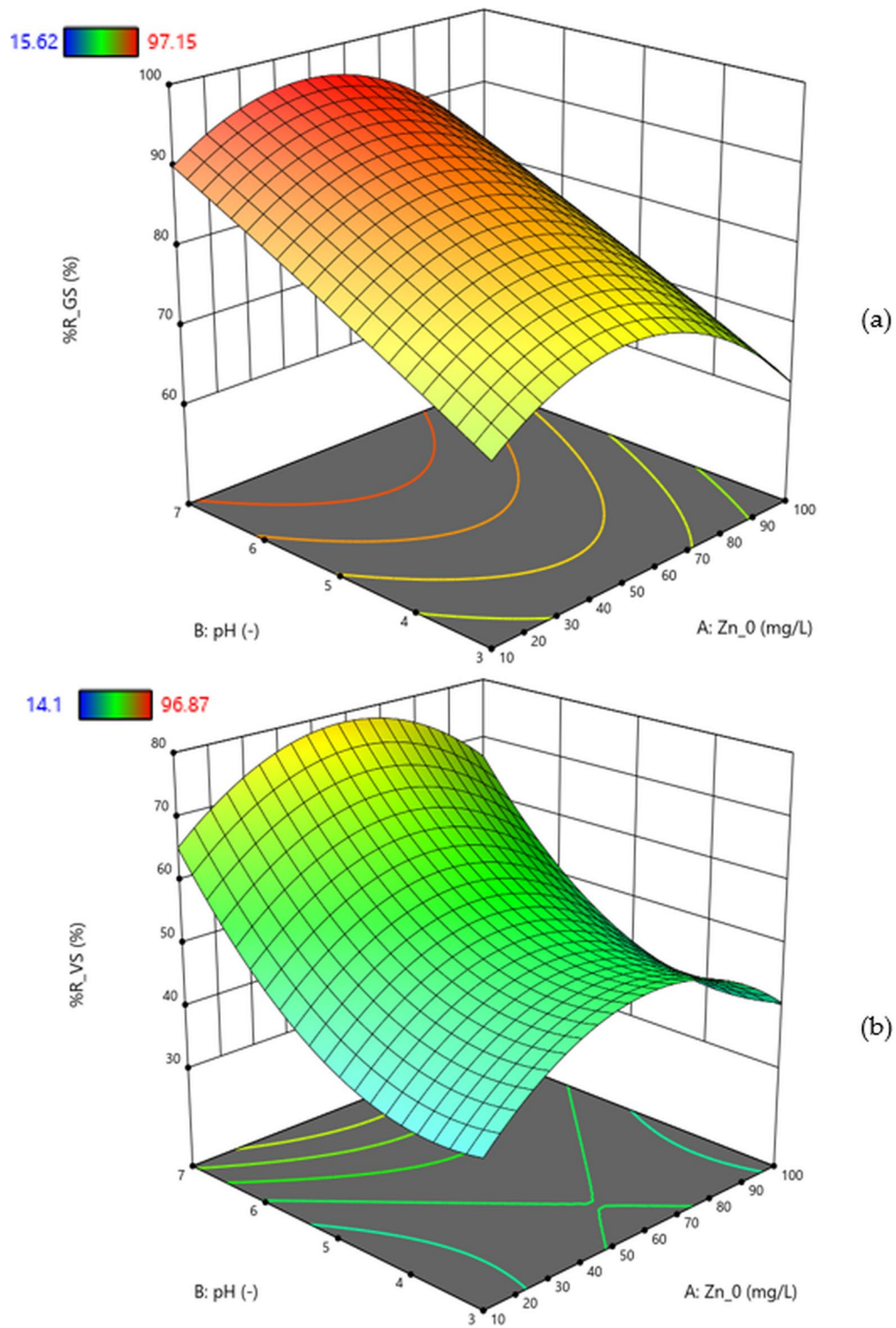


Fig. 3 Influence of Zn_0 and pH on Zn(II) removal efficiency for **a** grape stems (%R_{GS}) and **b** vine shoots (%R_{VS})

further increases in Zn(II) concentration lead to a decline in efficiency due to the exhaustion of available binding sites (Zarei et al., 2024). Similar trends have been observed for other metal ions, including Cd(II) and Pb(II), where removal efficiency initially increases but levels off due to biosorbent saturation (Imran-Shaukat et al., 2022). For instance, a study by Rouibah et al., (2023) using *Inula viscosa* leaves showed that while an increase in Zn(II) concentration enhances biosorption capacity, removal efficiency declines at higher concentrations due to the limited number of active sites. Furthermore, lignocellulosic biosorbents, such as waste biomass-derived materials, exhibit a similar trend, where sorption capacity increases significantly with Zn(II) concentration, but removal efficiency decreases at high concentrations as the sorbent reaches saturation (Dang et al., 2021).

3.3.2 Influence of Biosorbent Dose and Stirring Time on Zn(II) Removal

The biosorbent dose (*Bio_D*) and stirring time (*Tim*) significantly influence Zn(II) removal efficiency, as they determine the availability of sorption sites and the interaction between the metal ions and the biosorbent. Figure 4 illustrates the impact of these parameters on the removal percentage for both grape stems (%*R_GS*), shown in Fig. 4(a), and vine shoots (%*R_VS*), shown Fig. 4(b).

Increasing *Bio_D* generally enhanced Zn(II) removal due to the greater availability of active sites (Dang et al., 2021). However, beyond a certain point, additional biosorbent only led to marginal improvements, likely due to site saturation and particle aggregation reducing the effective surface area (Kayranli et al., 2021). For grape stems, %*R_GS* increased from 40% at *Bio_D*=0.1 g to 60% at *Bio_D*=1.6 g, reaching 92% at *Bio_D*=3 g. A peak value of 95% was observed at *Bio_D*=2.4 g, suggesting an optimal biosorbent dose beyond which further increases did not lead to substantial improvements. A similar trend was observed for vine shoots, where %*R_VS* increased from 30% at *Bio_D*=0.1 g to 53% at *Bio_D*=1.6 g, reaching 58% at *Bio_D*=3 g, with a maximum value of 60% at *Bio_D*=2.4 g. This behavior aligns with previous studies on Zn(II) biosorption, which describe a two-phase biosorption process: an initial rapid uptake due to the abundance

of free binding sites, followed by a slower phase as equilibrium is approached (Priya et al., 2022). The rapid phase typically occurs within the first few minutes, where a substantial reduction in Zn(II) concentration (Karnwal, 2024). For instance, comparable results were observed in Zn(II) biosorption using tea waste, with maximum removal occurring within 2–10 min and equilibrium was reached within 30–60 min (Çelebi et al., 2020). Likewise, Zn(II) biosorption onto lignocellulosic materials peaked within 30 min, with no significant improvement thereafter (Rouibah et al., 2023).

Regarding *Tim*, the results show that at low contact times, the removal efficiency is lower, while prolonged contact times enhance Zn(II) uptake. For grape stems, %*R_GS* increased from 85.5% at 10 min to 86.3% at 95 min, reaching 89% at 180 min. For vine shoots, removal efficiency increased from 53.5% at 10 min to 54% at 95 min, and reached 63% at 180 min. The initial rapid phase of Zn(II) biosorption can be attributed to the availability of numerous active sites on the biosorbent surface, allowing a fast uptake of metal ions (Thakur et al., 2020). This is consistent with previous studies reporting that most of the Zn(II) removal occurs within the first few minutes of contact (Çelebi et al., 2020). For instance, in a study using lignocellulosic biosorbents, Zn(II) removal increased significantly within the first 10 min, reaching equilibrium within 30 min (Kayranli et al., 2021). Beyond a certain duration, extending the stirring time led to only slight enhancements in Zn(II) removal efficiency. This behavior is attributed to the progressive saturation of active sites, leading to a dynamic equilibrium between adsorption and desorption (Rouibah et al., 2023). Studies have shown that biosorption equilibrium is typically reached within 60 to 180 min, depending on the biosorbent characteristics (Ighalo & Eletta, 2020; Pereira et al., 2024). For instance, Zn(II) uptake by *Moringa oleifera* reached 90% within 40 min, with equilibrium established at 50 min (Joshi et al., 2023). Similarly, biosorption of Zn(II) using *Inula viscosa* leaves achieved maximum adsorption at 60 min (Rouibah et al., 2023).

3.4 Optimization of Zn(II) Biosorption and Life Cycle Assessment

Optimization involves identifying the most favorable values of controllable factors that influence a system or process to achieve the desired outcome in the

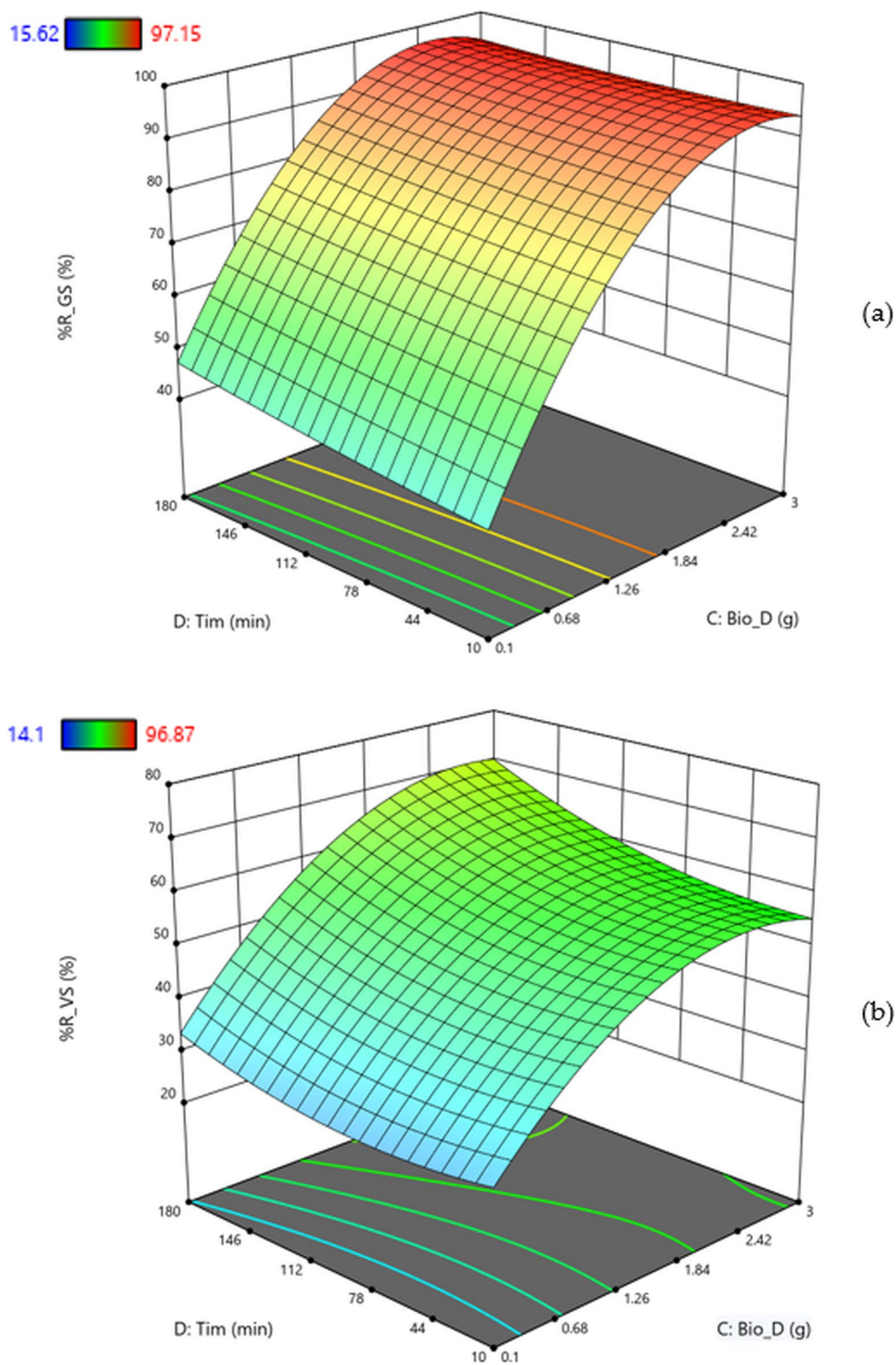


Fig. 4 Influence of *Bio_D* and *Tim* on Zn(II) removal efficiency for (a) grape stems (%R_{GS}) and (b) vine shoots (%R_{VS})

Table 5 Optimal experimental conditions and predicted Zn(II) removal efficiencies obtained from optimization 1

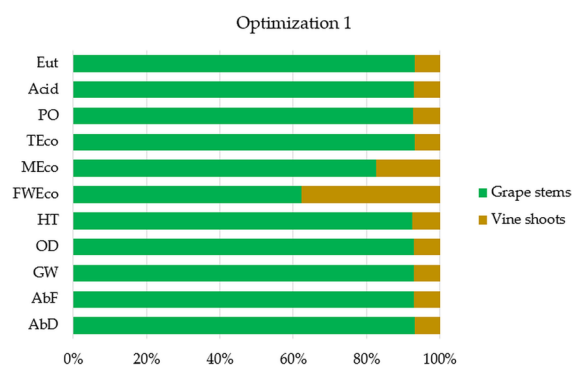
	Unit	Goal	Min	Max	Biosorbent	
					Grape stems	Vine shoots
<i>Zn₀</i>	mg/L	is in range	10	100	88	55
<i>pH</i>	-	is in range	2	7	7	7
<i>Bio_D</i>	min	minimize	0.1	3	1.3	1.4
<i>Tim</i>	g	minimize	10	180	10	10
<i>%R</i>	%	maximize	82.96	99.99	85.73	70.98

Table 6 Optimal experimental conditions and predicted Zn(II) removal efficiencies obtained from optimization 2

	Unit	Goal	Min	Max	Biosorbent	
					Grape stems	Vine shoots
<i>Zn₀</i>	mg/L	is in range	10	100	55	48
<i>pH</i>	-	is in range	2	7	7	7
<i>Bio_D</i>	min	is in range	0.1	3	2.1	2.5
<i>Tim</i>	g	is in range	10	180	25	18
<i>%R</i>	%	maximize	82.96	99.99	99.41	91.93

most favorable conditions (Zarei et al., 2024). Elleuch et al., (2021) further emphasize that determining optimal parameter values is crucial for obtaining the best possible results within system constraints. Table 5 presents the first optimization (O1), which aimed to enhance cost-effectiveness by minimizing *Bio_D* and *Tim* while maintaining high removal efficiency. Under these conditions, grape stems achieved a removal efficiency of 85.73%, while vine shoots reached 70.98%, requiring 1.3 g and 1.4 g of biosorbent, respectively. In contrast, Table 6 summarizes the second optimization (O2), where the primary objective was to maximize Zn(II) removal. This approach resulted in a significant improvement, with Zn(II) removal increasing to 99.41% for grape stems and 91.93% for vine shoots, while *Bio_D* and *Tim* were optimized to 2.1 g and 2.5 g, and 25 min and 18 min, respectively. Notably, in this scenario, *Zn₀* was lower than in O1, at 55 mg/L for grape stems and 48 mg/L for vine shoots, contributing to enhanced performance. In both cases, pH was kept constant at 7, as it was identified as the optimal value for Zn(II) biosorption.

Integrating Life Cycle Assessment (LCA) early in the development of technologies has the potential to enhance process optimization and improve understanding of how design choices impact the environmental performance of treatment systems, including those for metal removal (Harris et al., 2021). To assess the environmental performance of both optimization

**Fig. 5** Midpoint analysis results for Optimization 1, highlighting environmental impact categories under the optimized conditions

scenarios, an LCA was conducted, as illustrated in Figs. 5 and 6. The LCA considered the following impact categories: Abiotic Depletion (AbD), Abiotic Depletion (fossil fuels) (AbF), Global Warming (GW), Ozone Layer Depletion (OD), Human Toxicity (HT), Freshwater Aquatic Ecotoxicity (FWEco), Marine Aquatic Ecotoxicity (MEco), Terrestrial Ecotoxicity (TEco), Photochemical Oxidation (PO), Acidification (Acid), and Eutrophication (Eut). As shown in Table 7, the comparative results indicate that O1 generally exhibited lower environmental impacts than O2, confirming the expected benefits of reduced *Bio_D* and *Tim*. This aligns with previous findings

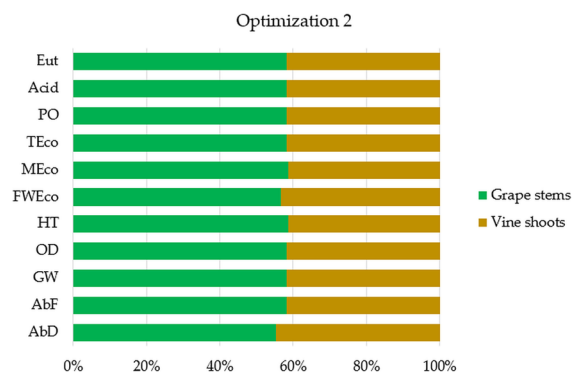


Fig. 6 Midpoint analysis results for optimization 2, highlighting environmental impact categories under the optimized conditions

highlighting how the optimization of sorption parameters directly influences environmental burdens (Filote et al., 2021). However, for grape stems, some impact categories such as GW and HT were higher in O1 than in O2, likely due to differences in Zn_0 concentration. Comparing the two biosorbents, grape stems

generally showed higher environmental impacts than vine shoots in both scenarios. For vine shoots, O1 displayed reduced AbD, PO, and Acid compared to O2. However, for grape stems, while O1 also had lower impacts in several categories, the reduction was less pronounced in FWEco and Eut.

3.5 Adsorption Kinetic Modeling

The adsorption kinetics of Zn(II) onto vine shoots and grape stems were evaluated using the pseudo-first-order and pseudo-second-order models. The kinetic parameters obtained for both biosorbents at different initial Zn(II) concentrations are presented in Tables 8 and 9.

For grape stems (Table 8), the pseudo-second-order model exhibited higher correlation coefficients ($R^2=0.9963$) compared to the pseudo-first-order model (ranging from 0.6969 to 0.8968), suggesting that chemisorption primarily governed the adsorption process (Kainth et al., 2024). The equilibrium adsorption capacity (Q_e) increased with the initial Zn(II)

Table 7 Midpoint impact category results of the LCA for both optimization scenarios

Impact category	Unit	Grape stems		Vine shoots	
		O1	O2	O1	O2
AbD	kg 1,4-DB eq	5.81E-06	4.18E-06	4.27E-07	3.38E-06
AbF	MJ	2.11E-02	5.73E-02	1.60E-03	4.11E-02
GW	kg 1,4-DB eq	1.84E-03	5.01E-03	1.40E-04	3.60E-03
OD	kg CO ₂ eq	2.43E-10	6.42E-10	1.85E-11	4.62E-10
HT	kg 1,4-DB eq	7.33E-04	3.74E-03	5.96E-05	2.63E-03
FWEco	kg 1,4-DB eq	2.58E-03	5.49E-03	1.57E-03	4.22E-03
MEco	kg SO ₂ eq	1.43E+00	8.67E+00	3.03E-01	6.10E+00
TEco	kg PO ₄ eq	1.60E-05	4.31E-05	1.18E-06	3.09E-05
PO	kg C ₂ H ₄ eq	3.47E-07	9.85E-07	2.76E-08	7.07E-07
Acid	kg SO ₂ eq	8.36E-06	2.44E-05	6.40E-07	1.70E-05
Eut	kg Sb eq	6.20E-06	1.75E-05	4.26E-07	1.26E-05

Table 8 Kinetic results for grape stems

Model	Parameter	Initial Zn(II) concentration			
		25 mg/L	50 mg/L	70 mg/L	100 mg/L
Pseudo-first-order	R^2	0.8764	0.8867	0.8968	0.6969
	Q_e (mg/g)	0.4613	0.1708	0.0574	0.3513
	k_1 (min ⁻¹)	0.0170	0.0184	0.0233	0.0099
Pseudo-second-order	R^2	0.9963	0.9985	0.9994	0.9999
	Q_e (mg/g)	12.1212	27.1003	38.0228	43.8596
	k_2 (g/mg min)	0.0135	0.0096	0.0114	0.0361

Table 9 Kinetic results for vine shoots

Model	Parameter	Initial Zn(II) concentration			
		25 mg/L	50 mg/L	70 mg/L	100 mg/L
Pseudo-first-order	R^2	0.9775	0.9465	0.9181	0.8511
	Q_e (mg/g)	0.4418	0.3517	0.6289	1.2078
	k_1 (min^{-1})	0.0166	0.0143	0.0129	0.0115
Pseudo-second-order	R^2	0.9876	0.9936	0.9953	0.9960
	Q_e (mg/g)	9.3809	24.0385	35.4610	45.2489
	k_2 (g/mg min)	0.0125	0.0069	0.0053	0.0045

concentration, reaching a maximum of 43.86 mg/g at 100 mg/L. The pseudo-second-order rate constant (k_2) varied with concentration, with the highest value at 100 mg/L (0.0361 g/mg·min). Similarly, for vine shoots (Table 9), the pseudo-second-order model provided a better fit ($R^2=0.9876$) than the pseudo-first-order model (ranging from 0.8511 to 0.9775). The equilibrium adsorption capacity of vine shoots was slightly lower than that of grape stems, with a maximum of 45.42 mg/g at 100 mg/L.

The results of this study align with previous research employing biomass for Zn(II) biosorption. For instance, Kayranli et al., (2021) investigated Zn(II) biosorption using banana peel and identified the pseudo-second-order model as the best fit. Similarly, Rouibah et al., (2023) found that *Inula viscosa* leaves followed the same kinetic model, as did Priya et al., (2022) with rice husk ash, further supporting the predominance of chemisorption in Zn(II) biosorption across different biosorbents.

To provide a clearer comparison of the kinetic model fits, nonlinear plots were generated for both pseudo-first-order and pseudo-second-order models across the full range of initial Zn(II) concentrations tested (25–100 mg/L). Figures 7 and 8 show the results obtained for grape stems and vine shoots, respectively. In each case, the experimental data are represented alongside the fitted curves for the two models.

3.6 Adsorption Isotherm Modeling

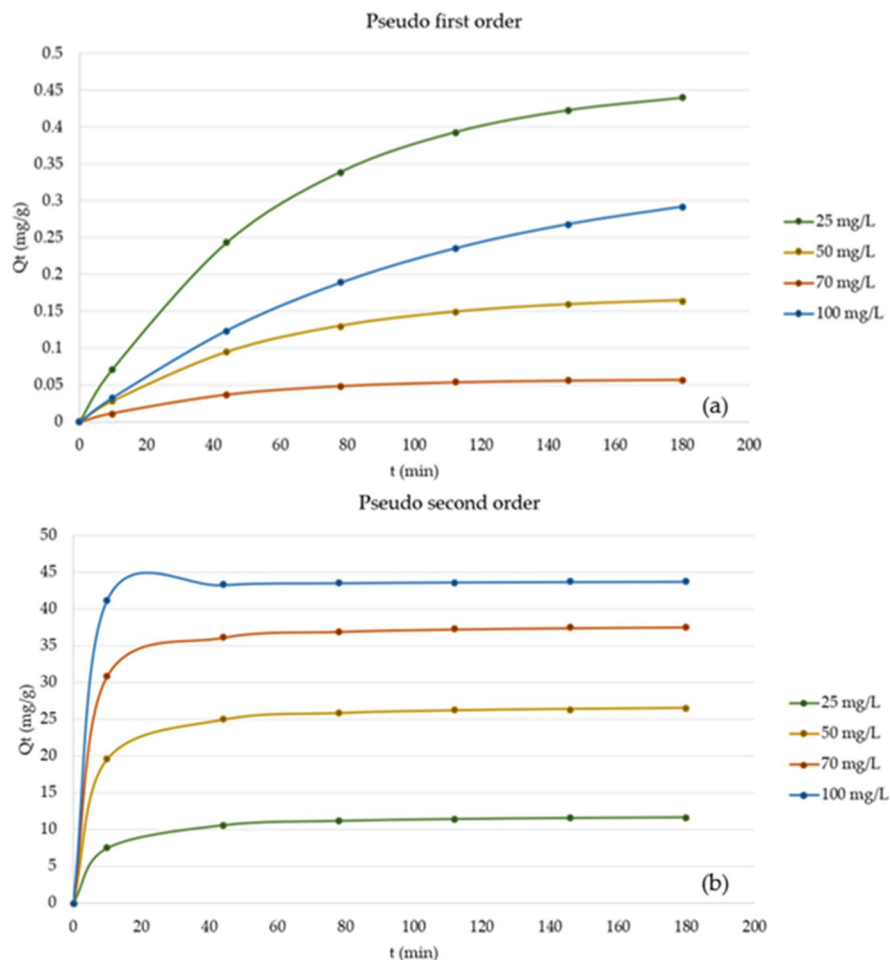
The equilibrium adsorption data were fitted to the Langmuir, Freundlich, and D-R models to evaluate the biosorption mechanism of Zn(II) onto grape stems and vine shoots. The obtained isotherm parameters and correlation coefficients (R^2) are summarized in Table 10. The Langmuir model provided a better fit for grape

stems ($R^2=0.9854$), suggesting that Zn(II) biosorption primarily follows a monolayer adsorption mechanism (Kainth et al., 2024). The maximum adsorption capacity (Q_m) value of 40.5039 mg/g suggests a high adsorption capacity for Zn(II). For vine shoots, the Freundlich model exhibited a higher correlation coefficient ($R^2=0.9876$), suggesting that biosorption occurs on a heterogeneous surface with multilayer interactions (Zarei et al., 2024). The Freundlich constant (n) was 1.3236 for grape stems, indicating favorable adsorption, whereas for vine shoots ($n=0.6861$), the biosorption process was less favorable but still effective.

Furthermore, the separation factor (R_L) ranged from 0.8075 to 0.2955 for grape stems and from 0.7820 to 0.2640 for vine shoots, confirming that Zn(II) biosorption was favorable under the studied conditions. As Zn_0 increased, the R_L value decreased, indicating enhanced adsorption capacity at higher initial concentrations.

The D–R model was also applied to provide further insight into the adsorption mechanism. The correlation coefficients ($R^2=0.9603$ for grape stems and 0.9674 for vine shoots) support the suitability of this model for describing Zn(II) biosorption onto both biosorbents. The estimated mean adsorption energy (E) was 345.77 J/mol for grape stems and 166.67 J/mol for vine shoots, which are both below 8 kJ/mol. These values indicate that the process is governed predominantly by physisorption, involving weak electrostatic interactions or van der Waals forces (Abdolali et al., 2014). This result is consistent with the surface heterogeneity suggested by the Freundlich model and further confirms that the Zn(II) uptake occurs mainly through physical interactions under the studied conditions (Hung et al., 2023). The Q_m values obtained from the D–R model were 10.85 mg/g for grape stems and 12.75 mg/g for vine shoots, which are lower than those from the Langmuir model, as expected for this type of analysis.

Fig. 7 Kinetic **a** pseudo first and **b** pseudo second order modeling for Zn(II) biosorption using grape stems



To further illustrate the performance of the applied isotherm models, nonlinear plots comparing the experimental data with the theoretical curves of Langmuir, Freundlich, and D–R models were generated for both biosorbents (Fig. 9). These visual representations confirm the numerical trends observed in Table 10. For grape stems (Fig. 9a), the Langmuir model shows the best agreement with the experimental data, especially in the mid-to-high concentration range, indicating a monolayer adsorption pattern. In contrast, vine shoots (Fig. 9b) align more closely with the Freundlich model, particularly at higher concentrations, supporting the notion of heterogeneous multilayer adsorption. The D–R model provided a reasonable fit in both cases, especially in the intermediate C_e range, highlighting the possible contribution of surface porosity and energetically non-uniform sites.

Table 11 presents a comparison with various biosorbents documented in the literature. For instance, graphene oxide exhibited the highest adsorption capacity ($Q_m = 313.4$ mg/g), while the adsorption capacities of other biosorbents varied depending on their composition and surface modifications. Among the lignocellulosic-based biosorbents, carboxylated biomass demonstrated the highest adsorption capacity ($Q_m = 46.49$ mg/g), followed by xanthated biomass ($Q_m = 36.59$ mg/g) and alkalinized biomass ($Q_m = 20.12$ mg/g).

3.7 FTIR Characterization of Lignocellulosic Biosorbents

The FTIR spectra of grape stems and vine shoots before and after Zn(II) biosorption are presented in Fig. 10. In the raw materials, a broad absorption

Fig. 8 Kinetic **a** pseudo first and **b** pseudo second order modeling for Zn(II) biosorption using vine shoots

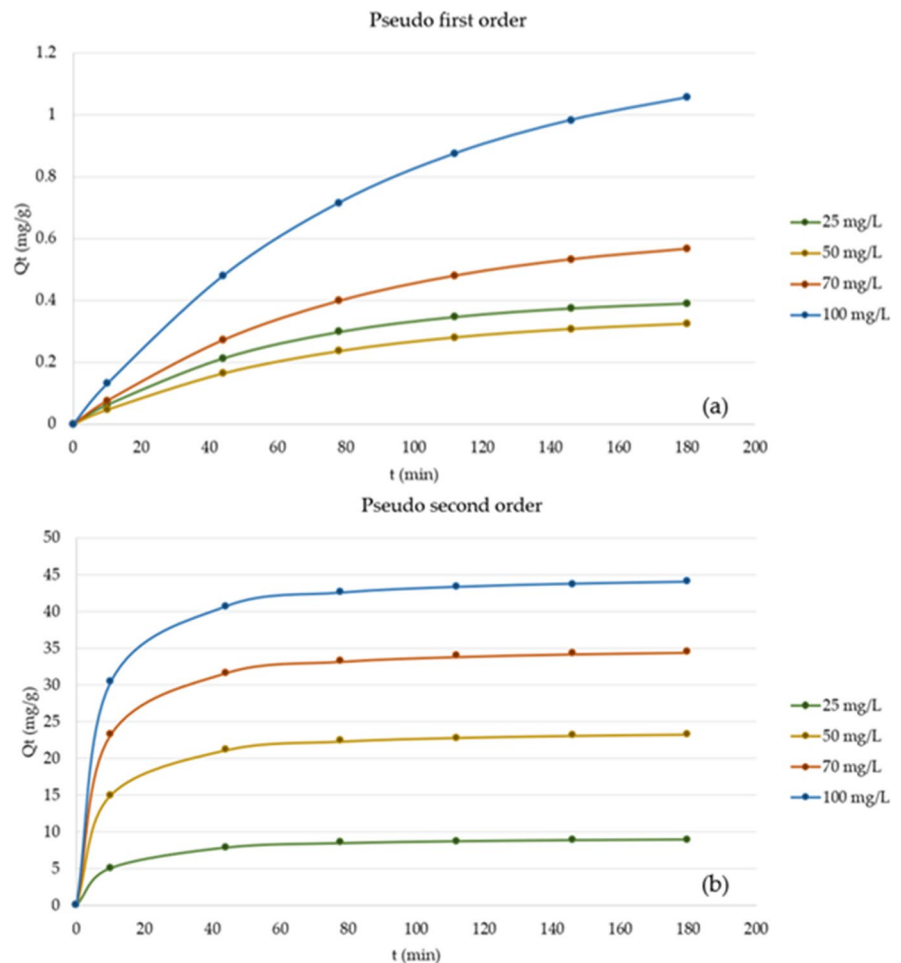


Table 10 Isotherm parameters for the Zn(II) biosorption process onto grape stems and vine shoots

Model	Parameter	Grape stems	Vine shoots
Langmuir	R^2	0.9854	0.9797
	Q_m (mg/g)	40.5039	10.1484
	k_L (L/mg)	0.0238	0.0279
Freundlich	R^2	0.9659	0.9876
	n	1.3236	0.6861
	k_F (mg/g)(L/mg) $^{1/n}$	1.3280	7.0049
Dubinin – Radushkevich (D–R)	R^2	0.9603	0.9674
	Q_m (mg/g)	10.8497	12.7472
	E (J/mol)	345.77	166.67
	β (mol ² /J ²)	$4.18 \cdot 10^{-6}$	$1.80 \cdot 10^{-5}$

band around 3330–3350 cm^{-1} was observed, corresponding to O–H stretching vibrations typically associated with hydroxyl groups in cellulose and lignin (Jayakumar et al., 2022). Peaks located at approximately 2920 cm^{-1} and 2850 cm^{-1} were assigned to asymmetric and symmetric C–H stretching in aliphatic chains, likely from hemicellulose and lignin structures (Tokay & Akpınar, 2021). A distinct peak near 1730 cm^{-1} was detected, indicating the presence of C=O stretching vibrations from carboxylic and ester functional groups, which are essential for metal coordination (Kajeiou et al., 2020). This was accompanied by a prominent band near 1605–1610 cm^{-1} , attributable to C=C stretching in aromatic rings, likely from the lignin

Fig. 9 Equilibrium isotherm modeling for Zn(II) biosorption using **a** grape stems and **b** vine shoots. Experimental data are fitted to Langmuir, Freundlich, and Dubinin–Radushkevich models

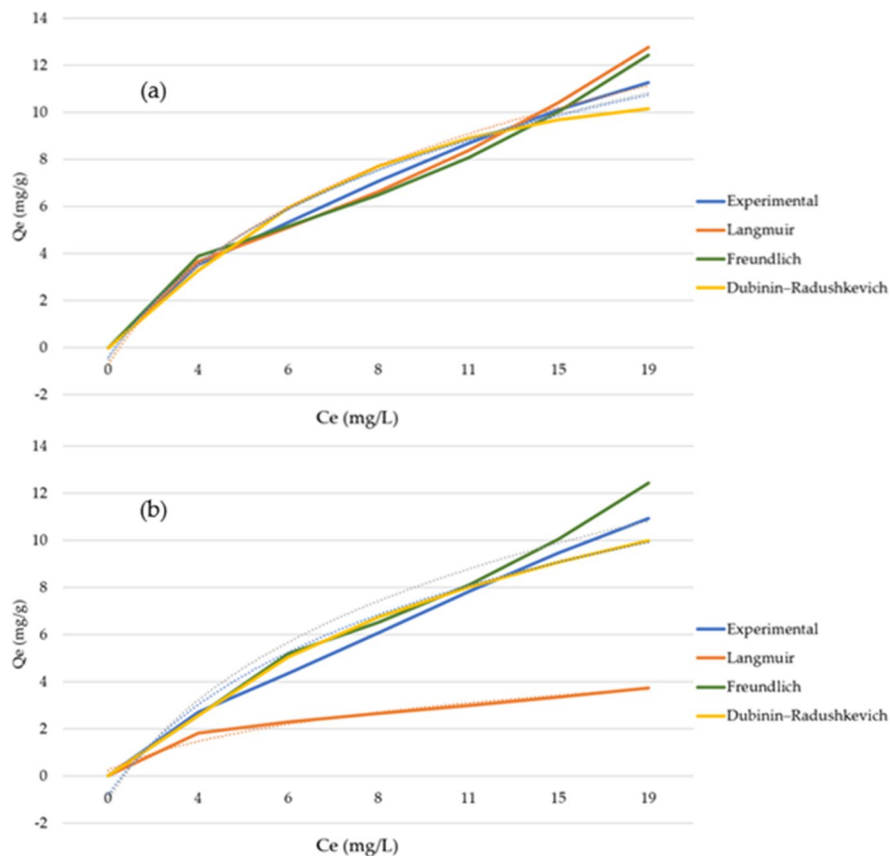


Table 11 Comparative adsorption capacities of various biosorbents for Zn(II) removal

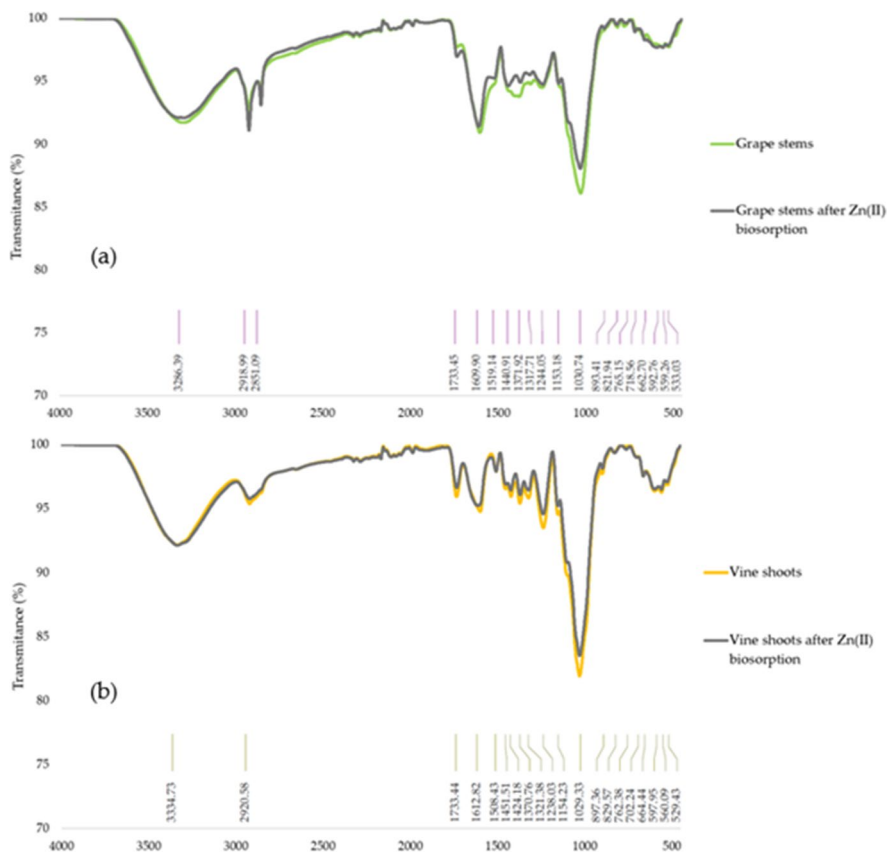
Sorbent type	Isotherm model	Q_m (mg/g)	Reference
Graphene oxide	Langmuir	313.4	Guerrero-Fajardo et al., (2020)
Alkalized residual biomass	Langmuir	20.12	Dang et al., (2021)
Xanthated residual biomass	Langmuir	36.59	Dang et al., (2021)
Carboxylated residual biomass	Langmuir	46.49	Dang et al., (2021)
ZnCl ₂ -activated biochar derived from sawdust	Freundlich	-	Maiti et al., (2023)
<i>Inula viscosa</i> leaves	Langmuir	10.66	Rouibah et al., (2023)
<i>Micropogonias undulatus</i> scales	Freundlich	-	Joshi et al., (2023)
<i>Sargassum polycystum</i> biomass	Langmuir	116.2	Joshi et al., (2023)
Banana peel-derived activated carbon	Langmuir	49.5	Pereira et al., (2024)

component. Additionally, a series of peaks between 1250 and 1030 cm^{-1} was observed, which can be attributed to C–O stretching vibrations in alcohols, esters, and ethers, indicating the lignin and polysaccharide nature of the materials (Joshi et al., 2023).

After Zn(II) biosorption, changes in peak positions and intensities were noted. The O–H stretching

band exhibited a slight shift to lower wavenumbers, indicating the participation of hydroxyl groups in hydrogen bonding or metal chelation during Zn(II) interaction (Jayakumar et al., 2022). Similarly, the C=O band at 1730 cm^{-1} also showed minor shifts, suggesting interaction with metal ions. The intensity of the C=C band at 1605–1610 cm^{-1} decreased

Fig. 10 FTIR spectra of lignocellulosic biosorbents before and after Zn(II) biosorption: **a** raw grape stems and grape stems after Zn(II) biosorption, **b** raw vine shoots and vine shoots after Zn(II) biosorption



slightly, as did the bands in the 1030–1250 cm^{-1} region, indicating possible involvement of these functional groups in Zn(II) complexation. These findings are in line with previous research, such as the work by Kayranli et al., (2021), who reported similar C=O shifts during Zn(II) adsorption onto fruit-waste-based biosorbents. Likewise, (Ighalo & Eletta, 2020) observed reductions in aromatic and C–O band intensities during Zn(II) biosorption using *Micropogonias undulatus* scales, further supporting the current results.

3.8 SEM–EDX Characterization of Zn(II) Biosorption on Lignocellulosic Biosorbents

The surface morphology and elemental composition of grape stems and vine shoots were analyzed before and after Zn(II) biosorption using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). The SEM images, presented in Fig. 11, reveal significant structural differences between the raw and Zn(II)-adsorbed biosorbents. Prior

to Zn(II) biosorption, both grape stems (Fig. 11a) and vine shoots (Fig. 11b) exhibited a well-defined fibrous structure with a relatively smooth surface, characteristic of lignocellulosic materials. After Zn(II) biosorption, the surfaces of grape stems (Fig. 11c) and vine shoots (Fig. 11d) appeared rougher and more aggregated, suggesting the deposition of Zn(II) ions and potential structural modifications.

The EDX spectra, shown in Fig. 12, confirms the successful adsorption of Zn(II) onto the biosorbents. The atomic concentration of Zn in grape stems (Area A1) was 3.11%, whereas in vine shoots (Area B1), it was 1.05%, indicating a higher Zn(II) uptake by grape stems. Additionally, the elemental analysis identified the presence of calcium (Ca) and phosphorus (P) in the samples. The presence of Ca suggests that Zn(II) biosorption involves ion exchange, where Zn(II) displaces Ca from the biosorbent's functional groups, a mechanism frequently observed in lignocellulosic-based adsorption processes (Cardoso et al., 2020). This ion exchange typically occurs when Zn(II) ions interact with negatively charged

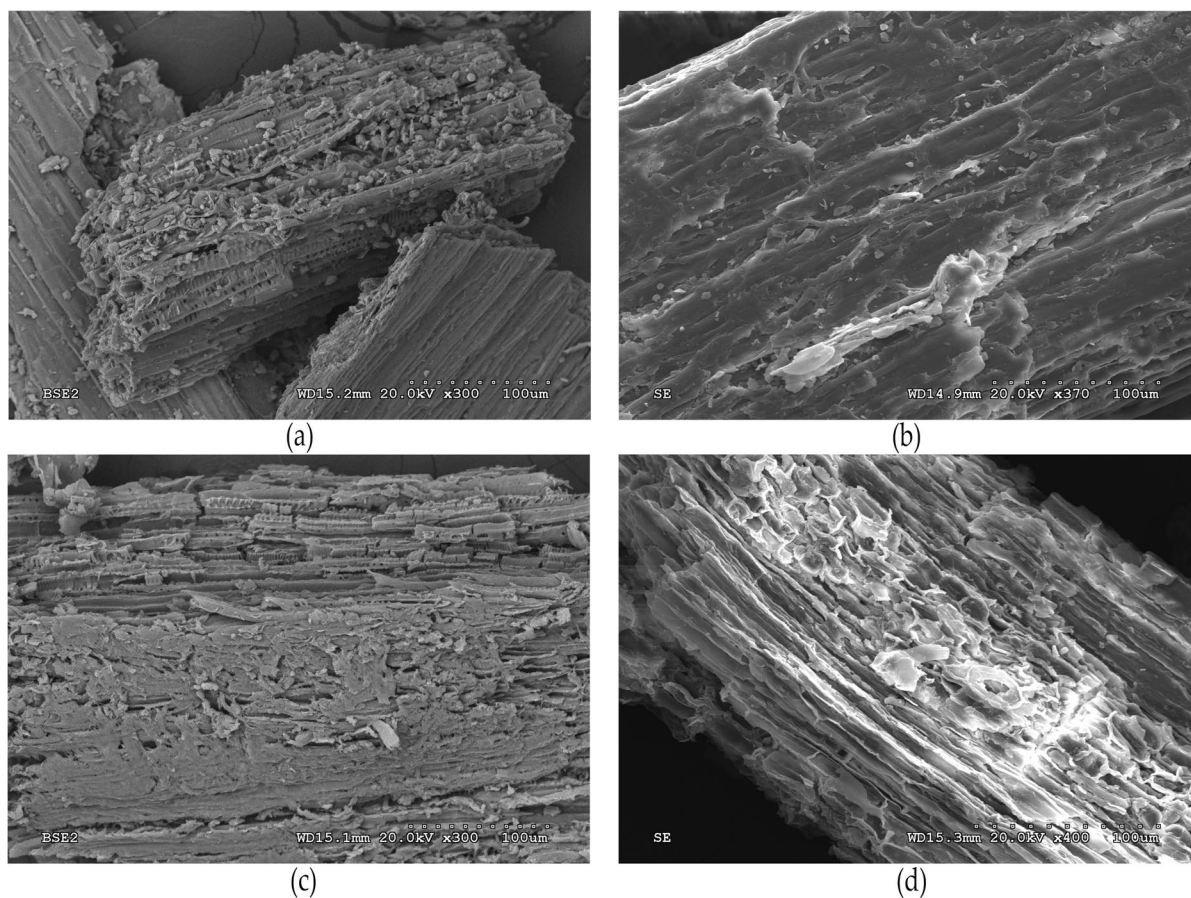


Fig. 11 SEM images of **a** raw grape stems before Zn(II) biosorption, **b** raw vine shoots before Zn(II) biosorption, **c** grape stems after Zn(II) biosorption, and **d** vine shoots after Zn(II) biosorption

sites, such as carboxyl and hydroxyl groups, effectively replacing the Ca ions that were previously bound (Dias et al., 2023). Meanwhile, the detected P may play a role in Zn(II) retention via phosphate-based interactions, forming stable surface complexes that enhance the efficiency of metal adsorption (Li et al., 2022). These findings are consistent with previous research by Li et al., (2021), where Zn(II) biosorption onto lignocellulosic materials was facilitated by both ion exchange and surface complexation mechanisms, significantly enhancing metal uptake efficiency.

3.9 Insights into the Zn(II) Adsorption Mechanism

The combination of equilibrium, kinetic, and physicochemical characterization results provides a comprehensive understanding of the Zn(II) biosorption

mechanism onto grape stems and vine shoots. The FTIR analysis revealed noticeable shifts and intensity reductions in peaks associated with hydroxyl ($-OH$), carboxyl ($-COOH$), and carbonyl ($C=O$) functional groups after biosorption, indicating their involvement in the binding of Zn(II) ions. These observations suggest that these groups acted as active sites through surface complexation or electrostatic interactions (Imran-Shaukat et al., 2022).

SEM images showed significant morphological changes in the surface texture of both biosorbents after Zn(II) biosorption, suggesting metal ion deposition and potential surface saturation. EDX analysis confirmed the presence of Zn on the biosorbent surface after the process, while simultaneously detecting a reduction in native cations such as Ca^{2+} and K^{+} . This finding supports the occurrence of ion exchange mechanisms, where original metal ions are displaced

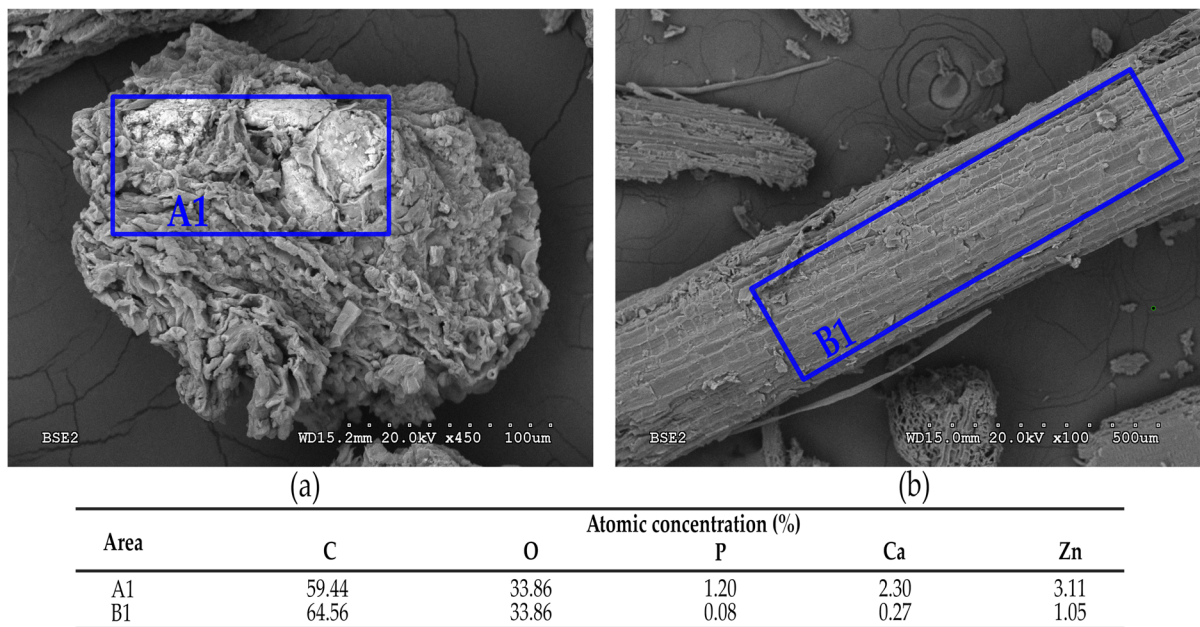


Fig. 12 EDX spectra and elemental analysis of Zn(II) biosorption on **a** grape stems and **b** vine shoots

by Zn(II) during biosorption. This behavior is consistent with observations reported in other biosorption studies. For instance, Cardoso et al., (2020) noted that light metal ions such as Ca^{2+} , Na^+ , Mg^{2+} , and K^+ , which are naturally present on biosorbent surfaces, are released into the solution during zinc uptake, resulting in a measurable depletion of these elements on the solid phase. Similarly, Šehović et al., (2022) reported a significant decrease in Na^+ and Ca^{2+} content on banana peel biosorbents used for the removal of Zn(II), Cu(II), and Pb(II), further supporting the hypothesis that ion exchange plays a relevant role in the metal binding process.

The isotherm modeling further supports this interpretation. The Langmuir model, which assumes monolayer adsorption on homogeneous surfaces (Liu et al., 2023), showed the best fit for grape stems, while the Freundlich model, which describes adsorption on heterogeneous surfaces (Syeda et al., 2022), was more suitable for vine shoots. The additional application of the Dubinin–Radushkevich (D–R) model revealed low values of mean adsorption energy ($E < 8$ kJ/mol), clearly indicating that the process is dominated by physisorption, primarily through weak electrostatic forces and van der Waals interactions (Karnwal, 2024).

Regarding the kinetic modeling, the pseudo-second-order model provided the best fit for the experimental data, which is often linked to chemisorption processes involving electron sharing or exchange between metal ions and the active sites on the biosorbent surface (Kayranli et al., 2021). However, the mean adsorption energy (E) values derived from the D–R isotherm, clearly indicating that the dominant interactions are of a physical nature, such as van der Waals forces or electrostatic attraction. Similar findings have been frequently reported in literature and are typically interpreted as evidence of hybrid adsorption mechanisms. Indeed, studies on Zn(II) biosorption using biosorbents such as alginate-extraction residues (Cardoso et al., 2020) and phosphate-accumulating biomass (Li et al., 2022), have shown that low E values from D–R coexist with pseudo-second-order kinetics, reflecting processes where physisorption predominates, but low-energy chemisorption steps, such as ion exchange or surface complexation, play a complementary role. In such systems, the rate-limiting step may involve subtle electron redistribution or surface-level ionic interactions, which are chemically driven but do not involve strong covalent

bonding (Syeda et al., 2022). Therefore, the coexistence of pseudo-second-order kinetics and low D–R energies in this study supports the interpretation of Zn(II) biosorption as a multifaceted process, primarily governed by physisorption, yet facilitated by mild chemisorption pathways, including ion exchange and weak complexation with surface functional groups.

4 Conclusions

This study demonstrates the effectiveness of using lignocellulosic materials derived from *Vitis vinifera*, specifically grape stems and vine shoots, for the biosorption of Zn(II) ions from wastewater. The optimized biosorption process achieved Zn(II) ion removal efficiencies of up to 99.41% for grape stems and 91.93% for vine shoots under optimal conditions, which included a pH of 7, a biosorbent dose of 2.1 g for grape stems and 2.5 g for vine shoots, and a stirring time of 25 min for grape stems and 18 min for vine shoots. Adsorption kinetics were best described by the pseudo-second-order model, while equilibrium isotherms were well-fitted by the Langmuir model for grape stems, and the Freundlich model for vine shoots. FTIR and SEM coupled EDX confirmed the involvement of functional groups including hydroxyl, carbonyl, and carbonyl in the biosorption process, revealing changes in surface morphology after Zn(II) ion biosorption. LCA indicated that the first optimization scenario, which focused on cost-effectiveness, generally exhibited lower environmental impacts compared to the second scenario, which prioritized maximum Zn(II) ion removal, highlighting the importance of balancing sustainability and performance in biosorption processes. The use of grape stems and vine shoots as biosorbents not only provides an effective solution for Zn(II) ion removal from wastewater but also contributes to sustainable waste management by repurposing agricultural residues, aligning with circular economy principles and offering an economical solution compared to traditional wastewater treatment methods.

Future work should explore the scalability of this biosorption process to ensure its feasibility for large-scale applications. This includes investigating the performance of grape stems and vine shoots as biosorbents in pilot-scale and full-scale wastewater treatment

systems. Additionally, research should focus on the regeneration and reuse of these biosorbents to evaluate their long-term effectiveness and economic viability. It is also important to study the applicability of this biosorption process to other heavy metals, such as cadmium, nickel, or chromium, to broaden its potential use in various industrial wastewater scenarios.

Acknowledgements The authors wish to thank the La Rioja Government as well as to the Institute of Riojan Studies (IER) for funding part of this research.

Author Contribution **Celia Sabando-Fraile**: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Software; Validation; Visualization; Roles/Writing—original draft; Writing—review & editing. **Marina Corral-Bobadilla**: Conceptualization; Data curation; Formal analysis; Funding acquisition; Investigation; Methodology; Resources; Supervision; Validation; Visualization; Roles/Writing—original draft; Writing—review & editing. **Elisa Sainz-García**: Formal analysis; Data curation; Methodology; Writing—review & editing. **Ignacio Muro-Fraguas**: Formal analysis; Data curation; Methodology; Writing—review & editing.

Funding Open Access funding provided thanks to the CRUE-CSIC agreement with Springer Nature.

Data Availability The datasets used during the current study are available from the corresponding author on reasonable request.

Declarations

Competing Interests The authors declare no competing interests.

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