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Optimizing the Efficacy of Immobilized Fungal Biosorbent for Toxic Metal Removal (Pb, Cu, Ni) from Aqueous Media

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Abstract. Amidst global industrialization, rising release of harmful pollutants, like heavy metals, into water sources raises concerns for human health. In response, this study aimed to assess the efficacy of immobilized fungal biomass as a biosorbent for the removal of heavy metals like lead (Pb), copper (Cu) and nickel (Ni) from contaminated water. An economical biomaterial was developed by immobilization with fungal cells of *Aspergillus oryzae* onto *Saccharum munja.* The efficiency of this biosorbent was gauged through an atomic absorption spectrophotometer and by controlling the various process parameters such as pH, initial metal concentration, contact time, dosing rate and temperature. To comprehend the adsorption mechanism, the study employed kinetic modeling, adsorption isotherm analysis and thermodynamic investigations. For this pseudo first order, pseudo second order kinetics model and isotherm i.e. Langmuir and Freundlich's models were executed. Furthermore, the experimental adsorption data was used to calculate the Gibbs free energy, enthalpy and entropy changes. The kinetic studies revealed a high correlation coefficient (R^2) of less than 0.997, 0.999 and 0.998 for Pb, Ni and Cu, respectively, indicating a pseudo second-order reaction. The equilibrium modeling revealed that the Langmuir model was more compatible than the Freundlich model. The maximum adsorption efficiency for Ni, Pb and Cu was found to be 18.86, 83.3 and 22.7 mg/g, respectively. The thermodynamic studies revealed that the adsorption process was both feasible and spontaneous. The immobilized fungal biosorbent emerges as an eco-friendly and cost-efficient method to eliminate a significant amount of metal ions from water and wastewater.

Keywords: immobilization, *Saccharum munja*, adsorption, heavy metals, kinetics, biomaterial

Introduction

Heavy metals are naturally occurring elements that exist in the environment in varying concentrations, characterized by a density exceeding 5 g/cm^3. They are identified as the primary sources of pollution in water and wastewater, causing significant harm to both humans and aquatic life. When water remains untreated or becomes polluted, it absorbs harmful heavy metals that infiltrate human tissues, leading to various detrimental diseases and disorders. Industries involved in chemicals and textiles produce substantial amounts of wastewater, containing both organic and inorganic pollutants, which ultimately find their way into nearby rivers or lakes. This mixing process disrupts the quality of water and intensifies the levels of heavy metals, impacting not just aquatic creature but also various animals. As a result, the consumption of such contaminated resources directly or indirectly exposes humans to severe toxic effects on their health. The heightened presence of toxic metals like lead (Pb), copper (Cu), nickel (Ni) and cadmium (Cd) inhibits the growth of living organisms and poses a grave threat to human well-being (Contreras-Cortés *et al*., 2020).

Lead is a heavy metal with a bluish-gray colour, finds widespread use in multiple processes including paint production, cosmetics, fuel ignition and mining. Consequently, it is discharged into nearby water bodies as wastewater from numerous industries (Ali, 2020). Initial indications of Pb exposure manifest as headaches, dizziness and impacts on the central nervous system (CNS). Short-term effects of Pb exposure encompass organ damage, whereas long-term effects involve elevated blood pressure and metabolic disturbances (Ibrahim *et al*., 2016; Ab Latif Wani and Usmani, 2015). Similarly, Ni is a hazardous transition metal, can lead

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to carcinogenic effects when present in higher concentrations (Wuana and Okieimen, 2011). Ni has the potential to accumulate in the tissues of aquatic organisms and can result in high concentrations of nickel in the food chain, posing risks to both aquatic species and those consuming contaminated seafood. Acute exposure to Ni can result in gastrointestinal disturbances, asthma, skin irritation, sickness, birth defects, respiratory problems, while chronic exposure may contribute to lung and nasal cancers and cardiovascular conditions (Sehrenth *et al*., 2020). Cu, classified as a transition metal, occurs naturally in soil, water, air and it ranks as the third most commonly utilized metal worldwide. Cu serves as an essential micronutrient for living organisms, albeit in limited quantities (Bashir *et al*., 2021). The world health organization has proposed an acceptable level of 2.0 mg/L of Cu in drinking water. Nevertheless, an overabundance of copper intake may result in adverse effects such as gastrointestinal discomfort, harm to the liver and kidneys, vomiting, neurological disorders, potential carcinogenic effects, elevated anxiety level and an increased risk of heart disease (Li *et al*., 2022; Taylor *et al*., 2020). Hence, it is crucial to eliminate these toxic metals from water and wastewater to prevent their harmful effects.

Several techniques are available for removing metals from water, including photocatalysis, membrane filtration, ion-exchange, precipitation and coagulation, ozonation and biosorption (Fei and Hu, 2023; Irfan *et al*., 2017). Ozonation demonstrates its effectiveness in the decomposition of both organic and inorganic substances. Nevertheless, a single-phase ozonation system has its constraints, including reduced ozone solubility, diminished ozone stability and a deficiency in selective oxidation potential (Mouele *et al*., 2015). Chemical precipitation, on the other hand, generates harmful sludge and waste materials (Znad *et al*., 2022; Kwikima *et al*., 2021). Photocatalysis and ion exchange both require high operating costs (Chong *et al*., 2010). Consequently, biological approaches are generally preferred over chemical methods due to their ability to mitigate these issues (Irfan *et al*., 2021). The biosorption method is the most effective choice among them, since it does not require large energy costs, is simple and more economical (Bala *et al*., 2022; Sonawane *et al*., 2022). This study used an immobilized biosorption system, which is an economical method. This method has properties that are easy to handle and environmentally friendly when establishing biosorption capacity. The strength of immobilization can be increased by various auxiliary materials such as fungi, algae and some protozoa.

Different types of fungal biomass and other microorganisms have been utilized as biosorbents to aid in the process of biosorption for heavy metals. This method presents advantages such as the regeneration and recovery of metals, as well as its remarkable efficiency, affordability and alignment with environmental concerns (Tripathi *et al*., 2023; Kalak *et al*., 2020; Diaz-Alarcón *et al*., 2019). Furthermore, these agents have demonstrated their effectiveness in previous research when it comes to biosorbing heavy metals. Particularly noteworthy is *Aspergillus oryzae* which has been highlighted in numerous studies for its ability to effectively remove a range of heavy metals, including copper, cadmium, lead, zinc, nickel, manganese and aluminum (Zareh *et al*., 2023; Sinha *et al*., 2019). Thus, in this research, the utilization of *Aspergillus oryzae (AO)* which is a type of fungi and proposed as a complementary element in combination with a new plant species known as *Saccharum munja (SM)*. This plant species is rich in silica content and has demonstrated remarkable effectiveness in adsorbing diverse metal ions. Nevertheless, a considerable portion of the harvested SM leaves, more than 40%, are currently discarded into the environment, either through land disposal or incineration, contributing to various environmental challenges (Kaliannan *et al*., 2019). Consequently, the combination of suitable microbial and plant species could be a promising opportunity to enhance the capacity for metal accumulation while concurrently addressing the adverse effects of toxicity. Therefore in this study *SM* and *AO* were used together to remove heavy metals to increase biosorption capacity and mechanical strength. The advantage of using microbial remediation is that a less hazardous end product is obtained at a lower cost (Mahmoud *et al*., 2011). This study aims to evaluate the maximum achievable efficiency of immobilized fungal biosorbent in eliminating Pd, Cu and Ni from liquid solutions. Furthermore, the research explores the importance of analyzing kinetic, equilibrium and thermodynamic studies in evaluating data and response rates associated with different parameters.

Material and Methods

Preparation of immobilized biomass. The immobilized biosorbent was prepared using easily accessible biomass,

specifically *SM*, obtained from a local farm in Lahore, Pakistan. *SM* possesses a porous tissue-like structure. The biomass underwent multiple washes with distilled water to eliminate any dust impurities, followed by drying at 60 °C. Afterward, it was processed in a laboratory mill and sieved to attain a particle size of 60 microns, as illustrated in Fig. 1.

The *AO* strain was acquired from the First Fungal Culture Bank of Pakistan (FCBP), University of the Punjab, Lahore and the Institute of Agricultural Sciences (IAGS), Pakistan. The cultivation of *AO* took place on Potato Dextrose Agar (PDA) and was incubated at a temperature of 32 °C for duration of 6-7 days. After this period, fully grown spores were obtained and subsequently stored for future use.

To create the immobilized biosorbent, a biomass weighing 1 g was measured and introduced into 100 mL of a culture medium. The composition of the culture medium comprised the following ingredients: 0.0714 g of KH_2PO_4 (98-100% of Merck), 1 g of glucose (extra pure, Scharlau), 0.2 g of yeast extract (Biolite), 0.047 g of $(NH_4)_2SO_4$ (99%, Scharlau), 0.086 g of urea (99-100% Icon Chemicals), 0.02 g of $MgSO_4.H_2O$ (>97%, Riedel-de Haen), 0.02 g of $CaCl_2$ (95%, PanReac), 0.44 mg of $ZnSO_4.7H_2O$ (99%, Scharlau), 0.078 mg of $CuSO_4.5H_2O$ (99%, Scharlau), 0.0144 mg of $MnCl_2.4H_2O$ (99%, Fluka), 0.302 mg of $FeCl_3$ (98%, MP biomedicals), all dissolved in 100 mL of distilled water. Afterwards, the mixture in the flask was subjected to autoclaving at 121 °C for 15 min. This process yielded a spore suspension of *AO*, which was then introduced to the autoclaved culture medium under sterile conditions. The mixture was then placed in a shaking incubator and allowed to grow for 6 days at a temperature of 30 °C and a speed of 120 rpm. Following that, the resulting biomaterial was filtered and subsequently dried in an oven set to 60 °C. Lastly, the dried immobilized biosorbent was stored in a plastic container for future utilization.

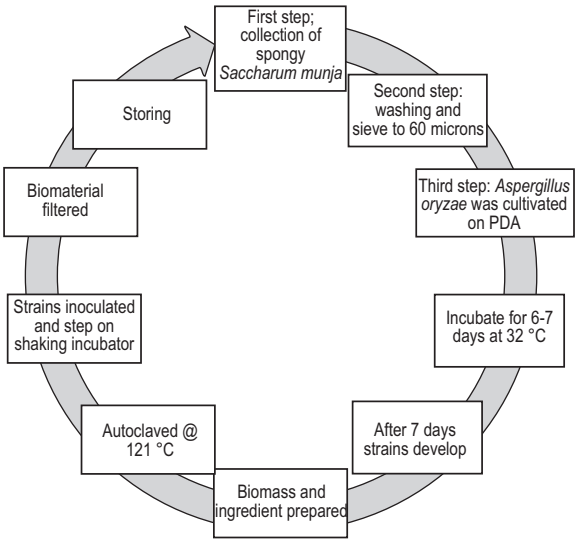

Fig. 1. Schematic diagrams of biomass preparation and immobilization.

Preparation of stock solution of heavy metal and analysis. Stock solutions (1000 mg/L) of Cu, Pb and Ni were prepared by dissolving 3.929 g of $CuSO_4 \cdot 5H_2O$, 5 g of $Ni(NO_3)_2 \cdot 6H_2O$ and 1.59 g of $Pb(NO_3)_2$ in liter of double distilled water (DDW) respectively. These chemicals were of analytical grade with >99%, 97%, 99% purity and were purchased from Scharlau, Honeywell and Fluka Chemicals, respectively. To conduct the absorption experiments, solutions of Cu, Pb and Ni were created by diluting the original solution with DDW, employing different concentrations. The pH of the metal solutions was altered to investigate its effects by using 0.1 M HCl or 0.1 M NaOH. The Atomic Absorption Spectrophotometer from thermo electron corporation was utilized to determine the metal concentration in the solution.

Optimization. To evaluate the sorption capacity of the prepared biosorbent, various parameters including the amount of adsorbent used, the duration of contact, pH levels and temperature were examined. The adsorption experiments were conducted in a 250 mL erlenmeyer flask with agitation at 120 rpm. The investigated variables en-compassed adsorbent dosage ranging from 0.25 g/50 mL to 0.75 g/50 mL, contact times spanning 15-60 min, pH levels from 4-6 and temperature between 30-50 °C. Subsequent to the adsorption process, the mixture was filtered and the concentrations of the remaining metals were determined through AAS.

Kinetics, isotherms and thermodynamic analysis. To grasp the mechanisms of adsorption, a range of analyses were carried out. These included using kinetic models and adsorption isotherms, as well as conducting thermodynamic investigations. To achieve this, the pseudo-first-order and pseudo-second-order kinetics models were employed, alongside Langmuir and Freundlich models as isotherms. Additionally, the experimental adsorption data enabled the calculation

of thermodynamic quantities such as Gibbs free energy (G°), enthalpy changes (H°) and entropy changes (S°). Different thermodynamic parameters, including ΔG°, ΔH° and ΔS° were derived and analyzed from the data for all metal ions.

Results and Discussion

The primary cause of water pollution is human activities, such as the discharge of industrial waste, domestic waste, sewage water and agricultural runoff. These pollutants pose a significant risk to the quality of drinking water. This research aims to combat metal pollution by using an innovative technique that employs a customized biosorbent created by immobilizing AO biomass.

Assessing the impact of adsorbent dosage on heavy metal removal. Figure 2(a) demonstrates the observation of Pb, Cu, and Ni adsorption on immobilized biosorbent by varying the adsorbent dosage within the range of 0.25-1 g. The findings suggest that as the dosage of the adsorbent is raised, the initial effect is an increase in the adsorption capacity of the immobilized biosorbent. However, beyond that point, the capacity either remains constant or decreases upon further increasing the adsorbent dosage. This increase in adsorption with higher adsorbent dosage can be attributed to the greater availability of active sites for binding metal ions (Irfan *et al*., 2021; Irfan *et al*., 2020; Rashid *et al*., 2016). Therefore, the percentage of metal ion removal was increased due to the higher availability of more active sites, which increase the rate of adsorption and increase the penetration of metal ions to the active sites of adsorption. However, upon achieving equilibrium, the adsorption percentage diminishes as doses of the biomass accumulate. This decrease happens because the growing accumulation can obstruct binding sites, leading to a reduction in total surface area (Irfan *et al*., 2020; Lu *et al*., 2020). The maximum percentage of removal of Pb, Cu and Ni was observed as 83.22, 99.47 and 83.05, respectively.

Examining the influence of contact time on heavy metal removal. The impact of contact time on the adsorption of studied metals is illustrated in Fig. 2(b). It was observed that increasing the contact time led to a significant increase in the percentage removal of heavy metal ions from the aqueous solution. It was observed that during the initial phase, there was a rapid increase in the percentage of removal, followed by a deceleration in the adsorption capacity. Eventually, the adsorption capacity reached a point where any noticeable changes in the later stages became insignificant. The equilibrium was established after 60, 60 and 75 min for Pb, Cu and Ni ions respectively. The process of metal ion adsorption onto the active sites of the adsorbent intensified with longer contact times. However, as the concentration of metal ions at these sites increased, the further movement of ions decreased due to the saturation of the adsorbent sites. Such saturation of the metal ions makes it difficult for the further movement of the metal ions towards the adsorbent sites, which resulted in the low adsorption efficiency of the material in the later stages (Beni and Esmaeili, 2020; Gupta and Balomajumder, 2015). This pattern of adsorption capacity versus contact time has also been reported in previous studies (Chiban *et al*., 2016; Verma *et al*., 2013).

Analyzing the effect of temperature on heavy metal removal. Temperature plays a significant role in the biosorption method and is also associated with thermodynamics. The biosorption of the studied ions shows a slight increase as the temperature elevates from 30 to 60 °C, as depicted in Fig. 2(c). This escalation in adsorption capacity suggests that the binding of immobilized SM to the surface is driven by an endothermic process. The heightened temperature furnishes the required energy for reactions to transpire more swiftly, thus promoting the interaction between heavy metal ions and the adsorbent material. Furthermore, the kinetic energy of both the adsorbent surface and the heavy metal ions intensifies, leading to heightened collisions and consequently yielding improved adsorption efficiency (Rashid *et al*., 2016). However, decrease of adsorption capacity at higher temperatures suggests a lack of strong supportive and interactive forces between the biosorbents (Rajalakshmi *et al*., 2009; Ho *et al*., 2005). Favorable adsorption has been observed on SM due to potential attractions between ions or biosorbent sites at specific temperature ranges (Zubair *et al*., 2008).

Investigating the impact of pH on heavy metal removal. The adsorption capacity of immobilized SM for heavy metal ions is significantly influenced by the pH level of the medium. This is because the pH level regulates the uptake of metals at adsorption sites and affects the solubility of metal ions as well as the ionization state of functional groups on the fungus cell wall (Jin *et al*., 2019; Taha *et al*., 2016). To examine the impact of pH on the biosorption capacity of immobilized SM towards heavy metal ions, a pH range of 2-8 was investigated as shown in Fig. 2d. Initially,

at a low pH value, a low percentage removal rate of metal ions was observed, which is associated with the protonation of the fungal biomass cell wall, which inhibited the adsorption capacity of materials. Nonetheless, as the pH increased, the cell became more negatively charged due to deprotonation, leading to a notable improvement in the efficacy of eliminating metal ions from aqueous solution (Say *et al*., 2003). The maximum percentage removal of metal ions was found to be 88.02%, 92.47% and 87.1 % for Pd, Cu and Ni, respectively. However, there was no significant difference observed in the percentage removal of metal ions in aqueous solution when the pH was increased towards a more alkaline region. Differences in metal ion adsorption across different pH levels may stem from varying surface charges caused by different degrees of ionization, the characteristics of the metal and the nature of the adsorbent surface. Metal ion adsorption could be constrained at extremely acidic and alkaline pH values due to the hydrophobic tendencies of the sorbate. The presence of functional groups is pivotal for metal binding and pH exerts an impact on these groups by either adding or removing protons. As a result, this could potentially decrease or augment the attraction to charged metal ions (Rashid *et al*., 2016). At a low pH, metal ions tended to form oxides of their metals, which decreased their solubility in an acidic environment and led to reduced diffusion to the biosorbent's active site, resulting in lower adsorption capacity. Conversely, when the pH of the solution was increased, these metal ions formed hydrates that were more soluble in aqueous solution. Moreover, Cu removal percentage was notably higher than other metals, which can be attributed to the higher solubility of Cu complexes in an aqueous alkaline medium (Negm *et al*., 2018).

Isotherm adsorption models. Adsorption, a highly utilized technique in environmental protection, is acknowledged as a crucial technology. Employing isotherm models for analyzing experimental data aids

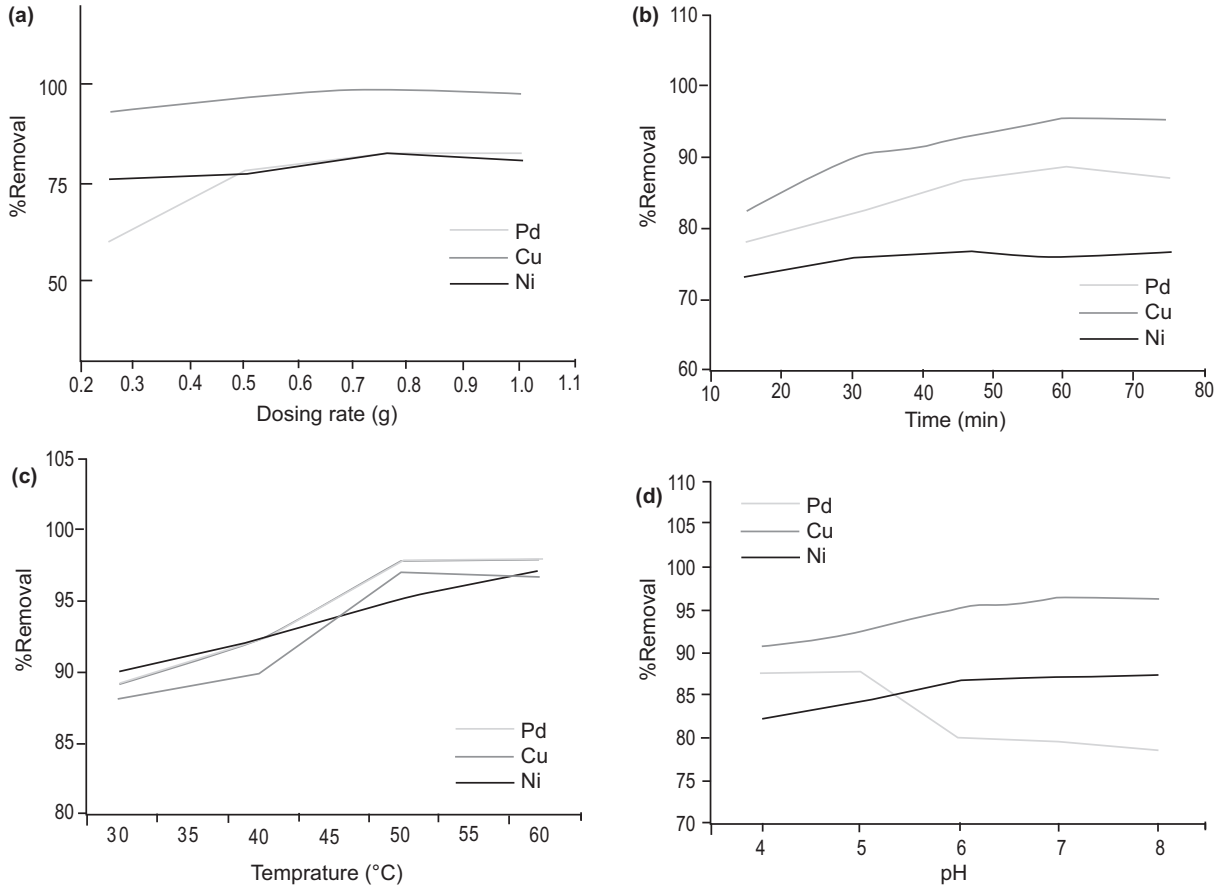

Fig. 2. Effect of various process parameters on the % removal of heavy metal ions i.e. Ni, Pb, Cu, **(a)** dosing rate **(b)** contact time **(c)** temperature **(d)** pH.

in comprehending the mechanism of adsorption, consequently contributing to the progress of the adsorption process (Chen, 2015). Consequently, two distinct isotherm models were utilized to investigate the adsorption behavior.

Langmuir and Freundlich isotherm model. The Langmuir isotherm model, named in honour of scientist Irving Langmuir, which was established to explain the occurrence of adsorption phenomena. This model illustrates a state of equilibrium and is grounded on four key assumptions: the constant surface of the substance being absorbed, the uniformity of all adsorption sites, the absence of interaction among adsorbed molecules and a consistent mechanism governing the adsorption process. According to the Langmuir model, a monolayer is formed when adsorption reaches high levels. This concept relies on the notion of dynamically similar adsorption sites present on the same type of adsorbent material. Various parameters, such as slope and intercept, were determined or observed and are presented in Table 1. These parameters are used to calculate the maximum adsorption capacity (q_{max}) in milligrams per gram (mg/g), as shown in Fig. 3. The correlation coefficients (R^2) for heavy metals Pb, Ni and Cu were found to be 0.996, 0.985 and 0.997, respectively, indicating a strong mathematical fit to the Langmuir model. These findings reveal a consistent adsorption pattern taking place on dynamically modified immobilized sites of SM. The greatest capacities for adsorbing were measured as 18.86, 83.3 and 22.72 mg/g for Ni, Pb and Cu respectively.

The Freundlich isotherm model is a mathematical model used to describe the adsorption of solute molecules onto the surface of a solid adsorbent. The Freundlich isotherm equation can be expressed as follows,

$$q= K.C^n$$

where:

q represents the quantity of solute adsorbed per unit mass of adsorbent at equilibrium, C stands for the equilibrium concentration of the solute in the liquid phase, K denotes the Freundlich constant, which is associated with the adsorption capacity and n represents the Freundlich exponent, which describes the intensity of adsorption.

To determine the Freundlich constants K and n, experimental data was plotted in a log-log format, with logq on the y-axis and logC on the x-axis as shown in Fig. 4. The slope and intercept of the line derived from this plot were used to estimate the Freundlich constants. This approach characterizes the Freundlich isotherm model as a heterogeneous system and the values of K and n are obtained from Table 1. The values for these two parameters and their magnitudes are determined: Ni (n=1.814, kf=5.3951 mg/g), Pb (n=1.14, kf=6.792 mg/g) and Cu (n=1.305, kf=4.405 mg/g). Correlation coefficients for Ni, Pb and Cu are provided in Table 1, showing values of 0.928, 0.989 and 0.999, respectively. Typically, the Freundlich exponent n is found to be between 1 and 10, showing as an indicator of the adsorption intensity. However, value of 1 corresponds to a linear relationship in the model, whereas higher values of n indicate more potent adsorption. Analysis of the experimental data reveals that the values of n are relatively close to 1, implying that the equilibrium data was examined using the linear form.

Kinetic studies. The investigation of adsorption data through kinetic studies entails examining the speed at which adsorption takes place and comprehending the mechanism of the adsorption process. These studies play a crucial role in optimizing adsorption processes across various applications, including water and wastewater treatment, environmental remediation, gas separation and purification. In this study, experimental data was utilized to explore the kinetics of 1st and 2nd order reactions. The kinetics of heavy metal (Cu, Pb, Ni) biosorption onto immobilized *SM* were observed at an initial concentration of 25 ppm. Pseudo 1st and 2nd order kinetics were determined and calculated based on the data presented in Table 2 and Fig. 5. The

Table 1. Parameters of Langmuir and Freundlich model

Metals	Langmuir model					Freundlich model				
	Slope	Intercept	R^2	q_{max}(mg/g)	b (dm^3/g)	Slope	Intercept	R^2	n	K_f
Ni	0.115	0.053	0.988	18.86	0.461	0.551	0.732	0.932	1.814	5.3951
Pb	0.130	0.012	0.996	83.3	0.092	0.874	0.832	0.989	1.14	6.792
Cu	0.170	0.044	0.997	22.72	0.258	0.766	0.644	0.995	1.305	4.405

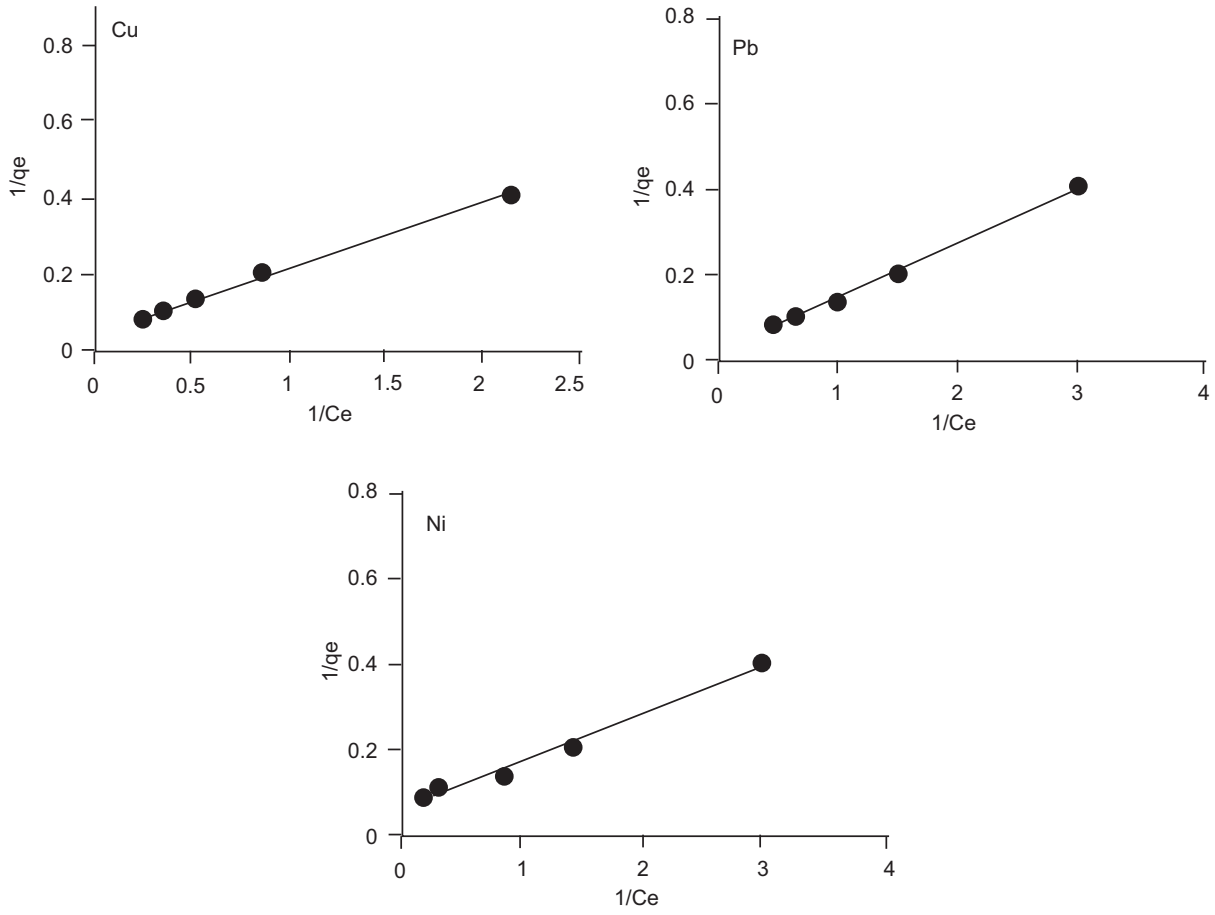

Fig. 3. Mathematical observations of Langmuir isotherm equilibrium curves of Cu, Pb and Ni.

Table 2. Observation of kinetic parameters

Metals	Pseudo first order						Pseudo second order					
	Slope	Intercept	R^2	$qe_{(exp)}$	K_1	$qe_{(calc)}$	Slope	Intercept	R^2	$qe_{(exp)}$	K_2	$qe_{(calc)}$
Ni	0.047	3.474	0.75	2.375	0.047	32.2	0.421	0.355	0.997	2.375	0.498	2.375
Pb	0.032	0.401	0.973	2.70	0.032	1.49	0.361	0.423	0.998	2.70	0.307	2.77
Cu	0.045	0.242	0.978	2.80	0.045	1.27	0.317	1.133	0.999	2.80	0.088	3.15

correlation coefficient (R^2) values for the Cu values for pseudo 1st and 2nd order kinetics were 0.978 and 0.999, respectively, as shown in Fig. 5(a,c). The values of Pb were found to be 0.671 and 0.995 for the pseudo 1st and 2nd orders, respectively, as depicted in Fig. 5(b,d). Additionally, the Ni values for pseudo 1st and 2nd order kinetics were 0.75 and 0.997, respectively, as shown in Fig. 5(c,f). The observed data for the metals indicated a closer adherence to the 2nd pseudo order due to the correlation coefficient approaching 1. Investigating the biosorption of Cu and Pb ions using immobilized *Penicillium simplicissimum* (Li *et al*., 2008). The dominance of the 2nd order kinetics suggests that the rate of adsorption is proportional to the square of the difference between the equilibrium adsorption capacity and the amount of adsorbate at any given time.

Thermodynamic studies. The study of thermodynamics in adsorption processes entails the analysis of the energy and equilibrium properties of this phenomenon. It serves as a framework for comprehending and quantifying the interactions between the substance undergoing adsorption and the material it

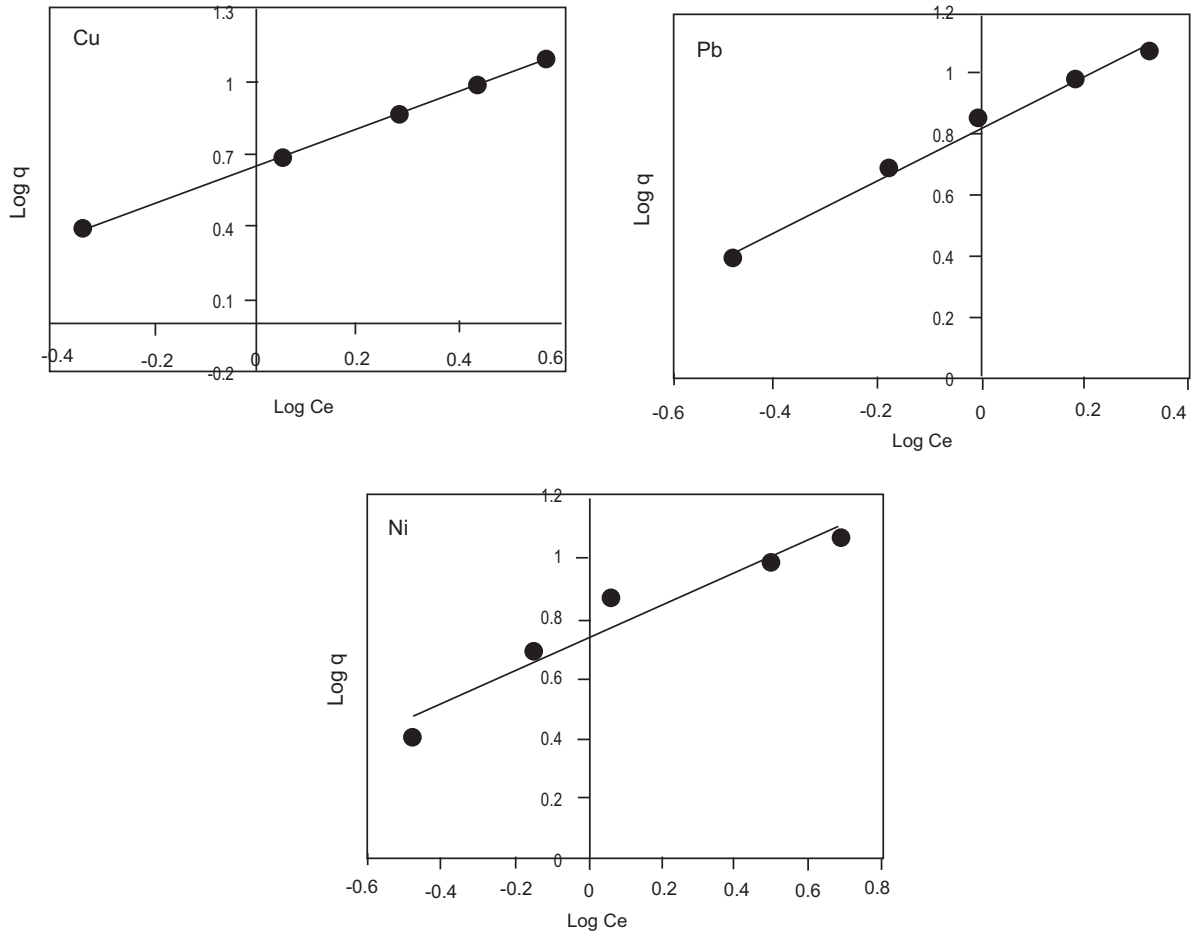

Fig. 4. Mathematical observations of Freundlich isotherm equilibrium curves of Cu, Pb and Ni.

adheres to. Parameters such as ΔG, ΔH° and ΔS° are used to characterize thermodynamic studies as shown in Fig. 6 and summarized in Table 3. The primary purpose of these studies is to determine whether the adsorption process is endothermic or exothermic. The temperature is represented by T, the gas constant by R, and the distribution coefficient by K. The experimental data from Table 3 demonstrates that a negative value of ΔG indicates that the process is energetically favourable, implying that it can occur spontaneously without the need for external energy. This implies that the products of the reaction have lower free energy than the reactants. The negative ΔG values confirm that the biosorption of heavy metals onto immobilized *SM* is a favourable process, thereby validating the strength of the immobilized sorbent (Yadav *et al*., 2013). The positive value of ΔH° also supports this conclusion. During adsorption, molecules or particles from a gas or liquid phase adhere to the surface of a solid or liquid phase. The adsorption process can either release or absorb energy depending on the nature of the interactions between the substance being adsorbed and the material it is being adsorbed onto. A positive ΔH value indicates that the adsorption process is accompanied by the absorption of heat from the surroundings. This phenomenon is further corroborated by the observed increase in the percentage of metal ion removal with an increase

Table 3. Parameter of thermodynamic curve

Heavy metal	Temperature °C	K_D	ΔG J/mol	ΔH J/mol	ΔS J/mol
Pb	303.16	13.45578	-6551.27	1944	9.014
	323.16	20.0136	-8050.04		
Cu	303.16	8.4152	-5521.21	7646	27.41
	323.16	42.5897	-9611.1		
Ni	303.16	10.25828	-5867.45	6035	22.23
	323.16	35.17021	-9564.68		

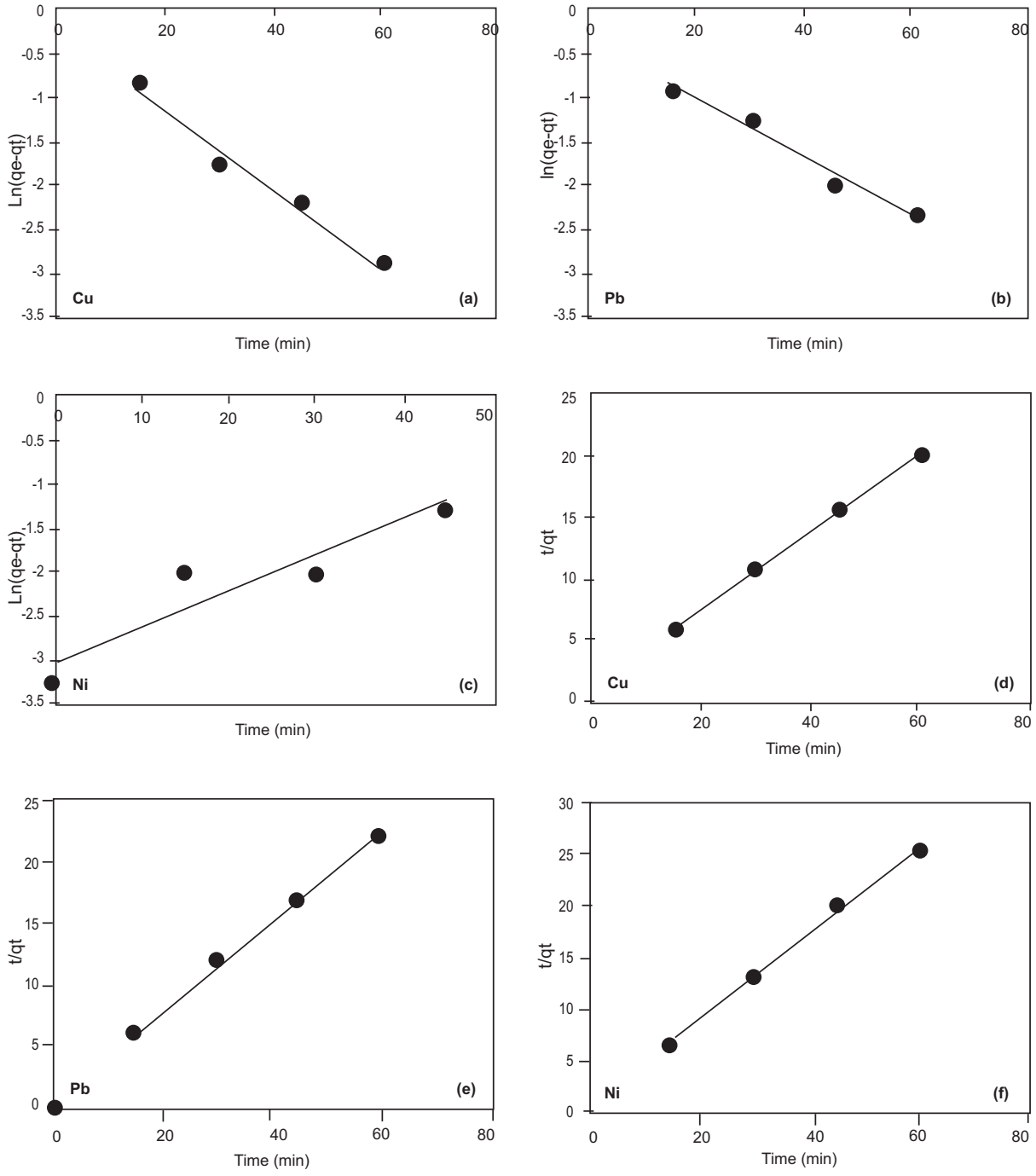

Fig. 5. Linear relationship for Kinetic studies of metal adsorption for pseudo 1st order of reaction for **(a)** Cu, **(b)** Pb , **(c)** Ni and for pseudo 2nd order of reaction for **(d)** Cu, **(e)** Pb, **(f)** Ni.

in temperature, as discussed in section 3.3. Additionally, a positive ΔS° value indicates an increase in un-predictability during the processing of heavy metals (Ni, Cu and Pb) onto immobilized *SM*. The values of ΔG, ΔH° and ΔS° are calculated and presented in Tables 3.

Conclusion

The immobilization of fungal biosorbents has been proven to be a highly effective and promising method for adsorbing metals, offering an environmentally friendly approach to remove heavy metals from polluted

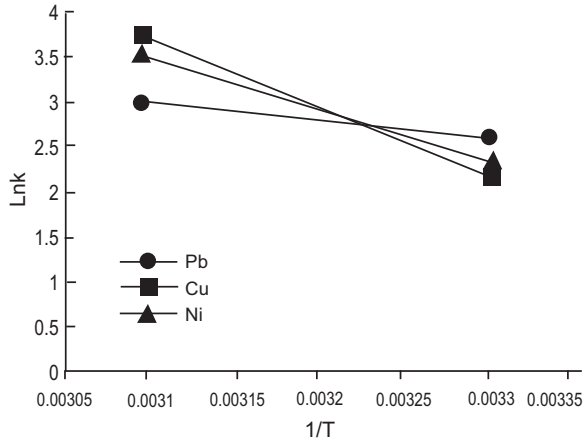

Fig. 6. Thermodynamic curves of Pb, Cu and Ni by taking an initial concentration 25 ppm, adsorbent dose 0.25 g and contact time 15 min.

water. This research showcases the use of *Saccharum munja* and presents compelling evidence for the effectiveness of this method in eliminating hazardous metals from water bodies. Various process parameters such as pH, temperature, contact time, biomass concentration and initial metal concentration significantly influence the metal adsorption capacity of fungal biosorbents. By optimizing these parameters, the adsorption efficiency of the biosorbent can be enhanced, making it a versatile and adaptable technology. Both thermodynamic and kinetic studies, coupled with equilibrium results, lend substantial support the notion that this biosorbent is well-suited for eliminating these toxic metals. Thermodynamic evaluations divulge that the adsorption process is spontaneous, endothermic and a feasible solution for heavy metal absorption in wastewater. In conclusion, this research underscores the synergy of fungal biomass, immobilization techniques and cost-effective operations, providing a sustainable and efficient approach for water and wastewater treatment, as well as metal recovery applications. This promising approach holds considerable promise for the eradication of heavy metals from aqueous solutions and could seamlessly transition into industrial wastewater treatment applications, while the study's findings lay a robust foundation, the realization of this integrated approach in industrial settings necessitates comprehensive exploration. Further characterization of the materials involved, meticulous fine-tuning of various process parameters and rigorous cost analyses in comparison to alternative materials are imperative steps towards successful implementation.

Conflict of Interest. The authors declare that they have no conflict of interest.

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