



Biosorption of Ni(II) from aqueous solutions by *Syzygium cumini* bark powder: Equilibrium and kinetic studies

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ABSTRACT

The present work deals with the use of *Syzygium cumini* bark powder as a biosorbent for Ni(II) removal from aqueous solution. The biosorption characteristics of Ni(II) onto *S. cumini* bark powder was investigated as a function of pH, contact time, biosorbent dosage, and initial Ni(II) ion concentration. Langmuir and Freundlich isotherms were used to fit the experimental data. The best interpretation for the equilibrium data was given by the Langmuir isotherm. The maximum biosorption capacity was found to be 294.1 mg/g for Ni(II) at pH 5.0 and at room temperature. The biosorbent was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy analyses. The equilibrium biosorption data were well fitted with the pseudo-second-order kinetic equation. The chi-square (χ^2) and sum of the square error tests were also carried out to find the best-fit biosorption isotherm and kinetic model. The FTIR results revealed that carboxyl, hydroxyl, and amine groups are responsible for Ni(II) biosorption onto *S. cumini* bark powder.

Keywords: Biosorption; Ni(II); *Syzygium cumini* bark powder; Equilibrium modeling

1. Introduction

The regulations concerning the discharge of contaminants to the environment are becoming more and more stringent. For example, metal ions may induce strong impact on the quality of water bodies, on wild and domestic life, and consequently on human health. Additionally, in many countries the discharge of a waste material in landfill is only authorized when the user has proved that the material cannot be valorized or recycled. These constraints have motivated a num-

ber of processes for recovering metals from effluents or waste materials. For example, recycling and metal recovery from spent batteries has retained a great attention in the research community for the last decade, based on the evolution of discharge regulations [1].

Different methods were investigated and applied to remove nickel ions from water, such as adsorption, chemical precipitation, ion exchange, filtration, membrane separation, and reverse osmosis [2]. Since these methods are either inefficient or expensive when

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heavy metals exist in low concentrations, the use of agricultural residues or industrial by-products having biological activities has been received with considerable attention [3]. However, these processes frequently meet limiting criteria that make their application uncompetitive. Technical limitations (concentrations reached by the process), economical constraints (cost of the materials for large-size applications, energy consumption), and environmental criteria (production of highly contaminated sludge (or) sorbent, poorly recyclable or difficult valorizable) are some of the issues that may explain the need for alternative treatment processes.

Biosorption is an attractive technology and has the potential to contribute to the achievement of this goal. Biosorption is a process that uses inexpensive biomaterials to sequester metals from aqueous solutions [4], and the biomaterials used in this process are termed as biosorbents. The by-products from agricultural, food, and pharmaceutical industries provide economically viable sources of biosorbents; this makes biosorption an inexpensive alternative treatment method. Several researchers have reported on the potential use of agricultural by-products as good substances for the removal of metal ions from aqueous solutions and wastewaters [5–10].

Nickel is a major concern because the larger usages in developing countries and their no degradability nature. This metal is released into the environment by many processes such as electroplating, leather tanning, wood preservation, pulp processing, steel manufacturing, plastic pigments, and mining and metallurgical processes [11,12]. Ni(II) is more toxic and carcinogenic metal than Ni(IV) comparatively. Toxication associated with nickel is the inhibition of oxidative enzyme activity. Acute poisoning causes nausea, vomiting, chest pain, and rapid respiration. Dermatitis is common among workers involved in making nickel-containing jewelry and those using nickel-plated watches and nickel-containing detergents. It is highly carcinogenic, and high levels of nickel induce the reduction of nitrogen and impair growth. The deficiency of nickel in animals results in impaired growth and an increased fatal death rate.

The aim of the present study is to investigate the use of *Syzygium cumini* bark powder as a biosorbent for the removal of Ni(II) from aqueous solution. Though few researchers have used *S. cumini* leaves and ash as biosorbent for the removal of chromium and zinc ions [13,14], first time we make use of the *S. cumini* bark powder as a new biosorbent for the removal of Ni(II) ions from aqueous solutions. The effect of various parameters such as pH, initial metal ion concentration, adsorbent dosage, and contact time was studied. The pseudo-first-order,

pseudo-second-order, and intraparticle diffusion kinetic models were applied to study the kinetics of adsorption process. The data were fitted to Langmuir and Freundlich isotherms.

2. Materials and methods

2.1. Preparation of biosorbent

S. cumini bark after collection was thoroughly washed with distilled water to remove muddy materials. Then, *S. cumini* bark powder was soaked in 0.1N NaOH to remove lignin-based color materials followed by 0.1N H₂SO₄. Finally, it was washed with distilled water several times and dried in an oven at 80°C for 6 h and cooled at room temperature in desiccators. The dried bark was ground to a fine powder and used as biosorbent for Ni(II) adsorption without any pretreatment.

2.2. Chemicals and equipment

All the reagents used were of AR grade. Deionized double-distilled water was used throughout the experimental studies. Stock solution (1000 mg/L) was prepared by dissolving NiSO₄·6H₂O. This was further diluted to obtain the desired concentration for practical use. ACS reagent-grade HCl, NaOH, and buffer solutions (E. Merck) were used to adjust the pH of the solution. The pH meter (Elico LI-129) was calibrated using buffer standard solutions of pH 4.0, 7.0, and 10.0. Fourier transform infrared spectrophotometer (Nicolet IR-200) from Thermo-Nicolet FTIR, USA, and scanning electron microscopy (Model Evo 15) from Carl Zeiss, England, were used to analyze the organic functional groups of the biosorbent and to study the surface morphology of the biosorbent. The metal concentrations in the samples were determined using atomic absorption spectrophotometer (AA-6300, Shimadzu, Japan).

2.3. Batch adsorption studies

In order to explore the effect of influencing factors, such as pH, contact time, quantity of adsorbent, and the initial concentration of adsorbate, a series of batch experiments were conducted. Batch adsorption experiments were carried out by agitating specified amount of adsorbent in 100 mL of 100 mg/L metal solution of desired concentration at varying pH in 125-mL stoppered bottles. The sample was then filtered using Whatman No. 42 filter paper and analyzed for the concentration of metal ions remaining in the solution.

The metal removal efficiency (R) is calculated from Eq. (1):

$$R = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where C_i and C_e are initial and equilibrium metal concentrations, respectively. The adsorption capacity of the biosorbent at any time (q) can also be calculated from Eq. (2):

$$q = \frac{(C_i - C_e)V}{M} \quad (2)$$

where M (g) is the adsorbent dosage and V (L) is the volume of the solution.

3. Results and discussion

3.1. Characterization of the biomass

3.1.1. Fourier transform infrared (FTIR) studies

The FTIR spectral analysis is important to identify the characteristic functional groups, which are respon-

sible for biosorption of metal ions. FTIR spectrum of *S. cumini* bark powder (Fig. 1) shows distinct peaks at 3,377, 2,923.5, 1,644.5, 1,500.8, 1,373.6, 1,110.3, 1,044.1, and 1,022 cm^{-1} before adsorption. The broad and strong band at 3,377 cm^{-1} may be due to overlapping of $-\text{OH}$ and $-\text{NH}$ stretching. The peaks at 1,110.3 and 1,044.1 cm^{-1} are assigned to alcoholic $\text{C}-\text{O}$ and $\text{C}-\text{N}$ stretching vibration, thus showing the presence of hydroxyl and amine groups on the biomass surface. The strong peak at 1,644.5 cm^{-1} can be assigned to a $\text{C}=\text{O}$ stretching in carboxyl or amide groups. The bands at 2,923.5 and 1,500.8 cm^{-1} are attributed to $\text{C}-\text{H}$ stretching and $\text{N}-\text{H}$ bending, respectively. The peak at 1,500.8 cm^{-1} corresponding to $\text{N}-\text{H}$ bending shifts to the lower frequency (1,460 cm^{-1}) after the nickel adsorption on the adsorbent. Thus, it can reasonably be concluded that the amino group may be the main adsorption site for nickel attachment on the *S. cumini* bark powder. In addition, the FTIR spectrum shows the shift in peaks at wavenumbers 3,377 and 1,110.3 cm^{-1} , which may be attributed to the intensity of $-\text{OH}$ and $-\text{NH}_2$ groups with the sorbate. The decrease in the wavenumber of the peak at 1,644.5–1,624.1 cm^{-1} suggests that $\text{Ni}(\text{II})$ interacts with carbonyl functional group present in the *S. cumini* bark

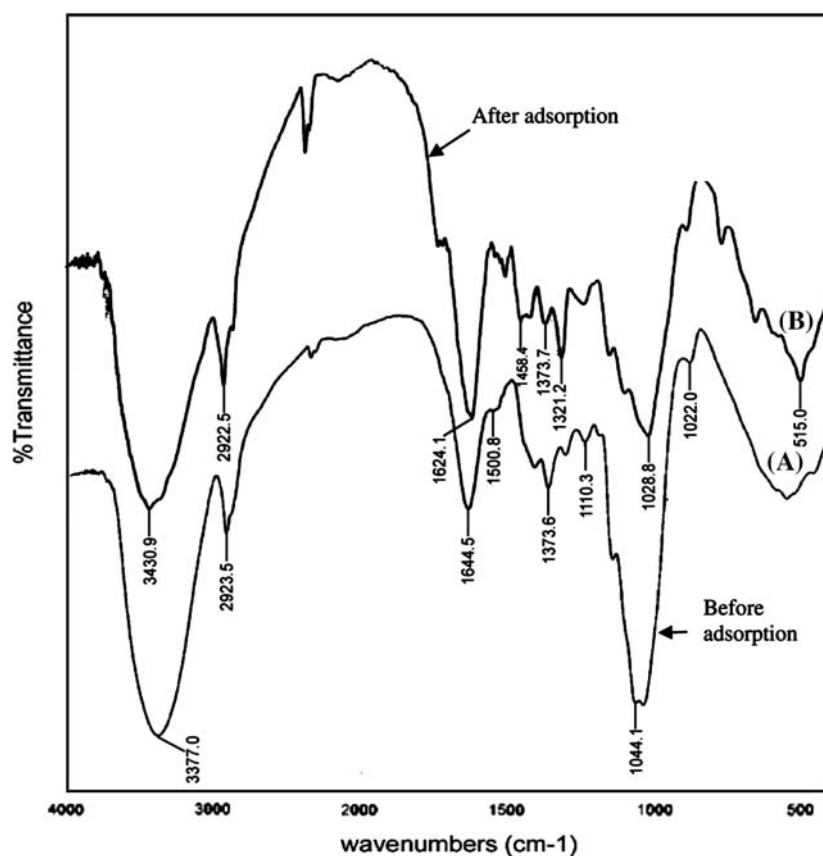


Fig. 1. FTIR spectra of *S. cumini* bark powder before and after biosorption of $\text{Ni}(\text{II})$.

powder. Hence, FTIR spectra reveal that functional groups such as $-\text{NH}_2$, $-\text{OH}$, and $-\text{C}=\text{O}$ present on the *S. cumini* bark powder surface are involved in nickel adsorption.

3.1.2. Scanning electron microscopy (SEM) analysis

In order to examine the textural structure of bark powder, SEM micrographs were taken before (Fig. 2 (A)) and after (Fig. 2(B)) the Ni(II) biosorption on *S. cumini* bark powder. These micrographs indicated clearly the deformation and presence of many new shiny bulky particles over the surface of Ni(II)-loaded

S. cumini bark powder, which were absent on the corrugated surface of biomass before loading with Ni(II). The unloaded bark powder has irregular pores with a diameter higher than $10\ \mu\text{m}$, which indicates that the biosorbent has a macroporous structure. There was also a decrease in pore sizes in Ni(II)-loaded bark powder, and this may be attributed to the fact that the macroporous structure plays a role in Ni(II) biosorption.

3.2. Effect of pH

The pH of solution greatly influences metal sorption, and the pH of maximum adsorption optima

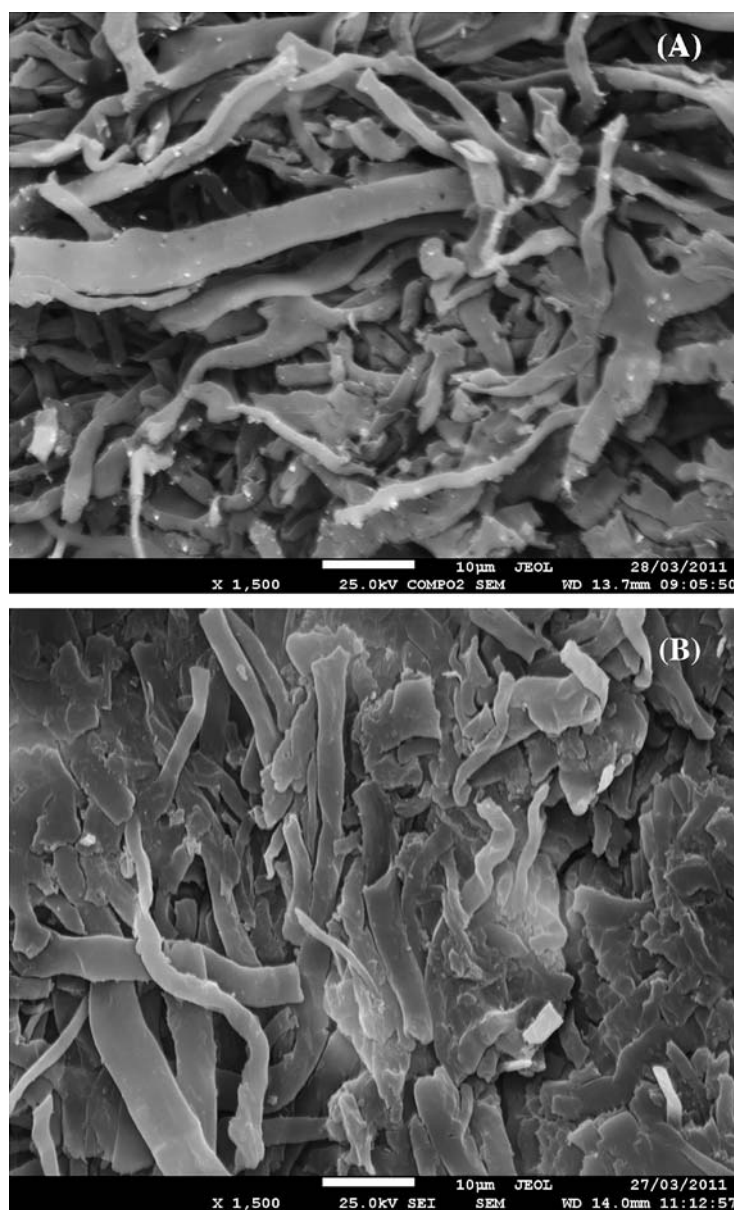


Fig. 2. SEM micrographs of *S. cumini* bark powder before (A) and after (B) biosorption of Ni(II).

depends on the nature of the biosorbent and the metal. Further, pH influences surface properties of the adsorbent by way of functional group dissociations and also surface charges [15,16]. Biosorption of nickel by *S. cumini* bark powder has been found to increase with increase in pH and reach maximum at 5.0 and then decrease with further increase in pH up to 8.0 (Fig. 3). The effect of pH was not studied beyond pH 8.0 because of the precipitation of nickel as hydroxide. At low pH values, the overall surface charge will be positive, which will inhibit the approach of metal cations. In the present case, nickel ions and protons compete for binding sites on the adsorbent at lower pH, resulting in a low adsorption of nickel. It has been suggested that at low pH, H_3O^+ ions are close to the binding sites of the bark and this restricts the approach of nickel ions due to repulsion [17]. As the pH of the solution increases, the number of protons dissociated from the functional groups on the cell wall increases, thus providing more negative groups on the adsorbent surface. As the adsorbent surface is negatively charged, the increasing electrostatic attraction between positively charged nickel ions and negatively charged adsorbent particles would lead to an increase in the adsorption of Ni(II) ions. Above the pH of maximum adsorption, the decrease in adsorption may be attributed to reduced solubility and precipitation of nickel [18,19].

3.3. Effect of biomass dosage

The effect of biomass dosage on the removal efficiency of Ni(II) was studied using varying amounts of biomass dosages (1–7 g/L), and the results are shown

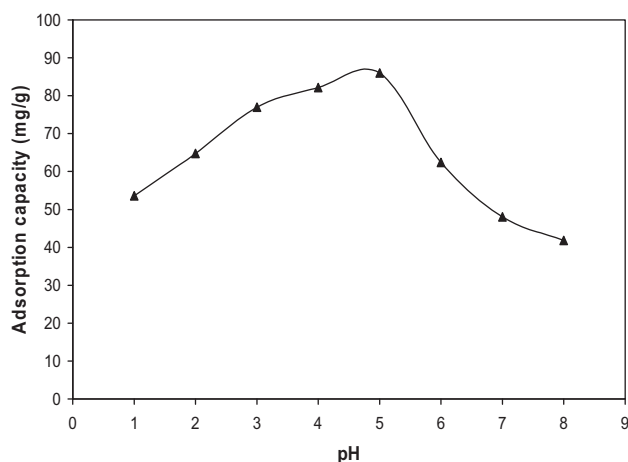


Fig. 3. Effect of pH on the biosorption of Ni(II) using *S. cumini* bark powder (initial metal ion concentration, 100 mg/L; pH, 1–8; adsorbent dose, 100 mg/100 mL; temperature, 28°C; contact time, 240 min).

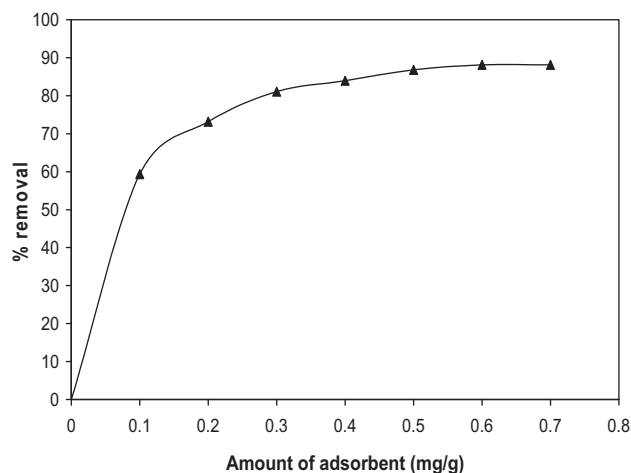


Fig. 4. Effect of biosorbent dose on biosorption of Ni(II) onto *S. cumini* bark powder (initial metal ion concentration, 100 mg/L; pH, 5; adsorbent dose, 100–700 mg/100 mL; temperature, 28°C; contact time, 240 min).

in Fig. 4. The efficiency of Ni(II) removal increased with increase in biomass dosage. The maximum removal efficiency attained was 88% at the dosage of 0.6 g/0.1 L. This suggests that the Ni(II) ion can be removed effectively by using <1 gm of the biosorbent. The increase in the biosorption percentage with rise in adsorbent dosage is due to increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the sorption sites [20]. Therefore, 0.6 g/0.1 L was selected as the adsorbent dosage for other experiments as the adsorption efficiency did not increase much thereafter.

3.4. Effect of contact time

The rate of biosorption was important for designing batch adsorption experiments. To understand the effect of time on the extent of adsorption, equilibrium concentrations of Ni(II) ions were determined at different time intervals with initial concentrations of 100, 150, and 200 mg/L, keeping the pH and amount of biosorbent constant. The biosorption yield of Ni(II) increased considerably until the contact time reached 180 min. Further increase in contact time did not enhance the biosorption, and thus contact time of 180 min was selected for further experiments. The data were used to study the kinetics of adsorption of Ni(II) on *S. cumini* bark biosorbent.

3.5. Biosorption kinetics

Biosorption kinetics depends on the sorbate–sorbent interactions and operating conditions. Several

kinetic models are available to understand the behavior of the adsorbent and also to examine the controlling mechanism [21]. In this study, the adsorption equilibrium data were analyzed using three kinetic models: pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

The linear form of the pseudo-first-order rate equation [22] is given as

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (3)$$

where q_t and q_e (mg/g) are the amounts of the Ni(II) ions sorbed at equilibrium (mg/g) and t (min), respectively, and K_1 is the rate constant of the equation (min^{-1}). The biosorption rate constants (K_1) can be determined experimentally by plotting $\log(q_e - q_t)$ vs. t (Fig. 5).

Experimental data were also tested by the pseudo-second-order kinetic model, which is given in the following form [23]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad (4)$$

where K_2 (g/mg min) is the rate constant of the second-order equation, q_t (mg/g) is the amount of biosorption at time t (min), and q_e is the amount of biosorption at equilibrium (mg/g). The biosorption rate constants (K_2) can be determined experimentally by plotting t/q_t vs. t (Fig. 6). The rate constants and R^2 values are also given in Table 1.

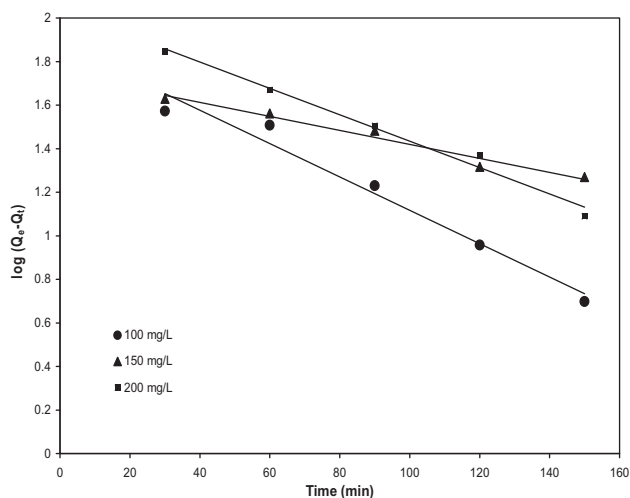


Fig. 5. Pseudo-first-order kinetic plots at different initial concentrations of Ni(II) onto *S. cumini* bark powder (initial metal ion concentrations, 100, 150, and 200 mg/L; adsorbent dose, 100 mg/100 mL; pH, 5; temperature, 28°C; contact time, 30–240 min).

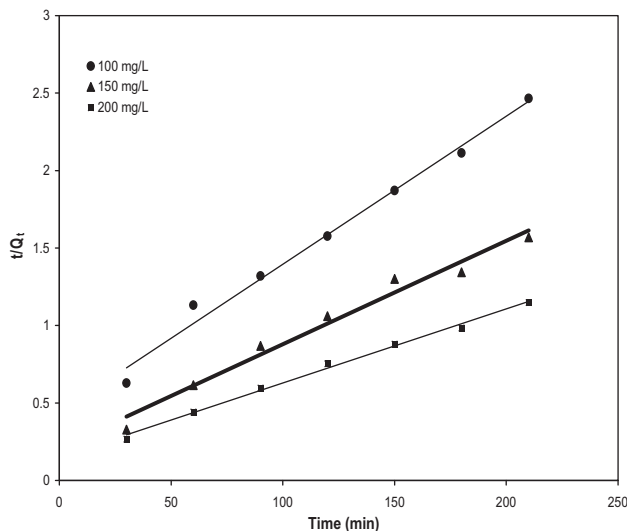


Fig. 6. Pseudo-second-order kinetic plots at different initial concentrations of Ni(II) onto *S. cumini* bark powder (initial metal ion concentrations, 100, 150, and 200 mg/L; adsorbent dose, 100 mg/100 mL; pH, 5; temperature, 28°C; contact time, 30–240 min).

The first-order kinetic process has been used for the description of reversible equilibrium between liquid and solid phases, whereas the second-order kinetic model assumes that the rate-limiting step may be chemical adsorption. In many cases, the first-order equation of Lagergren did not fit well to the whole range of contact time and was generally applicable over the initial stage of the adsorption process. The second-order kinetic model assumes that the rate-limiting step may be chemical adsorption. In many cases, the adsorption data could be well correlated by a second-order rate equation over the entire period of contact time. However, the correlation coefficients, R^2 , showed that the pseudo-second-order model, an indication of chemisorption mechanism, fits better with the experimental data than the pseudo-first-order model. In addition, the squared sum of error (SSE) test was also conducted to support the best-fit adsorption model.

The results are also analyzed in terms intraparticle diffusion model to investigate whether the intraparticle diffusion is the rate-controlling step in adsorption of metal ions on *S. cumini* bark powder. The intraparticle diffusion equation is expressed as [24]:

$$q_t = K_{id}t^{0.5} + C \quad (5)$$

where K_{id} is the intraparticle diffusion rate constant ($\text{mg}/(\text{g min}^{-0.5})$) and C is the intercept. The Weber–Morris plot for biosorption of Ni(II) is given in Fig. 7.

Table 1
Kinetic models for biosorption of Ni(II) on *S. cumini* bark powder associated with correlation coefficient

Concentration of nickel ion (mg/L)	Pseudo first order		Pseudo second order		Intraparticle diffusion			
	K_1	R^2	K_2	R^2	K_{id}	C	R^2	SSE
100	0.018	0.970	0.0002	0.988	5.910	7.424	0.961	0.866
150	0.008	0.969	0.0002	0.976	8.496	20.20	0.896	0.877
200	0.014	0.985	0.0001	0.995	12.17	24.60	0.927	0.871

It can be seen that all the plots have an initial curved portion, followed by a linear portion and a plateau regions. The initial curve of the plot is due to the diffusion of metal ions through the solution to the external surface of *S. cumini* bark powder. The linear portion of curves describes the gradual adsorption stage, where intraparticle diffusion of metal ion on *S. cumini* bark powder takes place, and final plateau region indicates equilibrium uptake. The rate constants of Weber–Morris intraparticle diffusion model are shown in Table 1. Based on the results, it may be concluded that intraparticle diffusion is not the only rate-determining factor.

3.6. The biosorption kinetic models

The kinetic models were evaluated for fitness of the sorption data by calculating the SSE. Lower values of SSE show a better fitness of the sorption data [25,26]. The SSE values were calculated by the equation:

$$SSE = \sum \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2} \tag{6}$$

where $q_{t,e}$ and $q_{t,m}$ are the experimental adsorption capacities of Ni(II) at time t and the corresponding values that are obtained from the kinetic models. SSE values for all the kinetic models are calculated and are summarized in Table 1. Pseudo-second-order model has lower SSE values, indicating that the adsorption of Ni(II) on the biosorbent follows second-order kinetic model.

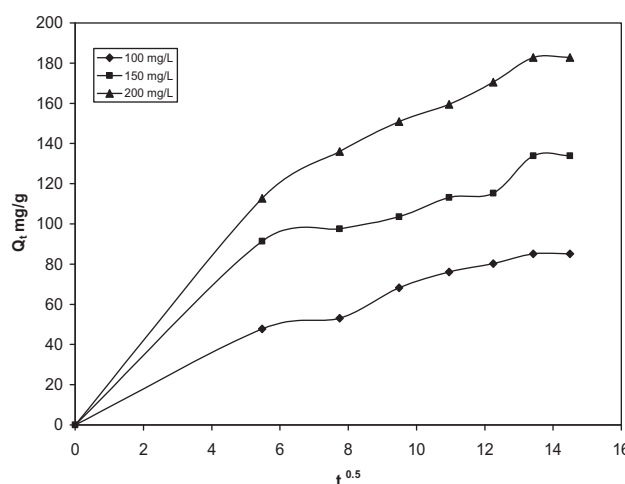


Fig. 7. Weber–Morris model for the biosorption of Ni(II) onto *S. cumini* bark powder (initial metal ion concentrations, 100, 150, and 200 mg/L; adsorbent dose, 100 mg/100 mL; pH, 5; temperature, 28°C; contact time, 30–240 min).

Table 2
Isotherms for biosorption of Ni(II) on *S. cumini* bark powder associated with correlation coefficient and χ^2 analysis

Langmuir	Freundlich					χ^2
	Q_0 (mg/g)	b (L/mg)	R^2	K_F (mg/g)	$1/n$ (L/mg)	
294.1	0.043	0.999	13.02	0.846	1.18	454.6

3.7. Biosorption isotherms

To describe the biosorption equilibrium between an adsorbent and a sorbate, two models were used—the Langmuir and Freundlich isotherms. The Langmuir isotherm assumes monolayer coverage of sorbate on the solid surface of the adsorbent, uniform energy of sorption, and no transmigration of sorbate in the surface [27]. At equilibrium, the Langmuir isotherm can be expressed as:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (7)$$

where q_e is the amount of metal adsorbed (mg/g) and C_e is the equilibrium concentration of solution (mg/L). Q_0 and b are Langmuir constants indicating adsorption capacity and energy, respectively. The Langmuir parameters are calculated from the linear Langmuir isotherm and represented in Table 2. As seen from the table, the coefficient of determination (R^2) was found to be 0.999. This result indicates that the biosorption of the Ni(II) onto *S. cumini* bark powder fitted well the Langmuir model. From this model, the maximum biosorption capacity of *S. cumini* bark powder was found to be 294.1 mg/g.

The Freundlich equation is often used as an empirical relationship between the concentration of a sorbate on the surface of an adsorbent and the concentration of the sorbate in the solution. The Freundlich equation based on the hypothesis of multi-layer biosorption has been widely used to examine the biosorption isotherm. Its linear form is given by the following equation [28]:

$$q_e = K_f C_e^{1/n} \quad (8)$$

where K_f and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich parameters are calculated from the Freundlich isotherm and represented in Table 2. The $1/n$ values were between 0 and 1, indicating that the biosorption of Ni(II) using *S. cumini* bark powder was favorable at the studied conditions. The R^2 value was found to be 0.958. These results indicated that the Freundlich model is not sufficient to describe the relationship between the amount of Ni(II) sorbed onto the biomass and its equilibrium concentration in the solution. In addition, the chi-square (χ^2) test was also carried out to find the best-fit adsorption isotherm model. The equation for evaluating the best-fit model is to be written as

$$\chi^2 = \sum \left(\frac{(q_e - q_{e,m})^2}{q_{e,m}} \right) \quad (9)$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is the equilibrium capacity (mg/g) from the experimental data. If the data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ, χ^2 will be a bigger number. Therefore, it is necessary also to analyze the data set using the non-linear χ^2 test to confirm the best-fit isotherm for the sorption system. The χ^2 values were calculated using Eq. (9) and are given in Table 2. The χ^2 values of both the isotherms are comparable, and hence the adsorption of Ni(II) follows both Freundlich and Langmuir isotherms and better fits to Langmuir model as its χ^2 value is less than that of Freundlich model.

4. Conclusions

The following conclusions were drawn from this study:

- The study revealed that *S. cumini* bark powder could be used as a biosorbent for the removal of Ni (II) from aqueous solution.
- The biosorption performances were strongly affected by the parameters such as pH of solution, biosorbent dosage, contact time, and initial Ni(II) concentration.
- The biosorption capacity of *S. cumini* bark powder for Ni(II) was found to be 294.1 mg/g at pH 5.0 and 0.6 g/0.1 L biosorbent dosage and 180 min equilibrium time at room temperature.
- The sorption of Ni(II) onto *S. cumini* bark powder follows pseudo-second-order kinetic model.
- The Langmuir and Freundlich isotherm models were used for Ni(II) sorption onto *S. cumini* bark powder, and it was found that the experimental data for Ni(II) ions would be described appropriately by the Langmuir model.
- The interactions between Ni(II) and functional groups on the cell wall surface of the biomass were confirmed by FTIR analysis.
- It can be concluded that the *S. cumini* bark powder can be used as an alternative biosorbent for the treatment of wastewater containing Ni(II) due to its low cost and high uptake capacity.

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