

# Biosorption of Nickel(II) from Aqueous Solution by the Fungal Mat of *Trametes versicolor* (Rainbow) Biomass: Equilibrium, Kinetics, and Thermodynamic Studies

Munagapati Venkata Subbaiah and Yeoung Sang Yun

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**Abstract** This study investigates the equilibrium, kinetics and thermodynamics of Nickel(II) biosorption from aqueous solution by the fungal mat of *Trametes versicolor* (rainbow) biomass. The optimum biosorption conditions like pH, contact time, biomass dosage, initial metal ion concentration and temperature were determined in the batch method. The biosorbent was characterized by FTIR, SEM and BET surface area analysis. The experimental data were analyzed in terms of pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models, further it was observed that the biosorption process of Ni(II) ions closely followed pseudo-second-order kinetics. The equilibrium data of Ni(II) ions at 303, 313, and 323 K were fitted to the Langmuir and Freundlich isotherm models. Langmuir isotherm provided a better fit to the equilibrium data and the maximum monolayer biosorption capacity of the *T. versicolor* (rainbow) biomass for Ni(II) was 212.5 mg/g at pH 4.0. The calculated thermodynamic parameters,  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ , demonstrated that the biosorption of Ni(II) ions onto the *T. versicolor* (rainbow) biomass was feasible, spontaneous and endothermic at 303 ~ 323 K. The performance of the proposed fungal biosorbent was also compared with that of many other reported sorbents for Nickel(II) removal and it was observed that the proposed biosorbent is effective in terms of its high sorption capacity.

**Keywords:** biosorption, *Trametes versicolor* (rainbow), isotherms, kinetics, thermodynamics

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## 1. Introduction

As a result of technological advances and enhanced industrial activities, a high volume of wastewater containing heavy metal ions is continually released into the natural environment. Heavy metal ions pose a significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature. According to the World Health Organization (WHO), the metals of most immediate concern are cadmium, chromium, cobalt, copper, lead, nickel, mercury, and zinc. Nickel finds its way into the environment through mining and metallurgical activities, and the industries of stainless steel, electroplating, battery and accumulators, pigments, ceramic and porcelain. Trace amounts of nickel may be beneficial as an activator of some enzyme systems but nickel(II) ion intake over the permissible levels causes various diseases such as pulmonary fibrosis, lung cancer, renal edema, skin dermatitis and gastrointestinal disorder [1-5]. Due to the detrimental effects of nickel, its removal from wastewater is an extremely significant step in the protection of the environment and human health.

Conventional treatment methods such as chemical precipitation, chemical oxidation, ion exchange, filtration, electrochemical treatment, solvent extraction, reverse osmosis and membrane technologies are not often feasible because of their high treatment cost, the need for continuous input of chemicals and the production of toxic sludge [6]. Biosorption technology is based on the interactions between toxic metals and the binding function groups on the cell wall structure of the microorganisms. These are mainly composed of polysaccharides, lipids and proteins. Biosorption has been recognized as a potential alternative method over the conventional separation techniques. Many microbial

species such as algae, bacteria, fungi, yeast and microbial biomass from fermentation and food industry were known to have high metal adsorbing capacities [7-9]. Among the main strains, fungal biomasses have a high percentage of cell wall material which demonstrates excellent metal-binding properties. Some low-cost fungal materials have been used as biosorbent for metal ions from aqueous water or wastewater, which included *Rhodococcus opacus* [10], *Aspergillus niger* [11], *Rhizopus arrhizus* [12], *Mucor hiemalis* [13], and *Mucor rouxii* [14].

Various biosorbents were chemically modified to increase the efficiency of metal ion removal. This chemical modification has either been too expensive or it has caused other problems, such as bleeding of excessive quantities of colored organic compounds, odor, or further pollution through the use of toxic chemicals [15]. Hence, attempts are made in this study to develop an inexpensive biosorbent for the removal of Ni(II) ions from aqueous solution using *T. versicolor* (rainbow) by simple treatment of washing with water. *Trametes versicolor* (rainbow) is a basidiomycete fungus and has many functional groups (carboxylate, hydroxyl, sulfate, phosphate and amino) involving the biosorption of heavy metals. The biomass of *T. versicolor* is a mat form and can be used as a biosorbent as is, whereas the powder form of bacterial biomasses should be immobilized prior to use as a biosorbent. This new biosorbent material was chosen for study as it is a natural, easily available and thus cost-effective biosorbent for dissolved metal ions.

This study focuses on the equilibrium, kinetic and thermodynamic reactions regarding the biosorption of Ni(II) ions on the *T. versicolor* (rainbow) biomass. To obtain a better understanding of the biosorption mechanisms for the removal of Ni(II) ions from aqueous solution. The objectives of this study included (i) characterizing the biosorbent through FTIR, SEM and BET surface area analysis; (ii) to establish a kinetic model for the biosorption of Ni(II) on the *T. versicolor* (rainbow) biomass; (iii) to investigate the biosorption isotherms, and to describe the biosorption thermodynamics.

## 2. Materials and Methods

### 2.1. Preparation of biomass

*Trametes versicolor* (rainbow) biomass was used as a biosorbent for the biosorption of Ni(II) ions. Samples of the biomass were collected from the Tirumala Tirupati Hills, Andhra Pradesh, India. Samples were washed several times using deionized water to remove extraneous and salts. They were then dried in an oven at 70°C for 24 h. The inactivated dried biomass was ground and sieved

through different particle sizes around 150 ~ 250 µm fractions, these particles were used in further biosorption experiments.

### 2.2. Preparation of metal ion solution

Nickel chloride hexahydrate is used as a source of divalent nickel. This stock solution of nickel is prepared by dissolving 4.049 g of NiCl<sub>2</sub>·6H<sub>2</sub>O in 1,000 mL of double distilled water such that each mL of the solution contains 1 mg of divalent nickel.

### 2.3. Reagents and equipment

Analytical grade nickel chloride, hydrochloric acid and sodium hydroxide were obtained from Merck (Mumbai, India). Double deionized water (Milli-Q Millipore 18.2 MΩ/cm conductivity) was used for all dilutions. The adsorbent was characterized by surface area analysis, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) studies. The surface properties of the adsorbent were measured by Brunauer-Emmett-Teller (BET) nitrogen adsorption technique (Model ASAP-2010, Micromeritics, USA). SEM (Model Evo-15, Carl Zeiss, England) studies were also conducted to observe the surface morphology. An FTIR (FTIR RX-1, Perkin-Elmer, USA) spectrometer was employed to determine the type of functional groups in the *T. versicolor* (rainbow) biomass responsible for metal adsorption. An atomic absorption spectrometer (AAS; Model AA-6300, Shimadzu, Japan) was used to determine the Ni(II) content in standard and treated solutions. The pH of the solution was measured with a Digisun electronics digital pH meter using a field-effect transistor (FET) solid electrode calibrated with standard buffer solutions.

### 2.4. Batch equilibrium studies

All batch biosorption experiments were carried out in 125 mL stoppered Erlenmeyer flasks containing 100 mL of aqueous Ni(II) solution with 100 mg of biosorbent. The flasks were agitated at a constant speed of 160 rpm for 4 h in an incubator shake. The pH values of the solution were adjusted with dilute 0.1 N HCl or NaOH. The time required for reaching the equilibrium was estimated by drawing samples at regular time intervals. The biosorbent was separated by filtration and the metal content in the filtrate was determined by flame atomic absorption spectrometer. All experiments were repeated three times and the average results were presented. The amount adsorbed per unit mass of adsorbent at equilibrium was obtained using the following equation:

$$q = \frac{(C_i - C_e)V}{M} \quad (1)$$

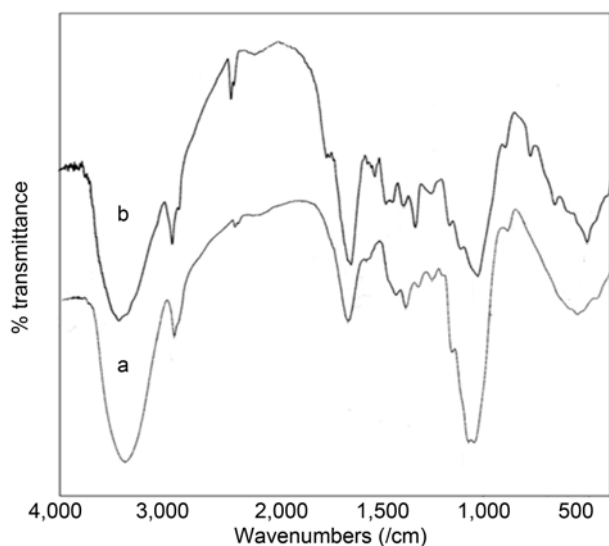
where,  $q$  (mg/g) is the biosorption capacity of equilibrium,  $C_i$  and  $C_e$  are the initial and equilibrium concentrations (mg/L) of Ni(II), respectively,  $M$  (g) is the mass of biosorbent, and  $V$  (L) is the solution volume.

### 3. Results and Discussion

#### 3.1. Characterization of the *T. versicolor* (rainbow) biomass

##### 3.1.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectroscopy method was used to obtain information on the nature of possible interactions between the functional groups of *T. versicolor* (rainbow) biomass and the Ni(II) ions. Fig. 1 presents the FTIR spectra of unloaded and Ni(II)-loaded *T. versicolor* (rainbow) biomass in the range of 4000 ~ 400/cm. The broad and strong band at 3377/cm may be due to the overlapping of O-H and N-H stretching vibration, indicating the presence of both surface free hydroxyl groups and chemisorbed. The peaks at 2923 and 1373/cm correspond to the C-H stretching and bending vibrations of the methyl group. The peak at 1644/cm may be attributed to the stretching vibration of the carboxyl group. The bands observed at 1110 and 1044/cm were assigned to alcoholic C-O and C-N stretching vibration, thus showing the presence of hydroxyl and amine groups on the biomass surface. After Ni(II) biosorption, the bands observed at 3377, 1644, and 1044/cm were shifted to 3430, 1624, and 1028/cm. The analysis of the FTIR spectra demonstrated the presence of ionisable functional groups (*i.e.*, carboxyl, hydroxyl, and amine) able to interact with



**Fig. 1.** FTIR spectra of fungus the *T. versicolor* (rainbow) biomass (a) before and (b) after adsorption of nickel.

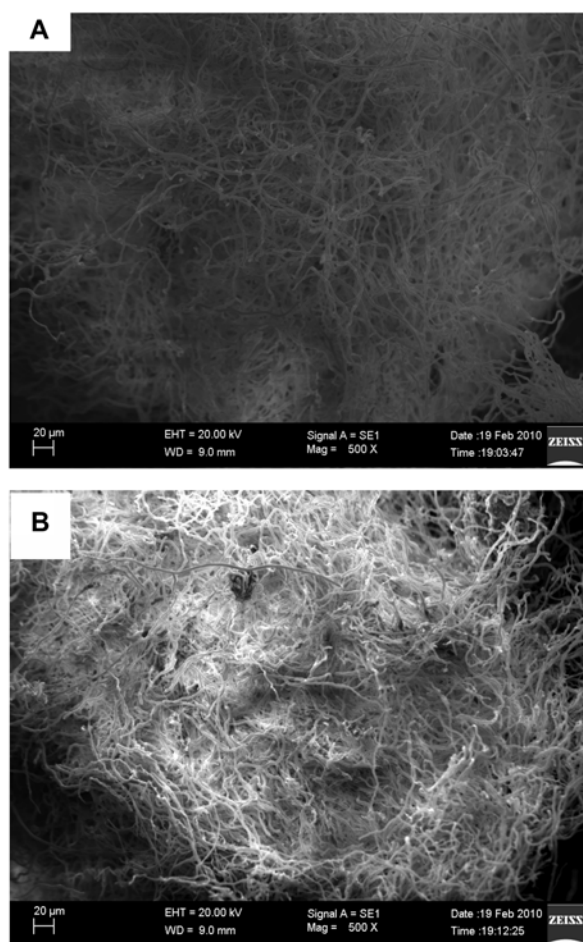
protons or metal ions. Similar FTIR results were reported for the biosorption of different heavy metals on various algae species [16,17].

##### 3.1.2. Surface area analysis

Surface area, pore volume and pore diameter of the *T. versicolor* (rainbow) biomass was determined on the basis of the Brunauer-Emmett-Teller (BET) method. The influence of the surface properties on the extent of biosorption was evaluated by measuring the surface area (2.95 m<sup>2</sup>/g), total pore volume (0.0061 cm<sup>3</sup>/g), and the average pore diameter (47.48 Å). The isotherm plots were used to calculate the specific surface area (N<sub>2</sub>-BET method) and average pore diameter of the *T. versicolor* (rainbow) biomass. Micropore volume was calculated from the volume of nitrogen adsorbed at P/P<sub>0</sub> 0.9966.

##### 3.1.3. Scanning electron microscopy (SEM) studies

Scanning electron micrographs were recorded using a software-controlled digital scanning electron microscope.

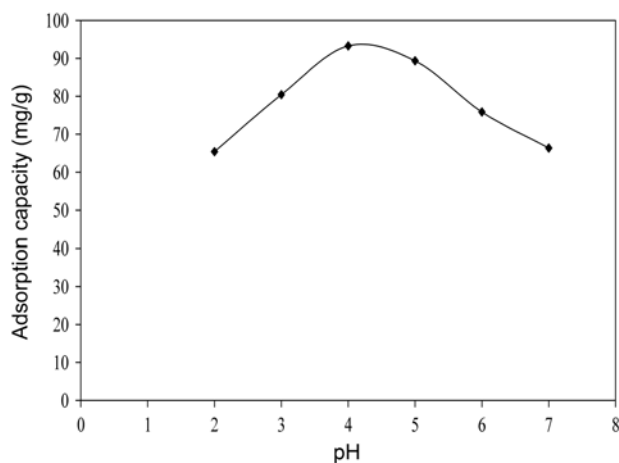


**Fig. 2.** SEM micrographs of the *T. versicolor* (rainbow) biomass (A) before and (B) after adsorption.

The SEM images of the samples were recorded to study the surface morphology. The SEM images of the biosorbent before and after sorption of the *T. versicolor* (rainbow) biomass are shown in Fig. 2. An examination of the SEM micrographs revealed the presence of many pores and small openings on the biosorbent surface. A comparison of these micrographs before and after adsorption revealed the absence of any significant change in the morphology of the surface regarding the biosorbent.

### 3.2. Effect of pH

The pH of the medium is an important parameter in the biosorption process of metal ions from aqueous solutions. Fig. 3 demonstrates the effect of pH on the biosorption of Ni(II) ions onto *T. versicolor* (rainbow) biomass was studied by changing pH values in the range of 2.0 ~ 7.0. From Fig. 3 it is evident that the extent of biosorption increased with increasing pH to a maximum at 4.0 and then decreased as the pH was further increased to 7.0. The pH of the biosorption mechanism is related to the metal-biosorption mechanism onto microorganism surfaces from water and reflects the nature of the physicochemical interaction of both the ion in solution and the nature of the call biosorption sites [18]. The effect of pH regarding the medium on the extent of biosorption can be explained with the involvement of hydronium ions in the biosorption process. At low pH values the concentration of hydronium ions is more than that of metal ions; hence these are bound to the adsorbent leaving the metal ions unbound [19]. When pH value is increased, more ligands such as amino, carboxyl, phosphate and imidazole groups would be exposed and carry negative charges with subsequent attraction of metallic ions with positive charge and biosorption onto the cell surface [20]. Under alkaline conditions, a decrease in



**Fig. 3.** Effect of pH on the biosorption of Ni(II) by the *T. versicolor* (rainbow) biomass (initial concentration: 100 mg/L, biomass dosage: 0.6 g/0.1 L, contact time: 210 min).

biosorption is due to the ionized nature of the cell wall surface of the *T. versicolor* (rainbow) biomass. Therefore, further experiments were carried out at an initial pH of 4.0. Previous studies also reported a maximum biosorption efficiency for Ni(II) metal ion [21,22].

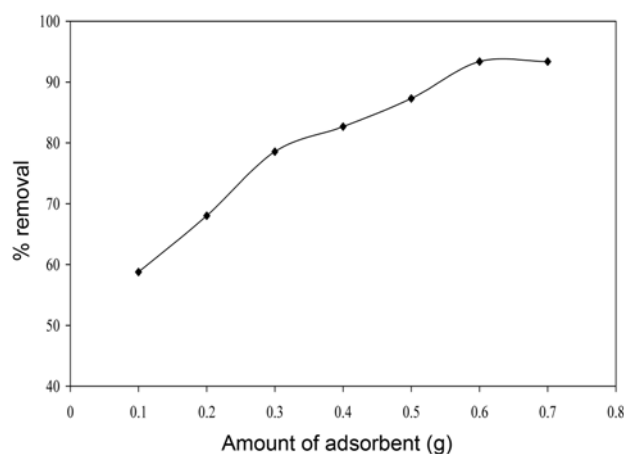
### 3.3. Effect of biomass dosage

The amount of sorbent is one of the important parameters in optimizing the biosorption process for practical applications. The effect of the biomass dose and Ni(II) removal efficiency is graphically presented in Fig. 4. As can be seen from this figure, the % removal of Ni(II) biosorbed increases with an increase in biomass dosage from 0.1 to 0.6 g/0.1 L. This is due to an increase in the mass of the biosorbent, thus increasing the number of active biosorption sites [23]. Further increases in biomass doses over 0.6 g/0.1 L do not lead to a significant improvement in biosorption yield due to the saturation of the biosorbent surface with Ni(II) ions. Therefore, the optimum biomass dosage is taken as 0.6 g/0.1 L for further experiments.

### 3.4. Effect of contact time and kinetic studies

Contact time is an important parameter for the successful use of biosorbents in practical applications [24]. The biosorption of Ni(II) increased considerably with increasing contact time up to 210 min, and remained constant thereafter. The mechanism of biosorption depends on the physical and chemical characteristics of the adsorbent, and on the mass transfer process. The results obtained from the experiments were used to study the kinetics of metal ion biosorption. The rate of Ni(II) biosorption on the *T. versicolor* (rainbow) biomass was analyzed using pseudo-first-order [25], pseudo-second-order [26] and intraparticle diffusion [27] models.

The pseudo-first-order kinetic model was proposed by



**Fig. 4.** Effect of sorbent dose on the biosorption of Ni(II) by the *T. versicolor* (rainbow) biomass (initial concentration: 100 mg/L, biomass dosage: 0.6 g/0.1 L, pH: 4.0, contact time: 210 min).

Lagergren. The integral form of the model is generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (2)$$

The kinetics of the biosorption process may also be described by the pseudo-second-order rate equation. The linearized form of the equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where  $q_e$  and  $q_t$  are the amount of the metal ions sorbed per unit mass of adsorbent (mg/g) at equilibrium and any time  $t$  (min), respectively, and  $K_1$  (1/min) and  $K_2$  (g/mg·min) are the rate constants of the first and second-order sorption, respectively.  $K_1$  is calculated from the linear plot of  $\log(q_e - q_t)$  versus  $t$  and  $K_2$  is determined by plotting  $t/q_t$  against  $t$ .

The values of the parameters and correlation coefficients are also presented in Table 1. The correlation coefficients of all examined data were found to be very high ( $R^2 > 0.999$ ). This shows that the model can be applied for the entire biosorption process and confirms that the sorption of Ni(II) ions onto *T. versicolor* (rainbow) biomass follows the pseudo-second-order kinetic model.

Biosorption is a multi-step process which involves transport of the solute molecules from the aqueous phase to the surface of the solid particulates followed by diffusion into the interior of the pores. The variation in the extent of biosorption with time at different initiation metal concentrations was preceded for evaluating the role of diffusion in the biosorption system. The intraparticle diffusion model is based on the theory proposed by Weber and Morris. According to this theory:

$$q_t = K_{id} t^{0.5} + c \quad (4)$$

where  $K_{id}$  is the intraparticle diffusion rate constant (mg/g min<sup>0.5</sup>) and the intercept  $C$  obtained by  $q_t$  versus  $t^{0.5}$  back to the axis is taken to be proportional to the extent of the boundary layer thickness. The intraparticle diffusion plots show multi-linearity in the biosorption process indicating that three steps are operational (figure not shown). The

initial sharply curved portions might be attributed to the external surface biosorption or instantaneous biosorption stage. The second portion was the gradual sorption stage where the intraparticle diffusion was rate-controlled, while the final linear portions might be due to the final equilibrium stage where the intraparticle diffusion started to slow down due to extremely low solute concentrations in the solution. These results indicate that intraparticle diffusion is not the only rate-controlling step [28,29]. The values of the intraparticle diffusion model are presented in Table 1.

### 3.5. Fitness of the biosorption kinetic models

The assessment of the kinetic models employed for fitting the sorption data was made by calculating the Sum of the Squared Errors (SSE). Lower values of SSE provide a better fit to sorption data and can give an indication of the sorption mechanism [30]. The SSE values were calculated by the equation:

$$SSE = \sum \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2} \quad (5)$$

where  $q_{t,e}$  and  $q_{t,m}$  are the experimental biosorption capacities of metal ions (mg/g) at time  $t$  and the corresponding values that are obtained from the kinetic models. The pseudo-second-order model had lower SSE values, indicating that the biosorption of Ni(II) ions onto *T. versicolor* (rainbow) biomass followed the pseudo-second-order kinetic model. The SSE values are presented in Table 1.

### 3.6. Equilibrium modeling

Optimization of biosorption equilibrium data is very important to evaluate the design parameters of a biosorption system. The parameters are helpful to provide sufficient physico-chemical information to understand the mechanism of biosorption. The sorption capacity of an adsorbent can also be described by an equilibrium sorption isotherm, which is characterized by definite constants whose values express the surface properties and affinity of an adsorbent. The commonly used equations for describing biosorption equilibrium for water and waste water treatment applications are Langmuir and Freundlich. For each isotherm, the initial concentrations

**Table 1.** Parameters of the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models

Metal ion	Pseudo-first-order			Pseudo-second-order			Intraparticle		
	$K_1$ (/min)	$R^2$	SSE	$K_2$ ((g/mg)min)	$R^2$	SSE	$K_{id}$ ((mg/g)min <sup>-0.5</sup> )	$R^2$	SSE
Ni(II)	0.02	0.995	0.998	0.0003	0.999	0.006	1.291	0.967	0.945
	0.02	0.969	0.999	0.0003	0.997	0.008	2.884	0.967	0.939
	0.01	0.992	0.998	0.0003	0.997	0.009	4.635	0.979	0.935
	0.01	0.983	0.999	0.0003	0.999	0.006	5.101	0.962	0.947

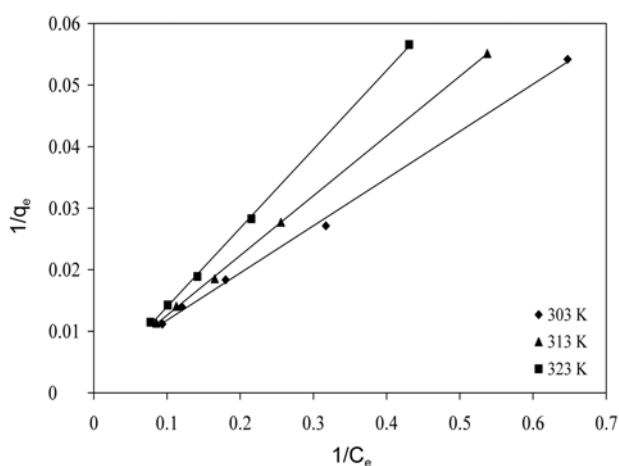
of Ni(II) ions were varied from 20 to 100 mg/L while the weight of the *T. versicolor* (rainbow) biomass and pH were kept constant. The biosorption capacity of *T. versicolor* (rainbow) increased with increasing initial metal ion concentration. The increased loading capacity of the biosorbent with increasing metal ion concentration may have been due to the higher probability of collision between the metal ions and biosorbent.

The assumptions from the Langmuir equation are (a) a finite number of identical sites which are energetically uniform are present on the solid surface; (b) the amount adsorbed has no influence on the rate of biosorption i.e., there is no interaction between adsorbed biomass; (c) when the surface reaches saturation a monolayer is formed. It assumes the form [31].

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (6)$$

where  $q_e$  is the equilibrium metal ion concentration on the sorbent (mg/g),  $C_e$  the equilibrium metal ion concentration in the solution (mg/L),  $q_m$  the monolayer sorption capacity of the sorbent (mg/g), and  $K_L$  the Langmuir sorption constant (L/mg) relating the free energy of biosorption. The Langmuir parameters  $q_m$  and  $K_L$  are calculated from the slope and intercept of the straight lines regarding plot  $1/C_e$  versus  $1/q_e$  (Fig. 5). The increase of maximum biosorption capacity ( $q_m$ ) and Langmuir constant ( $K_L$ ) with an increase of temperature reveals that the biosorption is favorable in high temperature and the process is endothermic in nature.

On the other hand, biosorption capacity of the *T. versicolor* (rainbow) biomass for Ni(II) is compared with various types of biosorbents reported in the literature [32–44] and shown in Table 3. Obviously the higher biosorption



**Fig. 5.** Langmuir isotherm plots for the biosorption of Ni(II) by the *T. versicolor* (rainbow) biomass at different temperatures.

capacity of *T. versicolor* (rainbow) biomass indicates its potential application in Ni(II) removal from aqueous solution.

The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The Freundlich model [45] is

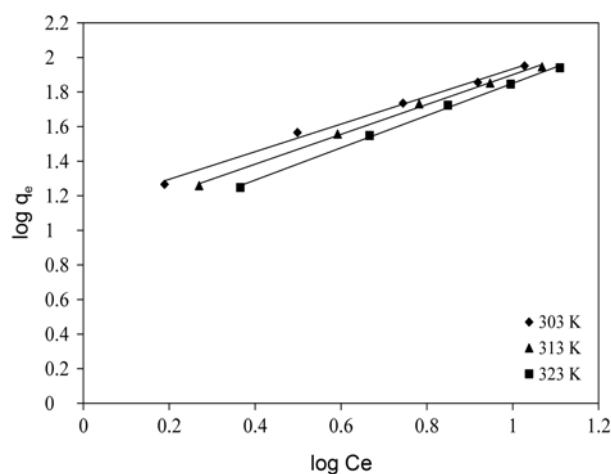
$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

where  $q_e$  is the amount of metal ions uptake (mg/g) at equilibrium,  $C_e$  is the equilibrium concentration (mg/L), and  $K_f$  and  $1/n$  are the Freundlich constants indicative of biosorption capacity and biosorption intensity, respectively. The constants  $K_f$  and  $1/n$  can be determined from the linear plot of  $\log C_e$  and  $\log q_e$  (Fig. 6). From the graphs, the  $K_f$  values were 2.64, 3.93, and 5.58 and the  $1/n$  values were 0.741, 0.813, and 0.869. The  $1/n$  values ranged between 0 and 1, indicating that the biosorption of Ni(II) ions onto the *T. versicolor* (rainbow) biomass was favourable at the studied conditions.

The Langmuir and Freundlich biosorption constants evaluated from the isotherms at different temperatures and their correlation coefficients are also present in Table 2. By comparing these results, it can be seen that the Langmuir isotherm can accurately describe the biosorption of Ni(II) ions onto *T. versicolor* (rainbow) biomass in this study.

### 3.7. $\chi^2$ Analysis

The Chi-squared test was carried out to identify the suitable isotherm for the biosorption of Ni(II) ions onto *T. versicolor* (rainbow) biomass. The chi-squared test statistic is basically the sum of squares for the differences between the experimental data and data obtained by calculating the models, with each squared difference divided by the corresponding data obtained by calculating the models [46]:



**Fig. 6.** Freundlich isotherm plots for the biosorption of Ni(II) by the *T. versicolor* (rainbow) biomass at different temperatures.

**Table 2.** Langmuir and Freundlich isotherm constants and correlation coefficients for the biosorption of Ni(II) by the *T. versicolor* (rainbow) biomass at different temperatures

Metal ion	Temp. (K)	Langmuir				Freundlich			
		$q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$	$\chi^2$	$K_f$	1/n	$R^2$	$\chi^2$
Ni(II)	303	140.2	6.04	0.996	0.233	2.64	0.741	0.988	1.152
	313	159.4	7.42	0.999	0.613	3.93	0.813	0.994	2.766
	323	212.5	8.41	0.999	0.789	5.58	0.869	0.997	3.483

**Table 3.** Comparison of maximum biosorption capacity of Ni(II) on different adsorbents in the literature

Biosorbent type	pH	$q_m$ (mg/g)	References
<i>Cassia fistula</i> (ponds bark)	6.0	188.4	[32]
<i>Moringa oleifera</i> bark	6.0	30.38	[33]
<i>Oedogonium hatei</i>	5.0	40.9	[34]
<i>Pseudomonas aeruginosa</i> ASU 6a	7.0	113.6	[35]
<i>Ulva</i> sp. and <i>Gracilaria</i> sp.	5.5	17	[36]
<i>Sargassum</i> sp. and <i>podina</i> sp.	5.5	35	[36]
<i>Sargassum muticum</i>	5.0	75.6	[37]
<i>Gracilaria caudata</i>	5.0	50.1	[37]
Cone biomass of <i>Thuja orientalis</i>	4.0	12.4	[38]
<i>Enteromorpha prolifera</i>	4.3	65.07	[39]
<i>Escherichia coli</i> biofilm supported on kaolin	5.7 ~ 6.2	6.9	[40]
<i>Streptomyces coelicolor</i> A3(2)	8.0	11.1	[41]
<i>Bacillus thuringiensis</i> (vegetative cell)	6.0	21.5	[42]
<i>Bacillus thuringiensis</i> (spore-crystal mixture)	6.0	34.3	[42]
<i>Synechocystis</i> sp.	5.0	189.8	[43]
Immobilized hybrid biosorbent(IHB)	5.0	101.1	[44]
<i>Trametes versicolor</i> (rainbow)	4.0	212.5	This study

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (8)$$

where  $q_{e,m}$  is equilibrium uptake obtained by calculating the models (mg/g) and  $q_e$  is the experimental data of the equilibrium uptake (mg/g). The  $\chi^2$  values of Langmuir isotherms are lower than the  $\chi^2$  values of the Freundlich isotherm, indicating that the Langmuir isotherm is more suitable for the biosorption of Ni(II) ions onto *T. versicolor* (rainbow) biomass. The  $\chi^2$  values are presented in Table 2.

### 3.8. Biosorption thermodynamics

Three thermodynamic parameters, the change in free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ), were used to describe the thermodynamic behaviour for the biosorption of Ni(II) ions onto the *T. versicolor* (rainbow) biomass.  $\Delta G^\circ$  value is estimated from the following equation:

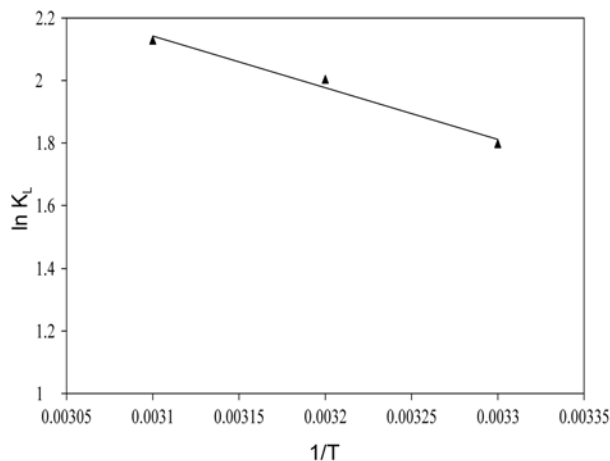
$$\Delta G^\circ = -RT \ln K_L \quad (9)$$

where  $R$  is the universal gas constant (8.314 J/mol K),  $T$  the temperature (K) and  $K_L$  the Langmuir constant.

The Van't Hoff equation (refer Eq. 10) is used to

determine the values of  $\Delta H^\circ$  and  $\Delta S^\circ$ . The resulted slope and intercept from the plot of  $\ln K_L$  versus  $1/T$  (Fig. 7) denote the values of the enthalpy and entropy, respectively.

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$



**Fig. 7.** Plot of  $\ln K_L$  versus  $1/T$  for the estimation of thermodynamic parameters for the biosorption of Ni(II) by *T. versicolor* (rainbow) biomass.

**Table 4.** Thermodynamic parameters for the adsorption of Ni(II) by the *T. versicolor* (rainbow) biomass at different temperatures

Metal ion	Temperature (K)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol K)	$\Delta H^\circ$ (kJ/mol)
Ni(II)	303	-4.530	75.4	18.3
	313	-5.215		
	323	-5.718		

The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for the biosorption of Ni(II) on the *T. versicolor* (rainbow) biomass are given in Table 4. The values of  $(-\Delta G^\circ)$  ranging from 4.530 to 5.718 kJ/mol at 303, 313, and 323 K are inversely proportional to the temperature. The negative value indicates that the biosorption is spontaneous in nature (The more negative the  $\Delta G^\circ$ , the stronger the driving force of biosorption reaction). The enthalpy changes ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of biosorption were 18.3 kJ/mol and 75.4 J/mol K, respectively. The positive value of  $\Delta H^\circ$  confirms that the overall biosorption of Ni(II) ions onto *T. versicolor* (rainbow) biomass is endothermic in nature. The positive value of  $\Delta S^\circ$  reflects the affinity of the *T. versicolor* (rainbow) biomass for Ni(II) and increased randomness at the solid/solution interface with some structural changes in the adsorbate and adsorbent. Furthermore, a positive  $\Delta S^\circ$  value corresponds to an increase in the degree of freedom for the adsorbed species [47].

#### 4. Conclusion

This study reports the biosorption performance of *T. versicolor* (rainbow) biomass for removal of Ni(II) ions from aqueous solutions.

The main conclusions are as follows:

- The *T. versicolor* (rainbow) biomass was an efficient biosorbent for the removal of Ni(II) ions from aqueous solutions compared to various biosorbents reported in the literature.
- The obtained results showed that the biosorption of Ni(II) ions was highly dependent on experimental parameters, such as pH, contact time, biomass dosage, initial metal ion concentration and temperature.
- The monolayer maximum biosorption capacity of the *T. versicolor* (rainbow) biomass was 212.5 mg/g at pH 4.0.
- The FTIR analysis confirmed the involvement of carboxyl, hydroxyl and amine groups in the binding of Ni(II) ions.
- The chi-square ( $\chi^2$ ) and sum of the squared errors (SSE) tests were also carried out to find the best fit biosorption isotherms and kinetics.
- The biosorption of Ni(II) ions onto *T. versicolor* (rainbow) biomass follows pseudo-second-order kinetics.

- The biosorption equilibrium was better described by the Langmuir isotherm model than the Freundlich isotherm model.
- The thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) are deduced for the biosorption of Ni(II) ions onto *T. versicolor* (rainbow) biomass and the results demonstrate that the biosorption is feasible, spontaneous and endothermic.

Based on the results *T. versicolor* (rainbow) biomass was an efficient and economic biosorbent material for the removal of nickel(II) from aqueous solutions.

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