



## Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) onto *Trametes versicolor* biomass

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### ABSTRACT

The ability of *Trametes versicolor* biomass for biosorption of Cu(II) ions from aqueous solution was studied in batch experiments. The effect of relevant parameters such as function of pH, biomass dosage, contact time, initial metal ion concentration and temperature was evaluated. Further, the biosorbent was characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and BET Surface area analysis. Experimental data were analyzed in terms of pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models. The results showed that the biosorption process of Cu(II) ions followed well pseudo-second order kinetics. The biosorption data of Cu(II) ions at 303, 313 and 323 K are fitted to Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin isotherms. Biosorption of Cu(II) onto *T. versicolor* biomass followed the Langmuir isotherm model ( $R^2 = 0.999$ ) with the maximum biosorption capacity of 140.9 mg/g. The calculated thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  showed that the biosorption of Cu(II) ions onto *T. versicolor* biomass was feasible, spontaneous and endothermic at 303–323 K.

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### 1. Introduction

Copper is widely used in electrical wiring, plumbing, gear wheel, selenium rectifier and roofing industries, due to its excellent physical and mechanical properties such as electrical and thermal conductivity, good corrosion resistance, ease of fabrication and installation. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production, and the fertilizer industry, etc., [1]. Ultra-trace amount of copper is essential for human, animals, and microorganisms. However, excessive copper is detrimental for the environment. For instance in human excessive intake will cause stomach upset and ulcer, mental retardation, liver and brain damage, and so on. Therefore, removal of copper from effluents is essential not only to protect the water resources but also to slow down the fast depletion of copper sources.

Conventional methods used to remove metal ions from industrial wastewater include chemical precipitation, electrochemical treatment, ion exchange process, membrane separation and evaporation [2,3]. However some of the conventional technologies are ineffective and unfavorable as they cause sludge disposal problem, expensive and incomplete removal [4,5]. The utilization of biosorption technology for the treatment of heavy metal contaminated wastewaters has become an alternative method to conventional treatments [6–9].

Biosorption utilizes various natural materials including fungi, yeast and bacteria that have been studied to sequester metal ions from aqueous solution [10]. Metal ions uptake by microorganisms involves several chemical processes including adsorption, ion exchange, covalent binding and co-ordination [11]. Fungi have been well-known for the removal of metal ions from industrial effluents [12]. Many fungal species such as *Aspergillus niger*, *Mucor* spp., *Phanerochaete chrysosporium*, *Rhizopus* spp. and *Saccharomyces* spp., have been extensively studied as a potential biosorbent in metal ions removal as it is inexpensive and abundant [8,13–19].

In some of these studies biosorbents used for copper removal were developed by manipulating the natural materials by chemically introducing the binding sites to improve the metal removal efficiency, which invariably increases the cost of the biosorbent. Hence attempts are made in this study to develop an inexpensive biosorbent for the removal of Cu(II) ion from wastewater using locally available fungal waste by simple treatment of washing with water. *Trametes versicolor* was chosen as biosorbent in this study due to being of its natural, renewable and thus cost-effective biomass.

The present work aims to investigate the biosorption potential of *T. versicolor* biomass as an alternative biosorbent material for the removal of Cu(II) ions from aqueous solution. The study includes an evaluation of the effects of various process parameters such as pH, contact time, initial metal ion concentration, biomass dosage and temperature. The experimental data are analyzed in terms of kinetic and equilibrium isotherm models. The results at different temperatures are used to evaluate thermodynamic parameters.

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2. Materials and methods

2.1. Biomass preparation

Samples of the biomass were collected from the Tirumala Hills, Tirupati, Andhra Pradesh, India. Samples were washed several times using deionized water to remove extraneous and salts. They were then dried in an oven at 105 °C for 48 h. The dried samples were ground to fine powder and the powder was sieved through different sizes and 200–300 μm fractions. This was stored in a desiccator and used in further experiments.

2.2. Chemicals and equipment

All chemicals used were of analytical reagent grade. Deionized double distilled water was used throughout the experimental studies. A stock solution of Cu(II) (1000 mg/L) was prepared by dissolving 3.801 g of Cu(NO<sub>3</sub>)<sub>2</sub> in 1000 mL slightly acidified distilled water. Working standards were prepared by progressive dilution of the stock copper solution. ACS reagent grade HCl, NaOH and buffer solutions (E. Merk) were used to adjust the solution pH.

An Elico (L1-129) pH meter was used for pH measurements. The pH meter was calibrated using standard buffer solution of pH 4.0, 7.0 and 9.2. The metal concentrations in the samples were determined using Atomic Absorption Spectrophotometer (Shimadzu AA-6300, Japan). FTIR spectrophotometer (Thermo-Nicolet FTIR, Nicolet IR-200, USA) was used for the IR spectral studies (4000–400 cm<sup>-1</sup>) of adsorbent. For IR spectral studies, 10 mg of sample was mixed and ground with 100 mg of KBr and made into pellet. The background absorbance was measured by using a pure KBr pellet. Surface area, density, pore volume, pore diameter and porosity of the composite biosorbent were determined with BET (Brunauer, Emmett and Teller) instrument (Micromeritics ASAP-2000, USA).

2.3. Surface area analysis

Surface area, density, pore volume, pore diameter and porosity of the composite biosorbent were determined with BET (Brunauer, Emmett and Teller). The isotherm plots were used to calculate the specific surface area (N<sub>2</sub>/BET method) and average pore diameter of biomass, while micropore volume was calculated from the volume of nitrogen adsorbed at P/P<sub>0</sub> 0.9966.

2.4. Batch equilibrium studies

In order to optimize the experimental conditions, the batch studies were performed for different metal concentrations (50–200 mg/L), contact times (30–210 min), pH (2–7), biomass dosages from (0.1 to 0.7 g/L) and temperature (303–323 K). The solutions including the metal ions and biosorbent were shaken during optimum contact time in an electrically thermostatic reciprocating shaker at 120 rpm. After the contents of the flask were filtered through Whatman no. 42 filter papers, the metal concentrations of filtrate were analyzed using AAS.

The sorption capacity of metal ion is the concentration of metal ion on the adsorbent, and it can be calculated based on the mass balance principle where;

$$q_e = \frac{(C_i - C_e)V}{M} \tag{1}$$

where,  $q_e$  (mg/g) is the adsorption capacity of the biosorbent at any time,  $M$  (g) is the biosorbent dosage, and  $V$  (L) is the volume of the solution.

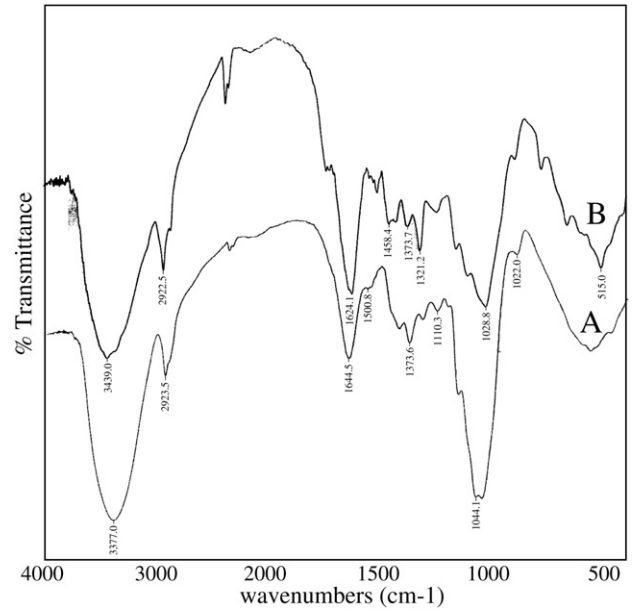


Fig. 1. FTIR spectra of fungus (*T. versicolor*) biomass before biosorption (A) and after biosorption of Cu(II) (B).

2.5. Fitness of the biosorption kinetic models

The kinetic models were evaluated for fitness of the sorption data by calculating the sum of squared error (SSE). The SSE values were calculated by the equation:

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

where  $q_{t,e}$  and  $q_{t,m}$  are the experimental biosorption capacities of Cu(II) ions (mg/g) at time  $t$  and the corresponding values that are obtained from the kinetic models.

2.6.  $\chi^2$  analysis

To identify the suitable isotherm for biosorption of Cu(II) ions onto *T. versicolor* biomass, the  $\chi^2$  analysis is carried out. The mathematical statement for  $\chi^2$  analysis is written as

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{3}$$

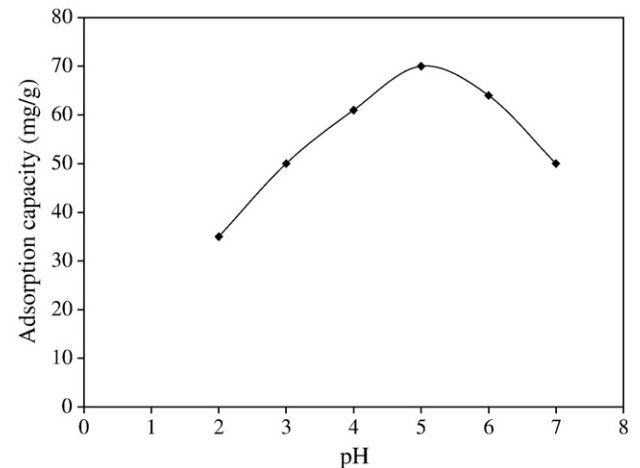


Fig. 2. Effect of pH on the biosorption of Cu(II) ions onto *T. versicolor* biomass.

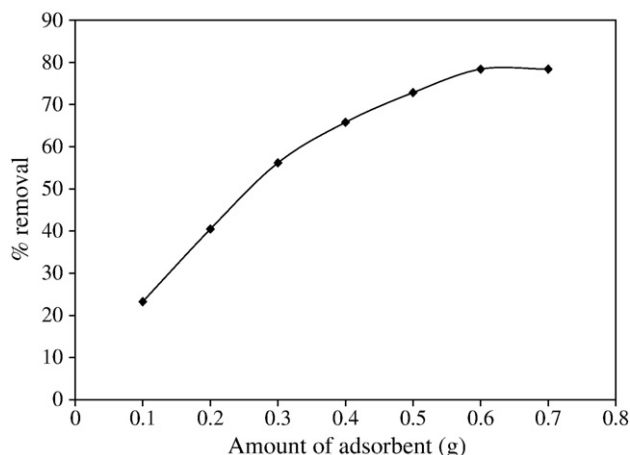


Fig. 3. Effect of adsorbent dose on the biosorption of Cu(II) onto *T. versicolor* biomass.

where  $q_{e,m}$  is the equilibrium capacity obtained by calculating from the model (mg/g) and  $q_e$  is the experimental data on the equilibrium capacity (mg/g).

### 3. Results and discussion

The biosorbent material shows an average surface area of 3.102 (m<sup>2</sup>/g), pore volume of 0.0061 (cm<sup>3</sup>/g), porosity of 62.91%, pore diameter of 0.197 nm and density of 1.490 (g/cm<sup>3</sup>).

#### 3.1. Fourier transform infrared (FTIR) studies

The FTIR spectral analysis is important to identify the characteristic functional groups, which are responsible for biosorption of metal ions. FTIR spectrum of *T. versicolor* biomass (Fig. 1A) shows distinct peaks at 3377, 2923, 1644, 1500, 1110, and 1044 cm<sup>-1</sup>. The broad and strong band at 3377 cm<sup>-1</sup> may be due to overlapping of -OH and -NH stretching. The bands at 2923 are attributed to C-H stretching vibrations. The bands 1500 cm<sup>-1</sup> are attributed to N-H bending, respectively, thus showing the presence of hydroxyl and amine groups on the biomass surface. The strong peak at 1644 cm<sup>-1</sup> can be assigned to a C=O stretching in carboxyl or amide groups. The peaks at 1110 and 1044 cm<sup>-1</sup> are assigned to alcoholic C-O and C-N stretching vibration, Fig. 1B shows the spectrum of *T. versicolor* biomass after the biosorption of Cu(II). FTIR spectrum shows the shift in peaks at wave numbers 3377 cm<sup>-1</sup> to 3430 cm<sup>-1</sup>, which may be attributed to the intensity of -OH and -NH<sub>2</sub> groups with the biosorbate. The decrease in the wave number of the peak at 1644 to 1624 cm<sup>-1</sup>, suggests that interacts with carbonyl functional group are present in the biomass. In addition the peak at 1500 cm<sup>-1</sup> corresponding to N-H bending shifts to the lower frequency (1458 cm<sup>-1</sup>) after Cu(II) uptake. Hence, FTIR spectra reveal that functional groups like -NH<sub>2</sub>, -OH and -C=O present on the *T. versicolor* biomass surface are involved in copper biosorption.

#### 3.2. Effect of pH

The pH of solution greatly influences metal sorption. Further, pH influences surface properties of the biosorbent by way of functional group dissociation and also surface charges. At pH 2 biosorption of Cu(II) onto *T. versicolor* biomass was found to be very low. It has been suggested that at low pH, H<sub>3</sub>O<sup>+</sup> ions are close to the binding sites of the biomass and this restricts the approach of Cu(II) ions due to repulsion [20]. With increase in pH, more ligands with negative charges are expected to be exposed and this will attract more positively charged Cu(II) ions for binding. Biosorption of Cu(II) by *T. versicolor* biomass had been found to increase with increase in pH and reach maximum at 5.0 and then decrease with further increase in pH up to 7.0 (Fig. 2). The effect of pH was not studied beyond pH 7.0 because of the precipitation of Cu(II) as hydroxide. Above the pH 7 the decrease in biosorption may be attributed to reduced solubility and precipitation of Cu(II) [21]. Therefore, further experiments were carried out with an initial pH value of 5.0. Previous studies also reported that the maximum biosorption efficiency for Cu(II) metal ion an biomass was observed at pH 5.0 [22–24].

#### 3.3. Effect of biomass dosage

The effect of biomass dosage on the removal efficiency of Cu(II) was studied using varying amounts of biomass dosages (0.1–0.7 g/0.1 L) and the results are shown in Fig. 3. The removal efficiency of Cu(II) was raised with increasing biomass dosage. The maximum removal efficiency was attained as the dosage was 0.6 g/0.1 L. The increase in the biosorption percentage with increase in biomass dosage is due to increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the sorption sites [25]. Therefore, 0.6 g/0.1 L was selected as optimum biosorbent dosage for further experiments.

#### 3.4. Effect of contact time

The rate of biosorption is important for designing batch biosorption experiments. Therefore, the effect of contact time on the biosorption of Cu(II) was investigated. The biosorption yield of Cu(II) increased considerably until the contact time reached 180 min. Further increase in contact time did not enhance the biosorption, so, the optimum contact time was selected as 180 min for further experiments.

#### 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 [26]. In this study, the biosorption equilibrium data were analyzed using three kinetic models, pseudo-first-order, pseudo-second-order and intraparticle diffusion model.

Table 1

Kinetic parameters obtained from pseudo-first-order, pseudo-second-order and intraparticle diffusion for Cu(II) biosorption onto *T. versicolor* biomass.

Metal ion	Lagergren first order			Pseudo-second-order			Weber and Morris		
	K <sub>1</sub> (min <sup>-1</sup> )	R <sup>2</sup>	SSE	K <sub>2</sub> ((g/mg)min)	R <sup>2</sup>	SSE	K <sub>id</sub> ((mg/g)min <sup>-0.5</sup> )	R <sup>2</sup>	SSE
Cu(II)	0.001	0.954	0.978	0.0006	0.999	0.018	1.128	0.983	0.922
	0.011	0.998	0.988	0.0006	0.997	0.003	1.460	0.981	0.953
	0.011	0.999	0.989	0.0006	0.998	0.004	2.204	0.988	0.951
	0.009	0.999	0.998	0.0005	0.999	0.003	2.533	0.985	0.954

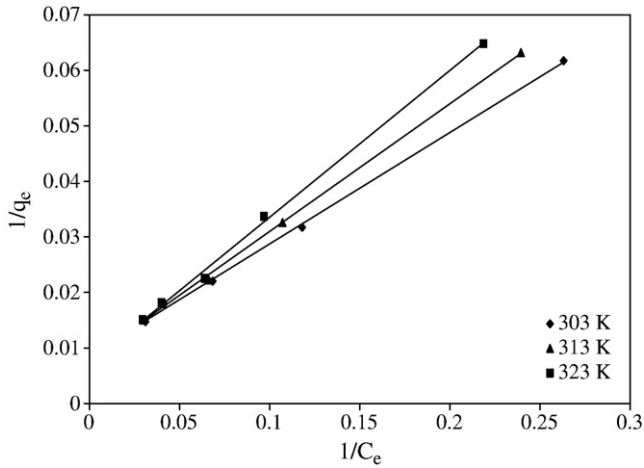


Fig. 4. Langmuir isotherm plots for the biosorption of Cu(II) onto *T. versicolor* biomass at different temperatures.

The linear form of the pseudo-first-order rate equation [27] is given as

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{4}$$

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

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [28]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where  $K_2$  (g/mg min) is the rate constant of the second-order equation,  $q_t$  (mg/g) is the amount of biosorption time  $t$  (min) and  $q_e$  is the amount of biosorption equilibrium (mg/g). The biosorption rate constants ( $K_2$ ) can be determined experimentally by plotting of  $t/q_t$  versus  $t$ .

The rate constants and  $R^2$  values are given in Table 1. However, the correlation coefficients,  $R^2$ , showed that the pseudo-second-order model fits better with the experimental data than the pseudo-first-order model. In addition, the sum of squared error (SSE) test was also done to support the best fit biosorption model (Table 1). SSE values were lower for pseudo-second-order model than the pseudo-first-order model. Based on  $R^2$  and SSE values it was confirmed that pseudo-second-order model best fits the biosorption data, an indication of chemisorption mechanism.

The results are also analyzed in terms of intraparticle diffusion model to investigate whether the intraparticle diffusion is the rate controlling step in biosorption of Cu(II) onto *T. versicolor* biomass. The intraparticle diffusion equation is expressed as [29]

$$q_t = K_{id} t^{0.5} + c \tag{6}$$

where  $K_{id}$  is the intraparticle diffusion rate constant ( $\text{mg}/(\text{g min}^{-0.5})$ ) and  $C$  is the intercept. It is observed that all the plots have an initial curved portion, followed by a linear portion and a plateau region. The initial curve of the plot is due to the diffusion of metal ion through the solution to the external surface of *T. versicolor* biomass. The linear portion of curves describes the gradual biosorption stage, where intraparticle diffusion of metal ion on *T. versicolor* takes place and final plateau region indicates equilibrium uptake. Based on the results it may be concluded that intraparticle diffusion is not only the rate determining factor. The rate constants of intraparticle diffusion model are shown in Table 1.

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 biosorption of Cu(II) on the biosorbent follows second order kinetic model. Lower values of SSE show a better fitness of the biosorption data [30,31].

### 3.6. Biosorption isotherm models

The successful representation of the dynamic biosorptive separation of solute from solution onto biosorbent depends upon appropriate description of the equilibrium separation between two phases [32]. In order to determine the mechanism of Cu(II) biosorption onto *T. versicolor* and to evaluate the relationship between biosorption temperatures, the experimental data was applied to the linear isotherms models, i.e. Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin.

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface [33].

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \tag{7}$$

where  $q_m$  is the monolayer biosorption capacity of the biosorbent (mg/g),  $q_e$  is the equilibrium metal ion concentration on the biosorbent (mg/g),  $C_e$  is the equilibrium metal ion concentration in the solution (mg/L), and  $b$  is the Langmuir biosorption constant (L/mg) related to the free energy of biosorption. Fig. 4 shows the Langmuir plots at different temperature and the constants  $q_m$  and  $b$  are tabulated in Table 2. The constants  $q_m$  and  $b$  increased with increase in temperature.

On the other hand, Table 3 presents the comparison of biosorption capacity ( $q_m$ ; mg/g) of *T. versicolor* biomass for Cu(II) with those of various biosorbents reported in literature [1,23,34–46]. Based on this table, it can be concluded that the *T. versicolor* has an important potential for the removal of Cu(II) from aqueous solution.

The Freundlich isotherm model assumes a heterogeneous sorption surface. The linear form of Freundlich isotherm is represented by the equation [47].

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{8}$$

where  $K_f$  is a constant relating the biosorption capacity and  $1/n$  is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material. From the graphs,  $K_f$  values were found to be 5.29, 6.30 and 7.22 and  $1/n$  values were found as 0.658, 0.685 and 0.735. The  $1/n$  values were between 0 and 1

Table 2  
Langmuir, Freundlich, Dubinin–Radushkevich and Temkin constants for the biosorption of Cu(II) on the *T. versicolor* biomass at different temperatures.

Metal ion	Temp. (K)	Langmuir				Freundlich				Dubinin–Radushkevich				Temkin				
		$q_m$	$b$	$R^2$	$\chi^2$	$K_f$	$1/n$	$R^2$	$\chi^2$	$q_m$	$\beta$	$E$	$R^2$	$\chi^2$	$B$	$K_T$	$R^2$	$\chi^2$
Cu(II)	303	114.9	0.0302	0.999	19.25	5.29	0.658	0.985	109.2	53.3	3.69	9.1	0.891	42.13	25.53	0.487	0.986	65.41
	313	125.0	0.0389	0.999	27.28	6.30	0.685	0.985	177.1	54.3	4.15	9.4	0.888	57.83	24.19	0.425	0.988	74.38
	323	140.9	0.0453	0.997	39.67	7.22	0.735	0.987	197.9	54.8	4.67	10.1	0.877	66.29	25.41	0.364	0.962	83.47

**Table 3**

A comparison of adsorption capacity ( $q_m$ : mg/g) of different biosorbents for Cu(II) removal.

Biosorbent	$q_m$ (mg/g)	Reference
Sugar beet pulp	31.4	[1]
<i>Sargassum vulgare</i>	88.80	[34]
<i>Sargassum filipendula</i>	74.19	[34]
<i>Sargassum fluitans</i>	78.68	[34]
<i>Pandina</i> sp.	84.30	[35]
<i>Sargassum</i> sp.	85.43	[35]
<i>Spirogyra</i> (green alga)	133.30	[36]
Rice bran	27.81	[37]
<i>Pycnoporus sanguineus</i>	2.76	[38]
Peanut hull	21.25	[39]
Soybean hulls	154.9	[40]
Modified orange peel	289.0	[41]
Wheat shell	10.84	[42]
Potato peels charcoal	0.3877	[43]
Carrot residue	32.74	[44]
Sour orange residue	21.70	[23]
Grape stalks waste	10.12	[45]
<i>Sargassum wightii</i>	52.6	[46]
<i>Trametes versicolor</i>	140.9	Present study

indicating that the biosorption of Cu(II) onto the *T. versicolor* was favorable at studied conditions. Fig. 5 shows the Freundlich plots at different temperature and the constants  $K_f$  and  $1/n$  are tabulated in Table 2.

Another equation that has been used to determine the possible biosorption mechanism is the Dubinin–Radushkevich equation, which assumes a constant sorption potential. The linear form of the D–R isotherm equation [48] is:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (9)$$

where  $q_e$  is the amount of metal ions adsorbed on per unit weight of biomass (mg/g),  $q_m$  is the maximum biosorption capacity (mg/g),  $\beta$  is the activity coefficient related to biosorption mean energy ( $\text{mol}^2/\text{kJ}^2$ ) and  $\varepsilon$  is the Polanyi potential described as

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (10)$$

where  $C_e$  is the equilibrium concentration of the Cu(II) in solution (mg/L),  $R$  is the gas constant (8.314 J/mol K), and  $T$  is the temperature

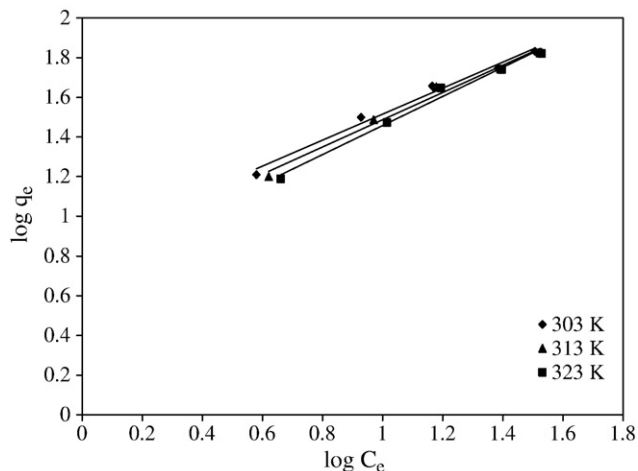


Fig. 5. Freundlich isotherm plots for the biosorption of Cu(II) onto *T. versicolor* biomass at different temperatures.

(K). The D–R isotherm parameters for the three different temperatures have been presented in Table 2.

The mean adsorption energy ( $E$ ) is calculated by using the following formula

$$E = \frac{1}{\sqrt{-2\beta}} \quad (11)$$

where  $E$  (kJ/mol) gives information about the physical and chemical features of adsorption. It can be seen that the mean sorption energy ( $E$ ) was evaluated at 9.1 to 10.1 kJ/mol for the biosorption of Cu(II) at temperature ranging from 303 to 323 K. According to the literature, the  $E$  value ranges from 1.0 to 8.0 kJ/mol for physical adsorption and from 9.0 to 16.0 kJ/mol for chemical ion-exchange adsorption [49,50]. Therefore, *T. versicolor* biomass may be attributed to chemical ion-exchange mechanism.

The Temkin isotherm [51] assumes that the heat of adsorption of all the molecules in the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions [52], and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum energy.

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (12)$$

$$q_e = B \ln K_T + B \ln C_e \quad (13)$$

where constant  $B = RT/b$ , which is related to the heat of adsorption,  $R$  is the universal gas constant (J/mol K),  $T$  is the temperature (K),  $b$  is the variation of a adsorption energy (J/mol) and  $K_T$  is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. A plot of  $q_e$  versus  $\ln C_e$  (Fig. 6) enables the determination of the isotherm constants  $B$  and  $K_T$  from the slope and the intercept, respectively. Temkin isotherm parameters are listed in Table 2.

By comparing the results, the values of  $\chi^2$  and the correlation coefficients ( $R^2$ ) (Table 2), it has been found that the Langmuir isotherm best represented the equilibrium biosorption of Cu(II) onto *T. versicolor* biomass. It is necessary to analyze the data set using the Chi-square test to confirm the best-fit isotherm for the biosorption system [53]. If the data from the model are similar to the experimental data,  $\chi^2$  will be a small number, while if they differ;  $\chi^2$  will be a bigger number. The  $\chi^2$  values of the isotherms are comparable and hence the biosorption of Cu(II) follows in the order as: Langmuir  $\geq$  Dubinin–Radushkevich (D–R)  $\geq$  Temkin  $\geq$  Freundlich isotherms.

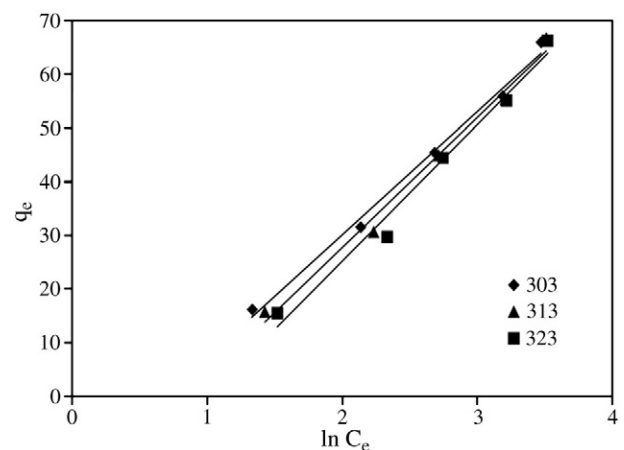


Fig. 6. Temkin isotherm for the biosorption of Cu(II) onto *T. versicolor* biomass at different temperatures.

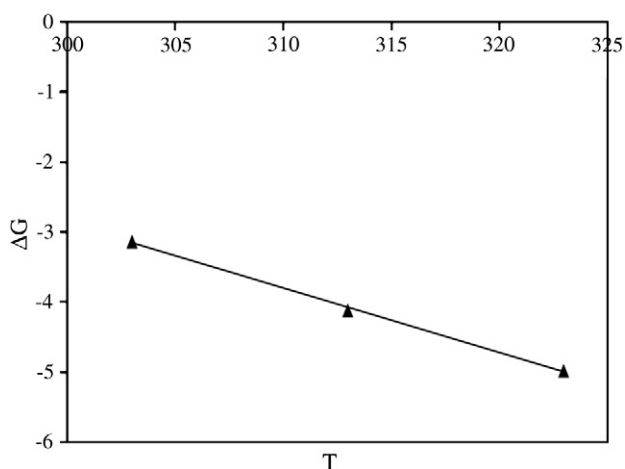


Fig. 7. Plot of  $\Delta G$  versus  $T$  for the estimation of thermodynamic parameters for biosorption of Cu(II) by *T. versicolor* biomass.

### 3.7. Biosorption thermodynamics

The thermodynamic parameters for the present system, including  $\Delta G$  (kJ/mol),  $\Delta H$  (kJ/mol) and  $\Delta S$  (kJ/mol K), were calculated using following equations Eqs. (14) and (15) [54]

$$\Delta G = -RT \ln K \quad (14)$$

$$\Delta G = \Delta H - T\Delta S \quad (15)$$

where  $T$  is the temperature (K),  $R$  is universal gas constant (8.314 J/mol K) and  $K$  (L/g) is an equilibrium constant obtained by multiplying the Langmuir constant  $q_m$  and  $b$  [55]. The values of  $\Delta H$  and  $\Delta S$  were calculated from the intercept and slope of a plot of  $\Delta G$  versus  $T$  (Fig. 7) according to Eq. (15) by linear regression analysis. The calculated thermodynamic parameters were listed in Table 4.

As shown in Table 4, the negative values of  $\Delta G$  indicated the spontaneous nature of the adsorption process. Positive value of  $\Delta S$  showed the increasing randomness at the solid–solution interface during the adsorption process [56]. The positive values of  $\Delta H$  suggested the endothermic nature of the adsorption interaction [57].

## 4. Conclusion

The present study focused on biosorption of Cu(II) from aqueous solution using the *T. versicolor* as a low cost biosorbent. The biosorbent was characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and BET Surface area analysis. The biosorption characteristic has been examined with the variations in the parameters of pH, contact time, biomass dosage, initial metal ion concentration and temperature. The experimental data were analyzed using Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin isotherm models. The equilibrium data fitted well with the Langmuir isotherm. The maximum biosorption capacity of *T. versicolor* biomass for Cu(II) was found to be 140.9 mg/g. The kinetic data were analyzed using pseudo-first order, pseudo-second order and intraparticle diffusion

Table 4

Thermodynamic parameters for the biosorption of Cu(II) on the *T. versicolor* biomass at different temperatures.

Metal ion	Temperature (K)	$\Delta G$ (kJ/mol)	$\Delta S$ (kJ/mol K)	$\Delta H$ (kJ/mol)
Cu(II)	303	-3.133		
	313	-4.115	0.092	24.7
	323	-4.977		

models. Among the kinetic models studied, the pseudo-second order equation was the best applicable model to describe the sorption process. Thermodynamic parameters suggested that the biosorption of Cu(II) ions on the *T. versicolor* was feasible, spontaneous and endothermic in nature. Furthermore, based on all results, it can be also concluded that the *T. versicolor* can be evaluated as an alternative adsorbent for the treatment of wastewater containing Cu(II) ions, due to its being a low-cost adsorbent and having a considerable high sorption capacity.

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