Research Article

Effective Biosorption of Nickel(II) from Aqueous Solutions Using *Trichoderma viride*

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The primary objective of the present study is to evaluate the optimization conditions such as kinetic and equilibrium isotherm models involved in the removal of Ni(II) from the aqueous solutions by *Trichoderma viride*. The biosorbent was characterized by FTIR and SEM. The optimum biosorption conditions were determined as a function of pH, biomass dosage, contact time, initial metal ion concentration, and temperature. The maximum Ni(II) biosorption was obtained at pH 4.5. The equilibrium data were better fit by the Langmuir isotherm model than by the Freundlich isotherm. The kinetic studies indicate that the biosorption process of the metal ion Ni(II) has followed well the pseudo-second-order model. The sum of the square errors (SSE) and chi-square (χ^2) tests were also carried out to find the best fit kinetic model and adsorption isotherm. The maximum biosorption capacity (q_m) of *T. viride* biomass was found to be 47.6 mg/g for Ni(II) ion. Therefore, it can be concluded that *T. viride* biomass was effective and low-cost potential adsorbent to remove the toxic metal Ni(II) from aqueous solutions. The recovery process of Ni(II) from *T. viride* biomass was found to be higher than 98% by using 0.25 M HNO₃. Besides the application of removal of toxic metal Ni(II) from aqueous solutions, the biosorbent *T. viride* can be reused for five consecutive sorption-desorption cycles was determined.

1. Introduction

Metal pollution has been a great concern for the past few decades. It is believed that the wide use of man-made chemicals, anthropogenic lifestyle, and rapid industrialization is the major source of metal toxicity [1]. Nickel is well known as a heavy metal pollutant, present in effluents of electroplating industries, smelting, and alloy manufacturing, mining, and refining industries [2]. According to WHO, the permissible limit of Ni(II) in drinking water is 0.5 mg/L [3]. The non-biodegradable and bioaccumulating properties of heavy metals may pose serious threats to living organisms, [4]. It has been reported that both occupational and environmental exposure to trace metals affects almost all compartments of animal systems including human health [1]. In humans and animals, nickel is an essential micronutrient [5] because of its importance in the metabolic pathways. Nickel is one of the cofactors for urease enzyme in plants [6]. Though, it is an essential micronutrient and/or cofactor, nickel is

one of the heavy metal toxicants at higher concentration and is a well-known human carcinogen [7]. Nickel has been implicated as an embryotoxin and teratogen [8]. The higher concentration of Nickel causes dermatitis, nausea, vomiting, behavioral, and respiratory problems in addition to cyanosis, gastrointestinal distress, and weakness [9]. All these biological disorder consequences alarm the need of nickel removal from the environment and to bring up its levels below the threshold limits from its sources. The classical physicochemical methods are commonly used for the removal of nickel from the industrial effluents, namely, evaporative recovery, filtration, ion exchange, and membrane technologies. Though they are promising to some extent, but these processes have high reagent or energy requirements and generate toxic sludge that requires careful disposal [10]. Furthermore, insufficient removal of traces of heavy metal ions, varying performances, and also high operating costs has limited the use of conventional physicochemical methods. Thus, there is a need for alternative methods for better efficacy

with low cost and complete removal of toxic metals from the water bodies.

In recent years, the exploitation of eco-friendly biosorption technology using inactive and dead biomasses to detoxify metal-contaminated effluents in the aquatic environment is gaining importance day by day [11, 12]. Moreover, the biosorbents have high specific metal binding ability in complex media in contrast to carbonaceous sorbents which tend to adsorb metal ions in a nonspecific manner. These advantages make biosorbents an economical alternative to commercial activated carbons in the removal of heavy metal-polluted water bodies [13].

The application of fungal organisms in the field of biosorption technology has become a part of active research by the environmental scientists. Fungal organisms like, *Aspergillus niger* [14], *Streptomyces noursei* [15], *Pseudomonas aeruginosa* [16], and *Rhizopus arrhizus* [17] have been reported for removal of heavy metals, such as Pb, Cd, and, in particular, Ni(II). Among the fungal organisms, the *T. viride* in biosorption process is little exploited [18]. The present study in our laboratory is mainly aimed at knowing the application of *T. viride* for sequestration of Ni(II) from contaminated water systems involving kinetic and equilibrium. The selection of this biosorbent *T. viride* is based on (1) inexpensive, (2) easily available, (3) no toxic effects of its own, and (4) some information suggests that metal-bioaccumulation properties of *T. viride* [19]. Hence, studies on the kinetic and equilibrium isotherm models have been studied, in order to systematically investigate the application of biomass, *T. viride* as biosorbent for the removal of nickel ions from water/industrial waste water. The optimum conditions for biosorption such as pH, initial metal ion concentration, biomass dosage, contact time, and equilibrium isotherm models in relation to the biosorption of Ni(II) onto *T. viride* have been investigated. In addition to this, the Ni(II) ion desorption studies have been performed over five sorption-desorption cycles to evaluate the sorbent *T. viride* for reusage.

2. Experimental

2.1. Collection and Preparation of Biomass (Adsorbent). The fungal biomass was collected from Microbial Type Culture Collection (MTCC), Chandigarh, India. The biomass was prepared in the sabouraud broth (peptone 10.0, dextrose 40.0, streptomycin 0.03, and agar 20.0 g/L) by inoculating the 0.1 mL spore suspension/100 mL of water in the 250 mL flasks and incubated at room temperature for 5–7 days. Samples were washed several times using deionized water to remove adhesive materials such as extraneous salts and then dried in oven at 60°C for 48 h and powdered to uniform size using a mortar.

2.2. Reagents and Equipments. A flame atomic absorption spectrophotometer (Shimadzu AA-6300, Japan) with nickel hollow cathode lamp was used for determination of Ni(II) before and after biosorption. Absorbance was measured at wavelength of 232 nm and spectral bandwidth was 0.2 nm.

FIGURE 1: FTIR spectra of *T. viride* biomass before adsorption (a) and after adsorption of Nickel (b).

Fourier Transform Infrared (FT-IR) spectrometer (Thermo-Nicolet FT-IR, Nicolet IR-200, USA) was used for IR spectral studies of dried biomass and Ni(II)-sorbed biomass in the range of 4000–400 cm^{-1} and Scanning Electron Microscopy (SEM, Model Evo15, Carl Zeiss, England) has been used to study the surface morphology of the biosorbent.

3. Results and Discussion

3.1. Characterization of Biomass. The FTIR spectra of free biomass and nickel sorbed biomass samples were showed in Figure 1. The spectra of free biomass (Figure 1(a)) has shown a broad and strong peak at 3354 cm^{-1} , which may be due to the overlapping of O–H and N–H stretching vibrations. The peak at 2924 cm^{-1} can be assigned to the –CH groups of an unloaded biomass sample. The peaks at 1642 and 1653 cm^{-1} may be attributed to asymmetric and symmetric stretching vibration of C=O groups, respectively. The spectrum of nickel sorbed biomass (Figure 1(b)) has revealed that the bands that have been observed at 3332, 1436, 1202, and 1079 cm^{-1} for free biomass are shifted to 3354, 1449, 1244, and 1028 cm^{-1} . The significant changes in the wave numbers of these specific peaks have suggested that amine, hydroxyl, C=O, and alcoholic C–O groups of biomass could be involved in the biosorption of nickel ion onto *T. viride*.

Figure 2 shows the morphology of *T. viride* before and after biosorption of Ni(II). Before Ni(II) biosorption on *T. viride* shows adhesive and small particles (Figure 2(a)). It has been shown that the morphology changed to a corn flake-like structure after Ni(II) biosorption onto *T. viride* biomass

(a)

(b)

FIGURE 2: SEM micrographs of *T. viride* biomass surface, (a) before adsorption of Ni(II) ions and (b) after adsorption of Ni(II) ions.

(Figure 2(b)). It can be seen that the surface modifications occurred by reducing the irregularity, after binding of Ni(II) ions onto the surface *T. viride* biomass.

3.2. Effect of PH. Biosorption of Ni(II) onto biomass of *T. viride* as a function of initial pH has been shown in Figure 3. It has been observed that the biosorption capacity is increased from pH 2.0 to 4.5. Beyond pH 4.5, the biosorption has gradually decreased. At lower pH, the cell wall of *T. viride* becomes positively charged due to the increase in hydrogen ion concentration which is responsible for reduction in biosorption of Ni(II) ions on adsorption sites. In contrast, at higher pH (>4.5), the cell wall surface becomes more negatively charged when compared to surface negative charges at lower pH. At pH greater than 4.5, nickel ions start binding with OH⁻ forming the insoluble nickel hydroxides that resulted in the reduction of biosorption.

3.3. Effect of Biosorbent Dose on Biosorption. The biosorbent dosage is an important parameter which determines the

FIGURE 3: Effect of pH on the biosorption of Ni(II) onto *T. viride* biomass.

FIGURE 4: Effect of biosorbent dosage level on the biosorption of Ni(II) *T. viride* biomass.

capacity of a biosorbent for a given initial concentration. The biosorption of Ni(II) ion as a function of the biosorbent dosage of 0.1 g to 0.7 g has been investigated and the results are shown in Figure 4. The percentage of biosorption has increased with the increase of biosorbent dose up to 0.5 g/0.1 L. At the initial concentration of 100 mg/L of Ni(II), the maximum percentage removal was 92.3% and remained constant at >0.5 g/0.1 L. Therefore, the optimum biosorbent dosage was taken as 0.5 g for further experiments to determine the effect of contact time, biosorption kinetics, and biosorption isotherm models.

3.4. Effect of Contact Time. The biosorption capacity of *T. viride* towards Ni(II) was investigated at different initial concentrations and fixed amount of fungi at different time intervals. The efficacy of biosorption increases with agitation time and reached equilibrium about 180 min for all the experimental concentrations performed. The rate of the uptake of metal ions was rapid in the early stages as expected, then the equilibrium was attained due to continuous formation of the

TABLE 1: Kinetic parameters for biosorption of Ni(II) by *T. viride* biomass.

Metal ion	Lagergren first order			Pseudo second order			Weber and Morris		
	K_1 (min^{-1})	R^2	SSE	K_2 ($\text{g}/(\text{mg min})$)	R^2	SSE	K_{id} ($\text{mg/g min}^{-0.5}$)	R^2	SSE
Ni(II)	0.0165	0.9982	0.995	0.0004	0.999	0.011	2.328	0.9498	0.922
	0.0158	0.9856	0.998	0.0004	0.997	0.003	2.934	0.9877	0.943
	0.0127	0.9921	0.999	0.0004	0.997	0.004	3.809	0.9869	0.951
	0.0134	0.9968	0.999	0.0004	0.999	0.003	4.559	0.9713	0.934

biosorption layer until saturation. The data obtained from the experiment has been further used to evaluate the kinetic parameters of the biosorption process.

3.5. Biosorption Kinetics. The mechanism of biosorption depends on the physical and chemical characteristics of the adsorbents as well as on the mass transfer process [20]. The results of rate kinetics of Ni(II) biosorption onto *T. viride* biomass are analyzed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The conformity between experimental data and the model predicted values was expressed by correlation coefficients (R^2).

The linear pseudo-first-order model [21] can be represented by the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}, \quad (1)$$

where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbed metal on the sorbent at the equilibrium time and at any time t , respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). The experimental data was fitted to (1) and various parameters obtained for biosorption of Ni(II) onto *T. viride* with different initial concentrations together with correlation coefficients are given in Table 1. The correlation coefficients for the pseudo-first-order equation obtained at all the studied concentrations were low. This suggests that this biosorption system does not follow the first-order reaction.

The kinetics of biosorption process may also be described by pseudo-second-order rate equation [22]. The linearized form of equation was given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (2)$$

where k_2 ($\text{g}/(\text{mg min})$) is the equilibrium rate constant of pseudo-second-order biosorption. The pseudo-second-order equation parameters obtained for biosorption of Ni(II) onto *T. viride* with different initial concentrations together with correlation coefficients are given in Table 1.

The biosorption results were analyzed using intraparticle diffusion model [23]. This is represented as

$$q_t = k_{id} t^{0.5} + c, \quad (3)$$

where q_t (mg/L) is the amount adsorbed at time t (min) and k_{id} ($\text{mg/g min}^{-0.5}$) is the rate constant of intraparticle diffusion. C is the value of intercept which gives an idea about the boundary layer thickness, that is, the larger intercept,

FIGURE 5: Weber and Morris plots for the biosorption of Ni(II) *T. viride* biomass.

the greater is the boundary effect. The Weber Morris plot for biosorption of Ni(II) is given in Figure 5. Based on the results, it can be concluded that both film diffusion and intraparticle diffusion are simultaneously operating during the biosorption of Ni(II) onto *T. viride* biomass.

3.6. Fitness of the Biosorption Kinetic Models. The values of rate constants and correlation coefficients for each model were shown in Table 1. The best fit among the kinetic models is assessed by the squared sum of error (SSE) values. It is assumed that the model which gives the lower SSE values is the best model for metal ion sorption on *T. viride*. The SSE values are calculated by the following equation:

$$\text{SSE} = \sum \left(\frac{(q_{t,e} - q_{t,m})^2}{q^2} \right), \quad (4)$$

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. SSE values for all the kinetic models are calculated and summarized in Table 1. The lower SSE values of pseudo-second-order model indicate that the biosorption of Ni(II) on the *T. viride* biosorbent follows the pseudo-second-order kinetic model.

3.7. Biosorption Isotherms Models. The equilibrium adsorption isotherm is of importance in the design of adsorption

systems [24]. The adsorption isotherms for Ni(II) adsorption onto *T. viride* biomass at the temperature of 20, 30, and 40°C are shown in Figures 6(a) and 6(b). The Langmuir treatment is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and there is no transmigration of adsorbate in the plane of the surface [25]. It is represented by

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}, \quad (5)$$

where q_e is the equilibrium metal ion concentration on the sorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer sorption capacity of the sorbent (mg/g), and K_L is the Langmuir sorption constant (L/mg) related to the free energy of sorption. Figure 6(a) shows the Langmuir plots at different temperatures and the constants q_m and K_L are tabulated in Table 2. On the other hand, Table 3 presents the comparison of biosorption capacity (mg/g) of *T. viride* for Ni(II) ions with that of various biosorbents reported in the literature [26–28].

The general form of Freundlich is given as follows:

$$q_e = k_f C_e^{1/n}, \quad (6)$$

where K_f is a constant related to the biosorption capacity and $1/n$ is an empirical parameter related to the biosorption intensity, which varies with the heterogeneity of the material. Figure 6(b) shows the Freundlich plots at different temperatures and the constant K_f and $1/n$ are tabulated in Table 2. The best fit biosorption isotherm model is confirmed by the correlation coefficients (R^2) and the chi-square (χ^2) tests. The equation for evaluating the best fit model is to be written as

$$\chi^2 = \sum \left(\frac{(q_e - q_{e,m})^2}{q_{e,m}} \right), \quad (7)$$

where q_e is the experimental data of the equilibrium capacity (mg/g) and $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g). χ^2 will be a small number if the data from the model are similar to the experimental data, while χ^2 will be a bigger number if they differ. Thus, it is also necessary to analyse the data set using the nonlinear χ^2 test to confirm the best-fit isotherm for the biosorption process and the χ^2 values are given in Table 2. The χ^2 values of both isotherms are comparable and hence the adsorption of metal ions follows both Freundlich and Langmuir isotherms and better fit to Langmuir as its χ^2 value is less than that of the Freundlich model.

3.8. Desorption Experiment. In addition to biosorption studies, desorption processes have equal importance due to the reuse of biomass material. Desorption mainly depends upon (a) type of eluents and (b) biomass material used. In the present study, HNO_3 solution was used as the eluent to remove Ni(II) from *T. viride*. Different concentrations

FIGURE 6: (a) Langmuir isotherm plots for the biosorption of Ni(II) *T. viride* biomass at different temperatures. (b) Freundlich isotherm plots for the biosorption of Ni(II) *T. viride* biomass at different temperatures.

(0.01–0.4 M) were used to desorb the Ni(II)-*T. viride* complex. The results of the present study indicate that the addition of acid at lower concentration 0.01 M HNO_3 desorbs the nickel from the complex and >55% adsorption was observed at 0.05 M HNO_3 . The maximum desorption (>98%) of nickel from the complex occurs at >0.25 M HNO_3 .

3.9. Recovery of Ni(II) by Adsorption-Desorption Cycle. In order to evaluate the reutilization of the *T. viride*, the biosorption-desorption cycles are repeated five times by treating the used biosorbent with 0.25 M HNO_3 . The desorption efficiency of 99.77% of Ni(II) was obtained by using 0.25 M HNO_3 in the first cycle and is, therefore, suitable for regeneration of biosorbent. There was a gradual decrease of

TABLE 2: Langmuir and Freundlich isotherm parameters for the biosorption of Ni(II) on *T. viride* biomass at different temperatures.

Metal ion	Temperatures (K)	Langmuir				Freundlich			
		$q_{\max}$ (mg/g)	K_L (L/mg)	R^2	χ^2	K_f (mg/g)	n	R^2	χ^2
Ni(II)	293	26.3	2.57	0.999	11.25	4.538	1.174	0.993	51.2
	303	37.0	3.15	0.999	17.28	3.566	1.1047	0.999	62.1
	313	47.6	3.68	0.999	21.67	2.875	1.076	0.999	69.9

TABLE 3: A comparison of biosorption capacity (mg/g) of different biomasses for Ni(II) removal.

Biomass	q_m (mg/g)	References
<i>Rhizopus nigricans</i>	5	[26]
<i>Streptomyces noursei</i>	0.8	[26]
Waste pomace of olive factory	14.80	[27]
PAC (Powdered activated carbon)	31.08	[28]
<i>T. viride</i>	47.6	(Present study)

Ni(II) biosorption on *T. viride* with an increase the number of desorption cycles. After a sequence of five cycles, it was observed that the Ni(II) uptake capacity of the *T. viride* has been reduced from 98.15% to 95.13%. The desorption efficiency more than 98% recovery of Ni(II) was observed in each cycle of all the five consecutive desorption cycles. The results indicate that the *T. viride* can be used repeatedly in the adsorption-desorption cycles.

4. Conclusion

This study is focused on the biosorption of Ni(II) ion onto *T. viride* biomass from aqueous solution. The operating parameters, pH of solution, biomass dosage, contact time, initial metal ion concentration, and temperature are effective on the biosorption efficiency of Ni(II). The biosorption capacity of *T. viride* biomass has been found to be 47.6 mg/g for Ni(II). Langmuir model has fitted the equilibrium data better than the Freundlich isotherm. The kinetic data has illustrated that pseudo-second-order model is more suitable than a pseudo-first-order model based on the lower SSE and correlation coefficients that are greater than 0.99. *T. viride* can be used for 5 cycles by regenerating with 0.25 M HNO_3 . Further, it can be evaluated as an alternative biosorbent to treat wastewater containing Ni(II) ion over the classical physicochemical methods. Hence, *T. viride* can be used as an effective, low-cost biosorbent for potential removal of heavy toxic metal Ni(II) from aqueous media. The significant advantage of *T. viride* is reusage of it when compared to other methods using different types of fungi for removal of Ni(II) from water media.

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