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Biosorption of cadmium from aqueous solutions by *Trichoderma* fungus: kinetic, thermodynamic, and equilibrium study

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ABSTRACT

Among toxic heavy metals, cadmium is one of the most dangerous for human health. Since cadmium is a well-known toxic metal, industrial effluents and wastewaters rich in cadmium must be treated prior to their disposal. Present study deals with the evaluation of biosorptive removal of cadmium by *Trichoderma* fungus. The effect of different important parameters such as initial pH, cadmium concentration, contact time, stirring rate, and temperature on cadmium sorption was investigated. Cadmium biosorption capacity and its removal efficiency increased along with the increase of pH of the solution, and maximum biosorption of cadmium(II) ions were observed at pH 6. Biosorption kinetics data were fitted using pseudo-first-order and pseudo-second-order models. It was found that the kinetics data fitted well the pseudo-first-order during the initial 120 min of biosorption, and when the biosorption time was 120 min, the experimental data fitted very well with the pseudo-second-order kinetics reaction. Thermodynamic parameters such as standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) were evaluated. The results confirmed that biosorption of cadmium(II) ions by *Trichoderma* fungus was spontaneous and endothermic nature.

Keywords: Biosorption; Cadmium; *Trichoderma* fungus; Isotherm; Kinetics

1. Introduction

The discharge of industrial effluents containing various heavy metals including cadmium(Cd), mercury, lead, chromium, copper, and manganese poses threat to the receiving freshwater resources due to their toxicity and cause several health problems with animals, plants, and human beings [1]. Among toxic heavy metals, cadmium is one of the most deleterious for human health. It is a highly toxic element and has been accepted as a category-1 (human) carcinogen by the International Agency for Research on Cancer [2]. Significant concentration of cadmium is present in different industrial effluents. These include effluents from cadmium electroplating, paint pigments, fertilizer industries, ceramic industries, battery manufacturing, alloy manufacturing, accumulator manufacturing, plastics manufacturing, smelting processes, mining processes, mineral processing, refining processes, and alloy industries [2–4].

The environmental cadmium pollution occurs due to its continuous release from the industrial and

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agricultural sources. It can easily translocate from plant roots to above-ground tissues and interferes with physiological processes [5,6]. Additionally, it can enter the human body by eating food, drinking water, breathing, or smoking. Most of the cadmium that enters the body goes to kidney and liver and can remain there for many years and can cause serious damage to kidney and bones (renal dysfunction, liver damage, bone degradation, and hypertension) [7–9]. The World Health Organization (WHO) has set a maximum guideline concentration of 0.003 mg/L for cadmium in drinking water [10].

Several physicochemical processes are available for the removal of cadmium from aqueous environments. These include the following: chemical precipitation, coagulation, filtration, solvent extraction, evaporation, reverse osmosis, chemical oxidation/reduction, electrochemical treatment, ion exchange, and membrane processes [11–13]. However, many of these approaches can be less cost-effective or difficult for practical use. Furthermore, most of these are either ineffective or excessively expensive when the metal concentrations are less than 100 mg/L [14]. In addition, these high technological processes have some significant disadvantages including incomplete metal ion removal, the requirement for expensive equipment and monitoring systems, high use of reagents, and large amount of sludge produced during the treatment and pretreated or other waste products that require disposal [15].

Biosorption is an alternative and innovative treatment technique utilizing biological materials such as bacteria, yeast, fungus, and algae [16,17]. This process involves a combination of active and passive transport mechanisms. The first phase, usually referred to as passive uptake, is an initial rapid and reversible accumulation step. The second phase, usually referred to as active uptake, is slower intracellular bioaccumulation, often irreversible and related to metabolic activity [18–20]. The major advantages of biosorption process include low operating cost, high efficiency, reusability of biosorbent, possibility of metal recovery, selectivity for specific metal ions, high efficiency in detoxifying very dilute liquid streams, reduction in the amount of chemicals, and no secondary sludge which might be toxic [21,22].

Cadmium biosorption by different living and non-living biomasses have been studied by several authors [23–26]. In this work, *Trichoderma* species that are non-parasitic and also non-pathogen fungi that are useful fungi for agriculture and recycling of biomass in nature were used for cadmium biosorption.

2. Materials and methods

2.1. Chemicals and analytical measurements

In this research work, the chemicals used were of analytical grade. Culture media were of biological grade. Stock solutions of cadmium was prepared by dissolving 2.744 g of $Cd(NO_3)_2 \cdot 4H_2O$ (Merck–Germany) in 1 L deionized water. The stock solutions were used to prepare dilute solutions of different working concentrations.

2.2. Preparation of fungal media as biosorbent

Trichoderma fungal species was obtained from the Laboratory of Mycology, Faculty of Medicine, Zahedan University of Medical Sciences. The samples were transferred to PDA (Potato Dextrose Agar) sterile media for *in vitro* testing consumption. When the fungal biomass was reached to maximal growth (after 3–4 d at 24℃), the samples were kept in the refrigerator at 4℃ until required. Generated colonies are appropriate for transferring to the new media and were used in our experiments as resource [27].

After fungal proper growth on the solid media, liquid media were prepared with the formula containing the amount of 250 g/L potato extract, 20 g/L of dextrose, and 0.25 g/L of tetracycline antibiotic (to prevent bacteria growth) in seven pH (2–8). Lactic acid and KOH (3%) were used for adjustment of the pH in the prepared media [28]. Finally before batch biosorption experiments to be started, liquid media were kept at an incubator equipped shaker for 24 h for fungal suitable growth before exposure with metallic ions (Cd(II)).

2.3. Analytical technique

At different interval time, samples were withdrawn and filtered, and the concentrations of cadmium ions were determined by the flame atomic absorption spectrometry using Atomic Absorption Spectrophotometer (Model Shimadzu AA 6650).

2.4. Batch biosorption experiments

The biosorption of cadmium(II) ions on the *Trichoderma* from aqueous solution was investigated in batch biosorption equilibrium experiments. The effect of solution pH, initial cadmium(II) ions concentration, contact time, mixing rate, and temperature on the biosorption capacity of cadmium(II) onto *Trichoderma* fungus was studied. In each experiment, one the above-mentioned factors were chosen as variable and the others were kept as constant.

The effect of initial pH of solution in the biosorption studies was studied at cadmium concentration of 25 mg/L. The pH of solutions was varied between 2 and 8 (which was adjusted at the beginning of the experiment and not controlled throughout the experiments). Biosorption data were obtained in a set of Erlenmeyer flasks (250 mL) at constant temperature (25˚C) and mixing rate 150 rpm for reaction time 180 min, where working solutions with different initial pH (100 mL) were placed in these flasks. The pH values in the solutions were monitored by a Hanna pH meter (Romania).

The effect of initial cadmium(II) concentration in the biosorption studies was studied at pH 6 (which was adjusted at the beginning of the experiment and not controlled throughout the experiments). The concentration of cadmium(II) ions was varied between 25 and 150 mg/L, and similar procedures were repeated. The effect of contact time and mixing rate was varied between 30 and 240 min and 150 and 350 rpm, respectively. Finally, the effect of temperature (298, 303, 308, and 313 K) on cadmium biosorption was studied at optimum attained conditions, and thermodynamic parameters were determined.

To obtain the dry weight of the fungal biomass, it was placed in a glass dish and was hold in the desiccator at 105˚C for 48 h. The amount of cadmium(II) ions bound by the biosorbent was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where q_e is mg of metal ion biosorbed per g of biomass (mg/g), C_0 (mg/L) is the initial concentration, C_e (mg/L) is the final or equilibrium concentration, V (L) the volume of metal solution in the flask, and M (g) is the weight of biosorbent (fungal dry mass). Furthermore, to express the cadmium removal efficiency by studied fungi, the following equation was used:

$$E(\%) = \frac{(C_0 - C_f)}{C_0} \times 100 \tag{2}$$

In this equilibrium, E is the percentage of cadmium removal by the fungal biomass and C_0 and C_f represent the initial and final (after adsorption) cadmium concentrations, respectively. Each of the experiment was repeated three times (yielding an experimental error of less than 5%), and the average values were obtained.

2.5. Isotherm study

During the biosorption, a rapid equilibrium is established between metal ions on biosorbent (q_e) and metal ions remaining in solution (C_e). This equilibrium can be described by the Langmuir or Freundlich adsorption isotherms. The Langmuir equation assumes that (i) the solid surface presents a finite number of identical sites which are energetically uniform; (ii) there is no interaction between adsorbed species, meaning that the amount adsorbed has no influence on the rate of adsorption; and (iii) a monolayer is formed when the solid surface reaches saturation [9]. The isotherm equation assumes the following form:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where q_e is the amount of metal ions adsorbed per specific amount of biosorbent (mg/g), C_e is equilibrium concentration of cadmium ions (mg/L), K_L is Langmuir constant, and q_m is the maximum amount of cadmium ions required to form a monolayer (mg/g).

The empirical Freundlich equation based on sorption on a heterogeneous surface is given as:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{4}$$

These models can provide information of metal uptake capacity and difference in metal uptake among various species [23,29–33]. Biosorption isotherm experiments were studied as mentioned above with different concentrations of cadmium (25–150 mg/L) at pH 6.0 and at different temperatures (298–313 K).

3. Results and discussion

3.1. Influence of initial pH on cadmium removal

Concentration of hydrogen ion in the biosorption process is considered as one of the most critical factors that influence the biosorption behavior of metal ions in aqueous environments. In fact, heavy metals biosorption is significantly dependent on pH. It affects the solubility of the metal ions in the solution, replaces some of the positive ions found in the active sites, and affects the degree of ionization of the adsorbate during the reaction [27,34,35]. Hence, heavy metals biosorption is considerably dependent on pH. In this study, the effect of initial pH on the biosorption of cadmium ions onto *Trichoderma* fungus was evaluated within the pH range of 2–8. In this work, studies beyond pH 8 were not attempted because precipitation of the ions as hydroxides would be likely [36].

As presented in Fig. 1, cadmium biosorption capacity and its removal efficiency strongly depend on the initial pH and increased along with the increase of pH of the adsorbate solution, and maximum biosorption of cadmium(II) ions were observed at pH 6. The lowest removal efficiency and biosorption capacity (4.32% and 1.35 mg/g) were calculated at pH 2. The optimal removing was obtained 69.28% (21.65 mg/g based on fungus dry weight) at pH 6.

Similar findings about the pH effect had also been reported when other kinds of biomass were employed as biosorbents. For example, Zhou et al. reported optimum pH of 6 for *Wangia profunda* [37], Amini et al. reported optimum pH of 5.96 for *Aspergillus niger* [38], Arica et al. reported an optimum pH of 5.5 for Trametes versicolor [39]. Say et al. reported an optimum pH 6 for biosorption of cadmium, lead, and copper with the filamentous fungus *Phanerochaete chrysosporium* [40]. Chang et al. reported an optimum pH 6 for *Pseudomonas aersuginosa* PU21 [41]. Also, Mashitah and Yus Azila [35] reported the maximum biosorption of cadmium(II) ions at pH 6 by immobilized cells of *Pycnoporus sanguineus*.

Furthermore, comparable results have been observed using other biosorbents including black gram husk (*Cicer arientinum*) [42], fungus *A. niger* [43], and by-products of *Lentinus edodes* [44]. Generally, pH 3–6 has been found favorable for the biosorption of metal ions by microbial biomass [45].

The biosorption capacities of various biosorbents depend on the available binding sites provided by the functional groups existing in the surface of the biosorbents. Negatively charged groups at the biosorbents surface are necessary for the sorption process [42]. At low pH value, the biosorption capacity is less because large quantity of hydrogen ions competes with metal ions binding at sorption site (mostly due to competition between Cd^{2+} and H_3O^+ ions in the solution). Akhtar et al. [46] also demonstrated that carboxylic groups that are components of the cell wall of *A. niger* are sites for metal ions absorption and that in the very acidic pH values, the total surface charge of the cell is positive and consequently metal cations and protons are competing for the sites in on the cell wall and tend to reduce metal uptake. When the pH values increased in the solution, the deprotonation of acid functional groups, such as carboxyl, phosphonate, and phosphodiester, was strengthened and the attraction increased between negative charge on biomass and positive metal cations [44]. Decrease in biosorption at higher pH ($pH > 6.0$) is because of the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites; as a consequence, the retention would decrease again [47].

3.2. *Influence of initial cadmium concentration*

The equilibrium cadmium biosorption capacity of *Trichoderma* fungus at various initial concentrations of cadmium is depicted in Fig. 2. Cadmium sorption was studied in batch experiments (pH 6.0) using different initial cadmium concentrations of 25, 50, 75, 100, and 150 mg/L. As shown in Fig. 2, when the initial Cd(II) concentration is increased, the amounts of adsorbed metal also increased, so the removal of Cd(II) ions depends on the concentration of the cadmium. For example, when the initial concentration of Cd(II) increases from 25 to 150 mg/L (at contact time 120 min), the equilibrium biosorption capacity of *Trichoderma* fungus increased from 21.34 (68.3%) to 149.08 mg/g (79.51%).

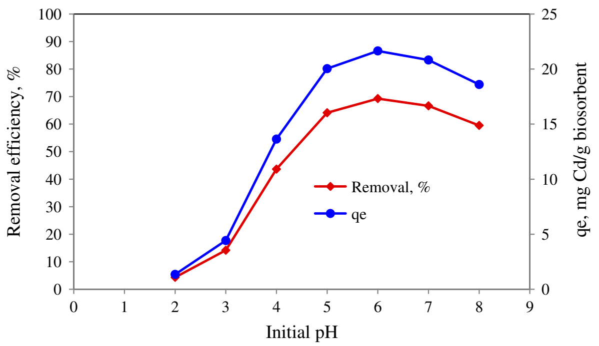

Fig. 1. Effect of initial pH on the removal efficiency of Cd(II) (initial Cd(II) concentration = 25 mg/L, mixing rate = 150 rpm, contact time = 120 min, *T* = 298 K).

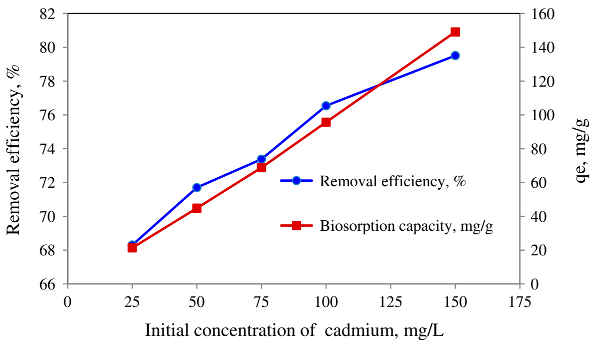

Fig. 2. Effect of initial concentration of cadmium on cadmium biosorption by *Trichoderma* fungus (optimal pH 6, mixing rate = 150 rpm, *T* = 298 K).

The initial concentration of the Cd(II) ions in the solution remarkably influenced the equilibrium uptake of Cd(II). It was noted that initial concentration increased the sorption of Cd(II) as is generally expected due to equilibrium process (Fig. 2). This increase in uptake capacity of the studied biosorbent with the increase in initial metal concentrations is probably due to higher availability of metal ions (Cd(II)), for the sorption. Moreover, higher initial concentration provides increased driving force to overcome all mass-transfer resistance of metal ions between the aqueous and solid phase resulting in higher probability of collision between metal ions and sorbents. This also results in higher metal uptake [48]. Similar findings have been reported by Das and Guha [49], for chromium (III) removal by biomass of *Termitomyces clypeatus,* and Rathinam et al. [50,51].

Some researchers [27,52] studied Cd biosorption by microorganism Actinomycete R 27, and approximately 69% biosorption was attained. Jianlong et al. [28] also reported 100% adsorption of lead by the fungus *A. niger* at the concentration of 10 ppm. Their results indicated the high absorption of heavy metal ions by the organism, at low concentrations. Therefore, the limitation of metal ions uptake at low concentrations is less than at high concentrations. Considering the high pollution of sewage of the factories and high concentrations of water soluble metals, using the biomass of microorganisms, especially the fungal biomass, can be very useful for bioremediation of heavy metals [53,54].

3.3. *Effect of the mixing rate on Cd(II) biosorption*

Theoretically, the mixing rate can influence the adsorption through improving the contact between the biosorbent and the pollutants in the aqueous environments and reducing the mass-transfer limitation of pollutants adhering onto the surface of the biosorbent. In this study, the effect of the mixing rate was investigated by varying the agitation rate between 150 and 350 rpm, using an initial pH of 6, initial concentration of Cd(II) 50 mg/L, and a contact time of 120 min.

It is evident from Fig. 3 that the rate of adsorption increases as the agitator speed increases. In fact, the removal efficiency and biosorption capacity of the Cd(II) ions increased from 70.74% and 44.21 mg/g to approximately 77.94% and 48.71 mg/g, respectively, when the mixing rate was increased from 150 to 250 rpm, and then, it increased slowly and attained or almost attained a plateau value at 300 rpm (78.12%) and higher (78.48% at 350 rpm). This effect can be attributed to the increased turbulence, and as a consequence, the decrease in boundary layer thickness around the adsorbent particles occured as a result of increasing the degree of mixing. Similar findings were reported by Al-Qodah et al. [55] and Pitakpoolsil and Hunsom [56].

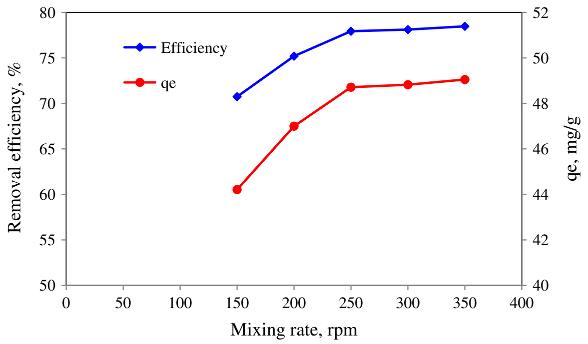

Fig. 3. Effect of mixing rate on the biosorption rate of Cd (II) ions onto *Trichoderma* fungus at 298 K (optimal pH 6, contact time = 120 min, initial Cd(II) concentration = 50 mg/L).

3.4. *Effect of temperature on cadmium biosorption*

Effect of temperature on the equilibrium sorption capacity of *Trichoderma* fungus for Cd(II) ions has been investigated in the temperature range of 298–313 K at different initial cadmium concentrations (25–150 mg/L) and optimum pH of 6.0 at contact time 120 min. As presented in Fig. 4, biosorption of cadmium increased from 68.3–79.5% to 75.5–80.5% with increase in temperature from 298 to 308 K for different initial cadmium concentrations (25–150 mg/L). Nevertheless, more increase of temperature reduced the cadmium removal efficiency, so removal efficiency at 313 K reached to 75.3–78.6%.

For biosorption processes, significant variations of the effect of temperature have been reported in the literatures, even conflicting results at times. For example, Aderhold et al. [57] reported that temperature

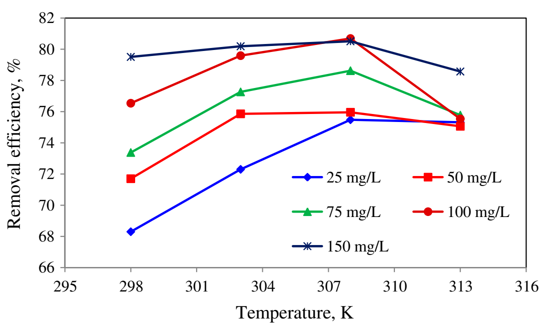

Fig. 4. Effect of temperature on Cd(II) ions biosorption onto *Trichoderma* fungus.

fluctuations between 283 and 308 K did not affect biosorption cadmium by seaweed, Ecklonia maxima. On the other hand, Dang et al. [58] reported that Cd (II) biosorption by wheat straw enhances with increasing temperature from 298 to 303 K. On the contrary, Cruz et al. [9] reported that increasing temperature in the range of 308–328 K decreases the capacity of cadmium sorption by *Sargassum* sp. biomass. The conflicting observations of the effect of temperature on biosorption among various studies might be due to various types of biosorbent used.

In order to determine the thermodynamic parameters, experiments were carried out at different temperature 298–313 K for Cd(II) biosorption. The free energy change (ΔG°) of the sorption reaction is given as:

$$\Delta G^\circ = -RT \ln K_a \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

where R is universal gas constant (8.314 J/mol/K) and T is the absolute temperature in K. The thermodynamic parameter, Gibb's free energy change, ΔG°, is calculated using K_a obtained from Freundlich Eq. (4) and shown in Table 3. The values of enthalpy (ΔH°) and entropy change (ΔS°) can be obtained from the slope of the plot of ΔG° vs. T.

A plot of Gibb's free energy change, ΔG°, against temperature, T, was found to be linear (Fig. 5). The enthalpy change, ΔH°, and the entropy change, ΔS°, for the biosorption process were obtained from the intercept and slope of Eq. (6) and found to be 55.29 kJ/mol and 0.187 kJ/mol/K, respectively. The negative values of ΔG° confirm the feasibility of the process and also the spontaneous nature of biosorption with a high preference of Cd(II) ions by *Trichoderma* fungus. Additionally, the decrease in the negative value of ΔG° with an increase in temperature indicates that the adsorption process of Cd(II) ions on *Trichoderma* fungus becomes more favorable at higher temperatures [59].

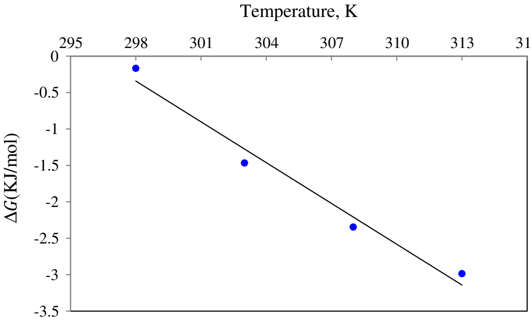

Fig. 5. Plot of Gibbs free energy change, ΔG°, vs. temperature, T.

Furthermore, adsorption process can be classified as physical adsorption and chemisorption by the magnitude of the enthalpy change. It is accepted that if magnitude of enthalpy change is less 84 kJ/mol, adsorption is physical. However, chemisorption takes place in the range from 84 to 420 kJ/mol [60]. From these results (Table 1), it is clear that physisorption is much more favorable for the biosorption of cadmium ions.

Also, the positive value of ΔH° indicates that the adsorption reaction is endothermic. Entropy has been defined as the degree of chaos of a system. The positive value of ΔS° suggests that some structural changes occur on the adsorbent and that the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process [61].

3.5. Biosorption kinetics

Biosorption rate gives important information for designing batch biosorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig. 6 shows the plot of cadmium biosorption vs. contact time. As presented in Fig. 6, the removal rate of cadmium was fast during the initial stages of the adsorption processes, especially for an initial cadmium concentration of 100 and 150 mg/L. However, the adsorption equilibrium was reached at 120 min for all the five concentrations tested.

In the initial stages, the removal efficiency of Cd (II) at all concentrations increased rapidly due to the abundant availability of active binding sites on the biomass, and with gradual occupancy of these sites, the sorption became less efficient in the later stages [62]. In fact, the biosorption kinetics of heavy metal ions consisted of two phases: an initial rapid phase where the biosorption was rapid and contributed significantly to the equilibrium biosorption, and a slower second phase whose contribution to the total metal biosorption was relatively small. The first phase of biosorption kinetics lasted for almost an hour. The trend of Cd(II) biosorption was typical of metal binding to biomass by means of physicochemical interactions. Such particular behavior could have been due to the non-homogeneity of the biomass surface which possesses functional groups differing in dissociability and in cadmium adsorption rates [63].

Table 1
Thermodynamics parameters for Cd(II) ions biosorption on *Trichoderma* fungus

Temperature (°K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol/K)
298	−0.167629173	55.29	0.187
303	−1.466683821		
308	−2.346356673		
313	−2.98586475		

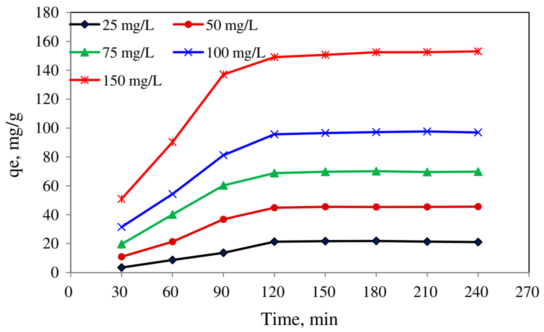

Fig. 6. Effect of contact time on Cd(II) biosorption using biosorbent *Trichoderma* fungus at different initial concentrations at 298 K (optimal pH 6, mixing rate = 150 rpm).

Adsorption kinetics is important in characterizing the efficiency of a sorbent for use in the adsorption process. Several kinetic models are available to understand the behavior of biosorbent and also to examine the rate-controlling mechanism of adsorption process. In this study, two chemical kinetic models were used to determine the respective biosorption rate of Cd(II) ions by Trichoderma. The first kinetic model evaluated was the pseudo-first-order Lagergren's equation [64], shown in Eq. (7):

$$\log\,(q_e - q_t) = \log q_e - K_1 t/2.303 \tag{7}$$

Thus, a plot of log $(q_e - q_t)$ vs. t provides the kinetic parameters k_1 and log q_e from the slope and intercept, respectively.

The second-order kinetic model [65] is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where k_2 is the pseudo-second-order rate constant (g/mg/min), q_e the quantity of metal ions sorbed at equilibrium (mg/g), q_t the quantity of metal ions sorbed at time t (mg/g), and t is the time (min).

If second-order kinetics is applicable, a plot of t/q_t vs. t should show a linear correlation and the rate constant of the second-order adsorption k_2 and q_e can be calculated from the slope and intercept of this plot, respectively. This model is more likely to predict the behavior over the whole range of adsorption and is in agreement with chemical sorption being the rate-controlling step [66]. The rate constants and the correlation coefficient are also summarized in Table 2. Fig. 7 shows the plot of log $(q_e - q_t)$ vs. time for the experimental data obtained under the optimized conditions (pH 6 and mixing rate 150 rpm). It can be seen that a linear relationship of log $(q_e - q_t)$ against time was observed during the initial 120 min of biosorption and then deviates from linearity from 120 min onwards. Therefore, the attachment of Cd(II)

Table 2
Kinetic parameters for the biosorption of Cd(II) ions by *Trichoderma* fungus for different initial concentrations of Cd(II) at pH 6

	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
Cd(II) concentration (mg/L)	K_1	q_e (mg/g)	R^2	K_2	q_e (mg/g)	R^2
25	0.0067	20.04	0.7575	5.9618	0.0154	0.3524
50	0.0108	42.10	0.6309	1.7798	0.0126	0.8075
75	0.0107	50.89	0.5611	0.8597	0.00978	0.9035
100	0.0099	76.28	0.7194	0.5689	0.0073	0.9414
150	0.0114	170.26	0.8959	0.3273	0.0048	0.9476

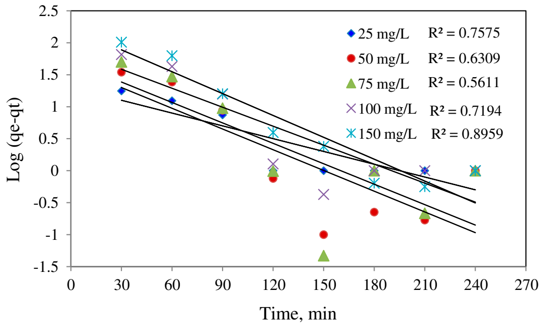

Fig. 7. Pseudo-first-order reaction of the biosorption of the Cd(II) by *Trichoderma* fungus at the optimized conditions (pH 6, mixing rate = 150 rpm).

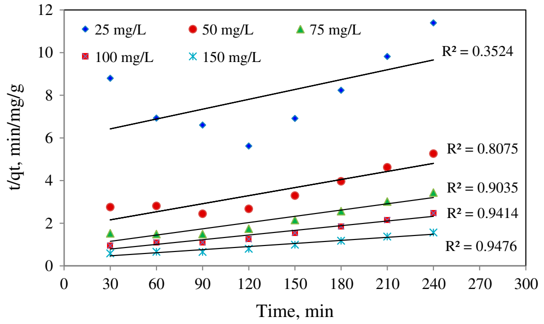

Fig. 8. Pseudo-second-order reaction of the biosorption of the Cd(II) by *Trichoderma* fungus at the optimized conditions (pH 6, mixing rate = 150 rpm).

ions to the biosorbent surface controlled the initial adsorption of pollutants. However, when the biosorption time was 120 min, the experimental data fitted very well with the pseudo-second-order kinetics reaction (Fig. 8). Similar kinetic results were reported in the treatment of biodiesel wastewater by adsorption with commercial chitosan flakes [56].

3.6. Equilibrium adsorption isotherm

An important physiochemical aspect in terms of the evaluation of sorption processes is the sorption equilibrium. In fact, the isotherm provides a relationship between the concentration of pollutant in solution and the amount of pollutant adsorbed on the solid phase when both phases are in equilibrium. Many sorption isotherm models are usually used to fit the adsorption data in order to obtain a linear regression data to predict the maximum adsorption capacity of the adsorbent. In this study, in order to investigate the adsorption isotherm, two equilibrium isotherms were analyzed: the Langmuir and Freundlich isotherms. Langmuir and Freundlich models are the most widely used models in the case of the adsorption of metal ions with biosorbents. Langmuir model suggests monolayer sorption on a homogeneous surface without interaction between sorbed molecules. In addition, the model assumes uniform energies of sorption onto the surface and no transmigration of the sorbate. The basic assumption of Freundlich theory is that the sorption surface is heterogeneous and binding sites have different sorption energies.

As presented in Table 3, equilibrium data obtained from biosorption of Cd(II) ions onto *Trichoderma* fungus were well fitted to the Langmuir and Freundlich isotherm equations. Nevertheless, it was found that biosorption of cadmium(II) ions onto the biosorbent was better suitable to Freundlich than Langmuir adsorption model. In a study that was performed by Rostami and Joodaki [67] on cadmium adsorption by *A. niger*, the adsorption data were fitted to Langmuir and Freundlich models and R^2 higher than 0.97 and 0.98 was obtained. Similar findings were reported by Chen et al. [44] on cadmium removal from simulated wastewater to biomass by-product of *L. edodes*.

Table 3
Isotherm parameters for Cd(II) biosorption at different temperatures (initial Cd(II) concentration = 25–150 mg/L, pH 6, biosorbent dosage 0.8 g/L)

	Langmuir isotherm			Freundlich isotherm		
Temperature (K)	q_m (mg/g)	K_L (L/mg)	R^2	K_f	n	R^2
298	133.33	0.02	0.9992	1.07	0.71	0.9924
303	158.73	0.02	0.9955	1.79	0.76	0.9979
308	270.27	0.01	0.9962	2.50	0.82	0.9918
313	1,250	0.0029	0.9986	3.15	0.92	0.9925

4. Conclusion

This work reports the results of the study of Cd(II) ions removal from aqueous solutions by *Trichoderma* fungus using batch biosorption technique. The biosorption studies were carried out as a function of pH, contact time, initial metal concentration, mixing rate, and temperature. The maximum biosorption occurred at pH 6. The rate of biosorption increased as the agitator speed increased. The equilibrium metal uptake was increased with an increase in the initial concentration of Cd(II) ions. Biosorption kinetics data were fitted using pseudo-first-order and pseudo-second-order models. It was found that the kinetics data fitted well the pseudo-first-order during the initial 120 min of biosorption, and when the biosorption time was 120 min, the experimental data fitted very well with the pseudo-second-order kinetics reaction. The results of thermodynamic study confirmed that biosorption of cadmium(II) ions by *Trichoderma* fungus was spontaneous and endothermic nature.

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References

[1] A. Özer, H.B. Pirinççi, The adsorption of Cd(II) ions on sulphuric acid-treated wheat bran, J. Hazard. Mater. B 137 (2006) 849–855.

[2] Z. Hossain, F. Huq, Studies on the interaction between Cd^{2+} ions and nucleobases and nucleotides, J. Inorg. Biochem. 90 (2002) 97–105.

[3] M. Fayyaz, S. Ahmad, A. Haydara, A. Bhatti, A.J. Bari, Application of artificial neural network for the prediction of biosorption capacity of immobilized *Bacillus subtilis* for the removal of cadmium ions from aqueous solution, Biochem. Eng. J. 84 (2014) 83–90.

[4] E. Bazrafshan, F.K. Mostafapoor, M.A. Zazouli, Z. Eskandari, G.R. Jahed, Study on removal of cadmium from plating baths wastewater by electrochemical precipitation method, Pak. J. Biol. Sci. 9 (2006) 2107–2111.

[5] L. Järup, A. Åkesson, Current status of cadmium as an environmental health problem, Toxicol. Appl. Pharmacol. 238 (2009) 201–208.

[6] S. Chakraborty, A. Mukherjee, A.R. Khuda-Bukhsh, T. Das, Cadmium-induced oxidative stress tolerance in cadmium resistant *Aspergillus foetidus*: Its possible role in cadmium bioremediation, Ecotox. Environ. Saf. 106 (2014) 46–53.

[7] N. Barka, M. Abdennouri, A. Boussaoud, M. EL Makhfouk, Biosorption characteristics of Cadmium(II) onto *Scolymus hispanicus* L. as low-cost natural biosorbent, Desalination 258 (2010) 66–71.

[8] P. Chakravarty, N. Sen Sarma, H.P. Sarma, Biosorption of cadmium(II) from aqueous solution using heartwood powder of *Areca catechu*, Chem. Eng. J. 162 (2010) 949–955.

[9] C.C.V. Cruz, A.C.A. da Costa, C.A. Henriques, A.S. Luna, Kinetic modeling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp. biomass, Bioresour. Technol. 91 (2004) 249–257.

[10] WHO, Guidelines for Drinking Water Quality: Recommendations, third ed., vol. 1, World Health Organisation, Geneva, 2008.

[11] E. Bazrafshan, A.H. Mahvi, A.R. Mesdaghinia, F. Vaezi, S. Nazmara, Removal of cadmium from industrial effluents by electrocoagulation process using iron electrodes, Iran. J. Environ. Health Sci. Eng. 3(4) (2006) 261–266.

[12] T.M. Alslaibi, I. Abustan, M.A. Ahmad, A.A. Foul, Cadmium removal from aqueous solution using microwaved olive stone activated carbon, J. Environ. Chem. Eng. 1 (2013) 589–599.

[13] G.O. Oyetibo, M.O. Ilori, O.S. Obayori, O.O. Amund, Equilibrium studies of cadmium biosorption by presumed non-viable bacterial strains isolated from polluted sites, Int. Biodeterior. Biodegrad. 91 (2014) 37–44.

[14] S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98 (2007) 2243–2257.

[15] Y.C. Sharma, Thermodynamics of removal of cadmium by adsorption on an indigenous clay, Chem. Eng. J. 145 (2008) 64–68.

[16] S.O. Lesmana, N. Febriana, F.E. Soetaredjo, J. Sunarso, S. Ismadji, Studies on potential applications of biomass for the separation of heavy metals from water and wastewater, Biochem. Eng. J. 44 (2009) 19–41.

[17] S.Y. Kang, J.U. Lee, K.W. Kim, Biosorption of Cr(III) and Cr(VI) onto the cell surface of *Pseudomonas aeruginosa*, Biochem. Eng. J. 36 (2007) 54–58.

[18] Y. Sağ, T. Kutsal, Biosorption of heavy metals by *Zoogloea ramigera*: Use of adsorption isotherms and a comparison of biosorption characteristics, Chem. Eng. J. Biochem. Eng. J. 60 (1995) 181–188.

[19] M. Tsezos, B. Volesky, Biosorption of uranium and thorium, Biotechnol. Bioeng. 23 (1981) 583–604.

[20] Y.P. Ting, F. Lawson, I.G. Prince, Uptake of cadmium and zinc by the *algaChlorella vulgaris*: Part 1. Individual ion species, Biotechnol. Bioeng. 34 (1989) 990–999.

[21] C. Jeon, J.Y. Park, Y.J. Yoo, Novel immobilization of alginic acid for heavy metal removal, Biochem. Eng. J. 11 (2002) 159–166.

[22] B. Volesky, Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy 59 (2001) 203–216.

[23] N. Masoudzadeh, F. Zakeri, T. Bagheri Lotfabad, H. Sharafi, F. Masoomia, H. Shahbani Zahiri, G. Ahmadian, K. Akbari Noghabi, Biosorption of cadmium by *Brevundimonas* sp. ZF12 strain, a novel biosorbent isolated from hot-spring waters in high background radiation areas, J. Hazard. Mater. 197 (2011) 190–198.

[24] Z. Aksu, Equilibrium and kinetic modelling of cadmium(II) biosorption by *C. vulgaris* in a batch system: Effect of temperature, Sep. Purif. Technol. 21 (2001) 285–294.

[25] B. Benguella, H. Benaissa, Cadmium removal from aqueous solutions by chitin: Kinetic and equilibrium studies, Water Res. 36 (2002) 2463–2474.

[26] K.Y.H. Gin, Y.Z. Tang, M.A. Aziz, Derivation and application of a new model for heavy metal biosorption by algae, Water Res. 36 (2002) 1313–1323.

[27] C. Sing, Copper adsorption and removal from water by living mycelium of white-rot fungus *Phanerochaete chrysosporium*, Water Resour. 32 (1998) 2746–2752.

[28] W. Jianlong, Z. Xinmin, D. Decai, Z. Ding, Bioadsorption of Lead (II) from aqueous solution by fungal biomass of *Aspergillus niger*, J. Biotechnol. 87 (2002) 273–277.

[29] E. Bazrafshan, F. Kord Mostafapour, S. Rahdar, A.H. Mahvi, Equilibrium and thermodynamics studies for decolorization of Reactive Black 5 (RB5) by adsorption onto MWCNTs, Desalin. Water Treat. 54 (2015) 2241–2251.

[30] E. Bazrafshan, A.A. Zarei, H. Nadi, M.A. Zazouli, Adsorptive removal of Methyl Orange and Reactive Red 198 by *Moringa peregrina* ash, Indian J. Chem. Technol. 21 (2014) 105–113.

[31] F. Kord Mostafapour, E. Bazrafshan, M. Farzadkia, S. Amini, Arsenic removal from aqueous solutions by *Salvadora Persica* stem ash, J. Chem. 2013 (2013) 1–8.

[32] E. Bazrafshan, M. Ahmadabadi, A.H. Mahvi, Reactive Red-120 removal by activated carbon obtained from cumin herb wastes, Fresenius Environ. Bull. 22(2a) (2013) 584–590.

[33] E. Bazrafshan, F. Kord Mostafapour, A.R. Hosseini, A. Raksh Khorshid, A.H. Mahvi, Decolorisation of Reactive Red (120) dye by using single-walled carbon nanotubes in aqueous solutions, J. Chem. 2013 (2013) 1–8.

[34] E. Bazrafshan, F. Kord Mostafapour, A.H. Mahvi, Phenol removal from aqueous solutions using Pistachio-nut shell ash as a low cost adsorbent, Fresen, Environ. Bull. 21(10) (2012) 2962–2968.

[35] M.D. Mashitah, Y. Yus Azila, S. Bhatia, Biosorption of cadmium (II) ions by immobilized cells of *Pycnoporus sanguineus* from aqueous solution, Bioresour. Technol. 99 (2008) 4742–4748.

[36] R. Apiratikul, T.F. Marhaba, S. Wattanachira, P. Pavasant, Biosorption of binary mixtures of heavy metals by green macro alga *Caulerpa lentillifera* Songklanakarin, J. Sci. Technol. 26 (2004) 199–207.

[37] W. Zhou, J. Wang, B. Shen, W. Hou, Y. Zhang, Biosorption of copper(II) and cadmium(II) by a novel exopolysaccharide secreted from deep-sea mesophilic bacterium, Colloids Surf., B 72 (2009) 295–302.

[38] M. Amini, H. Younesi, N. Bahramifar, Statistical modeling and optimization of the cadmium biosorption process in an aqueous solution using *Aspergillus niger*, Colloids Surf., A 337 (2009) 67–73.

[39] M.Y. Arıca, Y. Kaçar, Ö. Genç, Entrapment of white-rot fungus *Trametes versicolor* in Ca-alginate beads: Preparation and biosorption kinetic analysis for cadmium removal from an aqueous solution, Bioresour. Technol. 80(2) (2001) 121–129.

[40] R. Say, A. Denizli, M.Y. Arika, Biosorption of cadmium(II), lead(II) and copper(II) with the filamentous fungus *Phanerochaete chrysosporium*, Bioresour. Technol. 76(1) (2001) 67–70.

[41] J.S. Chang, R. Law, C.C. Chang, Biosorption of lead, copper and cadmium by biomass of *Pseudomonas aeruginosa* PU21, Water Res. 31 (1997) 1651–1658.

[42] A. Saeed, M. Iqbal, Bioremoval of cadmium from aqueous solution by black gram husk (*Cicer arientinum*), Water Res. 37 (2003) 3472–3480.

[43] A. Kapoor, T. Viraraghavan, D. Cullimore, Removal of heavy metals using the fungus *Aspergillus niger*, Bioresour. Technol. 70 (1999) 95–104.

[44] G.Q. Chen, G.M. Zeng, L. Tang, C.Y. Du, X.Y. Jiang, G.H. Huang, H.L. Liu, G.L. Shen, Cadmium removal from simulated wastewater to biomass byproduct of *Lentinus edodes*, Bioresour. Technol. 99 (2008) 7034–7040.

[45] K. Vijayaraghavan, Y.S. Yun, Bacterial biosorbents and biosorption, Biotechnol. Adv. 26 (2008) 266–291.

[46] M. Akhtar, K. Sastry, P. Mohan, Mechanism of metal ion biosorption by fungal biomass, Biometals 9 (1996) 21–28.

[47] R. Vimala, N. Das, Biosorption of cadmium(II) and lead (II) from aqueous solutions using mushrooms: A comparative study, J. Hazard. Mater. 168 (2009) 376–382.

[48] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by *Mucor hiemalis*, Biochem. Eng. J. 23 (2005) 185–192.

[49] S.K. Das, A.K. Guha, Biosorption of chromium by *Termitomyces clypeatus*, Colloids Surf., B 60 (2007) 46–54.

[50] A. Rathinam, B. Maharshi, S. Kalarical Janardhanan, R. Rao Jonnalagadda, B. Unni Nair, Biosorption of cadmium metal ion from simulated wastewaters using *Hypnea valentiae* biomass: A kinetic and thermodynamic study, Bioresour. Technol. 101 (2010) 1466–1470.

[51] F. Mohsenzadeh, F. Shahrokhi, Biological removing of cadmium from contaminated media by fungal biomass of *Trichoderma* species, J. Environ. Health Sci. Eng. 12 (2014) 1–7.

[52] A. Chergui, Simultaneous biosorption of Cu, Zn and Cr from aqueous solution by *Streptomyces rimosus* biomass, Bioresour. Technol. 206 (2007) 179–184.

[53] X. Xu, L. Xia, Q. Huang, J.D. Gu, W. Chen, Biosorption of cadmium by metal-resistant filamentous fungus isolated from chicken manure compost, Environ. Technol. 2 (2012) 1–10.

[54] S.K. Das, I. Shome, A.K. Guha, Surface functionalization *of Aspergillus versicolor* mycelia: *in situ* fabrication of cadmium sulphide nanoparticles and removal of cadmium ions from aqueous solution, RSC Adv. 2 (2012) 3000–3007.

[55] Z. Al-Qodah, A.T. Shawaqfeh, W.K. Lafi, Adsorption of pesticides from aqueous solutions using oil shale ash, Desalination 208 (2007) 294–305.

[56] W. Pitakpoolsil, M. Hunsom, Treatment of biodiesel wastewater by adsorption with commercial chitosan flakes: Parameter optimization and process kinetics, J. Environ. Manage. 133 (2014) 284–292.

[57] D. Aderhold, C.J. Williams, R.G.J. Edyvean, The removal of heavy-metal ions by seaweeds and their derivatives, Bioresour. Technol. 58 (1996) 1–6.

[58] V.B.H. Dang, H.D. Doan, T. Dang-Vu, A. Lohi, Equilibrium and kinetics of biosorption of cadmium(II) and copper(II) ions by wheat straw, Bioresour. Technol. 100 (2009) 211–219.

[59] A.B. Zaki, M.Y. El-Sheikh, J. Evans, S.A. El-Safty, Kinetics and mechanism of the sorption of some aromatic amines onto amberlite IRA-904 anion-exchange resin, J. Colloid Interface Sci. 221 (2000) 58–63.

[60] E. Errais, J. Duplay, F. Darragi, I. M'Rabet, A. Aubert, F. Huber, G. Morvan, Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters, Desalination 275 (2011) 74–81.

[61] V.K. Gupta, Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent, Ind. Eng. Chem. Res. 37 (1998) 192–202.

[62] A.C.A. da Costa, S.G.C. Leite, Metals biosorption by sodium alginate immobilized*Chlorella homosphaera* cells, Biotechnol. Lett 13 (1991) 559–562.

[63] J.T. Matheickal, Q. Yu, G.M. Woodburn, Biosorption of cadmium(II) from aqueous solutions by pre-treated biomass of marine alga *DurvillAea potatorum*, Water Res. 33 (1999) 335–342.

[64] G. McKay, Y.S. Ho, The sorption of lead(II) on peat, Water Res. 33 (1999) 578–584.

[65] Z. Eren, F.N. Acar, Adsorption of Reactive Black 5 from an aqueous solution: equilibrium and kinetic studies, Desalination 194 (2006) 1–10.

[66] M.S. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads, J. Hazard. Mater. 93 (2002) 233–248.

[67] Kh. Rostami, M.R. Joodaki, Some studies of cadmium adsorption using *Aspergillus niger*, *Penicillium austurianum*, employing an airlift fermenter, Chem. Eng. J. 89 (2002) 239–252.