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Fungal biosorption of cadmium(II) onto *Fennelia nivea* from aqueous solution: equilibrium, thermodynamics, and kinetics

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ABSTRACT

Cadmium(II) is an important ecotoxic pollutant and may cause health problems if accumulated in the human body. This study focused on the removal of cadmium(II) from aqueous solutions using newly isolated fungus dry mass as the adsorber. The fungus was isolated from soil and identified as *Fenellia nivea*, based on 18S rRNA sequence analysis. Cadmium(II) biosorption studies were carried out as a function of pH, biomass dose, initial metal concentration, contact time, and temperature. The pH of the aqueous solution strongly influenced the removal percent of Cd(II). The highest cadmium removal yield was obtained at pH 7 (4.9 mg/g) as well as below pH 4, very low yield biosorption of Cd(II) was observed. In the first 5 min, almost 50% Cd(II) ions were removed from the solution and reached equilibrium within 1,440 min at pH 7. Adsorption isotherm follows Langmuir model as well as the dimensionless constant is zero that corresponds to the irreversible adsorption of Cd(II) ions on biomass. The reaction rate constant for the pseudo-second-order adsorption process was found as 3.74×10^{-3} g/mg min. The adsorption process was determined as endothermic and spontaneous with negative standard Gibbs energy change.

Keywords: Biosorption; Cadmium; *Fennelia nivea*; Heavy metal removal; Adsorption kinetics; Adsorption thermodynamics

1. Introduction

High concentrations of anthropogenic heavy metals are a chronic environmental problem in ecosystems. Since they cannot be destroyed, the only way to remove metals from the environment is to accumulate them in a controlled phase through processes such as filtration, reverse osmosis, precipitation, ion exchange, and chemical oxidation–reduction [1]. Some of these removal methods have major disadvantages in the application, because of the need for advanced technology, expensive operational costs, high reagent consumption, unpredictable removal performance, or the generation of excessive secondary wastes. Among these removal processes, biosorption is a flexible and cost-effective adsorption process in metal removal, that is why scientific interest in bio-adsorption mechanisms and new bio-adsorbents including fungal biomass, is continuous [2].

Various kinds of adsorbents such as chitin, chitosan, dead biomass, zeolite, clay, fly ash, moss, modified wool, and modified cotton have been used to remove heavy metals [3]. Among adsorbent materials activated carbon is a good adsorbent for heavy metal removal but commercial activated carbon is very expensive as a result alternative sorbent materials are always investigated [4]. Living, dead, and immobilized fungal cells can be used for the removal of heavy metal ions from aqueous solutions [5–7].

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Biomass of fungi can be easily obtained in large quantities by several methods. Furthermore, fungi can easily grow in inexpensive growth media [4]. In addition, the use of inactivated fungal biomass to remove toxic chemicals, including heavy metals, is an environmentally friendly and sustainable approach since it does not introduce any unnatural material into the environment, during the removal process [5]. Because of these reasons, the adsorption capacities of different fungal species are continuously investigated and are tried to enhanced to develop sustainable adsorbent material.

Cadmium is a well-known ecotoxic metal, which is also one of the most toxic heavy metals for human health [6]. Some of the cadmium compounds (such as $CdSO_4$ and $CdCl_2$) are highly soluble in water and extensively used in several industrial applications, as a stabilizer in PVC, anti-corrosive agents, color pigment, production in nickel–cadmium batteries, and neutron absorber in nuclear plants. As a result, cadmium is found in different concentrations in wastewater and industrial effluents as Cd(II) ions [7]. Cadmium causes gastrointestinal damage, kidney damage, reproductive abnormalities, and damages to the bones [8]. High concentrations of cadmium are observed when industrial wastewater is released or accidentally spilled into the environment [9]. Therefore the researchers have used Cd(II) as one of the model toxic metals during the development of different sorbent material from fungal species for the metal removal from aqueous solutions [5,10]. In a study, the adsorption capacity of white-rot fungus *Funalia trogii* for Hg^{2+}, Cd^{2+} and Zn^{2+} ions were found as 403.2, 191.6, and 54.0 mg/g, respectively [11]. Another study showed that aminopropyl trimethoxy silane treated *Rhizopus nigricans* biomass could adsorb Cr(IV) effectively [12]. *Fennelia nivea* is a mold-shaped fungus, thus inoculation and cultivation of this fungus are relatively simple. *F. nivea* has not been investigated for the adsorption of cadmium in aqueous solutions before.

In this paper, the adsorption mechanisms of Cd(II) onto *F. nivea* surface are reported for the first time in literature. Effects of inactivated biomass dose, initial Cd(II) concentration, and pH on the adsorption yield of Cd(II) are investigated. Kinetic modeling of adsorption is also developed in this study.

2. Materials and methods

2.1. Microorganism

F. nivea species was isolated from the soil samples which were collected from the forest area of Kocaeli Province of Turkey. The fungus species isolated from soil samples were identified as *F. nivea* CH-Y-1043 (GenBank databases under accession no FJ155814.1), based on the 18S rRNA sequence. The newly isolated fungal species were kept on slant potato dextrose agar up to 20 d at 4°C and transferred to a new solid media, periodically. The media which was used to obtain fungal biomass composed of (per liter): 1 g glucose, 1 g $(NH_4)_2SO_4$, 1 g KH_2PO_4, 0.5 g $MgSO_4{\cdot}7H_2O$, 0.1 g yeast extract, 0.1 g $CaCl_2{\cdot}2H_2O$. Fungal biomass was separated from the growth media by filtering through a 45 μm (Minisart®) filter. Fungal mass collected on the filter was washed with distilled water three times. To obtain heat-inactivated biomass, filtered fungal biomass was autoclaved at 110°C for 25 min. Heat inactivated biomass was kept on drying at 30°C for 4 d. Dried fungal biomass is grinded by using a marble hammer and pastel. To sort *F. nivea* powder, dried biomass was sieved through a 0.15 mm screen and stored in a brown precleaned bottle until used in experiments. All measurements were carried out using dry biomass.

2.2. Isotherm studies

During isotherm studies, initial Cd concentration, contact time, pH, and temperature were used as control parameters. These parameters were also used for the description of the adsorption mechanisms.

For isotherm studies, 0.1 g of fungal powder is put into 100 mL of Cd (II) solutions which had different initial concentrations (C_0). Each reactor concentration is prepared from the same stock solution. After the adsorption period, cadmium concentrations of filtered supernatants were measured with an atomic absorption spectrometer in flame mode (Perkin Elmer Analyst 800, United States). Adsorption mechanism of Cd(II) onto *F. nivea* biomass is modeled using Freundlich and Langmuir isotherm approaches. The best-fitted model (Langmuir) is accepted as the accumulation mechanism of Cd (II) onto *F. nivea* biomass. The Langmuir adsorption model assumes a monolayer and uniform adsorption, no adsorption, the process occurs once saturation is reached and there is no interaction between adsorbate particles [13]. The linearized Langmuir adsorption model is expressed with the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{\left(q_m K_L\right)} \tag{1}$$

in which C_e is the equilibrium concentration of adsorbate (mg/L), q_e is the amount of adsorbed metal ion per unit mass of adsorbent (mg/g), q_m is the maximum adsorption capacity (mg/g), and K_L is a factor that is related with adsorption free energy (L/mg) (expressed as Langmuir constant).

Dimensionless constant, R_L, one of the essential analysis of the Langmuir model, is given by the following equation [14]:

$$R_L = \frac{1}{\left(1 + K_L C_0\right)} \tag{2}$$

where K_L is Langmuir constant and C_0 is the initial adsorbate concentration (mg/L). The value R_L assigns the isotherm in case of unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$).

2.3. Cd(II) biosorption studies

Biosorption experiments were carried out in 250 mL Erlenmeyer flasks (a batch system) containing 100 mL solution. Analytical grade cadmium chloride was used to prepare Cd(II) ion solutions and pH values were adjusted with 0.1 M NaOH and 0.1 M HCl solutions. Media pH was controlled with pH meter (Hanna®, HI2020-01). All experiments were prepared using deionized water and stirred at 150 rpm with rotary shaker (Microtest, Turkey). Each set of experiments is prepared as three replicates and the average of measured concentration is reported.

Solutions that contain 5 mg/L Cd(II) and 0.1 g fungal biomass were prepared to investigate the effect of pH, from 4 to 11. To study the effects of biomass dose, 0.1 to 0.5 g dry fungal powder was added, on 5 mg/L Cd(II) solutions. Effect of initial pollutant concentration was studied by changing the Cd(II) concentrations from 5 to 20 mg/L. High concentrations of cadmium is observed in electroplating effluent [15–17]. So, a range of Cd concentration were investigated during the study. In these experiments, biomass was kept constant at 0.1 g. Contact time (5–1,680 min) and temperature (15°C, 30°C, and 60°C) effects were investigated with 0.1 g biomass and 5 mg/L Cd(II). The temperature and pH were adjusted to 30°C and 7, in all experiments, respectively. The reactors were used on rotary shakers at 150 rpm for 24 h.

The change of adsorption capacity with contact time was also investigated by sampling at predetermined time intervals (0–1,800 min).

Temperature studies were performed at 15°C, 30°C, and 60°C. An Erlenmeyer flask without inactivated biomass was prepared and analyzed for each test, as a control. In order to measure the residual Cd(II) concentration in the batch studies, solutions were centrifuged at 5,000 rpm for 15 min and supernatant fractions were separated. Each test was performed in triplicates.

2.4. Cadmium analysis

Supernatants of samples and the control reactor were filtered through 0.45 µm sterile cellulose acetate syringe filters (Minisart®). Initial and equilibrium concentrations of cadmium were measured by Perkin Elmer Analyst 800 atomic absorption spectrometer in the flame module. Each measurement was repeated at least three times and average values were used in the analysis.

Cd(II) adsorption capacity of dry biomass was calculated using the following equation:

$$q_e = \frac{\left(C_i - C_e\right)V}{m} \tag{3}$$

where q_e is the amount of Cd(II) adsorbed by biomass at equilibrium (mg/g), C_i is the initial concentration of Cd(II) ions (mg/L), C_e is the equilibrium concentration of metal ions (mg/L), m is the biomass dose in the adsorption media (g), and V is the volume of adsorption media (L).

2.5. Adsorption kinetics

It is necessary to describe the kinetics of adsorption to determine some parameters by various model equations and the used equations that can enhance the optimization of the adsorption mechanism and the effect of surface properties on the adsorption process [17,18]. The pseudo-first-order and pseudo-second-order kinetic models were tested for the adsorption of Cd(II) ions on biomass.

The pseudo-first-order kinetic model was evaluated by following the Lagergren equation [18]:

$$\ln\left(q_e - q_t\right) = \ln\left(q_e\right) - K_1 \tag{4}$$

where q_e is the amount of the adsorbate at equilibrium (mg/g) and q_t is the amount of the adsorbate at any time in interest (mg/g). K_1 (1/min) is the rate constant of pseudo-first-order adsorption.

The other widely used kinetic model for adsorption studies is a pseudo-second-order model that is proposed as [19]:

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

where q_e is the amount of the adsorbate at equilibrium (mg/g) and where q_t is the amount of the adsorbate at any time in interest (mg/g). K_2 (mg/g min) is the rate constant of the pseudo-second-order adsorption process.

2.6. Thermodynamic studies

Thermodynamic studies were conducted at pH 7 with 5 mg/L Cd(II) solution. 0.1 g biomass was used in the reactors which were mixed continuously at 100 rpm for 24 h at different temperatures (288, 303, and 333 K). The favorability of the adsorption process is observed by following the changes in standard Gibbs free energy (ΔG°, J/mol), standard enthalpy (ΔH°, J/mol), and standard entropy. The parameters were evaluated by the following equations:

$$K_e = \frac{q_e}{C_e} \tag{6}$$

$$\Delta G^\circ = -RT\ln K_e \tag{7}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

$$\ln K_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{\left(RT\right)} \tag{9}$$

where T is in units of absolute temperature K and R is universal gas constant in units of J/mol K and K_e is the thermodynamic equilibrium constant. The values of ΔH° and ΔS° were evaluated from the graph constructed $\ln K_e$ vs. $1/T$.

3. Results and discussion

The light microscope view of *F. nivea* before grinding is given in Fig. 1. Parameters that might be effective during the adsorption process are evaluated and the results are compared to other research findings, in the following sections.

3.1. Effect of pH

Since the initial pH of the solution affects functional groups on the cell wall and chemistry of metal ions is

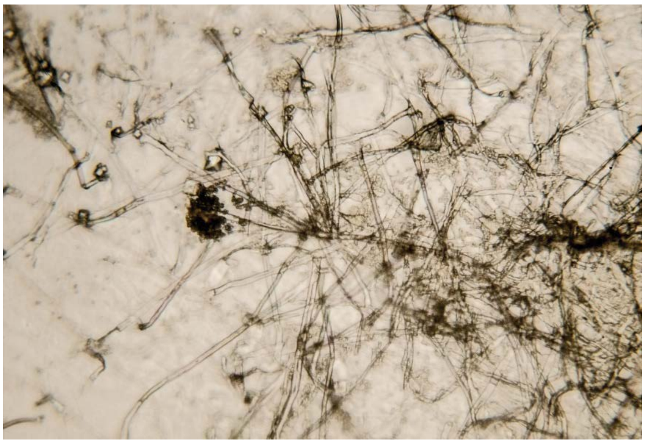

Fig. 1. Light microscope view of *F. nivea*.

accepted as one of the important parameters for the adsorption of metal ions [1]. Very low biosorption below pH 4 and a jump at pH 4 is observed during the experiments, results are given in Fig. 2. Maximum Cd(II) biosorption was obtained at pH 7 (4.9 mg/g). At low pH values (less than pH 4) biosorption of metal removal was inhibited because hydrogen ions compete with metal ions at the binding site of biomass [7].

At high pH values (>pH 4), heat-inactivated fungal cell surface is more negatively charged due to deprotonation of functional groups thus heavy metal removal capacity increased [20]. Due to the formation of hydroxylated metal complexes at higher pH levels (in this study, at pH 7) metal removal capacity of biomass starts to decrease [21]. Earlier similar adsorption trend was observed for *Phanerochaete chrysosporium* biomass which showed maximum cadmium adsorption at pH 6 [22]. Effect of pH on Cd(II) adsorption was also examined for fungus *Trametes versicolor* entrapped on alginate beds that an increase for biosorption with pH, maximum biosorption was observed between pH 5.0 and 6.0 and a decrease for adsorption starts with pH [23]. In another study, pH dependent cadmium biosorption on *Rhizopus cohnii* was observed as well, biosorption was increased between pH 2.0 and 4.5 values and a plateau up to pH 6.5 was reported [21]. The adsorption of cadmium on *Aspergillus niger* was rapidly increased between pH 3.0 and 4.0 and the lowest equilibrium concentration was observed between pH 4.0 and 5.5 [24]. The observed trend is an increase of adsorption through moderate pH values and a decrease at higher values. The optimum pH value is also dependent on the chemical structure of the fungus surface which plays an important role in the interaction of cadmium ions.

3.2. Effect of biomass dose and initial metal concentration

The biomass dosage is one of the important parameters that determine sorption capacity for a constant concentration of pollutant.

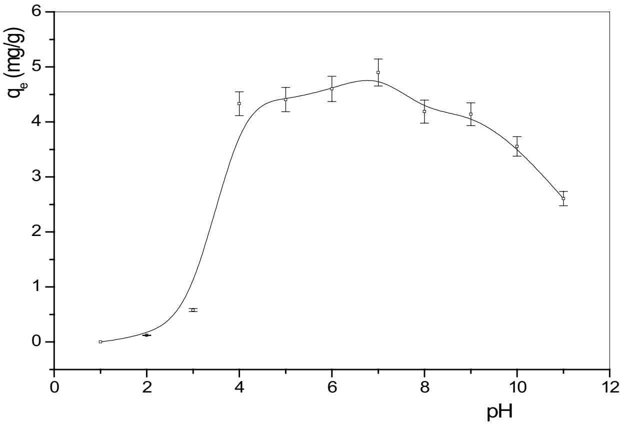

Fig. 2. Influence of pH on adsorption of aqueous Cd(II) ions on *Fennelia nivea*. T = 30°C, initial Cd(II) = 5 mg/L, fungal biomass = 0.1 g, and contact time = 24 h.

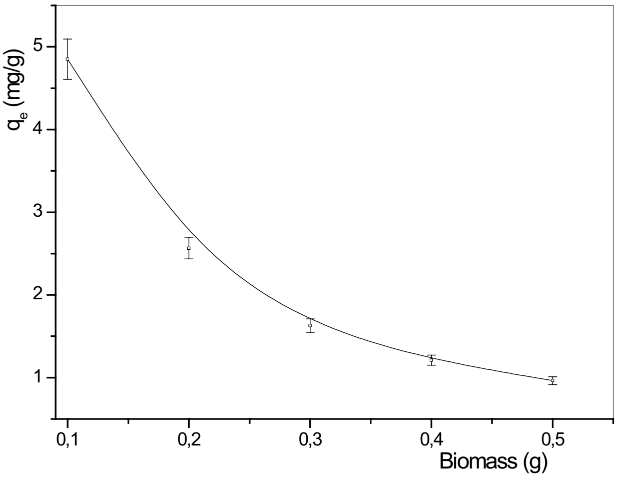

Fig. 3. Effect of the initial amount of biomass on adsorption of aqueous Cd(II) ions *on Fennelia nivea*. T = 30°C, initial Cd(II) = 5 mg/L, contact time = 24 h, and pH = 7.

Different amounts of heat-inactivated biomass (0.1–0.5 g) were tested in terms of Cd(II) biosorption capacity. As depicted in Fig. 3, biosorption capacity decreased with increasing biomass dose in the solution. The maximum adsorption capacity was obtained with 0.1 g *F. nivea* biomass (4.85 mg/g). Biosorption of cadmium by *A. niger* resulted in an increase in efficiency and a decrease in sorption capacity [24]. A previous study showed that the biosorption capacity of Cu(II), Ni(II), Zn(II), and Cr(VI) ions decreases with increasing biomass dose. However, the authors reported that the removal percentage of metal ions increases with the increase of *Pleurotus ostreatus* biomass [25]. Biosorption capacity of cadmium(II), zinc(II), and lead(II) decreased with increasing biomass of *Penicillium simplicissimum* [1]. Activated carbon derived from *Ceiba pentandra* hulls achieves maximum adsorption capacity with a dose of 0.5 g/50 mL (19.5 mg/g) [26]. When these results are compared to our study, researchers achieve almost 5-fold more adsorption capacity using 10 times higher biomass dosage (10 g/L). Another study investigated the effect of biomass dose on biosorption of Cd(II) by *Aspergillus* *fumigatus* that change with pH values of 5 and 6. The mass of *A. fumigatus* was examined up to 110 mg and the saturation was reached at 100 mg biomass for both pH values as well as the uptake efficiency was about 80% and 95% for pH 6 and 5, respectively [27]. In general, the results of this study show similar trends with the cited literature with better efficiency. Metal adsorption is a function of dried fungus mass since the available sorption sites increase with biomass dose.

Electrostatic interactions between biomass particles may be a significant factor in the biomass dose-dependency of metal adsorption, with a larger quantity of metal being adsorbed when the distance between particles is far enough [28].

Biosorption efficiency of Cd (II) onto *F. nivea* biomass increased with increasing initial metal concentration and became saturated at 15 mg/L Cd(II) concentration (Fig. 4). Higher metal ion concentration provides a driving force to overcome all mass transfer resistances between biosorbent and aqueous phase [29]. Consequently, high biosorption capacity was obtained at the higher metal concentration at 15 mg/L (7.01 mg/g). The maximum biosorption capacity of Cd(II) on *A. niger* was determined as 21 mg/g for 30 mg/L Cd(II) solution and a minor decrease was observed for higher Cd(II) concentrations [24]. *R. cohnii* was also used for Cd(II) biosorption from aqueous solution and its efficiency was compared with activated carbon. Although the uptake capacity of Cd(II) for activated carbon was higher, the results for *R. cohnii* was promising. The initial Cd(II) concentration varied from 0 to 1,000 mg/L and the biosorption capacity was followed, up to 100 ppm Cd(II) concentration, there is a steep change for Cd(II) uptake on *R. cohnii*, which is about 15 mg/L, and for higher Cd(II) concentrations, it is nearly constant about 18 mg/L [21]. Another study compared the adsorption of Cd(II), Zn(II), and Pb(II) on *P. simplicissimum* that showed relatively low adsorption capacity for Cd(II) rather than Zn(II) and Pb(II) at optimum conditions. An increase in adsorption capacity (52.50 mg/g was observed up to 200 mg/L Cd(II) and for higher concentrations, adsorption capacity decreased for a small value for 250 and 300 mg/L Cd(II) [21]. The adsorption capacity for different funguses increases at low Cd(II) concentrations and reaches saturation at higher Cd(II) concentrations. The saturation value depends on the structure and porosity of the fungus.

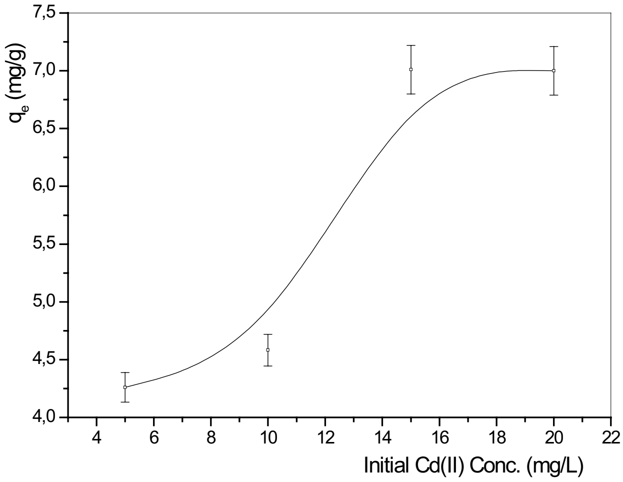

Fig. 4. Effect of the initial concentration of Cd(II) ions on adsorption of aqueous Cd(II) ions on *Fennelia nivea*. T = 30°C, fungal biomass = 0.1 g, contact time = 24 h, and pH = 7.

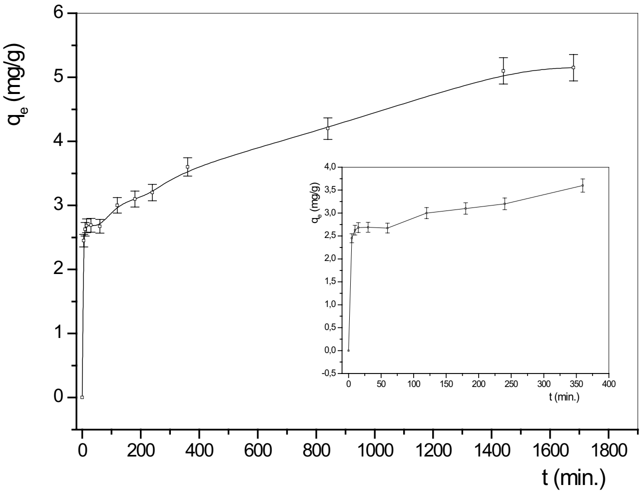

Fig. 5. Effect of contact time on adsorption of aqueous Cd(II) ions on *Fennelia nivea* (insert dilute region). T = 30°C, fungal biomass = 0.1 g, Cd(II) = 5 mg/L, and pH = 7.

3.3. Effect of contact time and temperature

The biosorption of cadmium ions onto fungal biomass as a function of contact time is given in Fig. 5, according to the results a rapid removal of Cd(II) was observed within the first 5 min.

Initially almost 50% of Cd(II) accumulated in the first 5 min then biosorption of Cd(II) reached equilibrium in 1,440 min at pH 7. Cd(II) biosorption occurred in two stages: in the first stage metal ions adsorbed quickly because of biosorbent has abundant active binding sites, in the second stage biosorption rate decreases and removal efficiency drops [21]. In a different paper, the biosorption of Cd(II) to *Aspergillus cristatus* surface showed a contact time-related uptake capacity, the cadmium uptake was 65% and 94% for 30 and 240 min, respectively for 100 ppm Cd(II) concentration [30]. Another study investigated the effect of contact time on biosorption of Cd(II) by *A. fumigatus* that change with pH At low pH values, the equilibrium was established for short contact times that is 30, 180, 90, and 90 min for 10 ppm Cd(II) concentration at pH values 3, 4, 5, and 6, respectively. The effect of pH is limited above certain values since the precipitation of Cd(II) starts as well as the active sites are designed for contact with metal ions depending on the pH [27]. The contact time for saturation depend on the concentration of Cd(II), structure of fungus, and pH.

As depicted in Fig. 6, biosorption capacity of heat-inactivated *F. nivea* biomass increased from 4.23 to 4.84 when the temperature was increased from 15°C to 60°C that corresponds to an endothermic process since the adsorption capacity increase with temperature [31]. This 15% non-linear increase in the adsorption capacity with

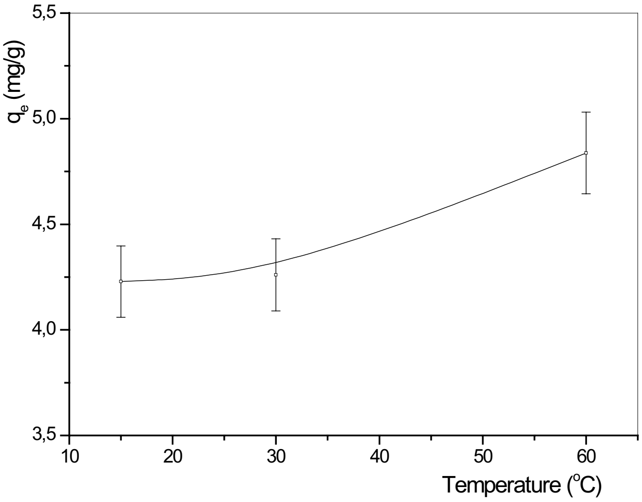

Fig. 6. Effect of temperature on adsorption of aqueous Cd(II) ions on *Fennelia nivea*. Fungal biomass = 0.1 g, Cd(II) = 5 mg/L, contact time = 24 h, and pH = 7.

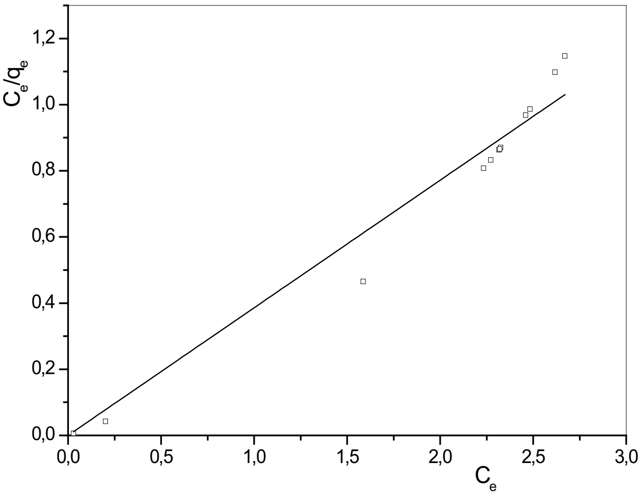

Fig. 7. Langmuir isotherm for adsorption of aqueous Cd(II) ions on *Fennelia nivea*. T = 30°C fungal biomass = 0.1 g, Cd(II) = 5 mg/L at pH 7.

temperature may be an advantage for the use of *F. nivea* at higher temperatures. Another study showed that biosorption of Cd(II), Zn(II), and Pb(II) on *P. simplicissimum* increased with temperature [1] and some reported that the temperature showed little effect on the biosorption of Cu(II), Ni(II), Zn(II), and Cr(VI) ions on *Schizophyllum commune* biomass [32]. Another study showed that a temperature range of 20°C–45°C had very little influence on biosorption of Cu(II), Ni(II), Zn(II), and Cr(VI) by *P. ostreatus* [25]. The effect of temperature on adsorption of Cd(II) on *P. chrysosporium* biomass was observed at pH 4.5 for 50 mg/L metal ions were examined as well, there is minor increase at the adsorption capacity from 25°C to 27°C and a minor decrease was observed at 30°C. A remarkable decrease is observed at 35°C [33]. Another study compared the effect of temperature on the adsorption of several metal ions including Cd(II) on two fungi, *Saprolegnia delica* and *Trichoderma viride.* The effect of temperature on adsorption percent was evaluated between 15°C and 35°C. A sharp increase was observed during the adsorption of Cd(II) on *S. delica* from 25.0% to 80.0% when the temperature was increased from 15°C to 20°C, respectively. It decreased 70% at 25°C and constant for further temperatures. The jump on adsorption (%) for cadmium on *T. viride* was similar to the results of the adsorption study conducted by using *S. delica* but it is lower at low temperatures when compared. The percent adsorption of Cd (II) on *T. viride* increase from 10.5% to 18.0% when the temperature was increased from 15°C to 20°C, respectively. The major adsorption percent was observed at 25°C with a value of 61%. There is a decrease in adsorption percent for further temperatures nearly constant at about 30% [34].

3.4. Adsorption isotherm

Fig. 7 shows the Langmuir isotherm for the adsorption of Cd(II) ions on biomass. The plot of experimental C_e/q_e vs. C_e fits well when regressed linear (with r^2 value of 0.993) where the intercept is 0 and slope is 0.386. The theoretical maximum adsorption capacity (q_m) was determined as 2.6 mg/g, which is rather lower than experimental data. The value of dimensionless constant, $R_L = 0$, corresponds to the irreversible adsorption of Cd(II) ions on biomass. The adsorption of Cd(II) on *F. nivea* seems to be more complex than physisorption Investigation of sorption efficiency of *P. chrysosporium* biomass showed maximum Cd(II) adsorption at pH 6 and obeyed Langmuir isotherm, with theoretical q_m value of 27.79 although observed one is 23.04 [22]. Another study adsorption of cadmium onto *R. cohnii* for 20, 50, and 100 mg/L Cd(II) concentration with q_e values of 3.8, 7.2, and 14.0 mg/g, respectively [35]. The theoretical q_m value of this system was 40.5 mg/g that follows the Langmuir adsorption isotherm. The biosorption isotherms of Cd(II) by *Cassia fistula* were investigated at different biomass doses for Langmuir adsorption isotherms from 0.25 to 1.5 g and theoretical q_m values were found to be between 7.24 and 2.56 mg/g, higher than the experimental for all biomass doses. The dimensionless constant, R_L was determined as smaller than 1 that shows the favorability of biosorption.

Although Freundlich isotherm is a widely used adsorption model to predict multilayer heterogeneous adsorption in pores [35]. The experimental data of this study did not fit the Freundlich adsorption model and its parameters (not given). Better fit of experimental results to Langmuir isotherm indicate a homogenous *F. nivea* surface for adsorption. There are papers in the literature where Freundlich isotherms analysis provided better results for adsorption of Cd(II); such as for *C. fistula* [36].

3.5. Adsorption kinetics

Fig. 8 shows the assumed pseudo-second-order model for adsorption of Cd(II) ions on biomass with linear regression coefficient value r^2 as 0.931. The theoretical amount of Cd(II) that can be adsorbed by biomass, q_e, was found as 4.53 mg/g from the slope of linear line. This value was determined as 4.80 mg/g experimentally. Also, the reaction rate

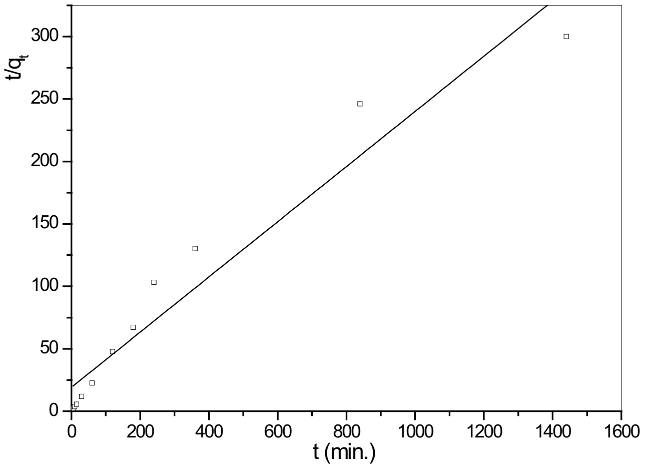

Fig. 8. Pseudo-second-order plot for the adsorption of aqueous Cd(II) ions on *Fennelia nivea*. T = 30°C fungal biomass = 0.1 g, Cd(II) = 5 mg/L.

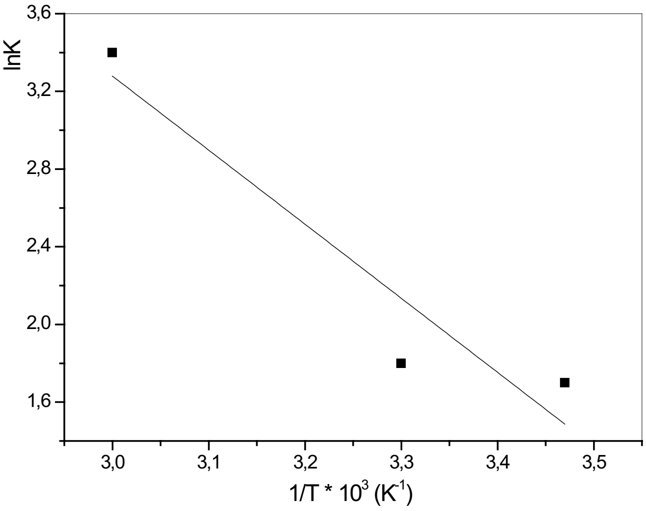

Fig. 9. Thermodynamic evaluation of the biosorption process.

constant for the pseudo-second-order adsorption process was found as 3.74 × 10^{-3} g/mg min from intercept for *Fenelia nivea*.

In a different study, adsorption capacity was found as 23.04 mg/g for *P. chrysosporium* biomass in 300 mg/L Cd(II) solution [22]. Some reported experimental q_e 14.6 and 69.6 mg/g for 20 and 100 ppm Cd(II) ions, respectively. In this study, the calculated are 15.2 and 71.1 mg/L, respectively with a reaction rate constant of 5.9 × 10^{-3} and 2.4 × 10^{-3} g/mg min with a pseudo-second-order adsorption process that follows Langmuir isotherm model [35]. When compared with data obtained for *Fenellia nivea,* the results are acceptable in 5 ppm Cd(II) solutions. The other research evaluated Cd(II) adsorption on *Penicillum simplicissimum* that followed Langmuir isotherm model with a $q_{\max}$ value of 61.35 mg/g for 50 ppm Cd(II) that obeys pseudo-second-order adsorption process with reaction rate constant of 2.41 × 10^{-3} g/mg min and calculated q_e is 19.61 mg/g that increase with temperature [1].

3.6. Thermodynamics of the biosorption

Thermodynamics of the biosorption process was evaluated to understand the favorability of biosorption (Fig. 9). The standard enthalpy change of adsorption ($\Delta H°$) was found to be 31.7 kJ/mol that is endothermic chemisorption as expected from previous data, the increase of adsorption capacity with temperature, and the value of dimensionless constant, R_L, that is zero that for irreversible processes. The standard entropy change of adsorption ($\Delta S°$) was found to be 0.12 kJ/mol. The reported values for the changes in standard Gibbs free energies were found to be –4.07, –4.53, and –9.41 kJ/mol for 288 K (15°C), 303 K (30°C), and 333 K (60°C), respectively, that indicate spontaneous biosorption. Thermodynamics of biosorption of Cd(II) on modified biomass ash, $\Delta H°$ and $\Delta S°$ were found to be 39.35 and 0.137 kJ/mol, respectively, that are close to the values in this study, $\Delta G°$ at 30°C, 45°C, and 60°C were found to be –2.31, –3.35, and –5.63 kJ/mol with a spontaneous biosorption process [37]. Thermodynamics of adsorption of Cd(II) on *Saccharum arundinaceum* was also evaluated by following adsorption data at different temperatures, $\Delta H°$ and $\Delta S°$ were found to be endothermic as 26.99 kJ/mol and as 2.11 kJ/mol K, respectively. The values of $\Delta G°$ were found to be –591.24, –612.34, –633.44, and –665.09 kJ/mol for 292, 303, 313, and 328 K, respectively [38].

4. Conclusions

In this study, newly isolated *F. nivea* biomass was used for the removal of toxic metal Cd(II). Batch experiments showed that the initial pH of the solution is the most significant parameter of cadmium biosorption and the highest Cd(II) removal occurred at higher pH values. Cadmium removal with *F. nivea* biomass is an endothermic process, Cd(II) removal rate increase with increasing temperature with positive standard molar enthalpy and entropy, negative standard Gibbs free energy that corresponds to spontaneous biosorption. Almost half the amount of Cd(II) is removed from the solution within the first 5 min of the reaction.

The adsorption of Cd(II) on biomass follows the Langmuir isotherm model with a value of dimensionless constant, R_L = 0, that corresponds to the irreversible adsorption process.

The kinetics of Cd(II) adsorption onto heat-inactivated *F. nivea* biomass fits better to pseudo-second-order model and theoretical adsorption capacity. q_e is determined as 4.53 mg/g where adsorption capacity is found as 4.80 mg/g, experimentally the similarity of theoretical and experimental results indicates that very efficient adsorption can be achieved in a short period of time for *F. nivea* biomass.

In conclusion, the results of this research show that heat-inactivated *F. nivea* biomass is a good candidate for metal removal, which is shown by using cadmium ions as model pollutants, from aqueous solutions.

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