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Original Research

Evaluating Forest Waste on Adsorption of Cd(II) from Aqueous Solution: Equilibrium and Thermodynamic Studies

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Abstract

The aim of this work was to investigate the adsorption potential of Uludag fir *(Abies nordmanniana subsp. bornmülleriana* Mattf.) on cadmium removal using batch experiments. The effect of parameters such as initial metal concentration, initial pH, biosorbent dosage, stirring speed, contact time and temperature was examined. The Langmuir and Freundlich models were applied to describe the equilibrium isotherms, and the biosorption process followed the Langmuir adsorption isotherms model with high coefficients of correlation at different temperatures. The kinetics of the sorption were analysed using the pseudo first-order and pseudo second-order kinetic models. The pseudo second-order kinetic model fit well in correlation with the experimental results. Moreover, the evaluated thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) showed that the sorption process was feasible, spontaneous and endothermic in nature. This study showed that Uludag fir *(Abies nordmanniana* subsp. *bornmülleriana* Mattf.) can be used as an effective and ecologically friendly biosorbent for removal of Cd(II) from aqueous solutions.

Keywords: adsorption, cadmium, Uludag fir (*Abies nordmanniana* subsp. *bornmülleriana* Mattf.), isotherms, kinetics

Introduction

The release of heavy metals to the environment due to industrialization and urbanization creates significant environmental pollution [1]. Heavy metals have direct toxic effects on living organisms unless there is a permanent dilution and sedimentation. Among the heavy metals, cadmium is one of the most widespread pollutants in the environment and is frequently released from various industries such as electroplating, metallurgy, phosphate fertilizers, pigments, nuclear, Ni-Cd batteries and other uses [2]. Cadmium usually is present as a divalent cation, Cd(II), and has high solubility in water in this form. Because it is not biodegradable in the environment, Cd(II) can easily be transported from one medium to another and eventually is enriched by bioaccumulation in the ecosystem [3]. Cd(II) enters into humans and other living organisms through contaminated water and the food chain, and can cause irreversible damage [4]. This

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Cd(II) pollution can lead to serious illnesses such as kidney damage, renal disorder, human carcinogen, and high blood pressure [5, 6]. For this reason, the use of an effective and economical method for removing Cd(II) from aquatic systems is an important issue for human health and the ecosystem [7].

Today, several techniques are applied to remove heavy metal contamination, such as chemical precipitation, reverse osmosis, membrane separation, ion-exchange methods and the biosorption process. Among these methods, the most economical and efficient process is biosorption process. Also, it is significantly necessary to develop alternative inorganic or organic sorbents that are inexpensive and abundant in the environment for removing heavy metals in biosorption processes. The search for cheap sorbents in biosorption applications has led to the search for the ability of forest and agricultural wastes to remove heavy metal ions. There are several studies on heavy metal removal using forest and agricultural waste such as bark from pinuspinaster [8]; sawdust of beech, linden and poplar trees [9]; pine cone powder [10]; castor seed hull [11]; cashew nut shell [12]; wheat straw [13]; bark, chestnut bur, sawdust, pinecone, pine needle and pine-nut cone [14]; and *Pinus sylvestris* L. [15].

In this study, Uludag fir (*Abies nordmanniana* subsp. *bornmülleriana* Mattf.) of forest waste was evaluated as a biosorbent for removing Cd(II) from aqueous solution using the batch sorption technique. The effect of parameters, including initial metal concentration, initial pH, biosorbent dosage, stirring speed, temperature and contact time were studied. Two isotherm models (Langmuir and Freundlich) were applied to describe the distribution of metal ions between the liquid phase and the solid phase at constant temperature. Moreover, kinetic (pseudo first-order and pseudo second-order) and thermodynamic (ΔG^0, ΔH^0, ΔS^0) behaviors of the Cd(II) ions onto Uludag fir were carried out to get information about adsorption studies.

Material and Methods

Chemicals

All purchased chemicals were analytical grade provided by Sigma Aldrich. Cd(II) solutions were prepared from the $CdCl_2$ salt in analytical purity. A standard stock Cd(II) solution was prepared at a concentration of 250 mg/L and desired concentrations (5-50 mg/L) of cadmium were prepared by making various dilutions using stock solution with distilled water. The pH was adjusted using diluted 0.1 M HCl and 0.1 M NaOH solution.

Preparation of Biosorbent

Uludag fir (*Abies nordmanniana* subsp. *bornmülleriana* Mattf.) was selected in these experiments as a biosorbent and obtained from Bartin, Turkey. This material was washed with distilled water and dried at 80ºC for 24 hours. The dried biomass was ground and sieved through a 0.5-1 mm particle size.

Experimental Apparatus

Biosorption experiments were carried out in 250-mL Erlenmeyer flasks using 100 mL (25 mg/L) metal-bearing solution with 5g/L of the dried adsorbents. The sample was stirred for 180 min. using an orbital shaker (Jeio Tech IST-4075R) at a constant stirring speed of 150 rpm. After the adsorption process, the solution was centrifuged for 5000 rpm using a Nüve NF200 centrifuge. The concentrations of Cd(II) in the solutions before and after adsorption were determined by a Shimadzu AA7000 atomic adsorption spectrophotometer.

Results and Discussion

Effect of Initial Metal Concentrations

The effect of initial Cd(II) concentrations onto adsorption performance in the range of 5 mg/L to 50 mg/L was studied. The results are shown in Fig. 1. It has been seen that the removal efficiency of Cd(II) decreased as the initial concentration was increased and the maximum initial metal concentration was found to be 5 mg/L (93.6%). Moreover, adsorption capacity increased from 0.94 mg/g to 5.79 mg/g while the initial Cd concentration was increased from 5 mg/L to 50 mg/L. As the concentration of Cd (II) increases, the driving force increases, and the diffusion of Cd(II) ions from the solution to the adsorbent surface accelerates. Moreover, adsorption efficiency decreased with increasing initial concentration because of the lack of active binding sites. It is easier to bind the Cd(II) ions to the biosorbent at low initial concentrations because there is sufficient binding area for the metal ions.

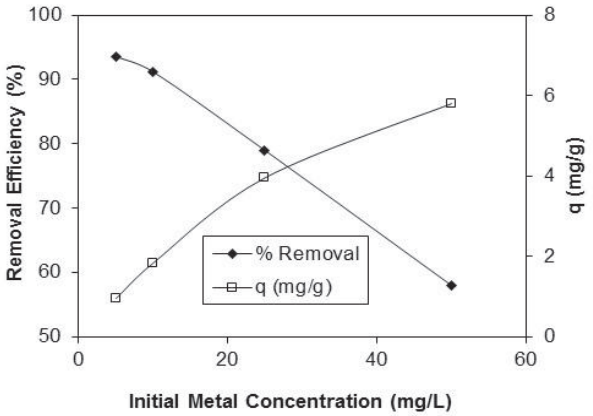

Fig. 1. Effect of initial Cd(II) concentrations.

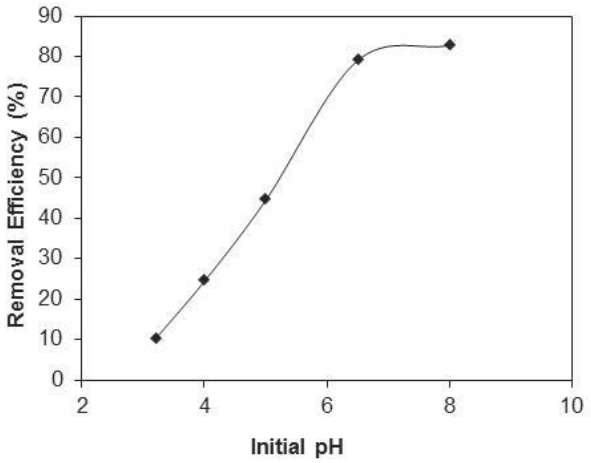

Fig. 2. Effect of initial pH.

Effect of Initial pH

The pH of the medium is an important parameter because hydrogen and hydroxyl ions may strongly affect the biosorption mechanism, such as the type of metal ions and the surface properties of the adsorbent. Thus, adsorption performance is significantly influenced by the initial pH for removal of metal ions. In this study, the effect of initial pH at 3.2-8.0 on Cd(II) removal was investigated and the results are presented in Fig. 2. The adsorption efficiency increased from 10.1% to 78.9% with the increase of pH from 3.2 to 6.5. Adsorption efficiency changed very little in pH range of 6.5-8.0. According to the results, hydrogen ions and metal ions are in competition, which leads to reduced efficiency at low pH values. As the pH value increases, the hydrogen ion concentration in the solution decreases and the negative charge on the adsorbent surface increases. This positively affects the adsorption of Cd(II) ions and increases adsorption efficiency [16]. The optimum pH value was found to be 6.5 and this pH value was used in subsequent studies.

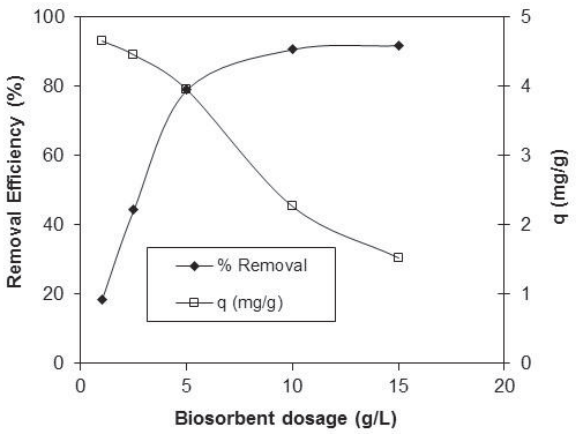

Fig. 3. Effect of biosorbent dosage.

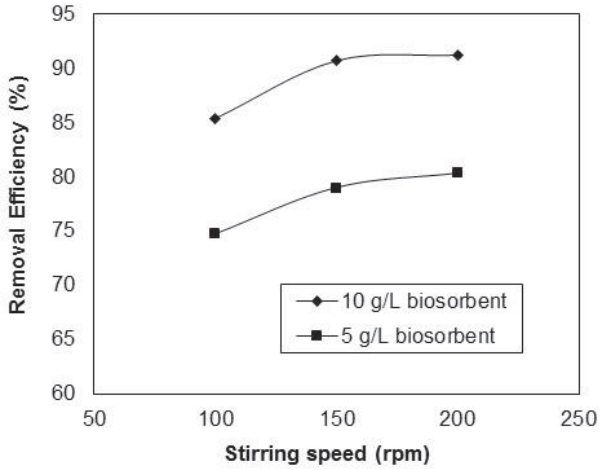

Fig. 4. Effect of stirring speed.

Effect of Biosorbent Dosage

The effect of biosorbent dosage was investigated in the range of 1-15 g/L and the results are presented in Fig. 3. The removal efficiency of Cd(II) increased from 18.6% to 91.8% as the biosorbent dosage was increased from 1g/L to 15 g/L. According to the results, when the biosorbent dosage is increased from 1 g/l to 10 g/L, the adsorption efficiency is increased rapidly. Moreover, there was no significant change in removal efficiency at 10 and 15 g/L biosorbent dosage. When the adsorbent dosage increases, the biosorbent surface area and suitable active binding sites for binding of the Cd(II) ions to the surface of biosorbent are increased, resulting in increased adsorption efficiency.

Effect of Stirring Speed

The effect of stirring speed was studied in the range of 100-200 rpm at 5 and 10 g/L and the results are shown in Fig. 4. According to the result, as the stirring speed increased from 100 to 200 rpm, removal efficiency of Cd(II) increased from 74.7% to 80.3% at 5 g/L and from 85.3% to 91.2% at 10 g/L. As seen from the results, stirring speed did not significantly affect removal efficiency – especially when the mixing speed was increased to 150 rpm or 200 rpm.

Effects of Temperature and Contact Time

In this study, the effect of temperature was investigated in the range of 15-45°C and the results are presented in Fig. 5. According to the obtained data, as the temperature increased from 15ºC to 45ºC, removal efficiency increased, but there was not much change in adsorption efficiency. Higher temperatures generally increase biosorption performance due to increased surface activity and kinetic energy of the solute [17]. The increase in surface activity suggests

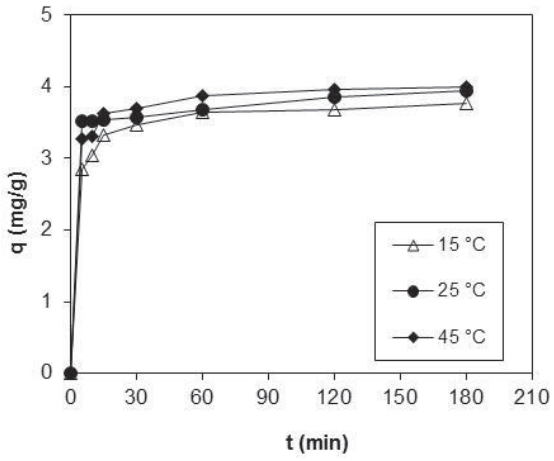

Fig. 5. Effect of temperature and contact time.

that the adsorption between Cd(II) and Uludag fir is endothermic. In addition, when the contact time is examined, it was observed that from Fig. 5, the adsorption of Cd is very fast because of the presence of many suitable binding sites and larger surface area in the first 15 min. The adsorption proceeds slowly after 15 min. due to the decrease of the binding sites, and the biosorption equilibrium occurred within 60 min. After this equilibrium time, the amount of biosorbed cadmium ions did not significantly change with time.

Adsorption Isotherms

The isotherms data were characterized by the Langmuir and Freundlich equations. Linear form of the Langmuir and Freundlich isotherms is given by Eqs. (1) and (2), respectively:

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

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

…where q_m is maximum adsorption capacity (mg/g) and K_L is the Langmuir constant (L/mg). When $1/q_e$ was plotted against $1/Ce$, the values of q_m and K_L were obtained from the slope and intercept of the fitted line, respectively. K_f and n are the Freundlich constants. These parameters can be determined from the plot of log q_e vs. logCe. In this study, the Langmuir and Freundlich models were applied to describe the equilibrium isotherms at different temperatures (15-45ºC). The biosorption isotherms are presented in Table 1. Comparing the R^2 values between Freundlich and Langmuir models, the Langmuir equation has better values for the adsorption of Cd(II) than the Freundlich equation at all temperature values. According to the obtained data, the biosorption process followed the Langmuir adsorption isotherms model with high coefficients of correlation at different temperatures (R^2>0.99). The maximum biosorption capacity q_m for Cd(II) at 45ºC was obtained as 3.915 mg/g.

Adsorption Kinetics

Knowledge of the kinetics of any biosorption process is crucial in order to explain the sorption mechanisms. The kinetic characteristics of adsorption process were described by pseudo first-order rate Eq. (3) and pseudo second-order equation Eq. (4):

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) \cdot t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{t}{q_e} \quad (4)$$

…where t is the contact time (min); k_1 is the first-order adsorption rate constant (min^{-1}), and q_e and q_t are adsorption capacity at equilibrium and time t, respectively (mg/g). When $log(q_e - q_t)$ was plotted against t, the values of q_e and k_1 were obtained from the slope and intercept of the fitted line, respectively. k_2 is the second-order adsorption rate constant (g/mg min). When t/q_t was plotted against t, the values q_e and k_2 were determined from the slope and intercept of the plot, respectively. Finally, initial sorption rate Eq. (5) is:

$$h = k_2 (q_e)^2 \quad (5)$$

…where h is the initial sorption rate (mg/g min). The kinetic studies were applied at 15ºC, 25ºC, and 45ºC, and the results are shown in Table 2 and Fig. 6 (a-b).

Table 1. Langmuir and Freundlich isotherm parameters for the biosorption of Cd(II).

Freundlich Isotherms				Langmuir Isotherms		
T (ºC)	K_f	n	R^2	q_m, (mg/g)	K_L, (L/mg)	R^2
15	1.553	2.554	0.932	2.672	1.941	0.999
25	1.726	2.320	0.975	3.508	1.501	0.995
45	1.904	2.359	0.962	3.915	1.589	0.991

Table 2. Kinetic parameters for biosorption of Cd(II).

T (°C)	Pseudo first-order				Pseudo- second order			
	$q_{e,exp}$	k_1(1/min)	$q_{e,cal}$(mg/g)	R^2	$q_{e,cal}$(mg/g)	k_2(g/mg min)	h(mg/g min)	R^2
15	3.680	0.024	1.073	0.705	3.805	0.107	1.549	0.999
25	3.910	0.020	0.852	0.570	3.962	0.114	1.785	0.999
45	3.950	0.032	1.074	0.820	4.031	0.125	2.035	0.999

In the pseudo second-order kinetic model, the R^2 value was found to be higher than the pseudo first-order model. Also $q_{e,cal}$ and $q_{e,exp}$ values are found to be closer in the pseudo second-order model. This indicates that the pseudo second-order model is more suitable for biosorption of Cd(II).

Activation Energy

Activation energy is determined according to the Arrhenius equation Eq. (6):

$$\ln k = \left(\frac{-E_a}{RT}\right) + \ln A \tag{6}$$

…where E_a is activation energy, T is temperature (Kelvin), R is the gas constant (8.314 J/mol.K) and A is a constant (frequency factor). E_a was calculated from the slope of *ln k* versus *1/T* plot. In this study, activation energy for the biosorption of Cd(II) onto Uludag fir was determined. The results are presented in Fig. 7. The activation energy of biosorption (E_a) and correlation coefficient (R^2) were found to be 3.984 kJ/mol and 0.99, respectively. According to the results, it can be said that biosorption of Cd(II) by Uludag fir is physisorption. There are two types of adsorption, including physical and chemical. The activation energy for physical adsorption is usually not more than 4.2 kJ/mol, since the forces involved in physical adsorption are weak. Chemical adsorption is specific and involves forces much stronger than in physical adsorption. Two kinds of chemical adsorption are encountered, activated and, less frequently, nonactivated. Activated chemical adsorption means that the rate varies with temperature according to a finite activation energy (between 8.4 and 83.7 kJ/mol) in the Arrhenius equation (high E_a). However, in some systems chemisorption occurs very rapidly, suggesting that the activation energy is near zero. This is termed non-activated chemisorption [18, 19].

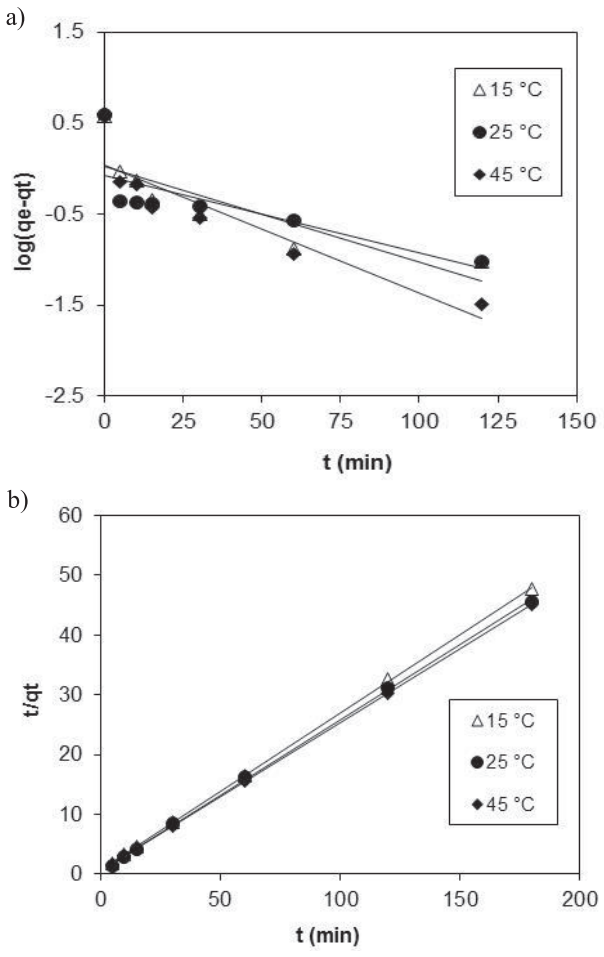

Fig. 6. Plots if biosorption kinetic equations: (a) pseudo first-order and (b) pseudo second-order biosorption kinetics.

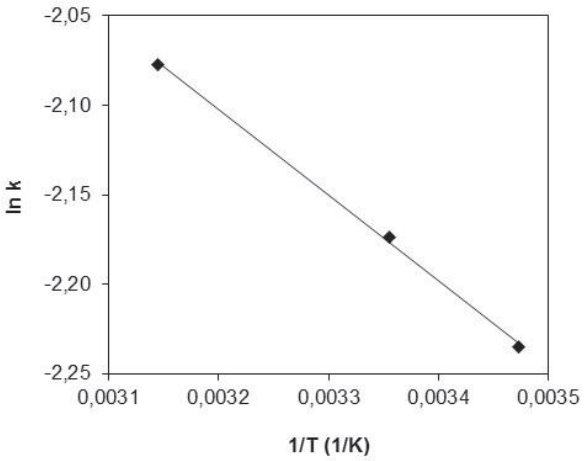

Fig. 7. Activation energy.

Table 3. Thermodynamic parameters for the biosorption of Cd(II).

ΔH^0 (kJ/Kmol)	ΔS^0 (J/mol K)	ΔG^0 (kJ/mol)		
		15	25	45
0.970	96.218	-17.895	-19.248	-20.840

Thermodynamic Parameters

Thermodynamic parameters of standard Gibbs free energy ($\Delta G°$), standard enthalpy ($\Delta H°$) and standard entropy ($\Delta S°$) were determined:

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (7)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (8)$$

$$K_d = \frac{q_e}{C_e} \quad (9)$$

...where K_d is the distribution coefficient for adsorption, T (K) is the temperature, and R ($J \cdot mol^{-1} \cdot K^{-1}$) is the gas constant. The amounts of $\Delta H°$ *and* $\Delta S°$ could be calculated from the slope and intercept of the straight line obtained by plotting ln *Kd* against 1/*T*, respectively. Values of thermodynamic parameters should be taken into consideration in order to determine the spontaneity, feasibility and nature of the biosorption process. [15, 20]. The values of ΔG^0, ΔH^0, and ΔS^0 are presented in Table 3. In this study, negative ΔG^0 values for all studied temperatures showed that the biosorption |process was feasible and spontaneous. The positive value of ΔH^0 (0.970 kJ/Kmol) indicated that the biosorption process is endothermic. Moreover, the positive value of ΔS^0 (96.218 J/mol K) indicates the randomness at the biosorbent-solution interface.

Conclusions

The objective of this work was to evaluate the application of Uludag fir (*Abies nordmanniana subsp. bornmülleriana* Mattf.) as biosorbent for the removal of Cd(II) from aqueous solutions by batch biosorption experiments. The parameters, including initial Cd(II) concentrations, initial pH, adsorbent dosage, stirring speed, temperature and contact time, were investigated. According to the results, the biosorption process was strongly affected by these parameters. Also, the Langmuir and Freundlich models were used to describe the equilibrium biosorption data of Cd(II) onto Uludag fir. The equilibrium data fits Langmuir adsorption isotherms model, and adsorption capacity was found to be 3.915 mg/g at optimized conditions. Adsorption kinetics of Cd(II) follow the pseudo second-order model. Thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) also showed that the sorption process was feasible, spontaneous and endothermic in nature. The activation energy of biosorption (E_a) and correlation coefficient (R^2) was found to be 3.984 kJ/mol and 0.99, respectively. The results obtained showed that this environmentally friendly, efficient and low-cost Uludag fir (*Abies nordmanniana subsp. bornmülleriana* Mattf.) as a biosorbent can be useful for the removal of Cd(II) from aqueous solutions.

Acknowledgements

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Conflict of Interest

The authors have not declared any conflict of interest.

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