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Dedicated to the memory of
Professor Candin Liteanu on his 100th anniversary

BIOSORPTION OF Cd(II) ON UNTREATED FIR CONE POWDER: KINETIC AND EQUILIBRIUM ISOTHERM STUDIES

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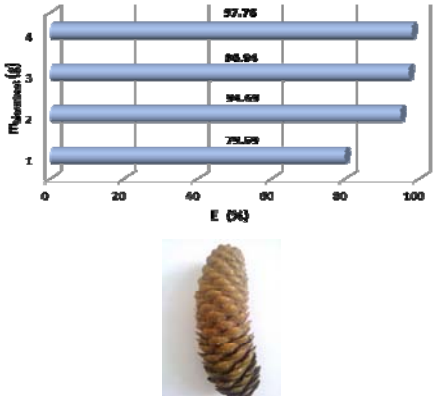
In the present paper, the biosorption of Cd(II) on untreated fir cone powder obtained from Roumanian fir tree (*Abies alba)* was investigated in aqueous solution. The effect of particle size, biomass quantity, agitation speed, contact time, initial Cd(II) concentration, initial pH of solution and temperature was studied in batch conditions mode. The favorable pH for maximum Cd(II) biosorption was at 8.2. Equilibrium data were analysed by the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models. The studies show that the Langmuir isotherm gave a better fit indicating monolayer coverage of the biosorbent surface. Pseudo-first-, pseudo- second-order, intra-particle and film diffusion models were used to describe the kinetics data. The pseudo-second order was found to better model in the kinetics of Cd(II) biosorption. It can be concluded that the fir cone powder could be a promising and effectively employed biosorbent for Cd(II) removal from aqueous solutions.



INTRODUCTION

The presence of heavy metals in environment becomes a problem due to their harmful effects on human health.[1] The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. The problem of removing pollutants from water and wastewater has grown with rapid industrialization.[2]

Cadmium (Cd) is one of the heavy metals considered being toxic to humans and aquatic life. Chronic exposure to cadmium can affect the nervous system, liver, cardiovascular system and may lead to renal failure and death in mammals and humans.[3,4]

At present, a number of technologies, such as chemical precipitation, evaporation, electroplating, adsorption and ion exchange processes are used for the treatment of heavy metal-containing wastewater streams.[3] Biosorption is considered a flexible and alternative method, easy to operate, with much less sludge disposal problems. Biosorption has been shown to be a cost effective and efficient option since the biosorbent material is naturally available and cheap.[5]

Fir (*Abies alba*) tree is a genus evergreen coniferous tree in the family *Pinaceae*, and there

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are present in large amounts across in the forests of Roumanian. Fire cones are the organ on plants in division *Pinophyta* (conifers) that contains the reproductive structures; these cones represent unutilized natural material that can be used as an ideal biosorbent on heavy metal removal from aqueous solutions.

Fir cone, like other natural materials: pine cone,[6] fly ash,[4,7] wood barks,[8,9]are buildup of lignocellulose materials, *i.e.* contains mainly cellulose, hemicellulose and lignin. Fir cone as pine cone is composed of mainly cellulose (18.8%), hemicellulose (46.5%), and lignin (37.4%).[6]

Fir tree (*Abies alba*) cone powder was chosen as a biosorbent material in this study because it is eco-friendly and economical, and there are no information in the literature regarding the removal of cadmium ions from aqueous solutions.

The aim of this work is to study the removal of Cd (II) from aqueous solution by adsorption on fir cone powder in batch mode. We determined the adsorption kinetics and isotherms, modeled by rate and diffusion equations using Langmuir, Freundlich, Dubinin-Radushkevich and Tempkin models. The influence of various operating parameters such as initial solution pH, temperature, particle size, biomass quantity, agitation speed, contact time and initial Cd(II) concentration of the solution onto biosorption process was investigated.

MATERIALS AND METHODS

1. Material

Fir tree (*Abies alba*) cones were collected from a botanical garden in Cluj-Napoca, Roumania. The fir cones were washed several times to remove surface impurities and then dried in an oven at 105°C for 24 h. The scales on the cones were then removed and crushed using a bead mill. Before using, the fir cone biomass was washed with distilled water several times until it yielded colorless filtered water. The obtained fir cone powder was then grinded and sieved, particles between 200 and 400 μm were collected and used for analysis.

2. Preparation of Cd(II) solutions

A stock solution of 1000 mg/L of cadmium(II) was prepared by dissolving a weighed amount of $Cd(NO_3)_2 \times 4H_2O$ in 1000 ml distilled water. The required concentrations for all the biosorption experiments were obtained by diluting with distilled water to the concentrations range between 49-240 mg/L of the stock solution. The initial pH of solution was adjusted using HCl and NaOH solutions. All chemicals were of analytical grad.

3. Batch experiments

The biosorption of cadmium onto fir cone powder was studied in batch conditions. Experiments were carried out contacting a known weight of biosorbent (1-4 g) at different stirring rates (200-400-500 rpm) was equilibrated with 100 mL of Cd (II) ions solution of known concentration (49-240 mg/L) in 250 ml of Berzelius glasses at different temperatures using a thermostat water bath (298-326 K). In order to establish the evolution of the removal process, samples of 100 μL were collected at different time intervals (5-240 min).

The collected samples at predetermined time intervals were filtered (ME cellulose 0.45μm microfilter) and the remaining concentration in aqueous phase was determined using an Atomic Absorption Spectrometer (SensAA Dual GBS Scientific Equipment, Australia). The evaluation of the Cd(II) uptake at equilibrium for the fir cone powder samples was realized using adsorption capacity, q_e (mg/g) and removal efficiency, E (%) values.

In order to study the initial pH influence over the biosorption process, the initial pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. The experiments carried out using 100 ml solution of 49 mg Cd(II)/L, which was contacted with 4 g fir cone powder at 23°C for 240 min.

All experiments were conducted in triplicate and mean values were used.

RESULTS AND DISCUSSION

1. Effect of particle size

Different particle sizes of biosorbent, 200-400-600-1200 μm, were used to examine the effect of the granularity to the biosorption. The percent removal of Cd(II) from particle size ranges of 1200-600 μm and 400-200 μm was 62.76%-73.67% and 77.14%-74.59%, respectively. Therefore, the removal efficiency for Cd(II) decreased with the increase in the particle sizes of fir cones biomass. These results are in accordance

with the increasing of particle surface size. Taking into account that after grinding large amounts of 200-400 μm particle size fir cone powder was obtained and the differences on the removal efficiency values between < 200 μm are very closed, therefore a particle size of 200-400 μm was chosen for the future experiments.

2. Effect of biomass quantity

The effect of biomass quantity on the equilibrium uptake of Cd(II) was investigated with biosorbent masses of 1, 2, 3 and 4 g, results are presented in Fig. 1. The increase in the biomass quantities, from 1 to 4 g, increases removal of Cd(II) ions from 79.59% to 97.76%. Major changes in the removal efficiency can be observed at quantities between 1 and 2 g, then a linear increase take place from 2 g to 4 g biomass quantity. This effect could be explained by the availability of more adsorption sites on biosorbent surface and by increasing on total functional groups. Higher biomass quantities do not enhance the removal efficiency, thus, optimum biomass quantity of fir cone powder for biosorption of Cd(II) is found to be 4 g.

3. Effect of agitation speed

Three different agitation speeds as 200, 400 and 500 rpm were selected for the biosorption of Cd(II) on fir cone powder biomass. The adsorption capacity (mg/g) of Cd(II), increased with increase in agitation speed. The removal of Cd(II) was found to be 3.48 mg/g, 3.62 mg/g and 3.68 mg/g for 200, 400 and 500 rpm agitation speed, respectively. So, all subsequent experiments conducted at an agitation speed of 500 rpm.

4. Effect of initial pH of solution and temperature

The effect of initial pH of solution onto Cd(II) biosorption from aqueous solution by fir cone powder was investigated over an initial of pH range between 2.7-8.2. As Fig. 2 shows, at initial pH = 2.7 the amount of cadmium removed from solution is smaller in comparison with the other initial pH tested. The low removal efficiency value (95.31%) obtained could be attributed to competition between Cd^{2+} ions and H^{+} for active sites on the biosorbent surface. As the initial solution pH increased, an increase in the removal efficiencies is observed, where the maximum removal percent was attained at initial pH = 8.2 (E = 98.65%). It was observed that during the biosorption process, the biosorbent set the initial pH value to 5.5 attained at equilibrium (after around 80 min) for all initial pH of solution studied. However, with increasing of pH, the competition protons (H^{+}) decreases and Cd(II) can be adsorbed on negatively charged sites of the bisosorbent surface. Studies beyond 8.2 were not attempted because precipitation of the hydroxides would be likely to occur.

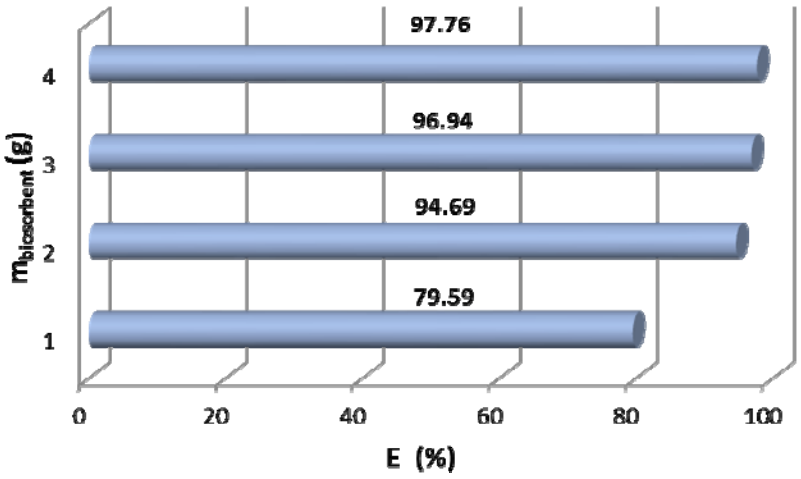

Fig. 1 – The effect of the fir cone powder quantity on Cd (II) biosorption over the removal efficiency; C_i = 49 mg Cd(II)/L, d = 200-400 μm, 296 K, 5.41 pH and 500 rpm.

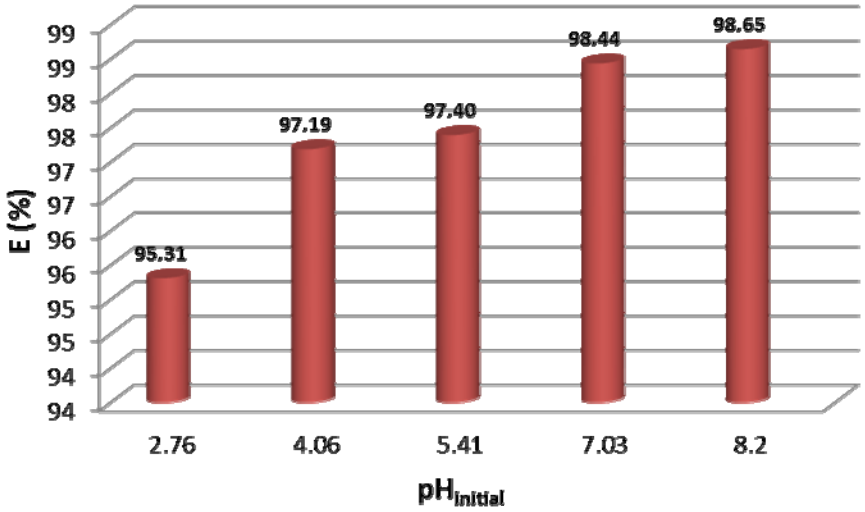

Fig. 2 – The effect of initial pH values on Cd (II) biosorption using fir cone powder; C_i = 49 mg Cd(II)/L, d = 200-400 µm, 4g biosorbent, 296 K and 500 rpm.

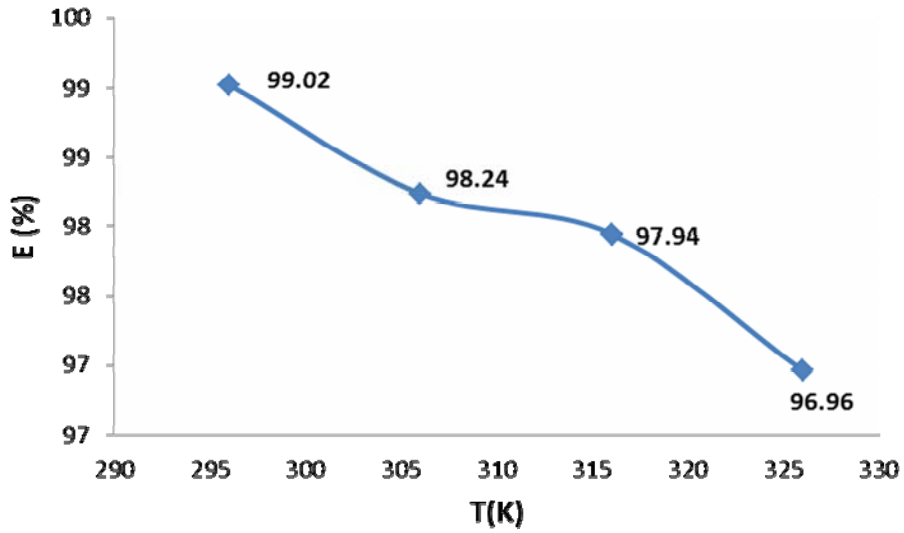

Fig. 3 – Temperature influence over the removal efficiency of Cd (II) on fir cone powder; C_i=49 mg Cd(II)/L, d = 200-400 µm, 4 g biosorbent, 5.41 pH and 500 rpm.

Similar results were reported for the removal of Cd(II) ions from aqueous solutions using activated fir tree cone with Fenton reagent.[10]

Fig. 3 shows the relationship between temperature and removal efficiency values for Cd(II) biosorption at various temperatures (using a thermostat water bath) from 23°C (296 K) up to 53°C (326 K). The result shows that with increase of medium temperature from 296 to 326 K, the maximum percentage for Cd(II) removal decrease gradually, which indicates an exothermic process. Recent study showed that the biosorption of Cd(II) using fir tree (*Abies alba*) sawdust is endothermic in nature,[11] compared with the present study (cones obtained from the same trees) who presents an exothermic process. This could be explained with the differences in the main constituents (cellulose, lignin and hemicellulose) percentage between the two biomasses.

It can be concluded that the Cd(II) biosorption is not enhanced by increased medium temperature.

5. Effect of initial Cd(II) concentration and contact time

The biosorption of Cd(II) was carried out at different initial ion concentrations ranging from 49 to 240 mg/L contacting 4 g fir cone powder, pH = 5.41, 500 rpm stirring rate at room temperature (23°C) with 240 min of contact time (until

equilibrium was reached). The studies showed that as higher was the initial Cd(II) concentration, more metal ions was adsorbed per unit weight at equilibrium, the results are presented in Fig. 4. From the experimental studies, it was shown that the adsorption capacity of Cd(II) ion increased from 1.20 mg/g (C_i = 49 mg Cd(II)/L) to 3.91 mg/g (C_i = 240 mg Cd(II)/L) with the increasing of the initial Cd(II) concentration. The increase in adsorption capacity is due to the higher adsorption rate and the utilization of all available active sites for adsorption at higher Cd(II) concentration. On the other hand, increasing the initial Cd(II) concentration, the adsorption capacity, the amount adsorbed per unit mass of biosorbent will decrease, mainly due to saturation of adsorption sites during the biosorption process.

The biosorption of Cd(II) was studied as a function of contact time and results are presented in Fig. 5. Biosorption increase rapidly with increasing contact time and equilibrium was attained in less than 80 min where a final plateau is observed. However, the contact time in this study was set to 240 min, time, where the final equilibrium was attained, thus completing the biosorption process.

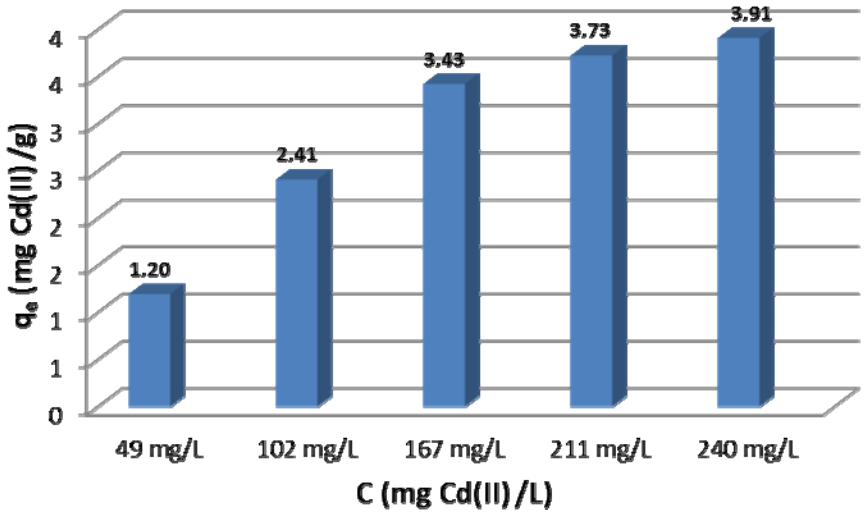

Fig. 4 – Influence of the initial Cd(II) concentration over the adsorption capacity on fir cone powder; 4g biosorbent, d = 200-400 µm, 296 K, 5.41 pH and 500 rpm.

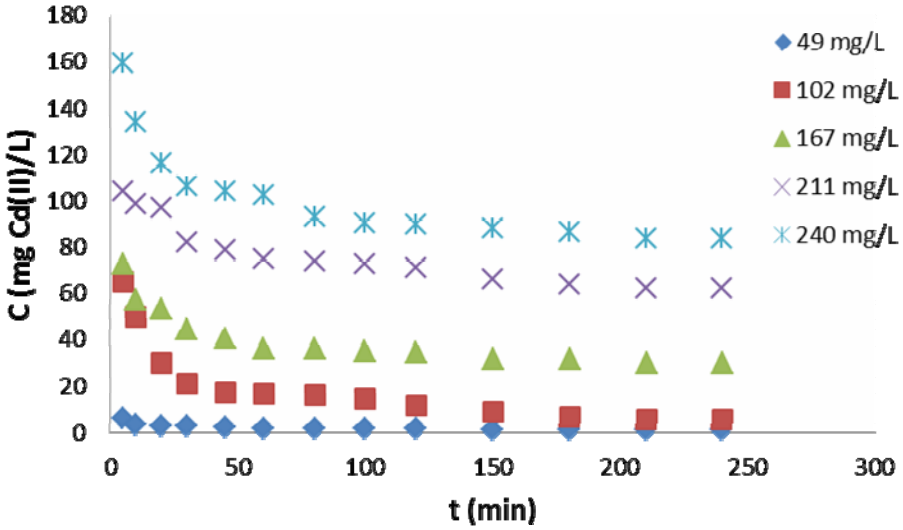

Fig. 5 – Effect of contact time over and initial concentration on the biosorption of Cd (II) ions on fir cone biosorbent; d = 200-400 µm, 296 K, 5.41pH, 500 rpm.

6. Biosorption kinetics

In order to investigate the mechanism of adsorption, pseudo-first-order and pseudo-second order, intra-particle and liquid film diffusions kinetic were used to test the experimental data.

Lagergren proposed a pseudo-first-order kinetic model, this model is the most widely used for the adsorption of a solute from a liquid solution.[12] This model was applied for our experimental data.

Experimental data were also tested using the Ho and McKay pseudo-second order model which is beside on the assumption that the adsorption follows second-order chemisorption.[13] A comparison of the pseudo-first-order and pseudo-second-order adsorption rate constant at different initial metal ions concentrations is presented in Table 1. The validity of the used models is verified by the correlation coefficient, R^2. The calculated correlation coefficients are less than 0.9048 for the first-order kinetic model, whereas the values of the correlation coefficient are bigger than 0.9991 for the pseudo-second kinetic order model. Moreover, the theoretical $q_{e,calc}$ values were closer to the experimental theoretical $q_{e,exp}$ values (Table 1). These results suggest that the pseudo-second-order mechanism is predominant and that chemisorption might be the rate-limiting steps that control the adsorption process. Chemisorption is usually restricted to just one layer of molecules on the surface, although it may be followed by additional layers of physically adsorbed molecules. [14, 15]

In order to study the mass transfer process, two diffusion models, intra-particle and liquid film models were applied.[16]

The possibility of intra-particle transport in the current study was explored by using the Weber-Morris equation, whereby the intra-particle diffusion is characterized by the relationship between specific sorption (q_t) and the square root of time ($t^{1/2}$). Intra-particle models show that the mass transfer process takes places in three steps, ascribed to boundary layer diffusion (liquid film diffusion), intra-particle diffusion, and to the final equilibrium stage.[16,17] This model were also applied and studied in detailed on the removal of Cd(II) using NaOH and H_2O_2 treated fir tree sawdust.[17] Plots of $t^{1/2}$ versus q_t are shown in Table 2 for the initial Cd(II) concentrations ranging from 49-240 mg/L. The plots reveal that the intra-particle diffusion line is straight line that does not pass through the origin indicated that intra-particle diffusion in not the only rate the determining mechanism and that some other mechanisms are involved.[18]

Table 1

Pseudo-first-order and pseudo-second-order rate constants, calculated and experimental q_e values for Cd(II) biosorption on fir cone powder biomass using different initial concentrations; C_i = 49-240 mg/L, 4g biosorbent,d = 200-400 μm, 296 K, pH 5.4, 500 rpm

C (mg/L)	q_e (exp) (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (1/min)	q_e (calc) (mg/g)	R^2	k_2 (g/mg·min)	q_e (calc) (mg/g)	R^2
49	1.20	1.93×10^{-2}	0.12	0.6728	79.07×10^{-2}	1.20	1
102	2.41	1.96×10^{-2}	0.22	0.9048	42.13×10^{-2}	2.49	0.9992
167	3.43	1.99×10^{-2}	0.97	0.8498	7.54×10^{-2}	3.47	0.9999
211	3.73	1.94×10^{-2}	1.05	0.8994	4.44×10^{-2}	3.79	0.9991
240	3.91	1.82×10^{-2}	1.34	0.8788	3.74×10^{-2}	4.00	0.9996

Table 2

Intra-particle diffusion rate coefficients for Cd(II) biosorption on fir cone powder biomass using different initial concentrations; C_i = 49-240 mg/L, 4g biosorbent, d = 200-400 μm, 296 K, pH 5.4, 500 rpm

C (mg/L)	D (cm^2/s)	Region 1, 10-45 minutes		Region 2, 45-150 minutes		Region 3, 150-240 minutes	
		k_{ip} (mg/g·$min^{1/2}$)	R^2	k_{ip} (mg/g·$min^{1/2}$)	R^2	k_{ip} (mg/g·$min^{1/2}$)	R^2
49	7.60×10^{-8}	0.019	0.6561	0.0028	0.8361	1.2×10^{-3}	0.7677
102	8.40×10^{-8}	0.275	0.9361	0.4580	0.9485	1.52×10^{-2}	0.7677
167	2.09×10^{-8}	0.169	0.9176	0.0229	0.8846	1.83×10^{-2}	0.7677
211	1.35×10^{-8}	0.150	0.9149	0.0468	0.8666	1.89×10^{-2}	0.7619
240	1.20×10^{-8}	0.305	0.8837	0.0731	0.7818	0.355×10^{-1}	0.7677
Intercept:		1.06 – 1.56		1.16 – 2.95		1.18 – 3.40	

Table 3

Liquid film diffusion rate coefficients for Cd(II) biosorption on fir cone powder biomass;
C_i = 49-240 mg/L, 4g biosorbent,d = 200-400 μm, 296 K, pH 5.4, 500 rpm

C (mg/L)	**k_{fd} (1/min)**	**Intercept**	**R^2**
49	0.015	- 2.81	0.9058
102	0.018	- 0.85	0.9183
167	0.017	- 1.57	0.9302
211	0.016	- 1.27	0.9463
240	0.018	- 1.13	0.9437

Table 4

Isotherm constants for Cd(II) biosorption on fir cone powder biomass;
C_i = 49-240 mg/L, 4g biosorbent, 200-400 μm, 296 K, pH 5.4, 500 rpm

Dubinin-Radushkevich			**Temkin**		
β (mol^2 kJ^2)	**E (kJ mol^{-1})**	**R^2**	**A_T (L g^{-1})**	**B (J mol^{-1})**	**R^2**
2×10^{-9}	5	0.9705	2.11	7×10^{-5}	0.9923
Langmuir			**Freundlich**		
K_L (L/mg)	**q_{max} (mg/g)**	**R^2**	**n**	**K_f($mg^{(1-1/n)}L^{1/n}$/g)**	**R^2**
0.169	3.74	0.9935	3.8	1.31	0.9481

The liquid film diffusion model namely external mass transfer may be a applied to determinate the transport of the solute molecules from the liquid phase up to the solid phase boundary.[18, 19] Liquid film diffusion rate constants -ln(1-F) against t plots intercepts, Table 3, were determined. The fact that none of the mentioned linear plots not exhibit zero intercepts, this suggest that the process is not controlled by diffusion through the liquid film surrounding the biosorbent grains.[19]

7. Biosorption isotherm model

The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable that can be used for design purpose. In the present study, the equilibrium data obtained for the biosorption of Cd(II) ions onto fir cone powder were analyzed by considering the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models.[11,20-22]

Langmuir isotherm represents the equilibrium distribution of cadmium ions between the solid and liquid phases, valid for monolayer adsorption onto specific homogenous sites. The Langmuir constant, q_m, which is measure of monolayer adsorption capacity is calculated as 3.74 mg/g and Langmuir constant, K_L, which denotes adsorption energy, is calculated as 0.169 L/mg which confirm favorable Cd(II) biosorption process using fir cone powder (Table 4).

The Freundlich isotherm is used to describe the adsorption characteristics for the heterogeneous surface. The Freundlich constants were calculated along with the coefficient of determination R^2 and these values are given in Table 4. The values for K_F and n are 3.8 and 1.31, respectively.

Comparing the coefficient of determination for these two models it can be concluded that the experimental data fitted better to Langmuir model (R^2 = 0.9935). They were worse fitted to Freundlich biosorption isotherm as it was evidence from the lower obtained value of R^2 (0.9481).

The Dubinin-Radushkevich isotherm expresses the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The Dubinin-Radushkevich isotherm parameters are shown in the Table 4. If E values are between 8 and 16 kJ mol^{-1}, the biosorption process is chemically and if E < 8 mol^{-1} the biosorption process is physically.[23,24] In our case the mean free energy was 5 mol^{-1} indicating a physisorption process.

Temkin assumes that the heat of adsorption of all molecules the layer would decrease linearly rather than logarithmic with coverage. Taking into consideration the calculated value of the constant related to heat of sorption, B, which has a value smaller than 20 kJ mol^{-1} we concluded that according to this isotherm the sorption process takes place as physisorption (Table 4).[23,25] This result confirms the result obtained from Dubinin-Radushkevich isotherm.

CONCLUSIONS

Biosorption study of untreated fir tree (*Abies alba*) cones biomass has proven to be a highly effective and promising adsorbent for the removal of cadmium ions from aqueous solutions. This biosorbent is widely available as a natural material, is mechanically stable, and most importantly it is eco-friendly. Cd(II) biosorptions and removal efficiency may be influenced by a number of factors, such as effective of particle size, biomass quantity, agitation speed, initial solution pH, temperature, contact time, and initial Cd(II) concentration. It was found that Cd(II) biosorption by fir cone powder is highly pH-dependent, the favorable initial pH of solution was attained at value of 8.2 where a removal efficiency of 98.65% was achieved.

Investigating the biosorption equilibrium in function of contact time at varying initial Cd(II concentrations, it can be concluded that maximum adsorption capacities were achieved almost in the first 80 min of contact.

Equilibrium (Langmuir, Freundlich, Dubinin-Radushkevich and Temkin) isotherm models and kinetics (pseudo-first-, pseudo-second models and intra-particle and liquid film diffusion) of the considered biosorption process were discussed in details.

Biosorption process followed Langmuir isotherm model. The calculated Cd(II) adsorption capacities for untreated fir cone powder obtained from Langmuir isotherm model (best fit, $R^2 = 0.9935$), were found to be 3.74 mg/g. From the values of activation energy of the process calculated according to Dubinin-Radushkevich and Temkin models, it is suggested that biosorption of Cd(II) by fir cone powder is physical in nature. The kinetics of Cd(II) biosorption was very well described by the pseudo-second-order kinetic model with correlation coefficient values exceeding 0.9991.

It can be concluded that the studied adsorption process at pseudo-second-order model indicates a chemisorption mechanism, where the chemisorption is usually restricted to just one layer of molecules on the surface, and it may be followed by additional layers of physically adsorbed molecules. As a result, this fact is proved by the Dubinin-Radushkevich and Temkin isotherm models, where the values obtained at mean free energy (Dubinin-Radushkevich) and the constant related to heat of sorption (Temkin) indicates a physisorption process.

In order to enhance the biosorption capacity and removal efficiency of the biomass on the removal of Cd(II) from aqueous solutions, further chemical treatments will be applied.

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