

Scientific paper

# Cadmium (II) Ions Removal from Aqueous Solutions Using Romanian Untreated fir Tree Sawdust – a Green Biosorbent

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## Abstract

Biosorption of cadmium ions from synthetic aqueous solution using popular Romanian fir tree sawdust (*Abies Alba*) as biosorbent, was investigated in this work. Prior to its utilization the considered biomass was washed, dried and sieved without further chemical treatments. The biosorbent was characterized using humidity, density and elemental analysis determinations and FTIR. FTIR analysis indicated that, on the biomass surface hydroxyl and carboxyl groups are presented. The effect of different biosorption parameters was studied. Higher biomass quantity, neutral pH, slightly elevated temperature and high cadmium ions concentration are all favouring the biosorption process. Equilibrium (Langmuir and Freundlich isotherm), kinetics and thermodynamics of the considered biosorption process were discussed in details. Equilibrium was best described by the Langmuir isotherm, while the kinetic of the process was best described by the pseudo-second-order model, suggesting monolayer coverage and a chemisorption process. Thermodynamic parameters showed that cadmium biosorption process on fir tree sawdust is an endothermic process.

**Keywords:** *Abies Alba* sawdust, cadmium ions, biosorption, equilibrium, kinetics, thermodynamics

## 1. Introduction

The production of a variety of chemical compounds and the large – scale industrialization contribute to global deterioration of environmental quality.

The pollution of water with toxic heavy metals is considered dangerous because of their great toxicity and their non-biodegradability. These heavy metals ions can be accumulated through the food chain even at low concentrations, leading to serious problems on aquatic life as well as to animal, plant life and human health.<sup>1</sup>

Wastewaters purification from heavy metals, as the most hazardous pollutants still attract considerable attention of scientists dealing with the protection and conservation of resources and ecosystem.<sup>2</sup>

Due to the complexity of the problems associated with metal removal and recovery from wastewaters, numerous techniques are available, such as, conventional technologies (chemical precipitation, electro-winning or

cementation of ions present in wastewater), separation and concentration methods (solvent extraction, adsorption or ion exchange, reverse osmosis, electrodialysis), etc, but these treatments are expensive.<sup>3</sup>

Sorption methods are particularly convenient to immobilized ions onto solid phase surface, from very dilute solutions such as wastewater. The application of low-cost materials, as by-products of furniture industries, to remove contaminants from water is one way to develop a low expensive treatment of hazardous wastes.<sup>4-7</sup>

Cadmium is a dangerous pollutant originating from metal plating, metallurgical alloying, mining, ceramics and other industrial operations.<sup>8</sup> According to Romanian legislation, the maximum concentration limit for Cd (II) discharge into surface waters is 0.2 mg/L and in potable water is  $5 \times 10^{-3}$  mg/L.<sup>9,10</sup>

Cadmium is considered as a non-essential and highly toxic element possibly because it forms a strong bond with sulphur and hence can displace essential metals, i.e.

Zn<sup>2+</sup> and Ca<sup>2+</sup> from the binding sites of certain enzymes.<sup>11</sup>

Over the past 10 years, extensive research has been carried out to identified new and economically priced adsorbent for cadmium ions removal/preconcentration such as different types of algae,<sup>12–16</sup> yeast biomass,<sup>17,18</sup> rice husk,<sup>19</sup> mushrooms,<sup>20</sup> orange peels,<sup>21</sup> papaya wood,<sup>22</sup> pine bark,<sup>23</sup> aquatic moss,<sup>24,25</sup> tea waste<sup>26</sup> and various types of sawdust.<sup>2,6,11,27–30</sup>

As we know, the sawdust is a solid by-product abundant, inexpensive and not enough exploited material, obtained from mechanical wood processing, which can be used as biosorbent for removing different heavy metals, cadmium (II) in particular, from aqueous waste solutions. The adsorption of heavy metals by these types of materials might be attributed to their lignin, cellulose and hemicellulose, which have proteins, carbohydrates and polyphenolic compounds with carboxyl, hydroxyl, sulphate, phosphate and amino groups that can bind metal ions.<sup>5</sup>

*Abies Alba* fir is a common tree from some forest areas in Transylvania (Romania). These trees are the main source in the local wood industry and their sawdust could be a good candidate as a green and economic alternative for Cd (II) removal from wastewater. The sawdust was evaluated without any chemical pretreatment.

The goal of this study was to realize the Cd (II) biosorption onto waste fir tree sawdust from Romanian wood industry and to offer an effective and economical alternative to more expensive adsorption processes (commercial active carbon and resins). Therefore, biosorbent quantity, Cd (II) concentration and pH influences over the biosorption process were investigated in batch conditions. Isotherm and kinetic models, and thermodynamics of the considered biosorption process were discussed in details.

## 2. Experimental

### 2.1. Biosorbent

The fir tree (*Abies Alba*) sawdust was obtained from a local sawmill in Huedin, Cluj County, Romania. Prior to its utilization the considered biomass was washed several times with distilled water in order to eliminate surface impurities, was dried at 105 °C for 24 h. Finally the dried biomass was grinded and sieved (400–600 μm). The sieved sawdust was then stored in an airtight box before its utilization. No further chemical treatments were considered at this stage.

### 2.2. Chemicals

The stock solution, 1 g/L of cadmium (II) was prepared by dissolving Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in distilled water. The required concentrations were obtained by diluting the stock solution to the desired concentrations, in 40–250 mg/L range. HCl (0.1 M) and NaOH (0.1 M) volumetric solu-

tions were used to adjust the solution pH. All chemicals used were of analytical grade.

## 2.3. Biomass Characterization

### 2.3.1. Humidity, Apparent Density and Elemental Analysis

For determination of residual humidity of the biosorbent, a known amount of biomass was dried in an oven at 105 °C (5 days). The biosorbent mass was measured twice a day until a constant value was reached. The biomass humidity (%) was calculated from the ratio of mass loss during drying to the initial biosorbent mass<sup>31</sup>:

$$W^a = \frac{m_1 - m_2}{m} \cdot 100 \quad (1)$$

where, W<sup>a</sup> is humidity of the analyzed sample (%), m is the sample mass (g), m<sub>1</sub> is the initial mass of the flask with the sample (g), and m<sub>2</sub> is the final flask mass with the sample, after drying (g).

The biomass density, ρ (g/cm<sup>3</sup>) was determined by pycnometry with ethanol, and calculated using the following formulas:

$$V_p = \frac{m_2 - m_1}{\rho^{20}} \quad (2)$$

where, m<sub>1</sub> is the mass of the empty pycnometer (g), m<sub>2</sub> is the mass of the pycnometer with distilled water (g), and ρ<sup>20</sup> = 0.9982 g/cm<sup>3</sup> the distilled water density at 20 °C.

$$\rho_c^{20} = \frac{m_3 - m_1}{V_p} \quad (3)$$

where, m<sub>1</sub> is the mass of empty pycnometer (g), and m<sub>3</sub> is the mass of pycnometer with ethanol, at 20 °C, in (g).

$$\rho = \frac{m}{(m_3 + m) - m_4} \cdot \rho_c^{20} \quad (4)$$

where, m is the mass of sawdust used for density determination (g), and m<sub>4</sub> is the mass of pycnometer with the sample of sawdust and ethanol (g).

Elemental analysis was performed using a Vario MICRO Element Analyzer CNHS, Elemental (Germany) 2 mg Chem 80 s method.

### 2.3.2. SEM Analyses

Scanning electron microscopy is utilized for characterizing surface microstructures, porosity and fundamental physical properties of different adsorbents. The surface morphology of fir tree (*Abies Alba*) sawdust was determined using a scanning electron microscope JEOL JSM 5510 LV.

### 2.3.3. FTIR Spectral Analysis

Fresh and used (separated from cadmium solution after adsorption and dried) sawdust samples were subjec-

ted to FTIR analysis. Sawdust samples were prepared by encapsulating 1.2 mg of finely grounded biomass particles in 300 mg of KBr. Infrared spectra were obtained using a JASCO 615 FTIR spectrometer, 400–4000  $\text{cm}^{-1}$ , resolution 2  $\text{cm}^{-1}$ .

## 2. 4. Adsorption Experiments

The adsorption experiments were performed in batch conditions, contacting various quantities of biosorbent (1–5 g) at 700 rpm with 100 mL aqueous solution of Cd (II) ions at different initial concentrations (40–250 mg/L). In order to determine the exact concentration of cadmium ions and establish the evolution of the removal process, samples of 100  $\mu\text{L}$  were collected at different time intervals up to 240 minutes.

At the end of the predetermined time, the suspension was filtered and the remaining concentration of metal in the aqueous phase was determined using an Atomic Absorption Spectrometer (SensAA Dual GBS Scientific Equipment, Australia). In order to evaluate the amount of cadmium ions retained per unit mass of sawdust, the adsorption capacity was calculated using the following equation:<sup>32</sup>

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (5)$$

where,  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_0$  is the initial metal ions concentration (mg/L),  $C_e$  is the equilibrium metal ions concentration (mg/L),  $V$  is the volume of the aqueous phase (L), and  $m$  is the biosorbent mass.

Removal efficiency,  $E$  (%), was calculated as a ratio between Cd (II) biosorbed at time  $t$  (mg/L) and the initial Cd (II) concentration (mg/L):<sup>32</sup>

$$E, (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (6)$$

The effect of pH of the initial solution on the equilibrium uptake of Cd (II) was analyzed over a 2 to 10 pH range. The initial pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. The experiments were carried out using 100 mL solution of 60 mg  $\text{Cd}^{2+}/\text{L}$  which was contacted with 5 g fir tree sawdust at 296 K for 240 minutes to reach equilibrium. In order to establish the thermodynamic parameters, 296, 306 and 316 K temperatures were used.

Experimental data were used to determine the equilibrium time, the optimum pH value, and the quantity of adsorbent for maximum efficiency, to establish isotherm and kinetics models and to calculate thermodynamic parameters. All the experiments were repeated three times, the values presented were calculated using averaged concentration values.

## 2. 5. Adsorption Kinetics

### 2. 5. 1. Pseudo-first-order Kinetic Model (Lagergren)

Lagergren suggested a first-order equation for the adsorption of liquid/solid system based on solid capacity, which can be expressed as follows:<sup>33</sup>

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (7)$$

Integrating eq. (6) from the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

where,  $q_e$  and  $q_t$  are the amounts of cadmium adsorbed (mg/g) at equilibrium and time  $t$ , respectively,  $k_1$  is the rate constant of first-order adsorption (1/min).

In order to determine the rate constant and equilibrium cadmium uptake, the straight line plots of  $\ln(q_e - q_t)$  against  $t$ , eq. (8), were made at different initial cadmium concentrations.

### 2. 5. 2. Pseudo-second-order Kinetic Model (Ho's Model)

Pseudo-second-order equations proposed initially by Ho and McKay are the most simplified and very frequently used kinetic equation. These equations are used to model the adsorption process for a wide range of solute-sorbent systems, including metal ions and natural sorbent.<sup>34</sup>

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

where,  $k_2$  is the rate constant of pseudo-second-order adsorption, and  $q_t$  and  $q_e$  are adsorption capacities at time  $t$  and equilibrium, respectively (mg/g).

Separating variables in equation (9) gives:

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt \quad (10)$$

Integrating equation (10) between  $t = 0$  and  $t = t$  gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (11)$$

If the pseudo-second-order kinetic model is applicable, the plot of equation (11) rearranged ( $t/q_t$  versus  $t$ ) gives a straight line whose slope is equal to  $k_2$ .

### 2. 5. 3. Pore (Intra-particle) Diffusion

When adsorption processes are studied, two important steps of mass transfer, external diffusion and internal diffusion (intra-particle diffusion), can also control the

process. When the adsorbate diffusion in the adsorbent pores, is the rate determining step, the intra-particle diffusion rate constant can be obtained from the Weber and Morris equation:<sup>29,35</sup>

$$q_t = k_{ip} \cdot t^{0.5} \quad (12)$$

where,  $q_t$  is the amount adsorbed (mg/g) at time  $t$  (min), and  $k_{ip}$  is the intra-particle diffusion rate constant (mg/gmin<sup>0.5</sup>).

If  $q_t$  against  $t^{0.5}$  plots gives straight lines passing through origin, internal diffusion is considered to be rate determining step. If the data exhibit multi-linear plots, then two or more steps influence the adsorption process.<sup>29</sup>

#### 2. 5. 4. External (Film) Diffusion

When the diffusion, (external diffusion), of the adsorbate from the liquid phase to the solid phase is the rate determining step, the liquid film diffusion model can be applied:<sup>36</sup>

$$\ln(1-F) = -k_{fd} \cdot t \quad (13)$$

where,  $F$  is the fraction attainment at equilibrium ( $F = q_t/q_e$ ), and  $k_{fd}$  is the liquid film diffusion rate constant (1/min).

A linear plot  $-\ln(1-F)$  against  $t$  with zero intercept would suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the adsorbent.

## 2. 6. Adsorption Equilibrium

Adsorption equilibrium can be described by a variety number of isotherm models. These models describe the solute-adsorbent interactions. The most applied are the Langmuir and the Freundlich models.<sup>37–39</sup>

### 2. 6. 1. Langmuir Isotherm

Langmuir model is frequently used for adsorption of heavy metal, dyes etc.,<sup>40, 41</sup> this is applicable for a monomolecular layer adsorption at specific homogenous sites on the adsorbent surface. This model expressed as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (14)$$

where,  $q_e$  and  $C_e$  are the solute concentration in liquid and solid phases at equilibrium, respectively  $q_m$  is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent and  $b$  is the adsorption equilibrium constant that is related to the apparent energy of adsorption.

A linear form of (14) is:

$$\frac{1}{q_e} = \frac{1}{q_m b} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad (15)$$

Isotherm parameters  $q_m$  and  $b$  can be obtained by plotting  $1/q_e$  against  $C_e$ .

### 2. 6. 2. Freundlich Isotherm

Freundlich isotherm is an empirical model that takes into account the heterogeneity of the surface of the adsorbent and is expressed by equation (16):

$$q_e = K_f C_e^{1/n} \quad (16)$$

with its logarithmic linear form:

$$\log q_e = \log K_f + \frac{1}{n} \cdot \log C_e \quad (17)$$

where  $K_f$  and  $n$  are the Freundlich constants, the  $K_f$  constant is an indicator of the adsorption capacity of the adsorbent while  $n$  indicates biosorption intensity.

The  $\ln q_e$  versus  $\ln C_e$  plot allows the determination of the Freundlich constants.

## 2. 7. Thermodynamic Parameters of Biosorption

The Gibbs free energy ( $\Delta G^\circ$ , kJ/mol), is the fundamental criterion of spontaneity of a process and can be determined using equilibrium constant  $K_d$  ( $q_e/C_e$ ) in the following equations:<sup>42</sup>

$$\Delta G^\circ = -RT \ln K_d \quad (18)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta \Delta^\circ \quad (19)$$

where,  $R$  is the universal gas constant ( $8.314 \times 10^{-3}$  kJ/Kmol),  $T$  is absolute temperature (K), and  $K_d$  is the distribution coefficient (L/g).

The enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) can also be computed using the following equation:

$$\ln K_d = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (20)$$

from the slope and intercept of the plot  $\ln K_d$  versus  $1/T$ .

## 2. Results and Discussion

### 3. 1. Biomass Characterization

Fir tree sawdust cell mainly consist of dry matter (96.93%) and it is part of the soft woods. The main chemical composition of sawdust is crude fiber, cellulose, hemi-

celluloses and lignin. *Abies Alba* contains a high quantity of cellulose 55.09% and lignin 33.3%.<sup>1,42</sup> As we know, cellulose and hemicellulose are structural components with a polysaccharide matrix. Hemicellulose is a branched polymer, while cellulose is unbranched. Lignin is a cross-linked racemic molecule from sawdust, with hydrophobic and aromatic nature. Their presence in sawdust structure it is likely to confer to this material biosorption properties.

### 3. 1. 1. Physical Characteristics and Elemental Analysis of the Fir Tree Sawdust

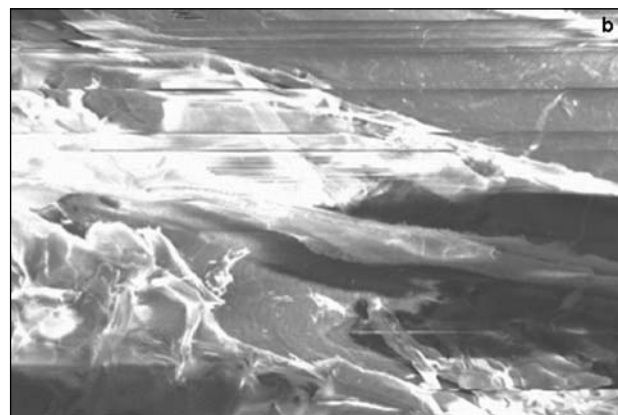
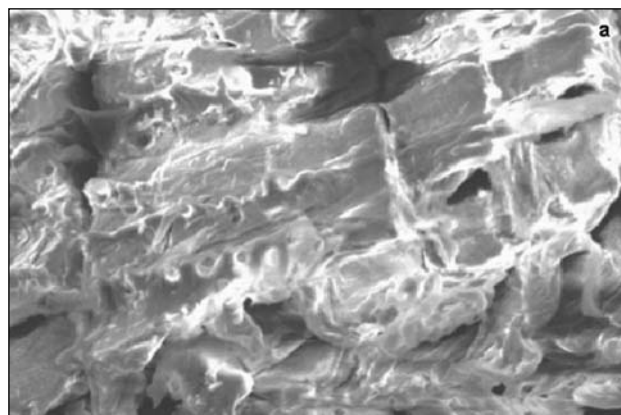
Humidity, apparent density and elemental analysis of the considered biosorbent (*Abies Alba*) were determined according to the procedures described above. The elemental analysis results were calculated for 1 mg of sawdust. The amount of S obtained percentage was under determination method detection limit and it was considered as negligible. Results are presented in Table 1.

**Table 1.** Physical characteristics and elemental analysis of the fir tree (*Abies Alba*) sawdust.

Particle size ( $\mu\text{m}$ )		$W^a$ (%)	$\rho_a$ ( $\text{g}/\text{cm}^3$ )
400–600		2.80	1.09
C	H	N	O
(%)			
25.457	3.668	0.004	70.871

### 3. 1. 2. SEM Analysis

Figure 1ab show the SEM micrographs of the sawdust before and after Cd (II) biosorption. Literature data show that hard woody material present cross-interconnected pores, while softer woody material presents fibrillar structure in nature.<sup>43</sup> Based on the image from Figure 1a it can be concluded that the fir tree sawdust fibers are not cross-linked. The surface seems to be rough and heterogeneous. After biosorption roughness attenuation was observed, this can be due to the effective adsorption of Cd (II) ions in the cavities and pores of fir tree sawdust.



**Figure 1.** SEM micrographs of fir tree (*Abies alba*) sawdust before (a) and after (b) Cd (II) biosorption.

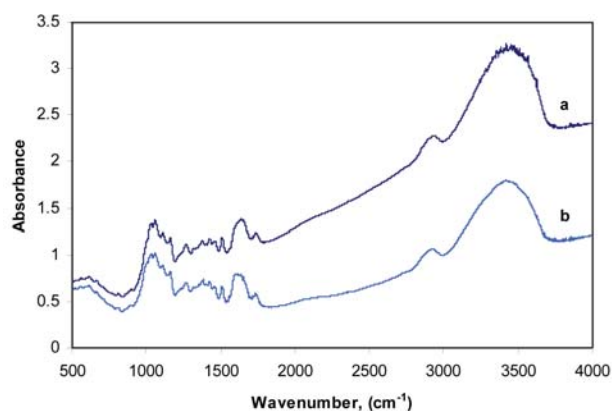
### 3. 1. 3. FTIR Spectral Analysis

Infrared analysis allows identification of some characteristic peaks that belongs to organic functional groups, including those implied in the biosorption process. Some chemical groups have been proposed to be responsible for the adsorption heavy metal ion. Carboxyl, hydroxyl, phenol, sulfonate groups are most important in sawdust.<sup>44</sup> In order to determine the functional groups involved in Cd (II) biosorption onto sawdust, a comparison between the FTIR spectra before (raw) and after biosorption (used) of cadmium was realized, Figure 2. Main identified peaks and their assignment is presented in Table 2. The FTIR data for the used fir tree sawdust show that some peaks were shifted (Figure 2 and Table 2). First change was observed in case of the strong peak which corresponds to O–H bond stretching of hydroxyl group from cellulose and lignin, and water, recorded at  $3421\text{ cm}^{-1}$  and  $3416\text{ cm}^{-1}$  respectively. Also this peak may be assigned to complexation of cadmium ions with the ionized O–H group of hydroxyl group and bonded O–H bands of carboxylic acids in the inter- and intramolecular hydrogen bonding of polymeric compounds.<sup>27,45</sup> A change was also observed in the  $2937\text{ cm}^{-1}$  peak (C–H stretch), which shifted to  $2924\text{ cm}^{-1}$  this indicating an ion exchange process between protons. C=O stretch was recorded at  $1735\text{ cm}^{-1}$  in both cases. An intense band appearing at  $1635$  and  $1604\text{ cm}^{-1}$  for raw and used biosorbent respectively, attributed to the N–H bend stretching from the amides group was also identified. In the  $1500\text{ cm}^{-1}$  region, at  $1512\text{ cm}^{-1}$  and  $1508\text{ cm}^{-1}$  another peak was observed, which belongs to the nitro groups ( $-\text{NO}_2$  stretching). The peaks at around  $1426\text{ cm}^{-1}$  represent O–H groups bending vibrations. The peak identified at around  $1268\text{ cm}^{-1}$  and the peaks from the broad band  $1000\text{--}1165\text{ cm}^{-1}$  are attributed to the surface C–O bond stretching of phenolic groups. FTIR studies revealed that several functional groups present in the fir tree sawdust are able to bind the heavy metal ions, in our case Cd (II) ions.

Physical and chemical characteristics of the fir tree (*Abies Alba*) sawdust suggest the fact that this material could be a good biosorbent for heavy metal ions.

**Table 2.** FTIR characteristic peaks of fir tree (*Abies Alba*) sawdust before and after Cd (II) biosorption.<sup>55–56</sup>

Wavelength range (cm <sup>-1</sup> )	Fir tree sawdust FTIR peaks (cm <sup>-1</sup> )			Assignment
	Before	After	Differences	
3400–3300	3421	3416	5	O–H stretching / hydroxyl groups
2950–2800	2937	2924	13	C–H stretching / methyl and methylene groups
1750–1690	1735	1735	–	C=O stretching / carboxylic acids groups
1640–1550	1635	1604	21	N–H bending / amides groups
1550–1490	1512	1508	4	–NO <sub>2</sub> stretching / nitro groups
1440–1400	1426	1424	2	O–H bending / carboxylic acids groups
1300–900	1268	1267	1	C–O stretching, phenolic groups
1300–900	1163	1162	1	C–O stretching, phenolic groups
1300–900	1061	1060	1	C–O stretching
650–510	618	618	0	C–Br stretch, alkyl halides group

**Figure 2.** FTIR spectra of fir tree sawdust (*Abies Alba*) before (a) and after (b) Cd (II) biosorption.

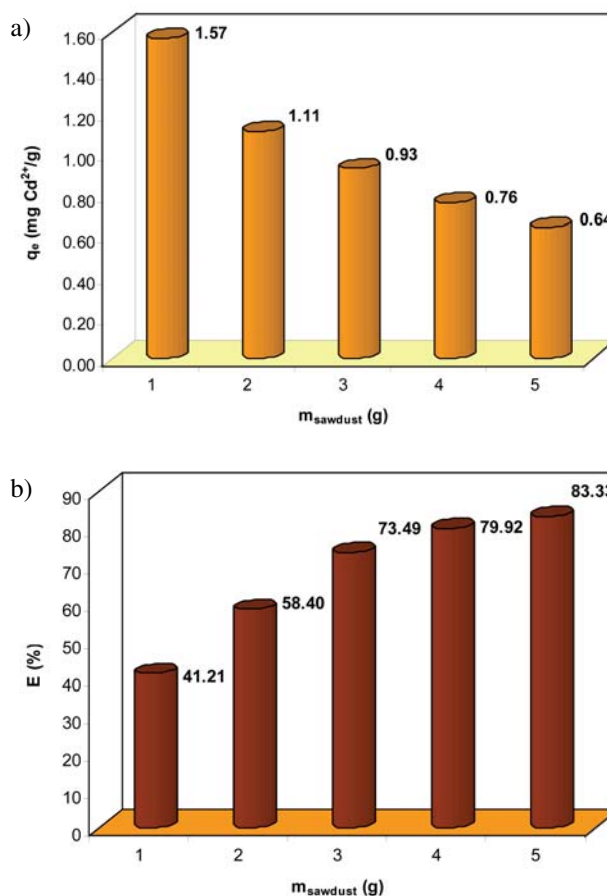
## 3. 2. Biosorption Results

### 3. 2. 1. Biosorbent Quantity, Cd (II)

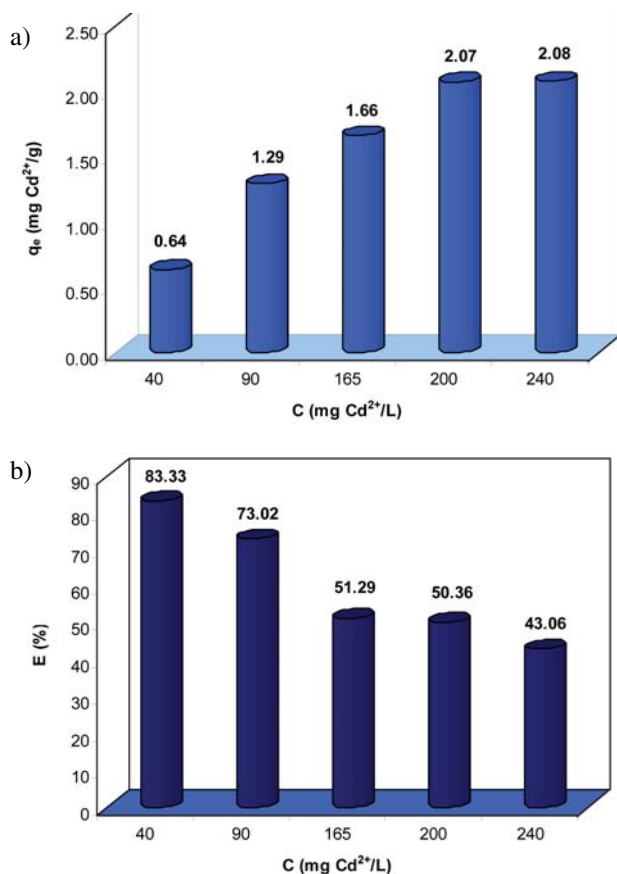
#### Concentration and pH Influences

Sawdust quantity (1–5 g) influence over the Cd (II) removal presented in Figure 3ab indicates that as the biosorbent quantity increases, adsorption capacity will decrease (reduced unsaturation, particle agglomeration which will increase diffusional path length<sup>46</sup> and removal efficiency will increase. Taking into consideration the fact that the fir tree sawdust is a by-product, therefore is available in large quantities and at very low cost, the experiments were further considered using 5 g for maximum removal efficiency.

When initial Cd (II) concentration was considered as a parameter which will influence the biosorption process, an increase in the adsorption capacity and a decrease of the removal efficiency with the increase in concentration (40–240 mg Cd<sup>2+</sup>/L) was observed, Figure 4ab. This indicates that if the metal ions concentration in solution increases, the difference in concentration between bulk solution and surface also increases, intensifying the mass transfer processes. Accordingly a higher quantity of metal will be adsorbed, proving that fir tree sawdust has a high adsorption capacity towards Cd (II).

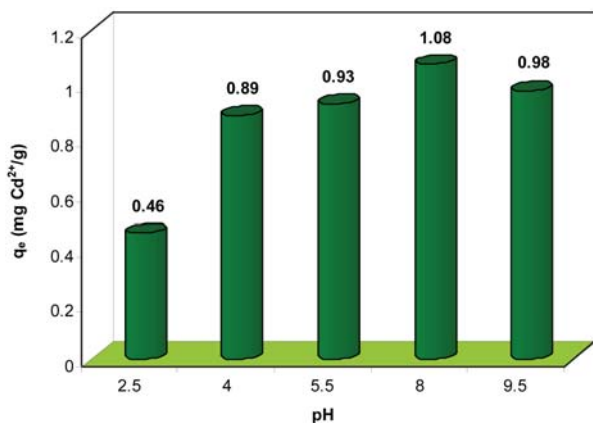
**Figure 3.** The effect of the fir tree sawdust (*Abies Alba*) quantity on Cd (II) biosorption over the (a) adsorption capacity and (b) removal efficiency; C<sub>i</sub> = 40 mg Cd<sup>2+</sup>/L, 296 K, 5.5 pH.

The pH is the most important controlling parameter in the adsorption process of heavy metal ions. Hydrogen ions affect metal complexation because they have a great affinity for many complexing and ion-exchange sites.<sup>47</sup> The pH values affect the surface charge of the adsorbent, the degree of ionization and speciation of adsorbate during the adsorption process.<sup>1</sup> In our study five different pH values were considered, ranging between 2 and 10, in order to establish pH influence on the adsorption capacity of cadmium



**Figure 4.** Influence of the initial Cd (II) concentration over the (a) adsorption capacity and (b) removal efficiency on fir tree sawdust (*Abies Alba*); 5g biosorbent, 296 K, 5.5 pH.

ions. The results are presented in Figure 5. As the biosorbent surface is positively charged at low pH, the electrostatic attraction between fir tree sawdust surface and cadmium ions leads to a decrease of the adsorption capacity. As the initial pH increases, the adsorption surface becomes less positive and therefore electrostatic attraction between the metal ions and sawdust surface is likely to be increased. The optimum pH that provides maximum removal of cad-

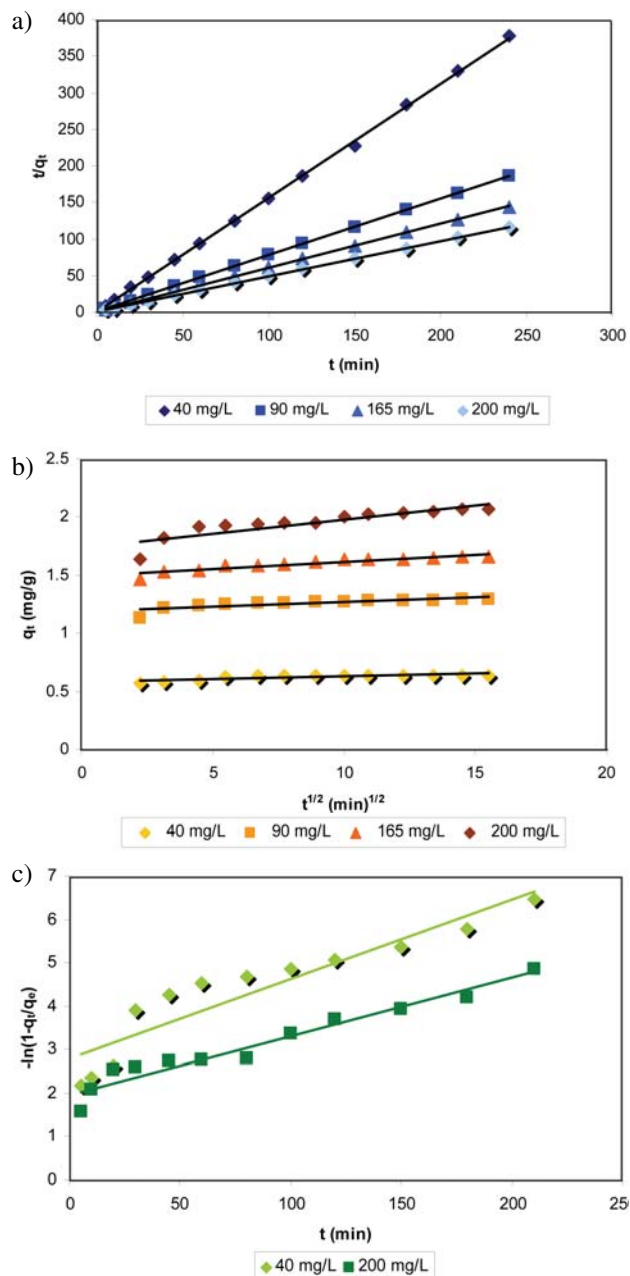


**Figure 5.** The effect of initial pH values on Cd (II) biosorption using fir tree sawdust (*Abies Alba*); C<sub>i</sub> = 60 mg Cd<sup>2+</sup>/L, 5g biosorbent, 296 K, 5.5 pH.

mium was an initial 8 pH. Similar results were reported using an Indian deciduous wood at pH 6.7.<sup>1</sup> At higher pH values (9.5), Cd (II) ions begin to precipitate, therefore the biosorption studies are significantly influenced.

### 3. 2. 2. Adsorption Kinetics

Correlation coefficients obtained when the pseudo-first-order kinetic model was applied to Cd (II) biosorption on fir tree sawdust data, ranging between 0.4231 and 0.8649, Table 3, led us to the conclusion that the considered biosorption process cannot be classified as first-order.



**Figure 6.** Plots of the (a) pseudo-second-order kinetic (b) intra-particle diffusion and (c) film diffusion models for Cd (II) biosorption on fir tree sawdust (*Abies Alba*); 5g biosorbent, 296 K, 5.5 pH.

Also values of calculated adsorption capacities show great differences by comparison to experimental values.

Application of the pseudo-second-order kinetic model for Cd (II) biosorption on fir tree sawdust is presented in Figure 6a. Values of pseudo-second-order ( $k_2$ ) rate constants and adsorption capacities were calculated from the slope and intercept of  $t/q_t$  vs.  $t$  plot represented for various Cd (II) initial concentrations. A comparison between calculated and experimental adsorption capacities, Table 3, showed a good agreement. The regression coefficients ( $R^2$ ) for the linear plots were higher than 0.999 indicating that the second-order-kinetic model describes well the removal of Cd (II) ions using fir tree sawdust as biosorbent, suggesting that the considered process takes place as chemisorption.

Intra-particle and liquid film diffusion rate constants, as well as  $q_t$  against  $t^{0.5}$  and  $-\ln(1-F)$  against  $t$  linear plots intercepts, Figures 6b and 6c, Table 3, were determined. The obtained results, and the fact that none of the mentioned linear plots pass through zero suggested that the two diffusion stages are not rate determining steps.

### 3. 2. 3. Adsorption Isotherm

The equilibrium adsorption study in aqueous phase is an important step in the design of adsorption systems.

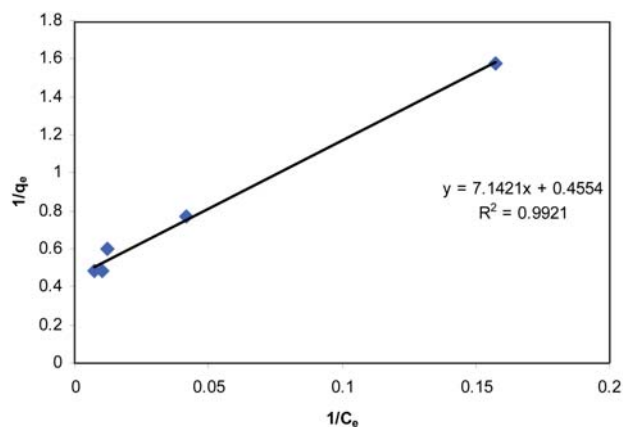


Fig. 7. Langmuir isotherm model for Cd (II) biosorption on fir tree sawdust (*Abies Alba*).

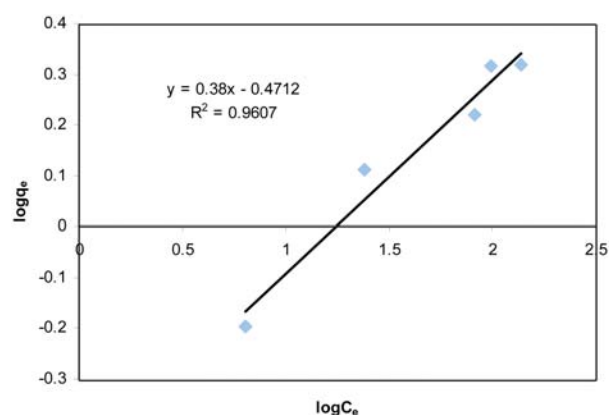


Fig. 8. Freundlich isotherm model for Cd (II) biosorption on fir tree sawdust (*Abies Alba*).

Table 3. Kinetic parameters for Cd (II) biosorption on fir tree (*Abies Alba*) sawdust

C (mg/L)	Pseudo-first-order		Pseudo-second-order		Intra-particle diffusion		Film diffusion		R <sup>2</sup>		
	q <sub>e,exp</sub> (mg/g)	q <sub>e,calc</sub> (mg/g)	k <sub>1</sub> × 10 <sup>2</sup> (1/min)	R <sup>2</sup>	q <sub>e,calc</sub> (mg/g)	k <sub>2</sub> (g/mg min)	R <sup>2</sup>	intercept		k <sub>fd</sub> × 10 <sup>2</sup> (1/min)	intercept
40	0.64	0.23	9.79	0.8649	0.64	5.21	0.9995	0.58	1.84	2.79	0.8689
90	1.29	0.32	6.28	0.6151	1.30	6.59 × 10 <sup>-1</sup>	1	1.18	1.78	2.73	0.9345
165	1.66	0.45	5.09	0.5614	1.67	3.19 × 10 <sup>-1</sup>	0.9999	1.49	1.71	2.28	0.9663
200	2.07	0.74	4.92	0.6327	2.08	1.69 × 10 <sup>-1</sup>	0.9998	1.74	1.34	1.97	0.9495
240	2.08	0.59	3.68	0.4231	2.10	1.54 × 10 <sup>-1</sup>	0.9997	1.79	1.91	1.80	0.9046



Adsorption isotherms are characterized by specific constants that express the surface properties and the affinity of the adsorbent towards Cd (II).<sup>29</sup> The equilibrium data for heavy metal and dyes adsorption on sawdust fit onto various isotherm models, which result in a suitable model that can be used for the design of an adsorption process.<sup>48–49</sup> In the present study two equilibrium models were considered, Langmuir and Freundlich isotherm model (Figure 7,8).

The monolayer saturation capacity of Cd (II) ions,  $q_m$  was calculated to be 2.1958 mg/g, while Langmuir constant, which is related to adsorption energy, was determined to be 3.25 L/mg. Freundlich isotherm constants were also calculated (Table 4). The linearity of the two plots, expressed by  $R^2$  can give information about the fitting between the experimental data and the isotherm model, the closest to linearity could be considered as describing better the adsorption equilibrium in a certain system.<sup>50,51</sup> In case of Cd (II) biosorption on fir tree sawdust, the results suggested that the experimental results fitted well on Langmuir isotherm model (Table 4).

The adsorption capacities of previously reported biomass for Cd (II) biosorption are presented in Table 5. As can be observed, fir tree sawdust presents intermediate adsorption capacities by comparison with other sawdust but smaller by comparison with almost all mushrooms or mosses.

**Table 4.** Comparison of individual constants obtained from Langmuir and Freundlich adsorption isotherm at Cd (II) biosorption on fir tree (*Abies Alba*) sawdust

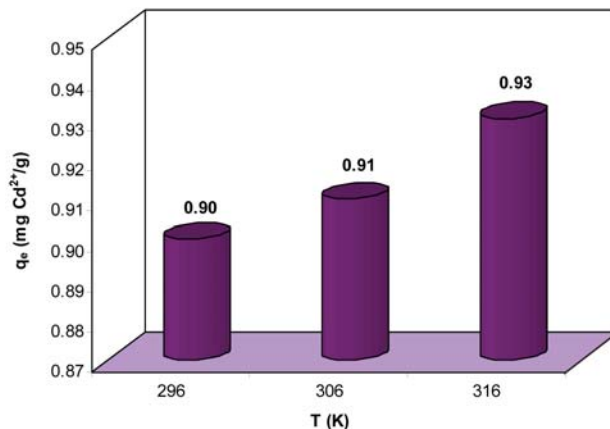
Langmuir isotherm			Freundlich isotherm		
b (L/mg)	$q_m$ (mg/g)	$R^2$	n	$K_f$ ( $\text{mg}^{(1-1/n)} \text{L}^{1/n}/\text{g}$ )	$R^2$
3.25	2.1958	0.9921	2.6315	0.3379	0.9607

**Table 5.** Previously reported adsorption capacities of different low-cost adsorbents for Cd (II)

Biosorbent	Biosorption capacity (mg/g)	Reference
Pinus halepensis sawdust	7.35	29
Poplar wood sawdust	0.0014	30
Fir tree ( <i>Abies Alba</i> ) sawdust	2.1958	Present study
Pine bark	0.126	23
Pleurotus platypus mushroom	34.96	20
Agaricus bisporus mushroom	29.67	20
Calocybe indica mushroom	24.09	20
Sargassum sp. macroalga	120.0	14
Cystoseira baccata marine macroalga	0.69	13
Gracillaria sp. marine algae	33.7	15
Spirulina sp. blue-green algae	159.0	16
Fontinalis antipyretica aquatic moss	28.0	25
Hylocomium splendens moss	32.50	24
Tea waste	11.29	26

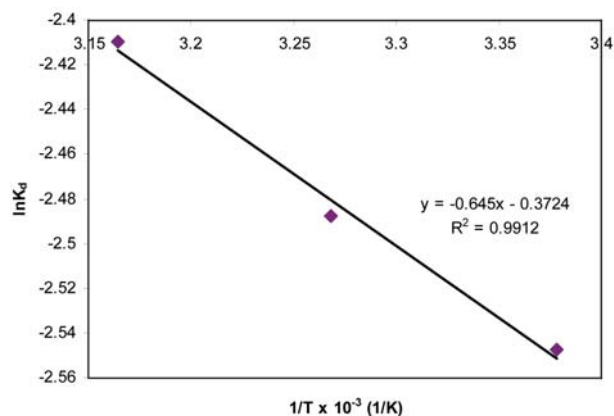
### 3. 2. 4. Thermodynamic of Biosorption

The influence of temperature on adsorption capacity of Cd (II) biosorption on fir tree sawdust is presented in Figure 9. As it can be observed an increase in temperature led to an increase of the adsorption capacity, suggesting that the biosorption process is endothermic.



**Figure 9.** Temperature influence over the adsorption capacity of Cd (II) on fir tree sawdust (*Abies Alba*);  $C_i = 55 \text{ mg Cd}^{2+}/\text{L}$ , 5g biosorbent, 5.5 pH.

Experimental results were used to calculate thermodynamics parameters, enthalpy ( $\Delta H^\circ$ , kJ/mol), entropy ( $\Delta S^\circ$ , kJ/Kmol), and Gibbs free energy ( $\Delta G^\circ$ , kJ/mol), Figure 10, Table 6. The positive value of the enthalpy (5.36 kJ/mol) confirmed that Cd (II) biosorption on fir tree sawdust is an endothermic process, where higher temperature makes the adsorption easier.<sup>52</sup> The endothermic process shows that the diffusion from bulk solution to adsorbent surface may require energy to overcome interaction of dissolved ions with solvation molecules.<sup>53</sup> Positive small values of free energy and a small negative value of entropy indicate the fact that the consi-



**Figure 10.** Plot of  $\ln K_d$  versus  $1/T$  for the estimation of the thermodynamic parameters for Cd (II) biosorption on fir tree sawdust (*Abies Alba*).

**Table 6.** Thermodynamic parameters for the adsorption of Cd (II) on fir tree sawdust (*Abies Alba*) at various temperatures

Ion	$\Delta S^\circ$	$\Delta H^\circ$	$\Delta G^\circ$ , (kJ/mol)		
	(kJ/K mol)	(kJ/mol)	296 K	306 K	316 K
Cd <sup>2+</sup>	$-3.10 \times 10^{-3}$	5.36	6.28	6.31	6.34

dered biosorption process will be promoted by specific temperature conditions, leading to increased adsorption capacities.<sup>54</sup>

### 3. Conclusions

This study presented results obtained at Cd (II) biosorption on popular Romanian fir tree sawdust (*Abies Alba*) as biosorbent (Transylvanian forests). The biomass was subjected only to mechanical preparation in order to obtain the final biomass (washing, drying and sieving). Humidity, density and specific surface area, and Fourier Transformed Infrared Analysis (FTIR) analysis were considered. FTIR analysis indicated the presence on the biomass surface of the hydroxyl and carboxyl groups which play an important role in the biosorption process, suggesting that the process takes place mainly by ionic exchange.

The effects of the initial biomass quantity, pH, temperature, initial cadmium ions concentration in solution were studied. Higher biomass quantity, pH in 5.5–8 range, slightly elevated temperature and high cadmium ions concentration are all favouring the biosorption process. Removal efficiencies up to around 83% and a maximum adsorption capacity of 2.08 mg/g Cd<sup>2+</sup> obtained experimentally and 2.1958 mg/g Cd<sup>2+</sup> obtained from Langmuir isotherm model.

Equilibrium (Langmuir and Freundlich isotherm), kinetics (pseudo-first- and pseudo-second-order, intraparticle and film diffusion models) and thermodynamics of the considered biosorption process were discussed in detail. Equilibrium was best described by the Langmuir isotherm, while the kinetic of the process was best described by the pseudo-second-order model, suggesting monolayer coverage and a chemisorption process. Thermodynamic parameters showed that cadmium biosorption process on fir tree sawdust is an endothermic process. According to the obtained results it can be concluded that the fir tree (*Abies Alba*) sawdust it is a good biosorbent for Cd (II) from aqueous solutions.

### 4. Acknowledgements

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### 5. References

1. M. S. Rahman, M. R. Islam, *Chem. Eng. J.* **2009**, *149*, 273–280.
2. D. Bozic, V. Stankovic, M. Gorgievski, G. Bogdanovic, R. Kovacevic, *J. Hazard. Mater.* **2009**, *171*, 684–692.
3. A. G. S. Prado, A. O. Moura, M. S. Holanda, T. O. Carvalho, R. D. A. Andrade, I. C. Pescara, A. H. A. de Oliveira, E. Y. A. Okino, T. C. M. Pastore, D. J. Silva, L. F. Zara, *Chem. Eng. J.* **2010**, *16*, 549–555.
4. A. Bhatnagar, M. Sillanpaa, *Chem. Eng. J.* **2010**, *157*, 277–296.
5. Y. Bulut, T. Zeki, *J. Environ. Sci. Eng.* **2007**, *19*, 160–166.
6. V. C. T. Costodes, H. Fauduet, C. Porte, A. Delacroix, *J. Hazard. Mater.* **2003**, *105*, 121–142.
7. A. G. S. Prado, A. O. Moura, R. D. A. Andrade, I. C. Pescara, V. S. Ferreira, E. A. Faria, A. H. A. de Oliveira, E. Y. A. Okino, L. F. Zara, *J. Therm. Anal. Calorim.* **2010**, *99*, 681–687.
8. C. Majdik, S. Burcă, C. Indolean, A. Măicăneanu, M. Stanca, Sz. Tonk, P. Mezey, *Rev. Roum. Chim.* **2010**, *55*, 871–877.
9. \*\*\*Romanian Government decision, HG 188/2002 modified with HG 352/2005.
10. \*\*\*Romanian Law 458/2002 modified with Law 311/2004.
11. S. Q. Memon, N. Memon, S. W. Shah, M. Y. Khuhawar, M. I. Bhangar, *J. Hazard. Mater.* **2007**, *139*, 116–121.
12. Y. Liu, Q. Cao, F. Luo, J. Chen, *J. Hazard. Mater.* **2009**, *163*, 931–938.
13. P. Lodeiro, J. L. Barriada, R. Herrero, M. E. Sastre de Vicente, *Environ. Pollut. (Oxford, U.K.)* **2006**, *142*, 264–273.
14. C. C. V. Cruz, A. C. A. da Costa, et.al., *Bioresour. Technol.* **2004**, *91*, 249–257.
15. P. X. Sheng, Y.-P. Ting, J. P. Chen, L. Hong, *J. Colloid Interface Sci.* **2004**, *275*, 131–141.
16. K. Chojnacka, A. Chojnacki, H. Górecka, *Chemosphere* **2005**, *59*, 75–84.
17. G. Yekta, U. Sibel, G. Ulgar, *Bioresour. Technol.* **2005**, *96*, 103–109.
18. Sz. Tonk, A. Măicăneanu, C. Indolean, S. Burca, C. Majdik, *J. Serb. Chem. Soc.* **2011**, *76*, 363–373.
19. K. Upendra, B. Manas, *Bioresour. Technol.* **2006**, *97*, 104–109.
20. R. Vimala, N. Das, *J. Hazard. Mater.* **2009**, *168*, 376–382.
21. X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, *Colloids Surf.* **2008**, *A 317*, 512–521.
22. S. Asma, A. M. Waheed, I. Muhammed, *Sep. Purif. Technol.* **2005**, *45*, 25–31.
23. S. Al-Asheh, F. Banat, R. Al-Omari, Z. Duvnjak, *Chemosphere* **2000**, *41*, 659–665.
24. A. Sari, D. Mendil, M. Tuzen, M. Soylak, *Chem. Eng. J.* **2008**, *144*, 1–9.
25. J. E. Ramiro, R. Martins, R. Pardo, A. R. Boaventura, *Water Res.* **2004**, *38*, 693–699.
26. S. Cay, A. Uyanýk, A. Ozasik, *Sep. Purif. Technol.* **2004**, *38*, 273–280.

27. P. Chakravarty, N. S. Sarma, H. P. Sarma, *Chem. Eng. J.* **2010**, *162*, 949–955.
28. G. V. Cullen, N. G. Siviour, *Water Res.* **1982**, *16*, 1357–1366.
29. L. Semerjian, *J. Hazard. Mater.* **2010**, *1173*, 236–242.
30. M. Sciban, B. Radetici, et.al., *Bioresour. Technol.* **2007**, *98*, 402–409.
31. M. Stanca, A. Măicăneanu, C. Indolean (Ed.): Characterisation, valorisation and regeneration of the main raw materials from chemical and petrochemical industry (original title in Romanian: Caracterizarea, valorificarea și regenerarea principalelor materii prime din industria chimică și petrochimică), Cluj University Press, Cluj-Napoca, Romania, **2007**, pp.102–109.
32. B. Yasemin, T. Zeki, *J. Environ. Sci. Eng.* **2007**, *19*, 160–166.
33. S. Lagergren, *Handlingar*, **1898**, Band 24, 1–39.
34. Y. S. Ho, G. McKay, *The Water Res.* **2000**, *34*, 735–742.
35. W. J. Weber and J. C. Morris, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* **1963**, *89*, 31–60.
36. G. E. Boyd, A. W. Adamson, L. S. Myers Jr., *J. Am. Chem. Soc.* **1947**, *69*, 2836–2842.
37. I. Langmuir, *J. Am. Chem. Soc.* **1918**, *40*, 1361–1367.
38. H. M. F. Freundlich, *Zeitschrift fur Physicalische Chemie (Leipzig)*. **1906**, *57 A*, 385–470.
39. H. Kalavathy M, I. Regupathi, et.al., *Colloids Surf.* **2009**, *B 70*, 35–45.
40. U. K. Garg, M. P. Kaur, V. K. Garg, D. Sud, *J. Hazard. Mater.* **2007**, *140*, 60–68.
41. X. Yang, B. Al-Duri, *J. Colloid Interface Sci.* **2005**, *287*, 25–34.
42. A. Ahmad, M. Rafatullah O. Sulaiman, M. H. Ibrahim, Y. Chii and B. M. Siddique, *Desalination*. **2009**, *247*, 636–646.
43. R. Malik, M. Mukherjee, A. Swami, D. S. Ramteke, S. Rajkamal, *Carbon Sci.* **2004**, *5*, 75–80.
44. A. Sharma, K. G. Bhattacharyya, *Adsorption*. **2004**, *10*, 327–338.
45. M. A. Wahab, S. Jellali, N. Jedidi, *Bioresour. Technol.* **2010**, *101*, 5070–5075.
46. K. G. Bhattacharyya, S. S. Gupta, *Colloids Surf.* **2008**, *A 317*, 71–79.
47. F. N. Acar, Z. Eren, *J. Hazard. Mater.* **2006**, *B 137*, 909–914.
48. A. Ahmad, M. Rafatullah, et.al., *J. Hazard. Mater.* **2009**, *170*, 357–365.
49. S. Gupta, B. V. Babu, *Chem. Eng. J.* **2009**, *150*, 352–365.
50. A. Kamari, W. S. Wan Ngah, L. W. Wong, *Eur. J. Wood Prod.* **2009**, *67*, 417–426.
51. K. G. Bhattacharyya, S. S. Gupta, *Chem. Eng. J.* **2008**, *136*, 1–13.
52. K. G. Bhattacharyya and S. S. Gupta, *Appl. Clay Sci.* **2008**, *41*, 1–9.
53. Z. A. Zakaria, M. Suratman, et.al., *Desalination*. **2009**, *244*, 109–121.
54. R. M. Schneider, C. F. Cavalin, et.al., *Chem. Eng. J.* **2007**, *132*, 355–362.
55. M. Macoveanu, D. Bilba, N. Bilba, M. Gavrilesco, G. Soreanu (Ed.): Ionic exchange processes in environmental protection, (Original title in Romanian, Procese de schimb ionic în protecția mediului); Matrixrom Publishing House, București, Romania, **2002**, pp. 75–80.
56. G. Tan, D. Xiao, *J. Hazard. Mater.* **2009**, *164*, 1359–1363.
57. F. Asadi, H. Shariatmadari, N. Mirghaffari, *J. Hazard. Mater.* **2008**, *154*, 451–458.

## Povzetek

Raziskovali smo biosorpcijo kadmijevih ionov iz vodne raztopine na biosorbentu (žaganje romunske jelke *Abies Alba*). Biomaso smo pred eksperimentom sprali, sušili in presejali ter jo okarakterizirali z meritvami vlažnosti in gostote, FTIR spektroskopijo in z elementno analizo. FTIR analiza je pokazala, da so na površini prisotne hidroksilne in karboksilne skupine. S spreminjanjem različnih parametrov smo ugotovili, da večja količina biomase, nevtralni pH, rahlo povišana temperatura ter višja koncentracija kadmijevih ionov povečajo stopnjo adsorpcije. Podrobno smo proučili tudi ravnotežja (z uporabo Langmuirjeve in Freundlichove izoterme), kinetiko in termodinamiko procesa. Izkazalo se je, da proučevani proces bolje opiše Langmuirjeva izoterma, kinetično pa hitrostni zakon psevdodrugega reda. Te ugotovitve kažejo, da gre za enoplastno kemisorpcijo, ki jo spremlja povečanje entalpije.