

Removal of cadmium (II) from aqueous effluents by sorption on Romanian silver fir tree bark (*Abies alba* Mill.) wastes

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Abstract

In last decades the search for new low cost sorbents that have heavy metal ions binding capabilities is a hot topic in the field of clean-up technologies. In this study, wastes of Romanian silver tree (*Abies alba*) bark were explored for first time as green and economical sorbent for the removal of Cd(II) ions from aqueous solutions. The effect of various experimental parameters such as initial solution pH, sorbent dose, initial Cd(II) concentration, temperature and contact time has been investigated under batch conditions.

The Langmuir and Freundlich models were used to describe the equilibrium isotherms and both models have been fitted very well. According to the evaluation using the Langmuir equation, the maximum sorption capacity of Cd (II) ions on *Abies alba* bark waste was found to be 11.98 mg g⁻¹ at 293 K. The thermodynamic parameters showed that the process of Cd(II) sorption on silver fir tree bark was feasible, spontaneous and endothermic. Kinetic data were properly fitted with the pseudo-second order model. The obtained results strongly suggest that Romanian silver tree (*Abies alba*) bark is eligible as an efficient sorbent for the decontamination of toxic metals from wastewaters.

Keywords: bark; cadmium; sorbent; isotherm; kinetic; thermodynamic.

1. Introduction

The population dynamics, rapid urbanization and non-uniform distribution of urban areas, the economy development associated with energy use and waste generation from domestic and industrial sources have considerably enhanced the release of heavy metals into the environment. The impacts of these metals on the ecosystems and on humans are relevant from the economic, environmental and public health point of view. According to a ranking of metal interest priorities, cadmium is of the tree most interesting heavy metals for removal

and/or recovery considering the combination of environmental risk and reserve depletion (Volensky, 2001).

Sorption has evolved into one of the most effective processes of cadmium removal/recovery, due to its advantages such as: high removal efficiencies, applicability for various concentrations, lack of sludge production, sorbent versatility, etc. (Rao *et al.*, 2010; Purkaystha *et al.*, 2014; Ghosh *et al.*, 2015). However, the removal efficiencies of cadmium by sorption, depend on several factors such as: initial loads of cadmium in the influent, purpose of treatment (drinking/industrial water production, wastewater treatment for disposal or recycling), costs of the overall process, properties and conditions for regeneration of the sorbent materials (Teodosiu *et al.*, 2014). In this context, the use of natural and waste materials that are biodegradable, readily available at little or no cost in place of conventional sorbents is in conformity with green chemistry and green environment, now in the front burn of global environmental issues (Okoro and Okoro, 2011; Salman *et al.*, 2016).

The use of different tree barks as heavy metal ion sorbents is of a special interest since they have significant sorption capacities even at low metal concentration, are abundant, renewable and low-cost, have reductive abilities, providing versatile applications in heavy metal effluent management (Al-Asheh and Duvnjak, 1997; Aoyama *et al.*, 2004; Escudero *et al.*, 2008; Gondogdu *et al.*, 2009; Jauberty *et al.*, 2011; Amalinei *et al.*, 2012; Tofan *et al.*, 2012; Sen *et al.*, 2015).

The silver fir tree (*Abies alba* Mill.) is a coniferous species in the family of Pinaceae that is widely spread across Europe. In Romania it grows naturally in the Carpathian Mountains, but it is also planted due to its economic, environmental and social importance. The silver fir tree occupies 5% of the Romanian forest area, being the second coniferous tree, as percentage, after spruce. The wood of

mature *Abies alba* Mill. tree is used in construction and furniture industries, the bark being the main waste product.

Previous studies have been emphasized that Romanian silver fir cone powder and sawdust (*Abies alba*) are able to retain cadmium(II) ions from aqueous solutions, the maximum sorption capacity having low values of 3.74 mg Cd g⁻¹ of cone powder and 2.159 mg Cd g⁻¹ of sawdust, respectively (Manzatu *et al.*, 2014; Nagy *et al.*, 2013). But among tree biomass components, bark has the highest capacity for heavy metal sorption, followed by cones, needles and wood (Sen *et al.*, 2015). Despite the large amounts of silver fir bark wastes generated in Romania from the industrial processing of the silver fir wood, no studies on the sorption capabilities of Romanian *Abies alba* bark have been carried out.

Against this background, the aim of the present work is to investigate the possibility of conversion of Romanian silver fir tree bark residues into a low-cost sorbent for the removal of Cd(II) ions from aqueous solutions.

2. Experimental

2.1. Plant Material

Patches of *Abies alba* Mill bark were collected in the Calimani Mountains (Romania) in March 2008. A full-grown tree was randomly selected for collection. The species was identified and authenticated by specialists from Botanical Garden, Iasi, Romania. The bark was shade-dried at room temperature for two weeks and powdered in a knife mill. A voucher sample was deposited in the Department of Pharmacognosy, Faculty of Pharmacy, "Gr. T. Popa" University of Medicine and Pharmacy, Iasi, Romania. Before use, the natural material was washed with deionized water several times and then dried at 40 °C for 24 h.

2.2. Chemicals

Stock solution of 1200 mg l⁻¹ was prepared by dissolution of analytical grade reagent CdSO₄·8H₂O (Sigma–Aldrich) in deionised water and was complexometrically standardized. Working solutions of Cd(II) were prepared by the appropriate dilutions of the stock solution.

In order to study the effect of medium acidity on the sorption process, a solution of H₂SO₄ with concentration of 10⁻² mol l⁻¹ has been used (340–A /SET 1 pH-meter).

2.3. Sorption procedure

Table 1. Sorption experimental conditions

Nature of investigation	Initial pH	Bark dose (g l ⁻¹)	Metal ion concentration (mg l ⁻¹)	Temperature (°C)	Contact time (h)
Solution pH effect	1 – 5	3	72.00	20±2	8
Bark dose effect	4.5 – 5	2 - 30	72.00	20±2	8
Initial concentration effect	4.5 – 5	3	22 – 192	4; 20; 60	8
Temperature effect	4.5 – 5	3	22 – 192	4; 20; 60	24
Effect of contact time	4.5 – 5	3	72.00 144.00	20±2	0.25 – 24

Batch sorption experiments for Cd(II) retention onto silver fir bark were performed according to the procedure presented in Fig. 1. The absorbance measurements were performed using a 210 VGB Buck Scientific atomic absorption spectrometer.

The effects of the experimental parameters such as pH, sorbent dose, metal concentration, temperature and contact time on the Cd(II) sorption by silver fir bark are systematized in Table 1. Each experiment was carried out by varying the parameter under study and maintaining the other parameters constant.

All the experiments were carried out in triplicate and the average of the values were used for the further calculation.

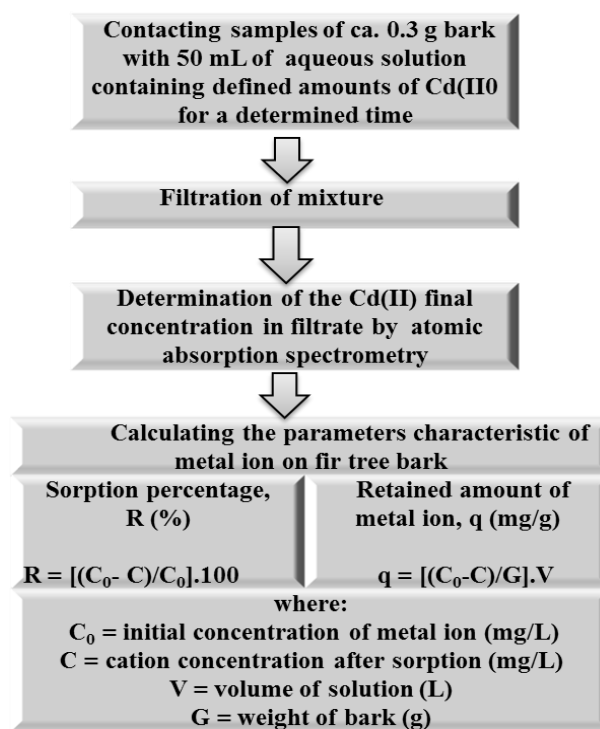


Figure 1. Sorption procedure

2.4. FT-IR spectra

The infrared spectra of the *Abies alba* bark samples before and after metal uptake were recorded, using a FT-IR spectrometer Vertex 70 model (Bruker-Germany-. range 4000–400 cm⁻¹). KBr was used as the embedding medium to make pellets

3. Results and Discussion

3.1. Characterization of the silver fir bark

Previous studies showed that the major chemical components of the raw *Abies alba* bark are cellulose (48.24–58.32%) and lignin (29.20–33.30%) (Nagy *et al.*, 2013). Their presence in the bark structure is responsible for the sorptive capabilities of this material.

Bark components offer a large variety of functional groups that are able to bind metals through chemical interactions (Fig.2). The most important bands of the silver fir bark and Cd-loaded silver fir bark with the respective assignments are:

- 3600-3200 cm^{-1} - corresponding to the deformation of O-H and N-H groups present in alcohols and phenols;
- 2950-2800 cm^{-1} - attributed to C-H asymmetrical and symmetrical stretching;
- 1650-1500 cm^{-1} - Represents the stretching vibration of C=O bonds, which originates from non-ionic carboxyl groups ($-\text{COOH}$, $-\text{COOCH}_3$), and may be denoted by carboxylic acids or corresponding esters.
- 1330-900 cm^{-1} - This band can be connected to the existence of stretching vibrations of C–O from phenolic groups.

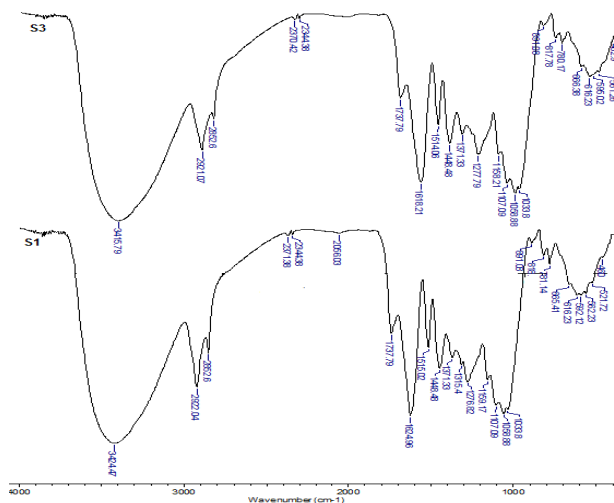


Figure 2. IR-spectra for: S1- silver fir bark; S3- silver fir bark-Cd(II) ions

3.2. Batch studies

3.2.1. Effect of initial pH on the Cd(II) retention by silver fir bark

The initial pH plays a vital role in the removal of cadmium ions from wastewaters by sorption due to its impact on both the surface functional groups of sorbents and the metal chemistry in water (Salman *et al.*, 2016). The effect of initial pH on the removal efficiency of Cd(II) by using wastes of Romanian silver fir bark was studied at different pH ranging from 1.0 to 5.0. It must be emphasized that the double positively charged ionic form of cadmium is

predominant at initial pH =1- 5 (Bayat, 2002) The pH sorption profile is shown in Fig 3.

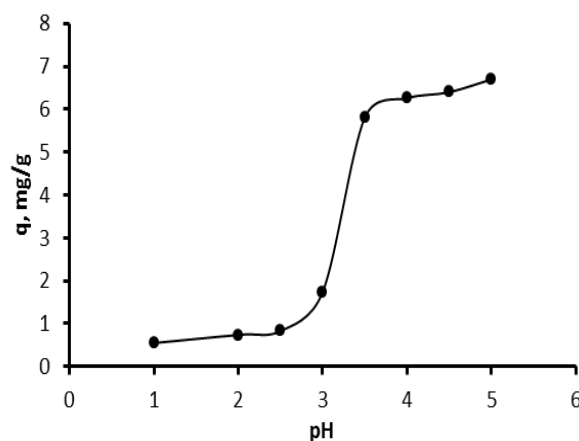


Figure 3. The influence of initial pH on the Cd(II) ions retention by *Abies alba* bark

It was observed that a sharp increase in the Cd(II) sorption ability of the *Abies alba* bark occurred when the pH of the initial solutions changed from 1 to 3.5 and after 3.5 a plateau is obtained. The explanation for the low Cd(II) sorption at strong acidic medium may be the electrostatic repulsion between the positive net charge on the *Abies alba* bark (as the result of its pronounced protonation) and the positively charged cadmium ions (Tofan *et al.*, 2012). The increased sorption of Cd(II) on *Abies alba* bark at higher values of initial pH may be due to the ionization of functional groups and the increase in the negative charge density on the bark surface which significantly improved the attraction of the tested cations (Amalinei *et al.*, 2012).

In this context, the influence of bark dose, Cd(II) initial concentration, temperature and contact time was performed with solutions of initial pH 4.5 – 5. This finding is in good agreement with literature data reporting that the metal sorption on barks normally occurs under slightly acidic conditions (Sen, 2015).

3.2.2. Effect of bark dose

The influence of silver fir bark dose on the sorption of Cd(II) is illustrated in Fig 4. It was observed that the Cd(II) removal efficiency increased rapidly from 32% to 87.8% with increasing of the bark concentration from 3 g l^{-1} from 20 g l^{-1} . This trend can be attributed to the increase in surface area resulting from the increase in sorbent mass, thus increasing the number of active sorption sites (Nguyen *et al.*, 2013). At higher sorbent dose, the equilibrium sorption of Cd(II) ions did not increase significantly with the increasing of the bark dose from 20 to 30 g l^{-1} . This behavior is expected due to the saturation level attained during the sorption process (Safiur Rahman and Rafiqul Islam, 2009).

3.2.3. Effect of Cd(II) concentration in initial solutions

The influence of metal ion initial concentration on Cd(II) biosorption by *Abies alba* bark is shown in Table 2. It can be seen from Table 2 that the amount of Cd(II) ions retained on the tested silver fir bark (q) increased with increasing

metal ion concentration. Conversely, the increase of initial metal concentration leads to the decrease of the removal efficiency (R%). The increasing trend may be attributed to the increase in the driving force of the Cd(II) concentration gradient produced by the increase in the initial metal ion concentration.

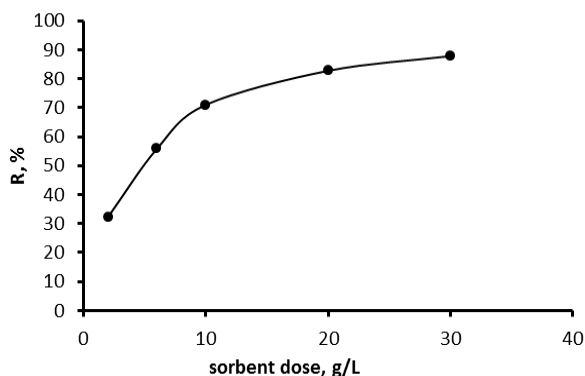


Figure 4. The effect of sorbent dose on the Cd(II) ions uptake by *Abies alba* bark

The lower removal efficiencies at higher Cd(II) initial concentrations might be closely associated with insufficient binding sites for sorption or to the saturation of the binding sites (Arief *et al.*, 2008). On the basis of this behavior it can be concluded that the wastes of Romanian silver fir bark may be a sustainable material for the efficient removal of Cd(II) from industrial effluents with low content in the tested cation.

Table 2. Effect of initial concentration (C_0) on Cd(II) sorption by *Abies alba* bark

Initial concentration C_0 , mg l ⁻¹	q , mg g ⁻¹	R, %
24.00	3.11	80.00
48.00	5.26	77.86
72.00	6.69	71.25
96.00	7.06	65.83
120.00	8.72	59.20
144.00	10.91	52.00
168.00	13.16	48.70
192.00	15.58	45.50

3.2.4. Isotherms of Cd(II) sorption

The sorption isotherms help in designing sorption process systems, since equilibrium studies determine the sorption capacities of the low – cost sorbents. In order to come up with an optimum design for successful sorptive removal of heavy metal ions from wastewaters it is imperative to establish the best correlation for the equilibrium isotherms (Moyo *et al.*, 2015). In present study, the equilibrium data obtained for Cd(II) removal using wastes of *Abies alba* bark were interpreted by means of two parameters isotherm models, Langmuir and Freundlich.

The **Langmuir model** is based on the reaction hypotheses and assumes monolayer sorption on a finite number localized sites that are equivalent with no lateral interaction and steric hindrance between the sorbed species, even on adjacent sites. Homogeneous sorption occurs with each molecule possessing constant enthalpies

and sorption activation energy without transmigration of the sorbate in the plane of the surface (Febrianto *et al.*, 2009). Fig. 5 shows the Langmuir isotherms for Cd(II) ions sorption on the investigated silver fir bark at three different temperatures. The Cd(II) ions sorption on the *Abies alba* bark under study is characterized in Table 3 by means of Langmuir constants obtained from the corresponding linear Langmuir plots.

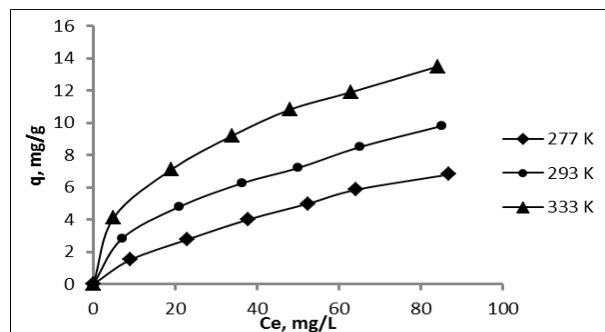


Figure 5. Langmuir isotherms of Cd(II) ions sorption on silver tree bark

The high values of K_L in Table 3 confirmed that the sorption of Cd(II) on Romanian silver fir tree bark was a favorable process. The maximum capacity of *Abies alba* bark for the uptake of Cd(II), derived from the application of Langmuir equation was 11.98 mg g⁻¹ at 20 °C in this work. This value for Romanian silver tree bark sorption capacity of Cd(II) was higher than other reported values for various barks, as summarized in Table 4. Although not being best of all, the *Abies alba* bark can be regarded as a good sorbent candidate in decontamination of waters containing Cd(II).

Freundlich isotherm describes the non-ideal and reversible multilayer sorption, with non uniform distribution of sorption heat and affinities over the heterogeneous surface (Manohar *et al.*, 2002). The stronger binding sites are occupied first, until sorption energies are exponentially decreased upon the completion of sorption process. The empirical values of the Freundlich constants at three different temperatures for Cd(II) ion-silver fir tree bark batch sorption system are recorded in Table 3. The n values are above unity, indicating favorable sorption of the Cd(II) ions by *Abies alba* bark under study at all working temperatures. The K_F values determined in this study are significantly higher than those determined in previous studies using other low-cost sorbents such as *Tamrix articulata* wastes or bottlebrush seeds (Al Othman *et al.*, 2010; Rao and Kashiffudin, 2014).

To compare the Langmuir and Freundlich isotherm models, the experimental data were statistically processed by linear regression. High values of the linear regression correlation coefficients (R^2) for both Langmuir and Freundlich plots (Table 3) suggest that monolayer sorption, as well as heterogeneous surface conditions may co-exist under applied experimental conditions. A similar behavior has been reported in the literature for the sorption of Cu(II) and Zn(II) ions on Romanian *Pinus sylvestris* L bark (Amalinei *et al.*, 2012).

Table 3. Isotherm parameters

Langmuir isotherm (Langmuir, 1916)					
Equation	Quantitative parameters				Isotherm parameters, significance
	T, K	K_L , L mol ⁻¹	q_0 , mg g ⁻¹	R ²	
$q = K_L \cdot C / (1 + K_L \cdot C)$	277	1543.20	11.76	0.9945	K_L – binding energy (relative sorption affinity) q_0 maximum capacity of sorption
	293	3597.12	11.98	0.9904	
	333	8403.36	13.10	0.9927	
Freundlich isotherm (Freundlich, 1906)					
Equation	Quantitative parameters				Isotherm parameters, significance
	T, K	K_F	n	R ²	
$\log q = \log K_F + (1/n)\log C$ (linearised form)	277	0.327	1.458	0.9989	K_F - sorption capacity n–energy of sorption
	293	1.071	2.023	0.9970	
	333	2.063	2.354	0.9996	

Table 4. Comparison of sorption capacity of various tree barks for Cd(II) from aqueous solution

Sorbent	Maximum Cd(II) sorption capacity, mg g ⁻¹	Reference
<i>Abies sachalinensis</i> bark	6.72	(Seki <i>et al.</i> , 1997)
<i>Pinus pinaster</i> bark	7.84	(Kumar, 2006)
<i>Juniperus monosperma</i> bark	10.08	(Shin <i>et al.</i> , 2007)
<i>Ceratonia siliqua</i> bark	14.27	(Farhan <i>et al.</i> , 2012)
Bark of Eucalyptus (globulus)	14.56	(Ghodbane <i>et al.</i> , 2008)
Romanian <i>Pinus sylvestris</i> L. Bark	27.32	(Tofan <i>et al.</i> , 2012)
<i>Eriobotrya japonica</i> Loquat bark	28.80	(Salem <i>et al.</i> , 2012)
<i>Harwickia binata</i> bark	33.60	(Seki <i>et al.</i> , 1997)
<i>Cassia siamea</i> bark	37.70	(John <i>et al.</i> , 2011)
Romanian <i>Abies alba</i> Mill. bark	11.98	This study

3.2.5 Effect of temperature and thermodynamic parameters

It is obvious from Fig. 5 and Table 5 that the temperature has a favorable effect within the sorption system under study. Both Langmuir and Freundlich constants (Table 3) increase with increasing temperature, showing that the sorption capacity and the intensity of sorption are enhanced at higher temperatures. This behavior may be

attributed to either increase in the number of active sites present on the surface of the sorbent or the increase in the attractive forces between the metal ions and the sorbent (Yuvaraja *et al.*, 2014)

The thermodynamic parameters, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated on the basis of Langmuir constant K_L at different temperatures by using the equations recorded in Table 5.

Table 5. The thermodynamic parameters of the sorption process of Cd(II) ions on Romanian *Abies alba* bark

Thermodynamic parameter	Equations (Khazali <i>et al.</i> , 2007)	T, K	Obtained values
Free energy change, ΔG , (kJ mol ⁻¹)	$\Delta G = -RT \ln K_L$ R is the gas constant; T is the absolute temperature	277	- 16.520
		293	- 19.910
		333	- 25.004
Enthalpy change, (ΔH), kJ mol ⁻¹	$\ln K_L = \text{constant} = - \frac{\Delta H}{RT}$	277	21.90
		293	
		333	
Entropy change (ΔS), kJ mol ⁻¹	$\Delta S = \frac{\Delta H - \Delta G}{T}$	277	0.1380
		293	0.1420
		333	0.1400

The negative values of ΔG in Table 5 suggest that the sorption of Cd(II) on Romanian *Abies alba* bark is a spontaneous process and thermodynamically favorable under the experimental conditions. Furthermore, the decrease in the values of ΔG reflects that the Cd(II) sorption process is more spontaneous at higher temperatures (Chen *et al.*, 2010). The positive value of ΔH suggests that the process of Cd(II) sorption on the bark under study is endothermic. On the basis of the positive value of ΔS in

Table 5 it can be concluded that the process is entropy driven and with an increased randomness at the bark/solution interface during the sorption of Cd(II) on the Romanian *Abies alba* bark

3.2.6. Effect of contact time

The kinetic data for the sorption of Cd(II) ions by Romanian silver fir tree bark are plotted in Figure 6.

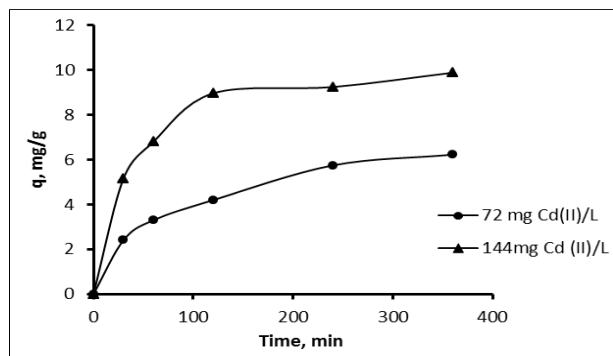


Figure 6. Effect of the contact time on Cd(II) ions retention by silver fir tree bark.

As shown in Figure 6, the removal rate of Cd(II) was rapid at the beginning and it became slow with increase of the contact time. It was observed that the process of Cd(II) sorption on Romanian *Abies alba* bark reached equilibrium at 120 minutes. It was showed no significant changes on silver fir tree bark with a further increasing contact time. The rapid uptake of Cd(II) ions at the initial period may be due to the availability of vacant sorption sites on the surface of the sorbent. The sorption process became slow later owing to the decrease of available sorption sites (Wang *et al.*, 2010).

3.2.7. Kinetic modeling

Table 6. Kinetic description of the Cd(II)- Romanian *Abies alba* bark sorption system

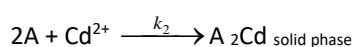
	$C_0, \text{mgCd(II) l}^{-1}$	72.00	144.00
Pseudo-first-order kinetics	$k_1, (\text{min}^{-1})$	$6.67 \cdot 10^{-3}$	$7.13 \cdot 10^{-3}$
	R^2	0.9890	0.9874
Pseudo-second-order kinetics	$k_2, (\text{g mg}^{-1} \text{min}^{-1})$	$1.75 \cdot 10^{-3}$	$2.99 \cdot 10^{-3}$
	$h, (\text{g mg}^{-1} \text{min}^{-1})$	0.0986	0.3420
	$q_0 (\text{g mg}^{-1})$	7.49	10.69
	R^2	0.9934	0.9984

The pseudo-second-order kinetic model implies that the rate of sorption sites covering is proportional to the square of the number of unoccupied and occupied sites (Ho, 2006). This model is based on the following equation (Ho and Mckay, 1999):

$$1/q_t = 1/h + (1/q_e) \cdot t$$

where k_2 is the rate constant of the pseudo-second-order model and $h = k_2 \cdot q_e^2$ ($\text{mg g}^{-1} \text{min}^{-1}$) can be regarded as the initial sorption rate constant of the pseudo-second-order sorption ($\text{g mg}^{-1} \text{min}^{-1}$).

According to this model, it can be assumed that one cadmium ion is sorbed onto two sorption sites on the bark surface

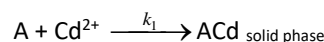


where A represents an unoccupied sorption site on the silver fir bark and k_2 is the pseudo-first-order rate constant.

The kinetic parameters derived from the plots of the linearized form of the pseudo-second-order equation are recorded in Table 6, along with the corresponding correlation coefficients. As shown in Table 6, the R^2 are very

Kinetics of sorption is one of the most important characteristics to be responsible for the efficiency of sorption (Mihailescu *et al.*, 2012). Kinetic studies gave detailed information on the mechanism of sorption and potential rate controlling steps. Kinetics of Cd(II) retention on the *Abies alba* bark under study was modeled by means of pseudo-first-order and pseudo-second-order kinetic models.

The pseudo-first-order model (Lagergren's equation) describes adsorption in solid-liquid systems based on the sorption capacity of solids (Ho, 2004). On the basis of this model one can assume that one cadmium ion is sorbed onto one sorption site on the silver fir tree bark surface:



where A represents an unoccupied sorption site on the bark and k_1 is the pseudo-first-order rate constant (min^{-1}).

The Lagergren pseudo-first-order kinetic model is represented by the following equation (Lagergren, 1898):

$$\log(q_e - q_t) = \log q_e - k_1 \cdot t / 2.303$$

The kinetic parameters obtained from the linear Lagergren plots for this study are given in Table 6, together with the corresponding determination coefficients (R^2). The R^2 values are less, suggesting that the sorption of Cd(II) on the bark under study does not follow pseudo-first-order model.

close to unity (0.99) for both Cd(II) concentrations, indicating the applicability of the pseudo-second order kinetic model to the sorption of Cd(II) on the Romanian *Abies alba* bark. According to literature data, the pseudo-second order kinetic model includes different sorption mechanisms such as surface complexation or ion exchange. The model is based on the assumption that the rate-limiting step is the chemisorption (Yuvaraja *et al.*, 2014). Furthermore, the sorption rate depends on the concentration of Cd(II) ions on the *Abies alba* bark surface (Table 6).

4. Conclusions

Romanian *Abies alba* bark - a low cost and abundant forest by-product - could act as potential sorbent for the removal of Cd(II) ions from wastewaters. The optimum value of initial pH for Cd(II) ions sorption was found to be 4.5 to 5. The Cd(II) removal efficiency increased rapidly from 32% to 87.8% with increasing of silver fir tree bark concentration from 3g l^{-1} to 20g l^{-1} . The amount of Cd(II) retained on the bark under study increased with the increasing of metal ion concentration, while the Cd(II)

sorption percentage decreased. The sorption isotherm studies clearly indicated that the sorptive behavior of Cd(II) ions on Romanian *Abies alba* bark under study satisfies not only the Langmuir assumptions, but also the Freundlich assumption. The calculated values for the isothermal thermodynamic parameters show that Cd(II) ions retention by silver fir tree bark is a spontaneous process of endothermic and chemical nature. The sorption kinetics for Cd(II) ions removal from aqueous solutions with initial pH of 4.5 to 5 was very well described by pseudo-second order model.

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