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REMEDIATION OF AQUEOUS SOLUTIONS CONTAINING Zn(II) IONS BY USING WASTES OF *ABIES ALBA* BARK

BY

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Abstract. Batch sorption capability of Romanian *Abies alba* bark wastes for the removal of Zn(II) ions from diluted aqueous solutions has been investigated as function of initial pH, sorbent dose, metal ion concentration, temperature, and contact time. The ability of the bark waste for Zn(II) sorption exhibited a maximum at pH 4.5-5. The percent removal of Zn(II) from solution with an initial concentration of 71.4 mg/L varied from 15% to 87.9% for an increase of bark waste dose to 2 at 30 g/L. The equilibrium data are best explained by both Langmuir and Freundlich sorption isotherm. Thermodynamic parameters also favor the sorption of heavy metal ions under study on *Abies alba* bark. Kinetics of sorption follows pseudo – first order rate equation. This valuable use of *Abies alba* bark may not only convert this waste material into low- cost effective sorbent, but also provide a viable solution to its disposal.

Keywords: *Abies alba*; bark; zinc; removal; waste.

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1. Introduction

Zinc is a significant heavy metals found in the aqueous environments from domestic and industrial discharges (Mishra, 2014). Although can act as an essential microelement, the zinc excess can be very harmful to human health (Fosmire, 1990).

A variety of processes may be used for the removal of zinc ions from water and wastewater, including but not limited to chemical precipitation, ion exchange, sorption, membrane filtration (Barakat, 2011; Fu and Wang, 2011; Kurniawan *et al*., 2006).

In order to remove zinc from aquatic environments the sorption processes are often used. The popularity of sorption is mainly due to its efficiency and versatile applicability (Zwain *et al*., 2014). One can not overlook that the sorption efficiency in the removal of zinc is conditioned by many factors whose action needs to be optimized (Teodosiu *et al*., 2014). Thus, there is a continuous interest in searching for low-cost, easy available and environmental friendly sorbents based on natural or waste materials, suitable for the remediation of zinc bearing waters before their discharge into the environment (Abas *et al*., 2013; De Gisi *et al*., 2016; Dhir, 2014; Emenike *et al*., 2016; Gupta *et al*., 2015; Kumar *et al*., 2011; Malik *et al*., 2017; Mishra, 2014; Nguyen *et al*., 2013; Tripathi and Ranjan, 2015; Zwain *et al*., 2014).

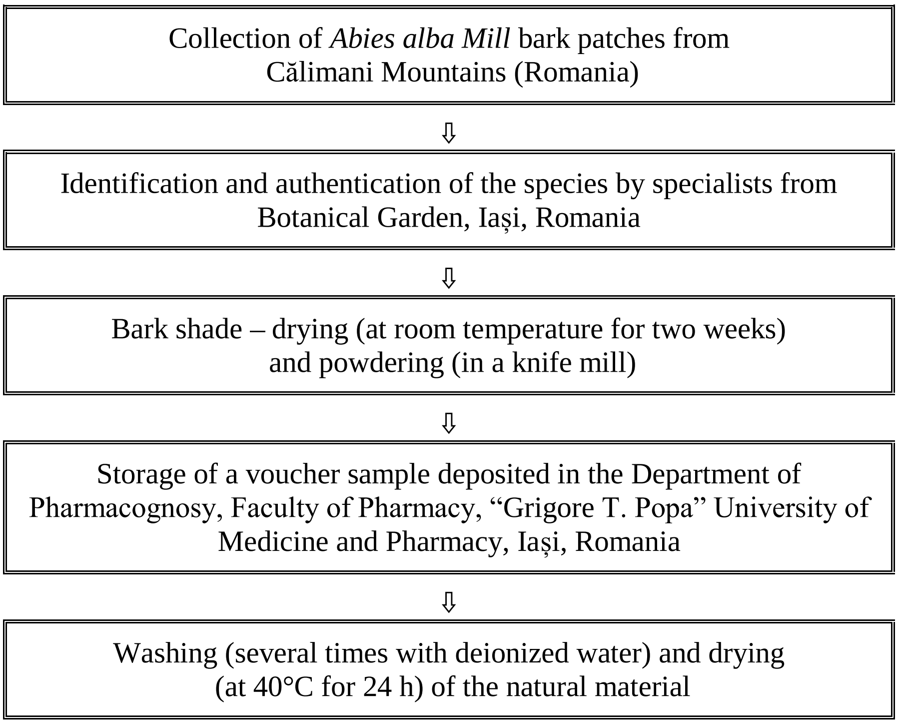
Wood bark, one of the most renewable resources, is a forestry waste of major importance. Currently, wood bark is disposed via burning or waste disposal, generating atmospheric pollutants harmful to the environment and to human health (Zhang *et al*., 2015). Extensive researches over last decades have been emphasized that the bark wastes can be converted into higher added value, sustainable sorbents for heavy metal removal treatments (Sen *et al*., 2015) Wastes of coniferous barks, hardwood bark, *Azadirachta indica* A. Juss. bark, Douglas fir barks, pelletized ponderosa pine bark, Romanian *Pinus sylvestris* L. bark or neem bark have been successfully used for the sorption removal of Zn(II) ions from aqueous solutions (Amălinei *et al*., 2012; Conrad and Hausen, 2007; Dupont *et al*., 2002; Jang *et al*., 2005; King *et al*., 2008; Maheshwari *et al*., 2015; Oh and Tshabalala, 2007).

The silver fir tree (class: *Pinopsida* (conifers); subclass: *Pinidae*; order: *Pinales*; family: *Pinaceae*; genus: *Abies alba*; species: *Abies alba* Mill.) grows naturally in the mountain regions of Romania. Because of its special importance and multiple industrial uses, the silver fir tree is also planted. The industrial uses of *Abies alba* tree wood generate significant amounts of waste, of which the most important is the bark. The possible therapeutic applications of Romanian *Abies alba* bark waste and its antioxidant potential have been emphasized (Vasincu *et al*., 2013). Previous studies emphasized another way of Romanian *Abies alba* bark waste valorization, as low –cost sorbent of Cu(II) and Cd(II) ions from diluted aqueous solutions (Tofan *et al*., 2016; Tofan *et al*., 2017). The aim of this work is to establish the optimum conditions of the batch sorption of Zn(II) by Romanian silver fir tree bark, to obtain equilibrium sorption isotherms and to evaluate the sorption capacity of *Abies alba* bark waste for Zn(II) ions present in the aqueous phase.

2. Materials and Methods

2.1. Biosorbent Preparation

The biosorbent under study was prepared according to the procedure presented in Fig. 1.



Collection of *Abies alba Mill* bark patches from
Călimani Mountains (Romania)

⇩

Identification and authentication of the species by specialists from
Botanical Garden, Iași, Romania

⇩

Bark shade – drying (at room temperature for two weeks)
and powdering (in a knife mill)

⇩

Storage of a voucher sample deposited in the Department of
Pharmacognosy, Faculty of Pharmacy, “Grigore T. Popa” University of
Medicine and Pharmacy, Iași, Romania

⇩

Washing (several times with deionized water) and drying
(at 40°C for 24 h) of the natural material

Fig. 1 – Schematic representation of the procedure applied for the biosorbent preparation.

2.2. Metal Solutions

Solution was prepared by dissolving corresponding analytical grade soluble $ZnSO_4 \cdot 7H_2O$ obtained from Sigma-Aldrich into distilled water. Subsequently this solution was standardized gravimetrically. The effect of medium acidity on the Zn(II) sorption was studied with a 10^{-2} mol/L solution of H_2SO_4 (340–A /SET 1 pH-meter).

2.3. Sorption Procedure

All the studies were carried out in batch sorption experiments. For this purpose, samples of about 0.5g *Abies alba* bark were equilibrated with 50 mL of aqueous solution containing defined amount of metal ion. The mixture was then separated from the sorbent by centrifugation (Premiere XC-2000) at 4000 rpm and the solution was analyzed for the cation content. The Zn(II) concentrations in solutions have been determined by atomic absorption spectrometry (210 VGB Buck Scientific atomic absorption spectrometer).

The amount of metal ions sorbed on bark was calculated from the difference between the initial and final concentrations of the solutions.

Sorption percentage, R, [%] $$R = [(C_0 - C)/C_0].100 \quad (1)$$

Retained amount of metal ion, q, [mg/g] $$q = [(C_0 - C)/G].V \quad (2)$$

where: C_0 – initial concentration of metal ion, [mg/L]; C – cation concentration after sorption, [mg/L]; V – volume of solution, [L]; G – weight of *Abies alba* bark, [g].

2.4. FTIR Characterization

In order to record the infrared spectra of the bark samples before and after zinc uptake, a FT-IR spectrometer Vertex 70 model (Bruker-Germany) have been used.

3. Results and Discussion

3.1. Sorbent Characterization

Infrared analysis provides valuable information about the mechanism of ion-binding zinc (II) on bark (Fig. 2). The assignment of the main absorption bands of the IR spectra shown in the crust before and after retaining the ions of Zn (II) is the following:

– 3600-3200 cm^{-1} - 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

– 1737- attributed to C=O from unionized carboxyl group

– 1650-1610 cm^{-1} - represents the stretching vibration of C=O bonds, from carboxylic acids or corresponding esters.

– 1315.4 cm^{-1} - attributed to –C-H from alkyl or carboxylic groups
– 1000-850 cm^{-1} stretching vibrations of C–O from phenolic groups.

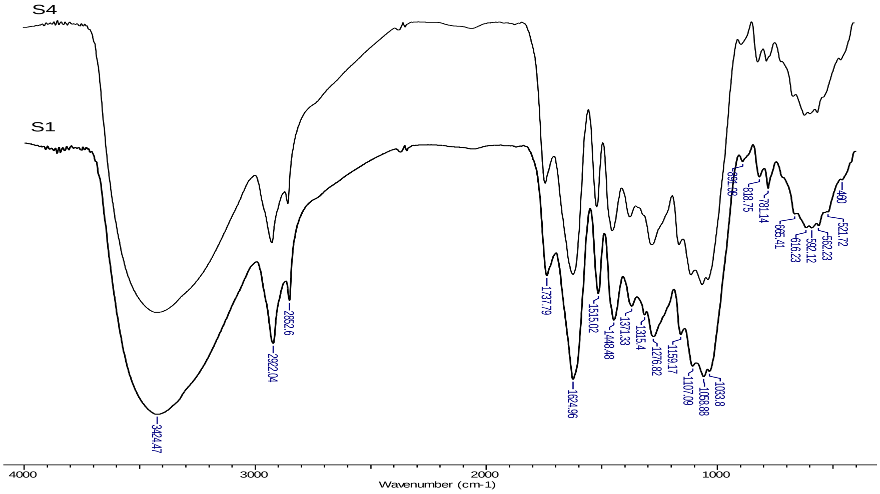
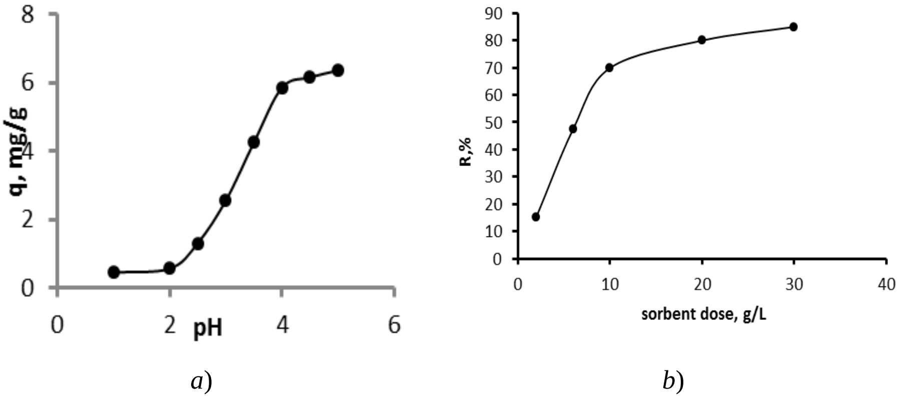


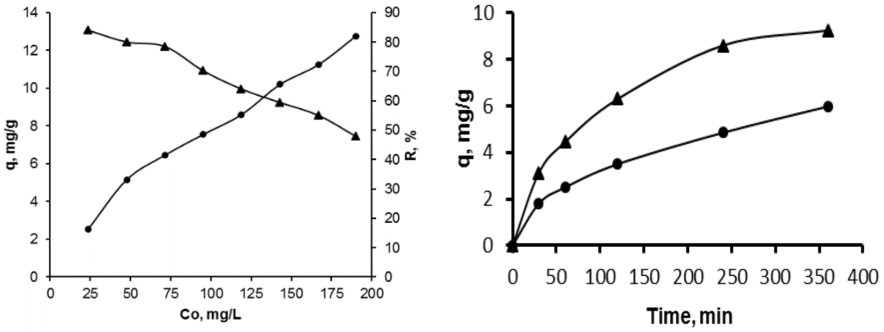
Fig. 2 – IR-spectra for: S1-*Abies alba* bark; S4-*Abies alba* bark –Zn(II) ions.

3.2. Effect of Various Experimental Factors

The removal of zinc ions from wastewater by sorption process is strongly influenced by the several physical and chemical factors which determine the overall sorption through affecting the uptake rate, selectivity and amount of heavy metals removed. Initial pH, bark dose, concentration of Zn(II) in initial solutions and contact time effect on the removal of Zn(II) from diluted aqueous solutions by using bark wastes under study are shown in Fig. 3 and explained in Table 1.



a) *b*)



c) (●)-q, mg/g; (▲)- R, % *d*) (●)71.4 mg/L; (▲) 143 mg/L

Fig. 3 – Effect of different factors [(*a*) – initial pH; (*b*) – sorbent dose; (*c*) – initial cation concentration; (*d*) – contact time] on the sorption removal of Zn(II) ions from aqueous solutions by *Abies alba* bark.

Table 1
The Impact of Major Experimental Factors on the Sorption of Zn(II) Ions by the Romanian Silver Fir Tree Bark

Factor	Findings	Explanation
Initial pH (Fig. 3*a*)	This estimation is most reliable at pH values where no hydroxide precipitation takes place and therefore the zinc pH dependence sorption on silver fir bark was studied in the initial pH range of 1→5. As follows from Fig. 3*a* the sorptive potential of the tested bark is minimum in strongly acidic media. Subsequently, the Zn(II) sorption rapidly increased in the initial pH range of 2–3.5. At the initial pH values higher than 3.5, the sorption did not increase further. This is the reason why we used solutions with initial pH of 4.5 – 5 for highlighting the effect of other experimental factors.	The decreased degree of the Zn(II) sorption at low pH is probably due to the positive charge of the bark and to the competition between hydrogen ions and zinc ions for the active sites on the bark surface. On the other hand, the increased sorption at higher values of pH can be correlated with the functional groups ionization and the increase in the density of negative charge on the surface of bark. This behaviour has led to a stronger attraction of the zinc cations (Sen *et al.*, 2015).

Table 1
Continuation

Factor	Findings	Explanation
Bark dose (Fig. 3*b*)	The dependence in Fig. 3*b* shows that the Zn(II) percentages of retention increase with increasing bark dose. Thus, the percent removal of Zn(II) from solution with an initial concentration of 71.4 mg/L varied from 15% to 87.9% for an increase of bark waste dose to 2 at 30 g/L.	This behavior can be explained as follows: rise in the mass of sorbent → active sorption sites number increase → surface area augmentation (Kumar *et al.*, 2006).
Initial Zn(II) concentration (Fig. 3*c*)	Fig. 3*c* shows that the zinc sorption is improved by the increase in the concentration of the initial solution. Contrariwise, a rise in the initial concentration resulted in a decrease of the removal efficiency of Zn(II). In this context, it may be concluded that the studied bark wastes could be efficiently used in the removal of the tested metal ions from wastewaters with low contents in Zn(II).	The increasing trend might be due to the increase in the backbone of the gradient of the concentration resulting from the augmentation in the initial concentration of zinc. The decreasing trend is probably generated by the rise in the number of ions competing for the available binding sites in the silver fir bark and also due to the lack of binding sites for the complexation of zinc ions at higher concentration levels (Amălinei *et al.*, 2012).
Contact time (Fig. 3*d*)	In the initial stages of the sorption process the amounts of Zn(II) retained on bark increased sharply with increasing contact time of the phases, reaching values that remained then almost constant. It can be considered that the retention of the tested ions on silver fir bark takes place in two different stages, a relatively quick step followed by a lower one.	The two-phases sorption may be explained by taken into account the fact that the active sites in a system is a fixed number and each active site can adsorb only one ion in a monolayer, the metal uptake by the sorbent surface will be rapid initially, showing down as the competition for decreasing availability of active sites intensifies by the metal ions remainingin solution (Li *et al.*, 2008).

3.3. Sorption Isotherms

An important element of the implementation of a metal ion separation process is the fitting of experimental data to an appropiate sorption isotherm model (Bartczak *et al.*, 2015). Analysis of the sorption isotherms provides very valuable information about the sorption mechanism and type (Febrianto *et al.*, 2009). The Langmuir and Freundlich sorption isotherms were tested to fit the recorded data.

The Langmuir sorption isotherm is based by the Eq. (3): (Langmuir, 1916).

$$Q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C} \tag{3}$$

where K_L is a constant that describe the binding energy (relative sorption affinity) and q_0 is the maximum capacity of sorption. The following assumptions are the basis of the Langmuir model: the sorption produces only a coverage in monolayer; all surface sites are alike and can only accommodate one adsorbed species; the ability of a species to be sorbed on a given site is independent from its neighboring sites occupancy; sorption is reversible; the sorbed species cannot migrate across the surface or interact with neighboring molecules (Febrianto *et al.*, 2009). The Langmuir isotherms for Zn(II) ions sorption on the wastes of Romanian *Abies alba* bark at three different temperatures are presented in Fig. 4.

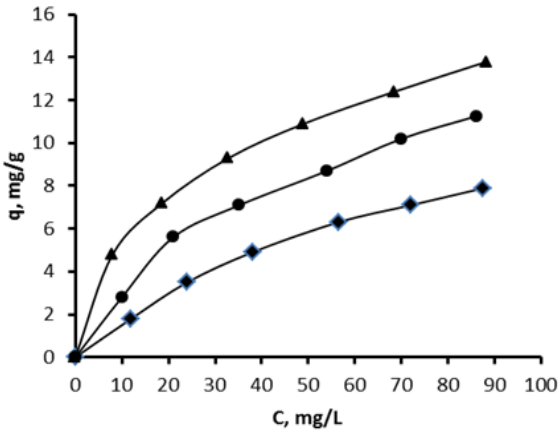


Fig. 4 – Langmuir isotherms of Zn(II) ions sorption on Romanian *Abies alba* bark at 277K (♦); 293 (●); 333 (▲).

Table 2 characterizes the Zn(II) ions retention on the silver bark under study through the Langmuir constants derived from the corresponding linear

Langmuir plots. The results in Table 2 strongly indicate that that Romanian *Abies alba* bark pine bark under study is a sustainable material for Zn(II) ions removal from waste streams.

Table 2
Quantitative Description of the Zn(II)– Abies Alba Bark Batch Sorption Systems on the Basis of Langmuir and Freundlich Models

Sorption isotherm model	Temperature [K]	Parameters values		R^2
Langmuir	277	K_L = 924.00 L/mol	q_0 = 14.12 mg/g	0.9961
	293	K_L = 1968.50 L/mol	q_0 = 14.38 mg/g	0.9929
	333	K_L = 2962.00 L/mol	q_0 = 16.08 mg/g	0.9951
Freundlich	277	K_F = 0.3177	n = 1.360	0.9940
	293	K_F = 0.7212	n = 1.590	0.9946
	333	K_F = 1.9500	n = 2.270	0.9977

Furthermore, it is clear from Table 3 that the tested silver fir bark is competitive against other reported low- sorbents based on tree barks, being suitable for the remediation of wastewaters containing Zn(II) ions. However, future experiments should be performed with industrial wastewaters to investigate silver fir bark sorption behavior in co-presence of other metals and organic matter.

Table 3
Bark of Different Trees as Sorbent for Zn(II) Removal from Wastewaters

Sorbent	Maximum capacity of Zn(II) sorption [mg/g]	Reference
Douglas fir barks (Pseudotsuga sp)	4.06	(Dupont *et al*., 2002)
Coniferous barks	7.4	(Conrad and Hansen, 2007)
Neem bark	11.90	(Maheshwari *et al*., 2015)
Hardwood bark	12.025 (pH = 5)	(King *et al*., 2008)
Romanian *Pinus sylvestris* L. bark	12.155 (pH = 6)	(Amălinei *et al*., 2012)
Pelletized ponderosa pine bark (*Pinus ponderosa*)	20.6 (pH = 5.1)	(Oh and Tshabalala, 2007)
Abies alba bark	14.38	This study

The linearised Freundlich sorption isotherm is in the following form: (Freundlich, 1906).

$$\log q = \log K_F + (1/n) \log C \tag{4}$$

where: q is the amount of Zn(II) taken up per 1g of bark, [mg/g]; C is the concentration of Zn(II) remaining in solution at equilibrium, [mg/mL]; K_F and n are the constants of the Freundlich isotherm associated with the factors affecting the retention process: sorption capacity (K_F) and energy of sorption (n), respectively. The Freundlich equation is based on a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites (Febrianto *et al*., 2009). Table 2 gives thevalues of the Freundlich constants for the batch sorption system under study. The favourability of the sorption of Zn(II) ions by the tested bark is highlighted by the values of the n values, which are greater than 1 at all working temperatures.

The linear regression was applied to the obtained data in order to compare the used isotherm models. The correlation coefficients of the linear regression (R^2) for both applied models have great values (Table 2). This indicates the possible co – existence of the sorption in monolayer and the conditions of heterogeneous surface (Amălinei *et al*., 2012; Gundogdu *et al*., 2009).

3.4. Thermodynamic Study

The increase of the values of the constants of both used models emphasizes a significant improvement of the capacity and intensity of sorption at higher temperatures (Table 2).

In order to evaluate the thermodynamic feasibility of the sorption process and to confirm its nature, the thermodynamic parameters, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated by using the following equations: (Khazali *et al*., 2007).

$$\Delta G = - RT \ln K_L; \tag{5}$$

$$\ln K_L = constant = - \frac{\Delta H}{RT}; \tag{6}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{7}$$

where: K_L are the values of the Langmuir constants at different temperatures; R is the gas constant; T is the absolute temperature.

Table 4

The Thermodynamic Parameters of the Sorption Process of Zn(II) Ions on Abies Alba Bark

T, [K]	ΔG, [KJ/mol]	ΔH, [KJ/mol]	ΔS, [J/mol K]
277	–15.698	10.02	0.0968
293	–18.456		0.0971
333	–22.110		0.0964

Evaluated thermodynamic parameters are presented in Table 4. Negative values of ΔG establish the feasibility of the Zn(II) sorption process. Also, the decrease in the values of ΔG with the increasing temperature indicates the spontaneity of the process at higher temperatures. The endothermic nature was confirmed from the positive value of the enthalpy change (ΔH), while good affinity of the Zn(II) ions towards the bark under study is revealed by the positive value of the entropy change (ΔS).

3.5. Kinetic Study

Kinetics of sorption describing the solute retention rate which, in turn, governs the residence time of sorption reaction is one of the important characteristics defining the efficiency of sorption. Hence, the kinetics of zinc removal has been carried out to understand the behavior of the bark. In order to analyze the sorption rate, the kinetic data were modeled using Lagergren pseudo-first-order and pseudo- second- order equations: (Lagergren, 1898; Ho and McKay, 1999).

Kinetic equation of pseudo-first-order (Lagergren):

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{8}$$

Kinetic equation of pseudo-second -order:

$$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + k_2 \cdot q_e \cdot t} \tag{9}$$

where q_t and q_e are the amounts of Zn(II) sorbed, [mg/g] at time and at equilibrium, respectively and k_1, [min^{-1}] and k_2, [mg/g min] are the rate constants of pseudo-first-order and pseudo-second order sorptions, respectively.

The values of the constants are calculated and listed in Table 5. The data presented in Table 5 indicate the increase of the sorption rate with the increase of the concentration of Zn(II). The correlation coefficient (R^2) values of the pseudo-first- and second order equations for the concentrations of 72 mg/L and 144 mg/L in Table 5 suggest that sorption kinetics of of Zn(II) ions on the tested bark follows better the pseudo-second-order kinetic model, which is in agreement with chemisorption being the rate-controlling step (Jang *et al.*, 2005).

Table 5

Kinetic Parameters Derived from Pseudo-First-Order and Pseudo-Second-Order Plots for Zn(II) Sorption by Abies Alba Bark

Initial concentration C_0, [mg L^{-1}]	Pseudo-first-order		Pseudo-second-order			
	k_1 [min^{-1}]	R^2	k_2 [g mg^{-1} min^{-1}]	h [mg $g^{-1}$$min^{-1}$]	q_0 [mg g^{-1}]	R^2
72	5.980 x10^{-3}	0.9818	1.371x10^{-3}	0.0680	7.042	0.9936
144	7.139x10^{-3}	0.9731	9.406x10^{-4}	0.1270	11.62	0.9964

4. Conclusions

1. *Abies alba* bark waste was explored as a low–cost sorbent for the removal of Zn(II) ions from aqueous solutions under batch conditions.

2. It is evident that initial pH, bark dose, initial Zn(II) ions concentration, contact time and temperature have marked effect on the sorption.

3. The dependence between the equilibrium concentrations of Zn(II) in the bark phase and aqueous solution phase was well described by both Langmuir and Freundlich models.

4. The obtained values for the thermodynamic parameters indicated the endothermic and chemical nature of the studied metal ions sorption on rapeseed.

5. In the concentration range under investigation, the sorption kinetics for Zn(II) ions at pH 4.5-5 fit with the pseudo-second-order model, indicating the chemisorption as the rate-controlling step.

6. The obtained results of are good prospects for the sorption of toxic heavy metals by silver fir tree bark in practical applications.

REFERENCES

Abas S.N.A., Ismail M.H.S., Lias K., Izhar H., *Adsorption Process of Heavy Metals by Low–Cost Sorbents*, World Appl. Sci. J., **28**, *11*, 1518-1530 (2013).

Amălinei R.L., Miron A., Volf I., Păduraru C., Tofan L., *Investigations on the Feasibility of Romanian Pine Bark Wastes Conversion into a Value–Added Sorbent for Cu(II) and Zn(II) Ions*, BioResources, **7**, *1*, 148-160 (2012).

Barakat M.A., *New Trends in Removing Heavy Metals from Industrial Wastewater*, Arab. J. Chem., **4**, *4*, 361-377 (2011).

Bartczak P., Norman M., Klapiszewski L., Karwańska N., Kawalec M., Baczyńska M., Wysokowski M., Zdarta J., Ciesielczyk F., Jesionowski T., *Removal of Nickel(II) and Lead(II) Ions from Aqueous Solution Using Peat as a Low-Cost Adsorbent: A Kinetic and Equilibrium Study*, Arab. J. Chem., DOI:10.1016/j.arabjc.2015.07.018 (2015).

Conrad K., Hansen H.C. B., *Sorption of Zinc and Lead on Coir*, Bioresour. Technol., **98**, *1*, 89-97 (2007).

De Gisi G., Lofrano G., Grassi M., Notarnicola M., *Characteristics and Adsorption Capacities of Low-Cost Sorbents for Wastewater Treatment: A Review*, Sust. Mater. & Technol., **9**, 10-40 (2016).

Dhir B., *Potential of Biological Materials for Removing Heavy Metals from Wastewater*, Environ. Sci. Pollut. Res., **21**, *3*, 1614-1627 (2014).

Dupont M.F., Gloaguen V., Granet R., Guilloton M., Moroan H., Krausz P., *Heavy Metal Removal by Crude Coniferous Barks: A Modeling Study.*, J. Environ. Sci. Health A, **37**, *6*, 1063-1073 (2002).

Emenike P.C., Omole D.O., Ngene B.U., Tenebe I.T., *Potentiality of Agricultural Adsorbent for the Sequestering of Metal Ions from Wastewater,* Global J. Environ. Sci. Manage., **2**, *5*, 411-442 (2016).

Febrianto J., Kosasih A.N., Sunarso J., Ju Y.H., Indraswati N., Ismadji S., *Equilibrium and Kinetic Studies in Adsorption of Heavy Metals Using Biosorbent: A Summary of Recent Studies*, J. Hazard. Mater., **162**, *2-3*, 616-645 (2009).

Fosmire G.J., *Zinc Toxicity*, Am. J. Clin. Nutr., **51**, *2*, 225-227 (1990).

Freundlich H.M., *Uber Die Adsorption in Lusungen*, Z. Phys. Chem., **57U**, *1*, 385-470 (1906).

Fu F., Wang Q., *Removal of Heavy Metal Ions from Wastewaters: A Review*, J. Environ. Manage., **92**, *3*, 407-418 (2011).

Gundogdu A., Ozdes D., Duran C., Bulut V.N., Soylak M., Senturk H.B., *Biosorption of Pb(II) Ions from Aqueous Solution by Pine Bark (Pinus Brutia Ten.),* Chem. Eng. J., **153**, *1-3*, 62-69 (2009).

Gupta V.K., Nayak A., Agarwal S., *Bioadsorbents for Remediation of Heavy Metals: Current Status and their Future Prospects*, Environ. Eng. Res., **20**, *1*, 1-18 (2015).

Ho Y.S., McKay G., *Pseudo–Second Order for the Sorption Process*, Biochemistry, **34**, *5*, 451-465 (1999).

Jang A., Slo Y., Bishop P.L., *The Removal of Heavy Metals in Urban Runoff by Sorption on Mulch*, Environ. Pollut., **133**, *1*, 117-127 (2005).

Khazali O., Abu–El–Halawa R., Sou Vod K.A., *Removal of Copper(II) from Aqueous Solution by Jordanian Pottery Materials*, J. Hazard. Mater., **139**, *1*, 67-71 (2007).

King P., Amuradha K., Beena Lahari S., Prasanna Kumar Y., Prasad V.S.R.K., *Biosorption of Zinc from Aqueous Solutions Using Azadirachta Indica Bark: Equilibrium and Kinetic Studies*, J. Hazard. Mater., **152**, *1*, 324-329 (2008).

Kumar J., Balomajunder C., Mondall P., *Application of Agro - Based Biomasses for Zinc Removal from Wastewater – A Review*, CLEAN– Soil, Air, Water, **39**, *7*, 641-652 (2011).

Kumar P.Y., King P., Prasad V.S.R.K., *Zinc Biosorption on Tecto Nagrandis L.f. Leaves Biomass: Equilibrium and Kinetic Studies*, Chem. Eng. J., **124**, *1-3*, 63-70 (2006).

Kurniawan T.A., Chan G.Y.S., Lo W.H., Babel S., *Physico–chemical Treatment Techniques for Wastewater Laden with Heavy Metals*, Chem. Eng. J., **118**, *1-2*, 83-98 (2006).

Lagergren S., *About the Theory of So-Called Adsorption of Solid Substance*, Handlinger, **24**, 1-39 (1898).

Langmuir I., *The Constitution and Fundamental Properties of Solids and Liquids*, J. Am. Chem. Soc., **38**, *11*, 2221-2295 (1916).

Li X., Tang Y., Cao X., Lu D., Luo F., Shao W., *Preparation and Evaluation of Orange Peel for Effective Removal of Cadmium, Zinc, Cobalt and Nickel*, Colloids Surf., A, **317**, *1-3*, 512-521 (2008).

Maheshwari U., Mathesan B., Gupta S., *Efficient Adsorbent for Simultaneous Removal of Cu(II), Zn(II) and Cr(VI): Kinetic, Thermodynamics and Mass Transfer Mechanism*, Process Saf. Environ. Prot., **98**, 198-210 (2015).

Malik D.S., Jain C.K., Yadav A.K., *Removal of Heavy Metals from Emerging Cellulosic Low-Cost Adsorbents*, Appl. Water Sci., **7**, *5*, 2113-2136 (2017).

Mishra V., *Biosorption of Zinc Ion: A Deep Comprehension*, Appl. Water Sci., **4**, *4*, 311-332 (2014).

Nguyen T.A.H., Ngo H.H., Guo W.S., Zhang J., Liang S., Yue Q.Y., Li Q., Nguyen T.V., *Applicability of Agricultural Wastes and by – Products for Adsorptive Removal of Heavy Metals from Wastewater*, Bioresour. Technol., **148**, 574-585 (2013).

Oh M., Tshabalala M., *Pelletized Ponderosa Pine Bark for Adsorption of Toxic Heavy Metals from Water*, BioResources, **2**, *1*, 66-81 (2007).

Sen A., Pereira H., Olivella M.A., Villaescusa I., *Heavy Metals Removal in Aqueous Environments Using Bark as a Biosorbent*, Int. J. Environ. Sci. Technol., **12**, *1*, 391-404 (2015).

Teodosiu C., Tofan L, Wenkert R., Păduraru C., *Advances in Preconcentration/Removal of Environmentally Relevant Heavy Metal Ions from Water and Wastewater by Sorbents Based on Polyurethane Foam*, Rev. Chem. Eng., **30**, *4*, 403-420 (2014).

Tofan L., Păduraru C., Mihăilescu Amălinei R.L., Bunia I., Miron A., *Valorization of Romanian Silver Tree Bark (Abies Alba Mill.) Wastes as Low–Cost Sorbent of Cu(II) Ions from Polluted Waters*, Water Sci. & Technol, **74**, *10*, 2314-2324 (2016).

Tofan L., Păduraru C., Mihăilescu Amălinei R.L., Bunia I., Miron A., *Removal of Cadmium(II) from Aqueous Effluents by Sorption on Romanian Silver Fir Tree Bark (Abbies Alba Mill.) Wastes*, Global NEST J., **19**, *1*, 107-114 (2017).

Tripathi A., Ranjan M.R., *Heavy Metal Removal from Wastewater Using Low Cost Adsorbents*, J. Bioremed. Biodegr., **6**, *6*, 315-319 (2015).

Vasincu A., Cretu E., Geagalau I., Amălinei R.L., Miron A., *Polyphenolic Content and Antioxidant Activity of an Extractive Fraction from Abies Alba Bark.*, Rev. Med. Chir. Soc. Med. Nat. Iași, **117**, *2*, 545-550 (2013).

Zhang J., Zhang W., Zhang Y., *Pore Structure of Activated Carbon Fibers Derived from Poplar Bark Liquefaction and their Use for Adsorption of Cu(II),* Bioresources, **10**, *1*, 566-574 (2015).

Zwain H.M., Vakili M., Dahlan I., *Waste Material Adsorbents for Zinc Removal from Wastewater: A Comprehensive Review*, Int. J. Chem. Eng. (2014).

ÎNDEPĂRTAREA IONILOR DE Zn(II) DIN SOLUȚII APOASE PRIN UTILIZAREA DEȘEURILOR DE SCOARȚĂ DE *ABIES ALBA*

(Rezumat)

Au fost studiate condițiile experimentale și influența unor parametri operaționali asupra procesului de sorbție în regim static a ionilor de Zn(II) pe scoarță de *Abies Alba.* Sorbția Zn(II) din soluții cu diferite concentrații de ion metalic a crescut progresiv la creșterea pH-ului inițial de la 1 la 5,5. Pentru o creștere a dozei de scoarță de la 4 la 30 g/L s-a înregistrat un procent de reținere de până la 89%. Procesul de reținere a ionilor metalici este bine descris atât de izoterma Langmuir cât și de izoterma Freundlich. Valorile calculate ale parametrilor termodinamici arată că reținerea ionilor de Zn(II) pe scoarță de *Abies Alba* este un proces spontan de natură endotermică și chimică. Analiza datelor ce descriu cinetica procesului de sorbție, arată ca procesul de reținere al ionilor Zn(II) este mai bine descris de modelul de ordin pseudo-doi.