# INVESTIGATIONS ON THE FEASIBILITY OF ROMANIAN PINE BARK WASTES CONVERSION INTO A VALUE-ADDED SORBENT FOR CU(II) AND ZN(II) IONS

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The batch sorption capability of Romanian pine bark for the removal of Cu(II) and Zn(II) ions from diluted aqueous solutions was investigated as a function of initial pH, contact time, and temperature. The metal sorption sequence is Cu > Zn. The experimental data for Cu(II) and Zn(II) ions retention on the tested bark of *Pinus sylvestris* L. showed a better compliance with the pseudo–second order kinetic model. The values of the maximum capacity of sorption, determined on the basis of the Langmuir isotherm model, are 14.7 mg g$^{-1}$ and 13.01mg g$^{-1}$ (at 20$^0$C) for Cu(II) and Zn(II) ions, respectively. The computed thermodynamic parameters indicate the spontaneous and endothermic nature of Cu(II) and Zn(II) ions sorption process by pine bark. The obtained results suggest that Romanian pine bark is a promising material for the development of a low–cost sorption technology for the removal of Cu(II) and Zn(II) ions from aqueous streams.

*Keywords: Pine bark; Sorbent; Removal; Copper; Zinc*

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## INTRODUCTION

In recent years, the use of environmentally sustainable biomaterials for removal of contaminants in aqueous solutions and industrial effluents has attracted once again considerable attention (Alluri et al. 2007; Demirbas 2008; Whang and Chen 2009; Opeolu et al. 2010).

Forest by-products and wastes are one of the most renewable resources available worldwide. Among these, bark accounts for a significant proportion of wood by-products generated by timber harvesting and timber processing. Usually, bark does not have a high added value as a fuel or as a humus component to increase the quality of vegetables.

*Pinus sylvestris* L. (Pinaceae, Scots Pine) is a coniferous species that is widely spread across Europe and Asia. In Romania it grows naturally in the Carpathian Mountains, but it is also planted due to its economic importance. *Pinus sylvestris* L. bark is rich in polyphenols, particularly condensed tannins (procyanidins) (Karonen et al. 2004). Procyanidins are pentahydroxyflavan oligomers and polymers. These molecules

bear ortho-dihydroxy phenolic groups that are able to chelate metal ions, leading to stable complexes (Chin et al. 2009). Many studies have shown that bark of different *Pinus* species has great potential for the removal of metals and organic pollutants and consequently, it can be used as a substitute for commercial sorbents such as active carbon.

Despite the large amounts of pine bark wastes generated in Romania from the industrial processing of pine wood, no studies on the sorption capabilities of Romanian pine bark have been carried out. The aim of the present work is to investigate the possibility of conversion of pine bark residues into a low-cost sorbent for removal of Cu(II) and Zn(II) ions from aqueous solutions. Cu(II) and Zn(II) were chosen as target ions because their presence in the environment, even in relatively low concentrations, is responsible for producing a variety of illnesses related with the risk of derma damage, respiratory problems, and several kinds of cancer (Rao et al. 2009). Furthermore, industrial wastewater containing Cu(II) and Zn(II) are common due to the fact that their metals are used in a large number of industries such as dyeing, paper, petroleum, acid mine drainage, electroplating, and metal finishing (Ucun et al. 2009)

## EXPERIMENTAL

### Plant Material

Patches of *Pinus sylvestris* L. bark were collected in the Calimani Mountains (Romania) in February 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.

### Chemicals

Stock solutions of 1202 mg $L^{-1}$ and 1000 mg $L^{-1}$ were prepared by dissolution of analytical grade reagents $CuSO_4 \cdot 5H_2O$ and $ZnSO_4 \cdot 7H_2O$, respectively, in deionized water and were complexonometrically standardized. Working solutions of Cu(II) and Zn(II) ions were prepared by the appropriate dilutions of the stock solutions.

In order to study the effect of medium acidity on the sorption process, a solution of $H_2SO_4$ with concentration of $10^{-2}$ mol $L^{-1}$ was used (Inolab pH/ion735).

### Sorption Procedure

The sorption experiments were performed in batch conditions. For this purpose, samples of about 0.3 g pine bark were equilibrated with 50 mL of each aqueous solution containing defined amounts of Cu(II) and Zn(II) ions, at desired temperature and pH. At the end of predetermined time intervals, pine bark was removed from the aqueous solutions by centrifugation (Rotofix 32A Hettich) at 4000 rpm for 10 min. Cu(II) and

Zn(II) ion concentrations in the final solutions were determined by atomic absorption spectrometry. The absorbance measurements were performed using a GBS Avanta 2007 Atomic Absorption Spectrometer equipped with an auto sampler and a furnace system.

The parameters characteristic to the metal ions sorption by pine bark were calculated with the following equations,

Retention percentage, *R (%)*        $R = [(C_0 - C)/C_0].100$                     (1)

Retained amount of metal ion, *q (mg g$^{-1}$)*      $q = [(C_0-C)/G]/V.$                     (2)

where $C_0$ is the initial concentration of metal ion (mg L$^{-1}$), $C$ is the cation concentration after sorption (mg L$^{-1}$), $V$ is the volume of solution (L); and $G$ is the weight of pine bark (g).

## FT-IR Spectra

The infrared spectra was obtained as KBr pellets, using a FT-IR spectrometer Bruker Vertex 70.

## RESULTS AND DISCUSSION

### Characterization of the Pine Bark under Investigation

Previous studies showed that the major chemical components of raw pine bark are cellulose and lignin (Argun et al. 2009). Pine bark proved to be a material of very low porosity, low specific surface area (1.41m$^2$/g), and strong carbon aromatic content, probably due to its content of polyphenols and lignin (Bras et al. 2004).

IR spectra of the pine bark under investigation before and after Cu(II) and Zn(II) ion sorption are given in Fig. 1.

The broad and strong band ranging from 3000 to 3600 cm$^{-1}$ indicates the presence of –OH and –NH groups, which is consistent with the peaks at 1035 and 1159 cm$^{-1}$ assigned to alcoholic C-O and C-N stretching vibration. The peaks observed near 2921 cm$^{-1}$ can be assigned to C-H groups. Bands near 1614 and 1635 cm$^{-1}$ are indicative of carboxyl groups (C=O). The IR spectra indicate that the carbons possess different surface structure (aliphatic, aromatic, cyclic), as one can observe the bands at 1447 cm$^{-1}$ and over the 1371 to 1276 cm$^{-1}$ range (Gundogdu et al. 2009).

### Effect of Initial Solution pH

Fig. 2 depicts the effect of initial pH on the sorption of Cu(II) and Zn(II) ions by pine bark under study. This major dependence was investigated in solutions with initial pH in the range of 1 to 5 where both metals exist in their double positively charged ionic forms (Cu$^{2+}$ and Zn$^{2+}$) and their precipitation as metal hydroxides is avoided (Tofan et al. 2008).

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**Fig. 1.** IR-spectra for 1-pine bark; 2-pine bark-Cu(II) ions; 3-pine bark-Zn(II) ions

It may be seen from Fig. 2 that the sorption for both metal ions under study decreased with reducing the initial pH. Thus, Cu(II) ions showed a maximum sorption of 6.98 mg g$^{-1}$ at pH 4.5 to 5, which decreased progressively to 4 mg g$^{-1}$ at pH 3 and 0.68 mg g$^{-1}$ at pH 1. The respective values for Zn(II) ions are 6.24 mg g$^{-1}$ at pH 4.5 to 5, 3.3 mg g$^{-1}$ at pH 3 and 0.54 mg g$^{-1}$ at pH 1. The decrease in the sorption of Cu(II) and Zn(II) ions at low pH can be attributed to the positive charge of the pine bark and to the competition between hydrogen ions and the heavy metal ions for the active sites on the bark surface. This behavior may be used to recover the metal ions by desorption with mineral acids from the loaded pine bark (Gundogdu et al. 2009). On the other hand, the increased sorption at higher values of pH may be due to the ionization of functional groups and an increase in the negative charge density on the bark surface which

significantly improved the attraction of the tested cations. A similar pH sorption profile was recently reported for the retention of Cu(II) and Zn(II) ions on a cone biomass of *Pinus sylvestris* L. and explained on the basis of the nature of chemical interactions of each metal with the various functional groups on the cone biomass (Ucun et al. 2009).
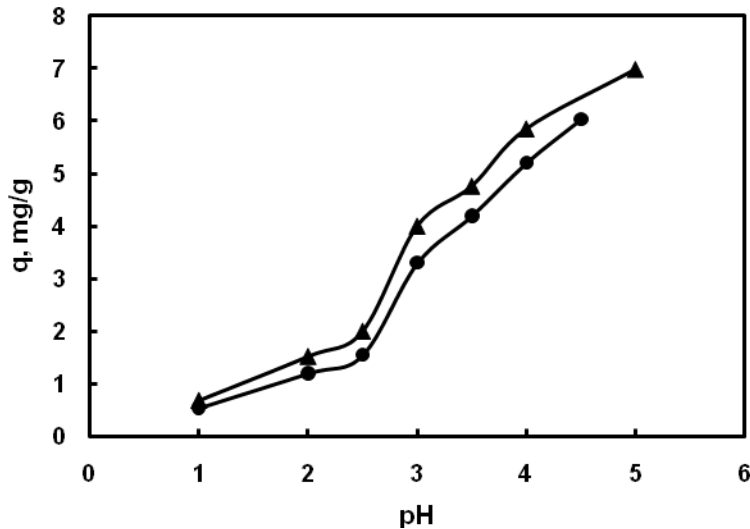


**Fig. 2.** The influence of initial pH on the Cu(II) ions (▲) and Zn(II) ions (●); retention by pine bark ( $C_0$= 72 mg Cu(II) $L^{-1}$; $C_0$=60 mg Zn(II) $L^{-1}$)

## Effect of Contact Time and Kinetic Modeling

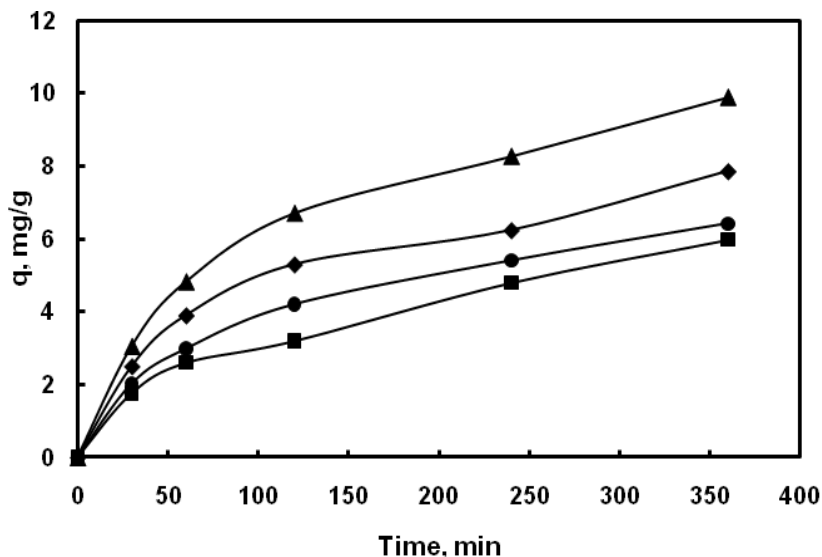The kinetic data for the sorption of Cu(II) and Zn(II) ions by pine bark are shown in Fig. 3.



**Fig. 3.** Effect of the contact time on Cu(II) and Zn(II) ion retention by pine bark. (Cu(II) (●)$C_0$= 72 mg $L^{-1}$; (▲)$C_0$= 96 mg $L^{-1}$; Zn(II) (■) $C_0$= 60 mg $L^{-1}$; (♦) $C_0$=100 mg $L^{-1}$: temperature=20$^o$C

According to Fig. 3, the kinetics of Cu(II) and Zn(II) ions removal by pine bark under study presents a shape characterized by a rapid rate of uptake of tested metal ions by pine bark during the first few minutes, followed by a slow continued uptake until the state of equilibrium is reached. In this context, it can be considered that the retention of Cu(II) and Zn(II) ions on *Pinus sylvestris* L. bark takes place in two distinct steps, a relatively fast phase followed by a slower one. The optimum time to reach equilibrium is about 4 hours, and an increase of the sorption time to 24 hours did not show notable effects. These findings are in good agreement with those reported in literature for removal of Pb(II) ions from aqueous solution by sorption on *Pinus brutia* Ten. bark (Gundogdu et al. 2009).

Batch sorption modeling is necessary to describe the response of the sorption systems to changes caused by variations in the experimental conditions and the properties of the sorbents, as well as the parametric sensitivity of the model to the process parameters. Kinetic studies give detailed information on the mechanism of sorption and potential rate controlling steps. Kinetics of Cu(II) and Zn(II) ions sorption on pine bark under study was modeled by the pseudo-first order and pseudo-second order equations, summarized in Table 1.

**Table 1.** Mathematical Form and Parameters of the Used Kinetic Models

| Kinetic model | Equation form | Kinetic parameters | Remarks | Reference |
|---|---|---|---|---|
| Pseudo-first order model (Lagergren model) | $log\,(q_e - q_t) =$ $log\,q_e - \dfrac{k_1}{2.303} \cdot t$ where $q_e$ and $q_t$ are the amounts of cation (mg g$^{-1}$) sorbed at equilibrium and at time t, respectively | $k_1$-rate constant of pseudo–first order model sorption (min$^{-1}$). | Based on adsorption capacity | Lagergren 1898 |
| Pseudo-second order model (Ho model) | $\dfrac{1}{q_t} = \dfrac{1}{h} + \dfrac{1}{q_e} \cdot t$ | $k_2$- the rate constant of the pseudo–second order model $h = k_2 \cdot q_e^2$ (mg g$^{-1}$ ·min$^{-1}$) can be regarded as initial sorption rate constant of the pseudo–second–order sorption (g.mg$^{-1}$·min$^{-1}$). | Based on adsorption capacity | Ho Y.S. 1999 |

The kinetic parameters derived from the plots of the linearized form of the pseudo-first order and pseudo-second order equations are recorded in Table 2, along with the corresponding coefficients of determination ($R^2$).

**Table 2.** Kinetic Characterization of the Sorption Systems based on Pine Bark

| Metal | 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$^{-1}$ | $q_{e, calc}$ (mg g$^{-1}$) | $R^2$ |
| Cu(II) | 72 | 0.64 x10$^{-2}$ | 0.9748 | 1.35x10$^{-3}$ | 0.0828 | 7.82 | 0.9944 |
| | 96 | 0.78x10$^{-2}$ | 0.957 | 0.809x10$^{-3}$ | 0.1943 | 10.83 | 0.9948 |
| Zn(II) | 60 | 0.62x10$^{-2}$ | 0.9811 | 1.16 x10$^{-3}$ | 0.0687 | 7.037 | 0.9975 |
| | 100 | 0.713x10$^{-2}$ | 0.9709 | 1.36x10$^{-3}$ | 0.0968 | 8.42 | 0.9929 |

According to $R^2$ values, it is obvious that the experimental results of Cu(II) and Zn(II) ions sorption on the tested pine bark showed a better compliance with pseudo–second order kinetic model. A similar behavior has been observed for the sorption of Cu(II) and Zn(II) ions onto a cone biomass of *Pinus sylvestris* L. (Ucun et al. 2010) and of Pb(II) ions from aqueous solutions by *Pinus brutia* Ten. bark (Gundogdu et al. 2009). 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 chemical sorption (chemisorption) involving valence forces through the sharing or exchange of electrons between the sorbent and the sorbate (Lazarevic et al. 2011). Furthermore, the sorption rate depends on the concentration of Cu(II) and Zn(II) ions on the pine bark surface (Table 2).

**Sorption Isotherms**

As there were no critical reasons to use more complex models, the experimental data were processed in the light of Langmuir and Freundlich models (Table 3).

**Table 3.** Concise Description of the Applied Isotherm Models

| Sorption isotherm model | Equation | Isotherm parameters, significance | Assumptions | Reference |
|---|---|---|---|---|
| Langmuir | $C/q = C/q_0 + 1/K_L \cdot q_0$ (linearised form) | $K_L$ – binding energy (relative sorption affinity) $q_0$ – maximum capacity of sorption | Formation of a monolayer coverage of metallic ion at the sorbent surface containing a finite number of homogeneous sites of sorption | Langmuir 1916 |
| Freundlich | $log\ q = log\ K_F + (1/n)log\ C$ (linearised form) | $K_F$ - sorption capacity n–energy of sorption | Logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites | Freundlich 1906 |

Figures 4 and 5 illustrate the Langmuir isotherms for Cu(II) and Zn(II) ions adsorbing on the investigated pine bark at three different temperatures. The Cu(II) and Zn(II) ions retention on the pine bark under study is characterized in Table 4 by means of

Langmuir constants obtained from the corresponding linear Langmuir plots.
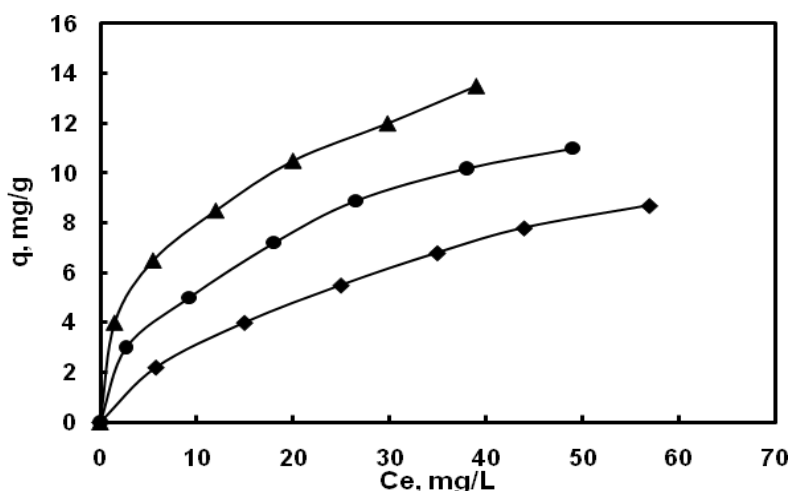


**Fig. 4.** Langmuir isotherms of Cu(II) ions sorption on pine bark at (▲) $60^0$C; (•) $20^0$C;(♦) $4^0$C (pH= 4.5-5; sorbent dose=6 g L$^{-1}$)
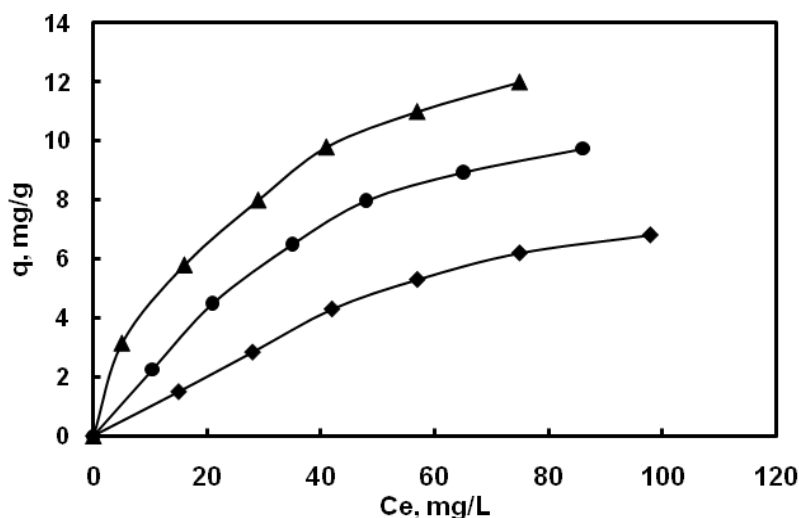


**Fig. 5.** Langmuir isotherms of Zn(II) ions sorption on pine bark at (▲) $60^0$C; (•) $20^0$C;(♦) $4^0$C (pH= 4.5-5; sorbent dose=6 g L$^{-1}$)

It can be seen from Table 4 that the conversion of pine bark waste under study to value-added sorbent for Cu(II) and Zn(II) ions is viable. The $K_L$ values in Table 4 derived from the Langmuir model suggest the following order of the metal binding affinity: Cu > Zn. The same metal sorption sequence (Cu > Zn) has been reported for Cu(II) and Zn(II) ions uptake by other silvichemical biomass materials (Yu et al. 2008). The low values for $q_0$ are comparable with those reported in literature for some other low-cost sorbents based on tree barks (Table 5).

**Table 4.** Quantitative Description of the Cu(II) Ion–Pine Bark and Zn(II) Ion–Pine Bark Batch Sorption Systems on the Basis of Langmuir and Freundlich Models

| Metal ion | T, K | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|---|
| | | $R^2$ | $q_0$, (mmol g$^{-1}$) | $K_L$ (L mol$^{-1}$) | $R^2$ | $K_F$ | $n$ |
| Cu(II) | 277 | 0.9832 | 0.2099 | 1892 | 0.9873 | 0.768 | 1.64 |
| | 293 | 0.9967 | 0.275 | 3591 | 0.9967 | 1.89 | 2.21 |
| | 333 | 0.9899 | 0.345 | 4543 | 0.9974 | 3.41 | 2.70 |
| Zn(II) | 277 | 0.9922 | 0.2057 | 648.9 | 0.9799 | 0.1688 | 1.20 |
| | 293 | 0.9948 | 0.242 | 1319 | 0.968 | 0.529 | 1.47 |
| | 333 | 0.987 | 0.257 | 2320 | 0.9957 | 1.39 | 1.954 |

The empirical values of the Freundlich constants for Cu(II) ion-pine bark and Zn(II) ion-pine bark batch sorption systems are recorded in Table 4 and indicate again that the sorption process is strongly dependent on the nature of the metal ion. The $n$ values are above unity, indicating favorable sorption of the tested cations by the pine bark under study at all working temperatures. The $K_F$ values determined in this study are higher than those determined in previous studies using other low-cost sorbents such as peanut hulls (Oliveira et al. 2010). This finding strongly indicates that the pine bark under study is a promising material for Cu(II) and Zn(II) ions removal from waste streams. However, future experiments should be performed with industrial wastewaters to investigate pine bark sorption behavior of these metals in co-presence of other metals and organic matter.

**Table 5.** Comparison of the Sorption Capacity for Cu(II) and Zn(II) Ions of Some Tree Barks

| Sorbent | $q_0$, mg g$^{-1}$ | | References |
|---|---|---|---|
| | Cu(II) | Zn(II) | |
| Coniferous barks | 5.08 – 9.525 | 7.4 | Yu et.al 2008; Conrad et al.2007 |
| Hardwood bark | 20.574(pH= 5) 22.796(pH = 6) | 12.025(pH = 5) 12.155(pH = 6) | Jang et al. 2005 |
| *Azadirachta indica* A. Juss. bark | | 33.49 | King et al. 2008 |
| *Casuarina equisetifolia* L. bark | 16.58(pH = 5) | | Mohan et al 2008 |
| Pelletized ponderosa pine bark (*Pinus ponderosa*) | 24.1(pH = 5.1) | 20.6(pH = 5.1) | Oh et al. 2007 |
| Natural radiata bark pine (*Pinus radiata* D. Don) | 20 – 50 | | Montes et al. 2003 |
| Pine bark | 9.46 | | Zacaria et al. 2002 |
| Douglas fir barks (Pseudotsuga sp.) | 7.0485 | 4.0625 | Dupont et al. 2002 |
| Romanian *Pinus sylvestris* L. bark | 14.7 | 13.01 | *This study* |

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 4) suggest that monolayer sorption, as well as heterogeneous surface conditions may co-exist under applied experimental conditions. A similar behavior has been recently reported in the literature for the sorption of Pb(II) ions on *Pinus brutia* Ten. bark (Gundogdu et al. 2009).

**Effect of Temperature and Thermodynamic Parameters**

It is obvious from Figs. 4 and 5 that the temperature has a favorable effect within the sorption systems under study. Both Langmuir and Freundlich constants (Table 4) increase with increasing temperature, showing that the sorption capacity and the intensity of sorption are enhanced at higher temperatures. This observed influence of the temperature may be a direct consequence of (i) opening up the cellulose structure, (ii) enhancing the mobility and extent of penetration within the bark structure, and (iii) overcoming the activation energy barrier and enhancing the rate of intraparticle diffusion (Shukla et. al 2002).

The thermodynamic parameters, free energy change ($\varDelta G$), enthalpy change ($\varDelta H$) and entropy change ($\varDelta S$) were calculated on the basis of Langmuir constant $K_L$ at different temperatures by using the following equations (Park et al. 2010),

$$\varDelta G = - RT \ln K_L \qquad \ln K_L = constant = -\frac{\Delta H}{RT} \qquad \Delta S = \frac{\Delta H - \Delta G}{T} \qquad (3)$$

where $R$ is the gas constant and $T$ is the absolute temperature.

The thermodynamic description of the sorption systems under study on the basis of experimental data is given in Table 6.

**Table 6.** The Thermodynamic Parameters of the Sorption Process of Cu(II) and Zn(II) Ions on Pine Bark

|  | $T$, K | $\varDelta G$ (KJ mol$^{-1}$) | $\varDelta H$ (KJ mol$^{-1}$) | $\varDelta S$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|---|
| Cu(II) | 277 | -17.35 | 10.54 | 0.102 |
|  | 293 | -19.78 |  | 0.104 |
|  | 333 | -23.3 |  | 0.101 |
| Zn(II) | 277 | -15.031 | 8.48 | 0.084 |
|  | 293 | -17.362 |  | 0.088 |
|  | 333 | -21.418 |  | 0.089 |

The negative values of $\varDelta G$ at all working temperatures show that the sorption process of Cu(II) and Zn(II) ions by pine bark is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature. The $\varDelta H$ positive values are characteristic for endothermic processes, favored by temperature increase. The positive values of entropy change $\varDelta S$ suggest the redistribution of energy between the heavy metal ions and the pine bark. Before the sorption occurs, the heavy metal ions near the surface of the sorbent will be more ordered than in the subsequent sorbed state and the ratio of free heavy metal ions to ions interacting with the pine bark will be higher than in the sorbed

phase. An explanation of this behavior might be that the adsorption of metal ions is accompanied by freeing up of water of hydration from those metal ions, and it is the increased freedom of the "freed" water molecules that contributes more to the entropy of the system. As a result, the distribution of the rotational and translational energy among a small number of molecules will increase with increasing sorption by producing a positive value of $\Delta S$ and the randomness will increase during the sorption process (Hefne et al. 2008).

## CONCLUSIONS

1. Pine bark under study provided a viable low-cost and eco-friendly sorbent for Cu(II) and Zn(II) ions from aqueous solutions.
2. The optimum value of initial pH for both Cu(II) and Zn(II) ions sorption was found to be 4.5 to 5.
3. The sorption kinetics for Cu(II) and Zn(II) ions removal from aqueous solutions with initial pH of 4.5 to 5 were very well described by the pseudo-second order model.
4. The sorption isotherm studies clearly indicated that the sorptive behavior of Cu(II) and Zn(II) ions on pine bark under study satisfies not only the Langmuir assumptions, but also the Freundlich assumption.
5. The calculated values for the isothermal thermodynamic parameters show that Cu(II) and Zn(II) ions retention by pine bark is a spontaneous process of endothermic nature.

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