# EQUILIBRIUM STUDY OF Pb(II) AND Hg(II) SORPTION FROM AQUEOUS SOLUTIONS BY MOSS PEAT

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**Abstract**

The sorption of Pb(II) and Hg(II) ions from aqueous solutions by moss peat (from Poiana Stampei, Romania) was studied in a batch system. The data obtained from experiments of a single-component sorption were analyzed using Langmuir and Freundlich models. The Langmuir equation describe sorption isotherm of Pb(II) and Hg(II) with high correlation coefficients, and better than Freundlich model. According to the Langmuir model, the maximum uptake capacities of moss peat for Pb(II) and Hg(II) were obtained as 117.58 mg/g and 81.97 mg/g, respectively. The effect of temperature on the Pb(II) and Hg(II) sorption process onto moss peat was also investigated, and various thermodynamic parameters, such as $\Delta G$, $\Delta H$, $\Delta S$ and $E_a$ have been calculated.

*Keywords:* equilibrium study, lead(II), mercury(II), moss peat, sorption

## 1. Introduction

Aqueous heavy metal pollution represents an important environmental problem due to their toxic effects and accumulation throughout the food chain. Heavy metals contaminants exist in aqueous wastewaters of many industries, such as metal plating facilities, mining operations and tanneries (Gogate and Pandit, 2004; Paterson, 1985, Srivastava et al., 1999). Among heavy metals, lead(II) and mercury(II) have high prior for removal from aqueous environments (Londrigan et al., 1990). The conventional methods for the removal of these heavy metals from wastewaters include chemical precipitation, membrane separation, ion exchange, adsorption and biosorption (Babel and Krniavan, 2003; Kumar, 2006; Rusten et al., 1997). But, these processes are not economically feasible even for small-scale industries, due to huge capital investment.

Adsorption of pollutants on solid adsorbents is an effective method used for heavy metals removal from aqueous solutions, in special when the adsorbent used is not very expensive (Babel and Krniavan, 2003; Bailey et al., 1999). Thus, natural materials that are available in large quantities or certain waste products from industrial or agricultural operations may have potential as inexpensive sorbents. The moss peat is one example of such low-cost sorbents which can be utilized for the heavy metals removal from aqueous solutions (Brown et al., 2000; Coupal and Spiff, 1999).

In generally, the moss peat is considered a complex natural organic material, resulted from partial degradation of vegetables, in water and in absence of oxygen (Syrovetnik, 2005). Even the moss peat cannot be included into biomass materials category, due mainly to the long time required for its formation, the interaction way with heavy metals from aqueous solutions is similar, with those observed in case of biomass materials. This similarity is determined by the major constituents, such as lignin, cellulose, humic substances, which are present both in moss peat and in biomass (Ho et al., 1996, Horsfall and Spiff, 2005).

Because of these constituents, the moss peat contains in its structure different polar functional groups (ex. –COOH, –OH, –NH$_2$ etc.), which bind metal ions from aqueous solutions. In addition, the

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moss peat is an inexpensive available material which can be used as an alternative sorbent from removing of heavy metals.

In this paper, the sorption of lead(II) and mercury(II) ions from aqueous solutions by moss peat (from Poiana Stampei, Romania) was studied in a batch system. The data obtained from experiments of a single-component sorption were analyzed using Langmuir and Freundlich isotherm models.

The effect of temperature on the Pb(II) and Hg(II) sorption process by moss peat was also investigated. The thermodynamic parameters ($\Delta G$, $\Delta H$, $\Delta S$, $E_a$), calculated from experimental results, show that the sorption process is spontaneous and endothermic. These suggest that the chemical interactions play an important role in controlling the sorption rate.

## 2. Experimental

### 2.1. Materials

The experiments were carried out using moss peat drawing at 0.5-1.0 m depth, from Poiana Stampei, Romania. The moss peat was dried in air for 4 hours, at $90 \pm 2$ °C, and then was grounded and sieved until the granulation less than 1-2 mm was obtained.

All chemical reagents were of analytical degree and were used without further purifications. The stock solutions of lead(II) and mercury(II), contains around 2000 mg M(II)/L, were prepared by metal nitrate (Reactivul Bucharest) dissolving in twice distilled water, following by solution standardization (Dean, 1995). The working solutions were obtained by diluting the stock solutions with twice distilled water. The initial pH values (pH 6.0) of working solutions were obtained using acetate buffer ($CH_3COOH/CH_3COONa$) in case of lead(II), and hexamethylene-tetraamine buffer (HMT / $HNO_3$) in case of mercury(II).

### 2.2. Methods

A volume of 25 mL of metal ion solution (lead(II) and mercury(II)) with varying initial metal ion concentration of 40 – 525 mg/L was added on cca 0.125 g of moss peat, in a 150 mL conical flask. The initial solution pH was obtained by adding 5.0 mL of certain buffer (pH 6.0) and was measured with a Radelkis OK-281 pH/ion-meter equipped with a combined glass electrode. A serried of such conical flasks was then intermittent shaken in a water bath at temperature of 5, 25 and 55 °C, respectively.

After shaking the flasks for 4 hours, the phases were separated by filtration, and the Pb(II) and Hg(II) concentrations in filtrate were spectrophotometrically determined (Table 1), using a calibration curve.

**Table 1.** The analytical characteristics of spectrophotometrical methods used for Pb(II) and Hg(II) analysis
(Flaska and Barnard, 1976; Popa and Moldovan, 1969)

|  | *Pb(II)* | *Hg(II)* |
|---|---|---|
| Reagent | 4-(2-pyridyl-azo)-resorcinol | Methyl-tymol-blue |
| Linearity domain | 0 – 3.0 mg/L | 0 – 4.0 mg/L |
| $\lambda_{max}$ | 530 nm | 610 nm |
| Reference | Blank solution | Distilled water |

## 3. Theory and data evaluation

The amount of metal ion adsorbed by the moss peat at each temperature was calculated using Eq. (1):

$$q = \frac{(c_0 - c) \cdot V}{m} \qquad (1)$$

where: $q$ – amount of metal ion adsorbed per unit mass of moss peat (mg/g), at equilibrium; $c_0$, $c$ – initial and residual concentration of metal ion in solution, respectively (measured in mg/L); $V$ – volume of initial metal ion solution used (L); $m$ – mass of dry moss peat (g).

Two models were used to describe the experimental sorption isotherms: Langmuir model and the Freundlich model (Cochrane et al., 2006; Ho et al., 2002; Nadeem et al., 2006). The Langmuir equation was chosen for to estimation of maximum adsorption capacity, corresponding to moss peat surface saturation. The liniarized form of Langmuir equation, after rearrangement is (Eq. 2):

$$\frac{c}{q} = \frac{1}{q_0 \cdot K_L} + \frac{c}{q_0} \qquad (2)$$

where: $K_L$ is a constant related to the adsorption/desorption energy (L/mg), and $q_0$ is the maximum adsorption upon complete saturation of the moss peat surface (mg/g). These constants were determined by plotting $c/q$ against $c$.

The Freundlich model was chosen to estimate the adsorption intensity of the metal ion towards moss peat, and the linear form is represented by Eq. (3):

$$lg\, q = lg\, K_F + \frac{1}{n} lg\, c \qquad (3)$$

where: $K_F$ – Freundlich constant, is an indicator of the sorption capacity; $n$ – constant that characterizes the affinity of the metal ion towards the moss peat. A plot of $lg\, q$ in function of $lg\, c$, yielding a straight line indicated the confirmation of the Freundlich adsorption isotherm. The Freundlich constants, $K_F$ and $n$, can be determined from the intercept and slope, respectively.

In these systems, the free Gibbs energy change (*ΔG*) is the driving force and the fundamental criteria of spontaneity. As is known, the processes occur spontaneously, at a given temperature if ΔG is a negative quantity. The free energy of the sorption process was calculated from the Langmuir constant using Eq. (4):

$$\Delta G = -RT \ln K_L \qquad (4)$$

where: *R* is the universal gas constant, 8.314 J/mol K; *T* is absolute temperature, *K*.

The other thermodynamic parameters, such as enthalpy change (*ΔH*) and entropy change (*ΔS*) may be determined from the slope of linear dependence *ln K_L* against *1/T*, and using Eq. (5):

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (5)$$

The activation energy (*E_a*) was obtained from the slope of plot *ln (1-θ)* against *1/T*, where the surface coverage (*θ*) was calculated from the relation (6):

$$\theta = \left( 1 - \frac{c}{c_0} \right) \qquad (6)$$

where: *c, c_0* are the initial and residual concentration of metal ion in solution, respectively (mg/L).

## 4. Results and discussion

### 4.1. Effect of temperature

The effect of temperature on the Pb(II) and Hg(II) sorption from aqueous solutions by moss peat was studied by varying the temperature between 5 and 55 °C. The results presented in Fig. 1a and 1b showed that the sorption of metal ions by moss peat increase with the increase of temperature.

This is because with the increasing of temperature, the attractive forces between moss peat surface and metal ions are stronger and the sorption increase. This behaviour is typical for the adsorption of most metal ions from their solutions onto natural materials (Chong and Volesky, 1995; Ho et al., 1996).

The temperature increase was observed to be in two stages, with exception of Pb(II) adsorption at lower temperature, when three stages are observed. The sorption equilibrium occurs rapidly at lower metal ion concentration, for all studied temperatures and becomes relatively constant at higher concentrations. The equilibrium concentration was obtained at 37 mg/L for Pb(II) and 49 mg/L for Hg(II), and are not significant different from a temperature to other. This indicate that increasing of the metal concentration above the equilibriums concentration of 37 – 49 mg/L may not have any

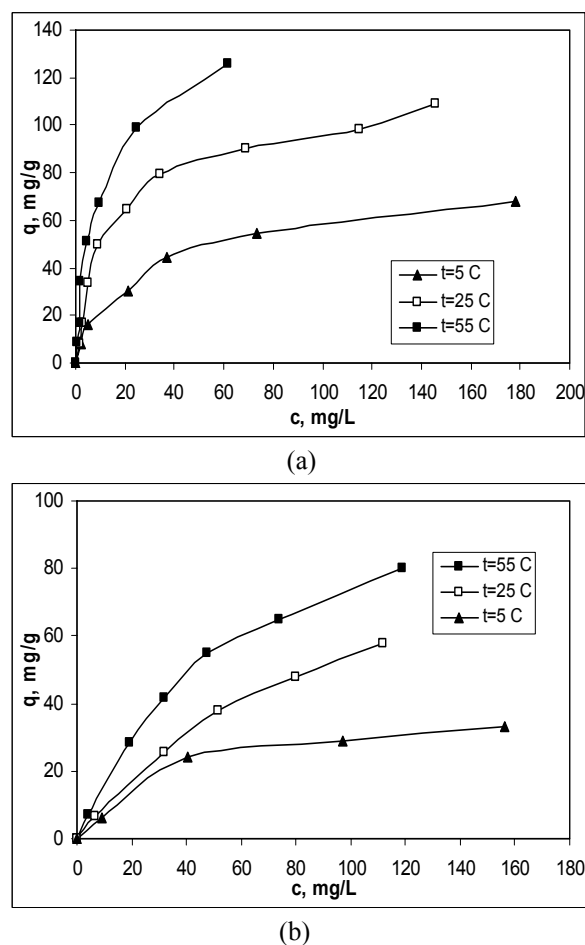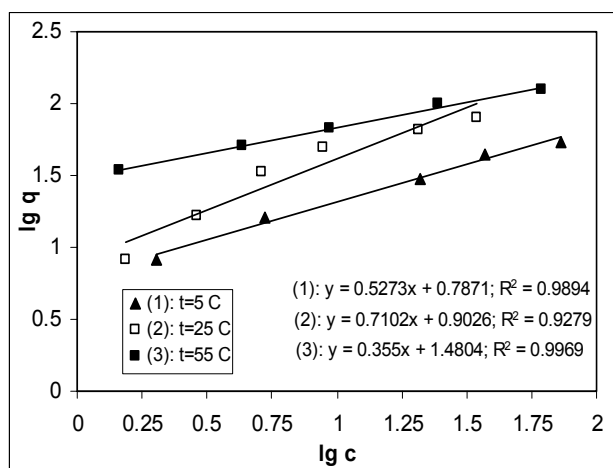significant increasing in the sorption of metal ions by moss peat.



(a)



(b)

**Fig. 1.** Effect of temperature on the adsorption on to moss peat: (a) – Pb(II); (b) – Hg(II)

At high temperature, the thickness of the boundary layer increase, due to the increased tendency of the metal to interact with the moss peat surface, which result in an increase in sorption as temperature increases (Do, 1998). The increase in the adsorption with increasing of temperature suggest strong adsorption interactions (ionic or / and covalent) between functional groups of moss peat surface and the metal ion, which support the chemo-sorption.
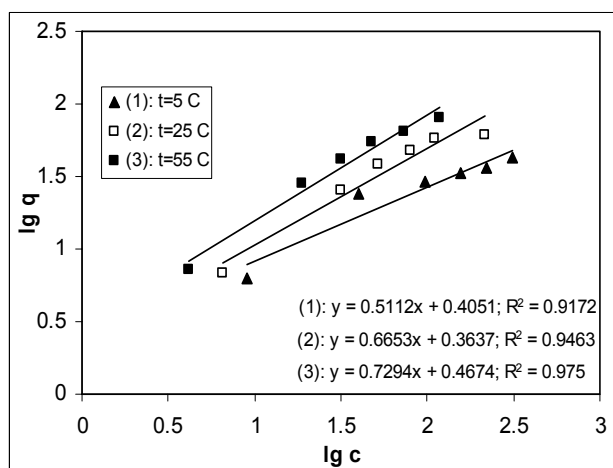
In order to estimate the adsorption capacities, at various temperatures, the experimental data were fitted into equilibrium isotherm models Freundlich and Langmuir. The liniarized profile of Freundlich and Langmuir sorption isotherms of Pb(II) and Hg(II) onto moss peat, are presented in Figs. 2 and 3. The values of *K_F, n, q_0* and *K_L*, calculated from the intercept and slope of the linear plots and the correlation coefficients ($R^2$), at each temperature, are summarized in Tables 2 and 3.

The values of correlation coefficients indicate that the Pb(II) and Hg(II) sorption data are very well represented by the Langmuir model ($R^2 >$

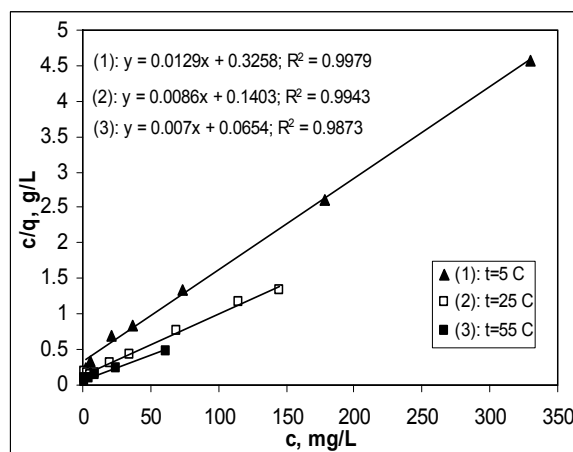0.98), in case of Freundlich model, these have lower values.



(a)



(b)

**Fig. 2.** Freundlich isotherm plots for the adsorption onto moss peat: (a) – Pb(II); (b) – Hg(II).

The Freundlich constant, n, which estimate the adsorption intensity of the metal ion on the moss peat surface, is higher than 1 for both metal ions at all studied temperatures, indicating the favourable sorption even at higher metal ion concentrations.
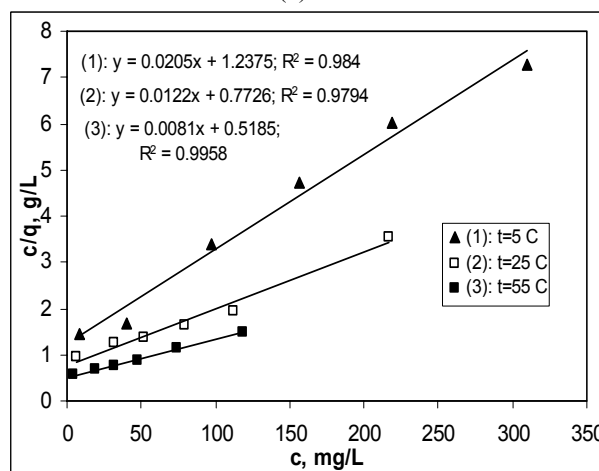
In addition, the values of this constant are higher in case of Pb(II) than in case of Hg(II) sorption onto moss peat, and increase with the increasing of temperature.

This suggest that the free $Pb^{2+}$ ions (predominant specie of Pb(II) at pH 6.0) have a higher affinity for superficial functional groups of moss peat than $HgO^+$ (predominant specie of Hg(II) at pH 6.0) (EpH-web diagrams, 2008).

But, because the experimental values of n, obtained in case of Pb(II) and Hg(II) sorption by moss peat have the same order of magnitude, suggest that the retention of metal ions from aqueous solutions probably take place, in the first moments, by ionic interactions. The values of $K_F$, which is a measure of the adsorption degree, increase with the increase of temperature.



(a)



(b)

**Fig. 3.** Langmuir isotherm plots for the adsorption onto moss peat: (a) – Pb(II); (b) – Hg(II).

**Table 2.** The values of constants from Freundlich model for Pb(II) and Hg(II) sorption by moss peat, at studied temperatures

| t, °C | Pb(II) | | | Hg(II) | | |
|---|---|---|---|---|---|---|
| | $R^2$ | n | $K_F$, mg $L^{1/n}$/g $mg^{1/n}$ | $R^2$ | n | $K_F$, mg $L^{1/n}$/g $mg^{1/n}$ |
| 5 | 0.9894 | 1.411 | 6.136 | 0.9172 | 1.372 | 2.310 |
| 25 | 0.9279 | 1.905 | 7.991 | 0.9463 | 1.506 | 2.541 |
| 55 | 0.9969 | 2.823 | 30.227 | 0.9750 | 1.966 | 2.933 |

**Table 3.** The values of constants from Langmuir model for Pb(II) and Hg(II) sorption by moss peat, at studied temperatures

| t, °C | *Pb(II)* | | | *Hg(II)* | | |
|---|---|---|---|---|---|---|
| | $R^2$ | $q_0$, mg/g | $K_L$, L/mg | $R^2$ | $q_0$, mg/g | $K_L$, L/mg |
| 5 | 0.9979 | 77.523 | 0.040 | 0.9840 | 48.782 | 0.010 |
| 25 | 0.9943 | 117.582 | 0.061 | 0.9794 | 81.975 | 0.015 |
| 55 | 0.9873 | 142.854 | 0.110 | 0.9958 | 123.451 | 0.016 |

The higher $K_F$ values at higher temperature indicate that more sorption would be expected at these temperatures, and this variation is more pronounced in case of Pb(II) sorption by moss peat than in case of Hg(II).

The most probable temperature of adsorption was further evaluated by the Langmuir model. The Langmuir maximum adsorption capacity ($q_0$, mg/g), and the Langmuir constants ($K_L$, L/mg) at the studied temperatures were obtained from the dependences given in Fig. 3. The constants values as show in Table 3 indicate that the optimal temperature of adsorption in utilizing moss peat for the removal of Pb(II) and Hg(II) from aqueous solutions is 55°C.

By comparison of experimental values of $K_L$ constants, obtained for Pb(II) and for Hg(II), it can be observed that on the sorbent surface is not a single sites type. Two or more sites with different affinity may be involved in metal ions sorption onto moss peat. On the other hand, the values of $q_0$ and $K_L$ increase with the increasing of temperature, showing that the adsorption capacity and intensity of adsorption are enhanced at higher temperatures.
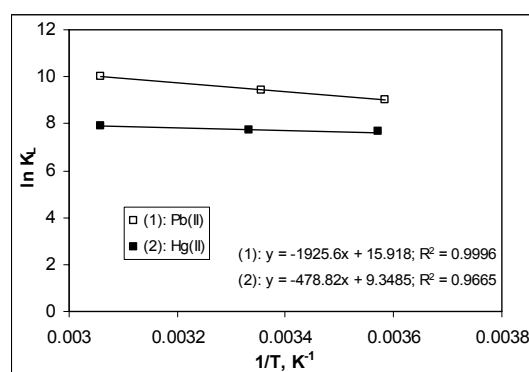
*4.1. Thermodynamic parameters of sorption process*

The thermodynamic treatment of the sorption experimental results shows that ΔG values were negative at all temperatures investigated, for both metal ions. The negative values of ΔG (Table 4) indicate the spontaneous nature of Pb(II) and Hg(II) adsorption by moss peat.

According to the studied from literature, a *ΔG* value up to -15 kJ/mol are connected with the physical interactions between sorption sites and metal ion (physical adsorption), while a *ΔG* values more negative than -30 kJ/mol involve charge transfer from sorbent surface to the metal ion to form a coordination bond (chemical adsorption) (Chong and Volesky, 1995; Ho et al., 1996). The *ΔG* values obtained in this study for both metal ions, are higher than -15 kJ/mol, but lower than -30 kJ/mol, indicating that in the sorption mechanism the chemical

interactions (both ionic and covalent) have the predominant role in the controlling sorption rate.

The values of *ΔH* and *ΔS* were obtained from the slope of plots *ln $K_L$* vs *1/T* (Fig. 4) and from Eq. (5), and are presented in Table 4. The positive values of *ΔH* for Pb(II) and Hg(II) on to moss peat further confirm the endothermic nature of the adsorption process. The positive values of *ΔS* (Table 4) show that the freedom of metal ions is not too restricted at the moss peat surface.



**Fig. 4.** Plot *ln $K_L$* against *1/T* for Pb(II) and Hg(II) sorption on moss peat

In order to further support the assertion that chemical adsorption is the predominant mechanism, the values of activation energy ($E_a$, kJ/mol) were estimated from experimental data. According with the modified Arrhenius equation, the plot of *ln (1-θ)* against *1/T* gave a linear plot with slope of $E_a/R$, as it is shown in Fig. 5.

The $E_a$ values calculated from the slope of plot were found to be 79.57 kJ/mol and 140.79 kJ/mol for Pb(II) and Hg(II) respectively. The positive values of $E_a$ indicate that the higher temperature favours the metal ion removal by adsorption onto moss peat. On the other hand, the high values of $E_a$ suggest that the metal ion adsorption is chemical controlled process.

**Table 4.** The thermodynamic parameters for the Pb(II) and Hg(II) adsorption onto moss peat.

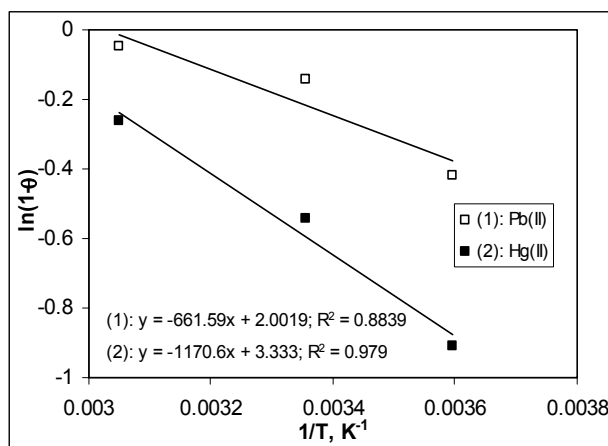| t, °C | *Pb(II)* | | | | *Hg(II)* | | | |
|---|---|---|---|---|---|---|---|---|
| | *ΔG, kJ/mol* | *ΔH, kJ/mol* | *ΔS, J/mol K* | *$E_a$, kJ/mol* | *ΔG, kJ/mol* | *ΔH, kJ/mol* | *ΔS, J/mol K* | *$E_a$, kJ/mol* |
| 5 | -20.92 | | 132.33 | | -17.81 | | 113.53 | |
| 25 | -23.39 | 16.00 | 131.58 | 79.57 | -19.26 | 13.98 | 110.80 | 140.79 |
| 55 | -27.00 | | 131.50 | | -21.46 | | 108.34 | |

**Fig. 5.** The dependence *ln(1-θ)* against *1/T* for Pb(II) and Hg(II) sorption on moss peat

## 5. Conclusions

The experimental results presented in this study clearly establish that the sorption of Pb(II) and Hg(II) onto moss peat is favoured at higher solutions temperatures. The studied temperature range (5 - 55°C) is favourable for the solubility of chemicals in wastewater treatment systems and will also enhance the adsorption rates. The equilibrium data agrees with the Langmuir isotherm. The sorption capacity of Pb(II) is higher than Hg(II), probable because to the nature of predominant species which are present in aqueous solutions with pH = 6.0 ($Pb^{2+}$, in case of Pb(II) and $HgO^+$, in case of Hg(II)). However, there is no significant difference in the sorption intensity of the moss peat towards the two metal ions. The values of thermodynamic parameters (*ΔG*, *ΔH* and *ΔS*) indicate that the sorption process is spontaneous for all studied temperatures and endothermic. The activation energy further support higher solution temperatures and the obtained values indicate that the metal ion adsorption is chemical controlled process.

## Acknowledgements

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