



УДК 547.992.2:544.72

## Sorption ability of humic substances from different origin peats of the Tula region in relation to Pb(II)

Siundiukova K.V., Dmitrieva E.D., Goryacheva A.A., Muzafarov E.N.

*Tula State University, Tula*

Поступила в редакцию 10.05.2016 г.

Sorption capacities of humic substances (HS) extracted from the peats of different origin were studied. These capacities were determined towards Pb(II). Sorption rate constants were calculated for whole samples of HS ( $0.01 \text{ s}^{-1}$ ) and separately, for low molecular weight fractions of HS ( $0.07 \text{ s}^{-1}$ ). Limiting sorption on the HS fractions was not observed that was due to their enrichment and availability of basic functional groups responsible for binding of lead cations.

**Keywords:** Humic substances, fractions, peat, heavy elements, sorption.

## Сорбционная способность гуминовых веществ торфов Тульской области различного происхождения по отношению к Pb(II)

Сюндюкова К.В., Дмитриева Е.Д., Горячева А.А., Музафаров Е.Н.

*Тульский государственный университет, Тула*

Определена сорбционная способность гуминовых веществ торфов различного происхождения по отношению к ионам Pb(II), рассчитаны константы скорости сорбции Pb(II) на гуминовых веществах ( $0.01 \text{ с}^{-1}$ ) и их низкомолекулярных фракциях ( $0.07 \text{ с}^{-1}$ ). На фракциях гуминовых веществ предельной сорбции ионов Pb(II) не наблюдается, что связано с их обогащенностью и доступностью основных функциональных групп, ответственных за связывание катионов свинца.

**Ключевые слова:** гуминовые вещества, фракции, торф, тяжелые металлы, сорбция.

### Introduction

Humic substances (HS) are ubiquitous in the environment and comprise the most abundant pool of organic matter [1, 2]. The HS are anionic polyelectrolytes which have heterogeneity in structure as well as in physical and chemical properties [3]. The average humic macromolecule consists of a hydrophobic aromatic core, that is highly substituted with functional groups (carboxyl and hydroxyl), and the side aliphatic chains. The core is ensconced in a periphery of hydrolysable carbohydrate-protein fragments [4, 5]. The structural complexity of HS creates opportunities for a broad range of chemical interactions with both trace elements and organic chemicals [6-8].

On an industrial scale, humic materials are produced from coal, sapropel and peat. The HS have the unique ability for environmental remediation [7, 9-11]. They play important role in the binding heavy metal and in controlling the transport of trace elements in water and soil [12, 13]. Heavy metals are the most prevalent pollutants in the environment,

which occur from industrial processes [14]. Lead, copper, nickel, cadmium, zinc and mercury are non-biodegradable and can accumulate in living tissues, creating threat to human health and the environment [15]. The last two decade, various methods have been proposed for efficient removal heavy metal, including their adsorption on HS. However, the most part of information exists about metal binding to HS, and less is known about the binding capacity of low molecular weight fractions (LMWF) of HS.

The aim of this work was to study the sorption capacities of HS extracted from peats of various origin and LMWF of HS to  $Pb^{2+}$ .

## Experimental

Materials and methods. Peatis a heterogeneous mixture plant material with various decomposed state that accumulated in a water saturated environment in the absence of oxygen [7]. Peats of two genesis were taken for that study: eutrophic – formed by black Alder (*Alnus glutinosa*) and mesotrophic – formed by Sphagnum. Peat samples were taken from the bog, allocated in Tula region, Russia. Eutrophic peat was formed in karst watered bog at depth of more than 5 m [16, 17], had decomposition degree was 35-40 % and consisted of alder bark and wood residues with the presence of grass. Mesotrophic peat was formed in a bog and had thickness of 1.5 m. Quagmire floats on the surface of a karst failure which has a depth of 7 m. Mesotrophic peat had a decomposition degree of 10-15% and consisted of sphagnum mosses stalks, microfossils of sedges residues, cotton grass, and cranberries. Samples were collected from the 0-20 cm of acrotelm layer in four locations and mixed afterwards to get one composite sample.

Humic substances were isolated from the peats by alkaline extraction (International Humic Substances Society). For the extraction, a 30 g of samples was taken and 0.1 N NaOH solution was added (1 : 6 ratio), mixture was heated for 2 h with constant stirring at 100°C and then stored for 24 h at room temperature ( $T=23\pm 2^\circ C$ ). Further, 10% HCl was added to solution to adjust the pH value to 2 for precipitation of HS. Precipitated HS were filtered through a paper filter (pore size 3-5  $\mu m$ ) and thoroughly washed with distilled water until the pH of washings was 7 units. The purification of HS from low molecular weight contaminants was performed by dialysis during 24 h (pore size of the dialysis membrane 12-14 kDa). Purified HS were dried in an oven at 40°C.

Fourier Transform Infrared Spectroscopy (FTIR) of HS. The 2 mg HS were grounded and mixed with 200 mg of dry KBr and then were pressed into discs using a hydraulic compressor. Infrared (IR) spectra were obtained by FTIR Spectrometer FSM 1201 (Russia). The 64 scans per sample were collected in the wavenumber range between 4000 and 500  $cm^{-1}$  in transmission mode at a spectral resolution of 4  $cm^{-1}$ .

Fractionation of HS. This method is based on precipitation of HS by salt solution with concentrations increasing. Salt interacts with HS and as a result the charges are compensated and HS fractions are precipitated. Coagulation occurs due to compression of the electrical double layer by increasing the ionic strength. This kind of coagulation is carried out with the addition of supporting electrolyte which is not capable to specific adsorption [18, 19].

The HS fractions were separated by coagulation them out from initial HS extract (40 g  $L^{-1}$  in 0.05 N NaOH) with increasing the  $Na_2SO_4$  or NaCl concentrations from 20 to 45%. The coagulated HA fractions were separated from the supernatants by centrifugation at 10000 rpm for 30 min. Fractionation of HS was stopped when the fraction mass was less than 30 mg (air-dried). The HS, that remained in supernatant, were precipitated by 10%

HCl and were not used for further experiments. The fractionation time of each fraction was 24 hours.

Elemental content and functional group analysis. Elemental analysis (C, N) was performed on a Vario EL elemental analyzer (ElementarAnalysensysteme GmbH, Germany). Representative samples were finely ground and dried to constant weight before analysis.

Indirect potentiometric titration was employed in characterizing the functional groups present in various types of HS and LMWF. Total acidity (TA) and carboxylic acidity (CA) were determined by indirect potentiometric titration method according to Schnitzer and Gupta. Phenolic acidity (PA) was determined by the difference between TA and CA [20].

Adsorption of lead on HS and HS fractions. The 0.1000 g of dry HS or low molecular weight fractions of HS were transferred in 100 mL flasks,  $\text{Pb}(\text{NO}_3)_2$  acid solution (40 mL,  $1 \text{ mg L}^{-1}$ ) of was added and samples were shaken at 700 rpm during 3 hours. Sorption experiments were conducted at room temperature ( $T=23\pm 2^\circ\text{C}$ ). Sorption equilibrium was established after 30 min.

The aliquots of supernatant (40 mL) were taken with 10 min interval and concentration of  $\text{Pb}^{2+}$  was determined by atomic absorption spectroscopy (AAS) method with electrothermal atomization on a atomic absorption spectrometer MGA-915M (Lumex Instruments, Russia). The amount of adsorbed  $\text{Pb}^{2+}$  was calculated as difference between concentration in the initial solution and in the supernatant. Data were used to calculate adsorption of  $\text{Pb}^{2+}$  according to the equation:

$$A = \frac{(C_0 - C) \cdot V}{m}; \quad (1)$$

where: A is adsorption of  $\text{Pb}^{2+}$  ( $\text{mg g}^{-1}$ ), C is the equilibrium concentration of  $\text{Pb}^{2+}$  ( $\text{mg L}^{-1}$ ),  $C_0$  is initial concentration of  $\text{Pb}^{2+}$  in the solution ( $1 \text{ mg L}^{-1}$ ), V is a volume of a stock solution of  $\text{Pb}^{2+}$  (0.04 L), m is a mass of adsorbent (mg).

Adsorption of  $\text{Pb}^{2+}$  on HS was approximated by two equations: Langmuir (Eq. 2) and Freundlich (Eq. 4) (Langmuir 1916, Freundlich, 1907, 1906):

$$\text{Langmuir equation: } A = A_\infty \frac{K_L C}{1 + K_L C}; \quad (2)$$

The above equation can be rearranged to the following linear form:

$$\frac{C}{A} = \frac{1}{K_L A_\infty} + \frac{1}{A_\infty} C; \quad (3)$$

where: C is the equilibrium concentration ( $\text{mg L}^{-1}$ ), A is the amount of  $\text{Pb}^{2+}$  sorbed ( $\text{mg g}^{-1}$ ),  $A_\infty$  is A for a complete monolayer ( $\text{mg g}^{-1}$ ),  $K_L$  is a sorption equilibrium constant ( $\text{L mg}^{-1}$ ).

Langmuir adsorption equation (2) is used in the following conditions: i) if the surface energy is uniform, ii) if there is no interactions between the adsorbed molecules and iii) if the adsorption is reversible.

$$\text{Freundlich equation: } A = K_F C^{1/n}; \quad (4)$$

where:  $K_F$  is a relative adsorption capacity constant of the adsorbent ( $\text{mg g}^{-1}$ ),  $1/n$  is the intensity of the adsorption constant, A is the amount of  $\text{Pb}^{2+}$  sorbed ( $\text{mg g}^{-1}$ ), C is the equilibrium concentration ( $\text{mg L}^{-1}$ ).

The Freundlich equation (4) is in the linear form,

$$\lg A = \lg K_L + \frac{1}{n} \lg C; \quad (5)$$

Freundlich adsorption equation (4) is valid when the surface is non-uniform, thus, adsorption carries out with various thermal effect.

In contrast, the Langmuir isotherm describes adsorption of metal cations on HS more accurately, than Freundlich isotherm. There are several reasons for that: I) the process of metal adsorption on HS is a monomolecular one, meaning that the number of adsorption sites is equal to the number of metal cations which can be sorbed, II) the Langmuir isotherm, in contrast to the Freundlich one, allows to determine the magnitude of the maximal adsorption more thoroughly and iii) sorption equilibrium constant in Langmuir equation has a certain magnitude, while the magnitude of sorption equilibrium constant in Freundlich equation varies dependently on the HS sort. Moreover, sorption equilibrium constant for Freundlich equation is descriptive (fitting) parameter, while in the Langmuir equation it has a strong thermodynamic meaning. Isobaric-isothermal potential  $\Delta G$  can be calculated from the Langmuir sorption constant due to it is a equilibrium constant of the adsorption-desorption processing heterogeneous system with metals and HS.

The simplified Henry's isotherm can be derived from the Langmuir one and applied for low surface coverage and/or for the nonselective sorbents with homogeneous surface. We used this approach to describe the experimental data for the LMWF of HS according to equation 6:

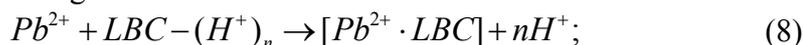
$$A = K_H C; \quad (6)$$

where: A is the amount of sorbed  $Pb^{2+}$  ( $mg\ g^{-1}$ ),  $K_H$  is the Henry constant ( $L\ g^{-1}$ ) and C is the equilibrium concentration ( $mg\ L^{-1}$ ). The  $K_H$  is calculated as tangent of the angle of the Henry's isotherm.

Lead sorption and pH changes. The pH values were monitored with 5 min intervals between measurements during a sorption course to calculate the adsorption rate constant. The adsorption was described as the process in a two-phase system to which the law of distribution was applicable. A distribution coefficient  $K_D$  characterizing a sorption equilibrium. It is a ratio of the total concentration of metal ions in the sorbent phase and its concentration in the equilibrated solution.

$$K_D = \frac{[Pb^{2+}]_{sorb}}{[Pb^{2+}]_{sol}} = \frac{C_0 - C}{C}; \quad (7)$$

$Pb^{2+}$  sorption on HS by ion exchange mechanism can be described as follows:



where: LBC is lead binding centers, ( $mg\ g^{-1}$ ),  $Pb^{2+}$  is equilibrium concentration of  $Pb^{2+}$  in the solution.

For the complexation process the equation for the concentration stability constant is:

$$k = \frac{[Pb^{2+} \cdot LBC] \cdot [H^+]^n}{[Pb^{2+}] \cdot [LBC - (H^+)_n]}; \quad (9)$$

$$K = k \cdot [LBC - (H^+)_n] = \frac{[Pb^{2+} \cdot LBC] \cdot [H^+]^n}{[Pb^{2+}]} = \frac{(C_0 - C) \cdot [H^+]^n}{C} = K_c \cdot [H^+]^n; \quad (10)$$

The linear form of the equation (10) is:

$$\lg K = \lg K_D + n \cdot \lg [H^+]; \quad (11)$$

$$\lg K_D = \lg K + n \cdot pH; \quad (12)$$

Equation (12) shows the empirical linear dependence between  $\lg K_D$  and pH. Tangent of the line slope is a measure of the  $Pb^{2+}$  sorption sensitivity on HS. The hypothesis about ion exchange for HS will be true if tangent of the angle to curve plotted in coordi-

rates  $\lg K_D - \text{pH}$  is equal to one (for singly charged ions) and when is equal to two for doubly charged metal cations.

## Results and discussion

Extraction of LMWF of HS. Addition of NaCl at 20% concentration into the tested humic substances allows selection of one LMWF only regardless to the origin and composition of the HS. It is known, that coagulation of the colloid particles increases with ionic strength of solution. Due to that chloride anion has weaker lyophobic properties compared to  $\text{SO}_4^{2-}$ , it posses weaker coagulation properties. For that reason, only  $\text{SO}_4^{2-}$  was used in further experiments for separation of LMWF from HS. Following fractionation, three and four HS fractions were separated from the Eutrophic and Mesotrophic peats, respectively. The HS fractions were separated according to their molecular weight and hydrophobicity.

The elemental composition of the obtained HS and the LMWF of HS showed, what the content of carbon was 46.2-48.8% for peats of various origin. The C content increased insignificantly in going from HS (40.9-57.9%) to LMWF (55.2-59.6%). It should be noted that all preparations insignificantly differed in the content of nitrogen (1.9-3.6%).

Functional structure of HS and their fractions was determined by acid-base titration. The results for the COOH content of HS 2.0-2.5  $\text{mmol g}^{-1}$ ; Fractions 3.2-4.4  $\text{mmol g}^{-1}$ , the OH content of HS 7.4- 8.2  $\text{mmol g}^{-1}$ ; Fractions 11.2- 13.7  $\text{mmol g}^{-1}$ . Fraction's enrichment of carboxylic and phenolic groups, as compared with HS, is the main factor of their greater sorption capacity in relation to heavy metal ions [5]. The FTIR spectra of HS extracted from the peats of various origins are shown in Fig. 1. Infrared spectra have a characteristic view for HS in the region between 3500 and 1500  $\text{cm}^{-1}$ .

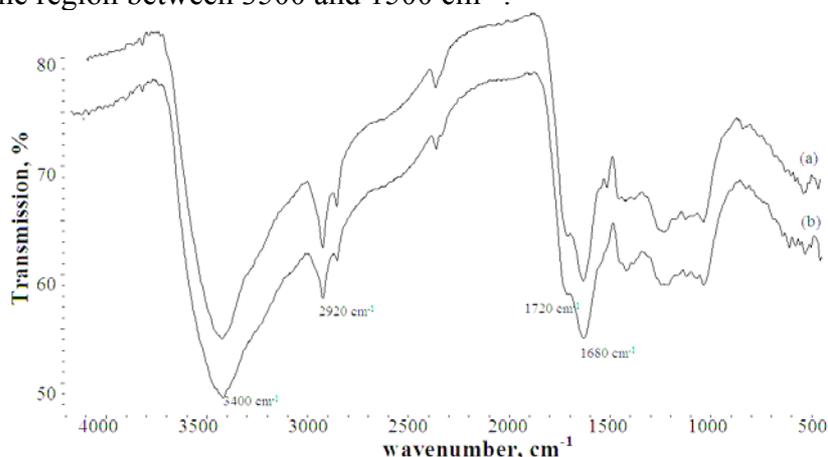


Fig. 1. FTIR spectra of HS from: a) Mesotrophic peat; b) Eutrophic peat

Following peaks have been identified: -OH hydroxyl groups in the region of 3500-3400  $\text{cm}^{-1}$  and mainly connected with intermolecular hydrogen bonds, -NH groups near the 3200  $\text{cm}^{-1}$ . The peaks at 2850 and 2920  $\text{cm}^{-1}$  are assigned to the aliphatic C-H stretching vibration. The bands at 1720  $\text{cm}^{-1}$  and 1700  $\text{cm}^{-1}$  correspond to carbonyl group which may be represented by ketones, aldehydes and carboxylic acids. The peaks between 1680 and 1640  $\text{cm}^{-1}$  are due to the stretching vibrations of the C=C bonds. Infrared spectra of the HS indicated the presence of aromatic moieties, oxygen – containing functional groups, that are able to bind heavy metals in the complex compounds by ionic and covalent mechanism.

Adsorption of Pb<sup>2+</sup> on LMWF of HS and unfractionated HS. Sorption isotherms play key role in the behavior analysis of adsorption system and they describe interaction between the substance dissolved in solution and the adsorbent (Fig. 2 a and b).

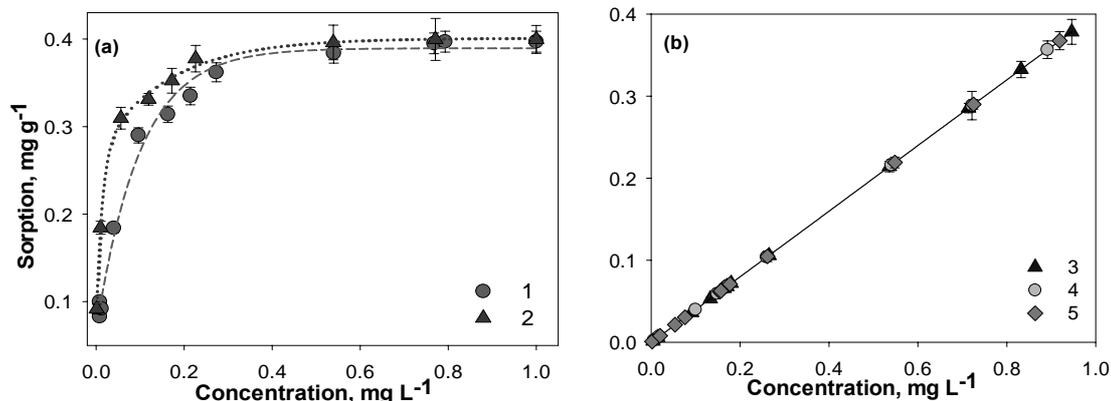


Fig. 2. Adsorption isotherms of Pb(II) *a*) –on HS extracted from peat of various origin (1) – HS (Mesotrophic peat), (2) – HS (Eutrophic peat); *b*) –on the low molecular weight fractions of HS (3) – Fraction I (Mesotrophic peat), (4) – Fraction I (Eutrophic peat), (5) – Fraction II (Eutrophic peat)

Sorption isotherms of Pb<sup>2+</sup> on LMWF of HS have the characteristic linear form (Fig. 2 b). At the experimental conditions used a limiting sorption capacity was not observed due to enrichment and availability of basic functional groups (CA and PA) responsible for binding of lead cations. A large number of functional groups of low molecular weight fractions are associated with breaking of hydrogen and intramolecular bonds during the fractionation of HS. Thus, experimental concentration of Pb<sup>2+</sup> was too low to obtain maximum adsorption, and in these conditions the sorption of Pb<sup>2+</sup> is directly proportional to its concentration in the solution. This means, that the Henry's constant is equal to Pb<sup>2+</sup> distribution coefficient between its concentration in solution and sorbed on the HS fraction. Calculated Henry's constant was 0.4 and was identical for the LMWF of HS extracted from peats of various origins. In this case the dispersion layers, where the metal binding centers are present, is the same for the various HS fractions.

Adsorption of Pb<sup>2+</sup> on HS was described by the Langmuir and Freundlich equation (Table 1). The calculated  $\Delta G$  had negative values, suggesting spontaneity of the sorption process and strong bonds between sorbent and sorbate.

Table 1. Parameters of adsorption isotherms of the Pb(II) on HS and LMWF of HS.

Langmuir isotherm					
Type of peat	Substance	K (L mg <sup>-1</sup> )	A <sub>∞</sub> (mg g <sup>-1</sup> )	R	ΔG (kJ mol <sup>-1</sup> )
Eutrophic	HS	1	0.4	0.994	-16
Mesotrophic	HS	1	0.4	0.996	-17
Freundlich isotherm					
		K (mg g <sup>-1</sup> )	n		R
Eutrophic	HS	0.008	1		1
Mesotrophic	HS	0.008	1		1
Henry isotherm					
		K (L mg <sup>-1</sup> )	R		
Eutrophic	LMWF	0.4	0.998		
Mesotrophic	LMWF	0.4	0.998		

The experiment showed, that adsorption of  $Pb^{2+}$  on non-fractionated HS was not dependent on their origin. So, physical adsorption and precipitation of metal cations on the surface of HS have significant contribution to the sorption process.

Analysis of pH changes in solution during the sorption process showed, that the equilibrium was established between 80-120 min and after 40 min, for the unfractionated HS and LMWF of HS, respectively (Fig. 3). This shows, that: i) sorption centers in the unfractionated HS were less available for  $Pb^{2+}$ , compare to LMWF of HS, ii) the LMWF of HS contain greater number of sorption sites available for bonding of  $Pb^{2+}$  compare to unfractionated HS and iii) close location of carboxyl groups, which increase absorption rates and direct effect on the sorption equilibrium.

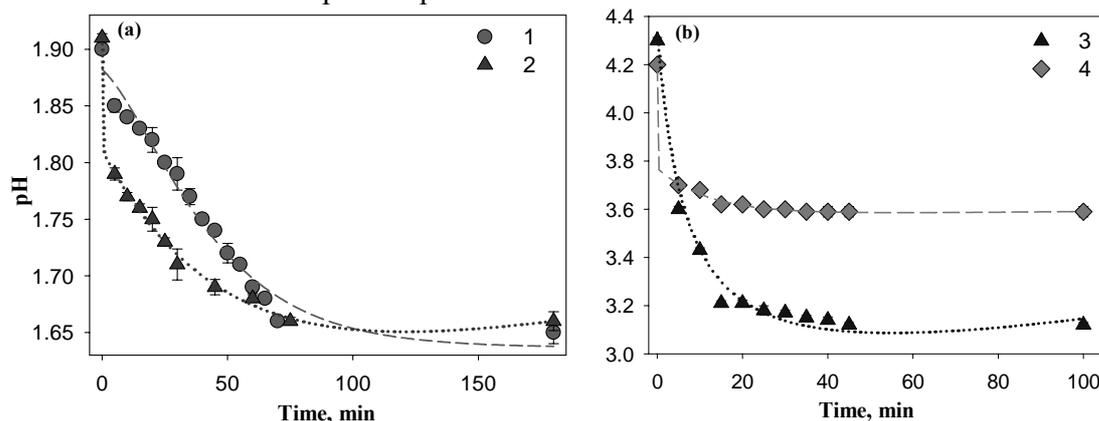


Fig. 3. pH changes during Pb(II) sorption as time function *a*)- on HS extracted from peat of various origin, (1) – HS (Mesotrophic peat), (2) – HS (Eutrophic peat); *b*)- on the LMWF of HS, (3) – Fraction II (Mesotrophic peat), (4) – Fraction II (Eutrophic peat)

The pH was changed to 0.25 units for unfractionated HS and for one unit for LMWF of HS during the sorption processes (Fig. 3). Thus, presence of a salt decreases the solution pH and in the same time increases the solubility of HS. This causes the formation of new active centers capable to bind the metal ions. Due to protons were released from the HS and LMWF into the solution during the sorption of  $Pb^{2+}$ , this type of sorption can be related to chemisorption. The  $Pb^{2+}$  concentration in solution plotted against pH values was used to reveal the mechanism of chemisorption (Fig. 4).

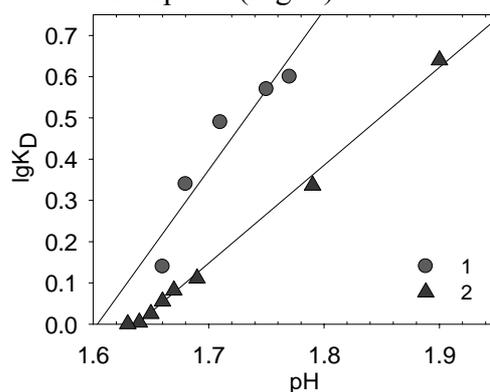


Fig. 4. Dependence of Pb(II) distribution on pH values: (1) – HS (Mesotrophic peat), (2) – HS (Eutrophic peat).

The calculated tangent to the curve slope had values 3.8 for HS originated from Eutrophic peat and 3.6 for HS from Mesotrophic peat. Due to these values were more than 2

(which should be for doubly charged cations), the sorption is not a simple ion exchange and additional mechanisms can contribute to that process.

The adsorption rate constants for  $Pb^{2+}$  were  $0.01\text{ s}^{-1}$  ( $R>0.995$ ) for the unfractionated HS and  $0.07\text{ s}^{-1}$  ( $R>0.997$ ) for the LMWF of HS, regardless of their origin. Therefore,  $Pb^{2+}$  sorbed better on HS fractions, due to greater availability of sorption sites for  $Pb^{2+}$ . These adsorption rate constants are comparable with the constants of  $Pb^{2+}$  sorption on lignite activated by potassium hydroxide ( $K=0.06\text{ s}^{-1}$ ) a known sorbent for the purification of waste and effluents. Also, present results were in the order for the adsorption of  $Pb^{2+}$  on nanoporous materials obtained by alkaline activation of brown coal ( $K=0.05\text{ s}^{-1}$ ). Thus, HS and their LMWF can be used as an effective natural sorbents for trace elements.

## Conclusions

Sorption capacity of HS and LMWF of HS to  $Pb^{2+}$  extracted from mesotrophic and eutrophic peats was studied. The IR spectra of HS extracted from peat of various origin had a characteristic view in the region from  $3500$  to  $1500\text{ cm}^{-1}$ . Aromatic moieties, oxygen-containing functional groups, capable of binding of heavy metals, were identified.

Sorption isotherm of  $Pb^{2+}$  from solution on HS had an exponential form and was well described by the Langmuir and Freundlich equations. The adsorption of  $Pb^{2+}$  on non-fractionated HS was not dependent on their origin.

Sorption of  $Pb^{2+}$  on the LMWF of HS was described by Henry's isotherm. Limiting adsorption at initial concentration of  $1.0\text{ mg L}^{-1}$  was not observed showing, that LMWF contain a large number of sorption sites able to bind of  $Pb^{2+}$ . Thus, the experimental concentration of the  $Pb^{2+}$  solution, applied for the study, is low to obtain a maximum adsorption. Fractionation of HS results in fraction preparation, that are enriched with basic functional groups responsible for binding of heavy metal ions and increase of total sorption capacity of HS.

The adsorption rate constant of  $Pb^{2+}$  on HS was  $0.01\text{ s}^{-1}$ , regardless of their origin, and was  $0.07\text{ s}^{-1}$  for LMWF. Therefore,  $Pb^{2+}$  sorbed faster on HS fractions due to greater availability of sorption sites compare to unfractionated HS. Sorption of  $Pb^{2+}$  occurred between 80 and 120 minutes for HS, and within 40 minutes for the LMWF of HS. Such different results are explained by higher amounts of sorption centers in LMWF of HS and which are in the same time high available.

Releasing of an equivalent amount of hydrogen ions to the solution during the ion-exchange by lead ions changed its pH value. Thus, sorption of  $Pb^{2+}$  on the HS and LMWF of HS is related to chemisorption. Due to sorption sensitivity was more than two, the processes of  $Pb^{2+}$  interaction with HS and LMWF of HS can not be related to the simple ion exchange.

*The work was carried out within the framework of the State Assignment of the Ministry of Education and Science of the Russian Federation (project No.5.241.2014/K).*

## References

1. Stevenson F.J. Humus chemistry: genesis, composition, reaction. 2nd ed.. N.Y.: John Wiley & Sons, 1994. 496 p.
2. Hedges J.I., Oades J.M., *Organic Geochemistry*, 1997, Vol. 27(7–8), pp. 319-361.
3. van Wandruszka, R. Humic acids: Their detergent qualities and potential uses in pollution remediation, *Geochemical Transactions*, 2000. 1. pp. 10-15

4. Chin Y.P., Aiken G., E. Oloughlin, *Environmental Science & Technology*, 1994, Vol. 28(11), pp. 1853-1858.
5. de Melo B.A.G., Motta F.L., Santana M.H.A. Humic acids: Structural properties and multiple functionalities for novel technological developments. *Materials Science and Engineering*, 2016, T. 62. pp. 967-974.
6. Khan S.U., Schnitzer M., *Geochimica et Cosmochimica Acta*, 1972, Vol. 36(7), pp. 745-754.
7. Perminova I.V., Hatfield K., Hertkorn N. Use of humic substances to remediate polluted environments: from theory to practice. *Dordrecht, Netherlands*, 2005. pp. 285-309.
8. Burlakovs J. et al., *APCBEE Procedia*, 2013, Vol. 5, pp. 192-196.
9. Yates L.M., Wandruszka R.V., *Environmental Science & Technology*, 1999, Vol. 33(12), pp. 2076-2080.
10. Stathi P., Deligiannakis Y., *Journal of Colloid and Interface Science*, 2010, Vol. 351(1), pp. 239-247.
11. Tang W.-W. et al., *Science of the Total Environment*, 2014, Vol. 468, pp. 1014-1027.
12. Burba P., Rocha J., Klockow D., *Fresenius Journal of Analytical Chemistry*, 1994, Vol. 349(12), pp. 800-807.
13. Murphy E.M. et al., *Environmental Science & Technology*, 1994, Vol. 28(7), pp. 1291-1299.
14. Jarup L., *British Medical Bulletin*, 2003, Vol. 68, pp. 167-182.
15. Lesmana S.O. et al., *Biochemical Engineering Journal*, 2009, Vol. 44(1), pp. 19-41.
16. Novenko E.Y. et al., *Quaternary International*, 2009, Vol. 207(1-2), pp. 93-103.
17. Dmitrieva E. et al., *Environmental Chemistry Letters*, 2015, Vol. 13(2), pp. 197-202.
18. Vanifatova N.G., Zavarzina A.G., Spivakov B.Y., *Journal of Chromatography A*, 2008. Vol. 1183(1-2), pp. 186-191.
19. Zavarzina A.G., Vanifatova N.G., Stepanov A.A., *Eurasian Soil Science*, 2008, Vol. 41(12), pp. 1294-1301.
20. Felbeck G.T., *Structural Chemistry of Soil Humic Substances*, in *Advances in Agronomy*, A.G. Norman, Editor 1965, Academic Press. pp. 327-368.

**Siundiukova Kristina V.** - postgraduate student of Tula State University, E-mail: [kristina-syundyukova@yandex.ru](mailto:kristina-syundyukova@yandex.ru)

**Goryacheva Anastasia A.** – candidate of chemical sciences, associate professor, Chemistry Department, Tula State University E-mail: [goryachevanastya@rambler.ru](mailto:goryachevanastya@rambler.ru)

**Dmitrieva Elena D.** – candidate of chemical sciences, associate professor, Chemistry Department, Tula State University, E-mail: [dmitrieva\\_ed@rambler.ru](mailto:dmitrieva_ed@rambler.ru)

**Muzafarov Eugeny N.** – Sc.D., professor, Head of the Department of Biology, Tula state University, E-mail: [enmuzafarov@mail.ru](mailto:enmuzafarov@mail.ru)