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## Application of Humic Sorbents for $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ and $\text{Hg}^{2+}$ ions preconcentration from aqueous solutions

Olga V. Vetrova <sup>a</sup> \*, Konstantin B. Konovalov <sup>b</sup>, Mikhail A. Gavrilenko <sup>c</sup>

<sup>a</sup> *Institute of Monitoring of Climatic and Ecological Systems of the Siberian Branch of the Russian Academy of Sciences,  
10/3 Akademicheskoy ave, Tomsk 634055, Russian Federation*

<sup>b</sup> *National Research Tomsk Polytechnic University, 30 Lenin ave, Tomsk 634050, Russian Federation*

<sup>c</sup> *National Research Tomsk State University, 36 Lenin ave, Tomsk 634050, Russian Federation*

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### Abstract

The sorbent prepared by sequential treatment of silica gel by polyhexamethylene guanidine of linear structure and humic acids is suggested for sorption concentration of metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ ) from aqueous solutions. Thermogravimetry and infrared spectroscopy have confirmed the success of the attachment of the humic acids onto modified silica surface. Sorption isotherms of lead (II), copper (II) and mercury (II) obtained in optimal conditions of metals sorption were analyzed by using Freundlich and Langmuir adsorption isotherms. Structural model of surface of humic sorbent was proposed based on the obtained results. The results demonstrated the potential applicability of supramolecular humic sorbent in the preconcentration of metal ions from aqueous solution.

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### 1. Introduction

One of the main ecological problems is environmental contamination with heavy metals. It represents a potential threat to humans, animals and plants. The metals do not undergo biodegradation. Many of them are soluble in water, therefore become more available for living systems and accumulate in the environment<sup>1</sup>.

The continuous monitoring of metal ions in environmental samples is of great importance. Preconcentration procedures have always been implemented when trace analysis of compounds in real matrices is contemplated, because of not only the matrices are complexes but target compounds have to be monitored at very low

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\* Corresponding author: Olga V. Vetrova. Tel.: +7-913-889-3329

E-mail address: [vetrovao.v@mail.ru](mailto:vetrovao.v@mail.ru)

concentrations. Sorption is widely used for preconcentration of the elements. It allows one to concentrate micro components from bulk concentrated by macro component solutions on relatively small weight of the sorbent<sup>2</sup>.

Nowadays chemically modified silicas with functional groups covalently bound to the surface are the most extensively used sorbents on inorganic oxide supports. Several approaches for non-covalent fixation of reagents have been suggested. One of such method is impregnation of the silica gel surface by humic acids (HA)<sup>3, 4</sup>. This way is characterized by not strong enough fixation of the reagents on the silica gel surface. The attachment of HA, which are a very important class of naturally occurring biogenic heterogeneous organic complex agents, can lead to materials with interesting properties. HA are formed by a mixture of weak-acid polyelectrolites, which present a complex class formed by organic macromolecules with a large variety of molar mass distributions, substructures and functionalities. Moreover, these natural materials present a high ability to adsorb and to complex metal ions, organic compounds and other possible contaminants. Thus, the preparation of hybrids with HA properties should lead to new materials with complexation characteristics of HA and with the insolubility, thermal and chemical stability characteristics of silica gel. These humic sorbent (HS) utilizes the immobilized humic acid for removing contaminants from water and/or other solvents, while avoiding humic acid loss by solubilisation. In addition, HS can be reused without waste.

It is necessary to make a surface layer with effective positive charge in order to fix reagents with negatively charged groups on the surface. Such a layer can be prepared during the sorption of polyamines, particularly, linear polyhexamethylene guanidine (PHMG), which has convenient amine group configurations. The strong fixation of PHMG on the surface of silica gel proceeds due to formation of multicentered hydrogen bonds between amine groups of PHMG and hydroxyl groups of the surface. Subsequent fixation of organic reagent is provided due to electrostatic interaction between negatively charged carboxylic groups of the HA and protonated amine groups of PHMG, which are not evolved in hydrogen bond formation with surface hydroxyl groups<sup>1, 3, 5</sup>.

In this work, Cu (II), Pb (II) and Hg (II) sorption by silica gel sequentially modified by PHMG and humic acids are considered.

## 2. Experimental

### 2.1. Materials and methods

Silica gel - silochrome C-80 (100–230 mesh, specific surface area of 80 m<sup>2</sup> g<sup>-1</sup>, and pore diameter of 50 nm) was used as a support for the humic sorbent synthesis. The extraction of HA from peat and their purification were performed using a traditional alkaline method described in<sup>1, 6, 9</sup>.

The manner of silica gel modification was as described in<sup>3</sup>. Prepared sorbent was separated from solution by decantation, washed by distilled water and dried at 85–90°C. After that 50 ml of alkaline solution of HA was added to silica gel modified by PHMG (SiO<sub>2</sub>–PHMG) and the mixture was stirred at ambient temperature. Prepared sorbent (SiO<sub>2</sub>–PHMG–NRS) was filtered and washed with NaCl solution and then with distilled water. Finally, HS was separated from solution by centrifugation, washed with distilled water and dried at 120°C.

### 2.2. Instrumentation

Termogravimetric curves were obtained from approximately 10 mg of humic sorbent sample, on a NETZSCH STA 449C thermogravimetric analyzer model in a dynamic air atmosphere, with heating from 25 up to 400°C at a heating rate of 5°C min<sup>-1</sup>. Infrared spectra of all samples were performed in KBr pellets in the 4000–500 cm<sup>-1</sup> region with a resolution of 4 cm<sup>-1</sup>, by using a «Nicolette 3700» spectrophotometer.

### 2.3. Adsorption experiments with HS

The sorption behaviors of metal ions (Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup>) were investigated by using Freundlich and Langmuir adsorption isotherms, which were analyzed by means of Scatchard plot analysis. Adsorption isotherms

were obtained by the batchwise method, in which a series of samples of 50.0 mg of HS were suspended in 20.0 cm<sup>3</sup> of aqueous solution with divalent metal ions concentration (Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup>), varying from 0 to 15.0 mmol/l. Samples were mechanically stirred for 24 h at 298.1K and the solid was separated by filtration. Adsorbed ion content was determined by difference between initial concentration and post-sorption concentration of metal ion in solution. The analysis of metal distribution was carried out by flame (acetylene–air) atomic absorption spectrometry using a Perkin-Elmer 2380 spectrometer. pH of solution has been adjusted using citric acid–phosphate buffers. HA were extracted from peat and purified as described in<sup>1, 5-8</sup>.

Concentration of adsorbed metal ions can be also determinate using diffuse reflectance spectroscopy without any further treatment.

### 3. Results and discussion

During sequential treatment by PHMG and HA supramolecular ensemble was generated on the silica gel surface. All three reagents in this ensemble are bound due to nonvalent interactions. In this case, the surface of the initial silica gel can be considered as a supramolecule with a large quantity of hydroxyl groups.

Thus, during sorbent synthesis supramolecular ensembles on the silica gel surface have three kinds of groups: surface hydroxyl groups, amine groups of PHMG, and functional groups of HA, which can interact with extractable metal ions under appropriate conditions.

#### 3.1. Thermogravimetric analysis

Thermogravimetric curves see Fig 1 for modified silicas were obtained in order to determine the thermal stability and confirm the amount of material immobilized on the surface.

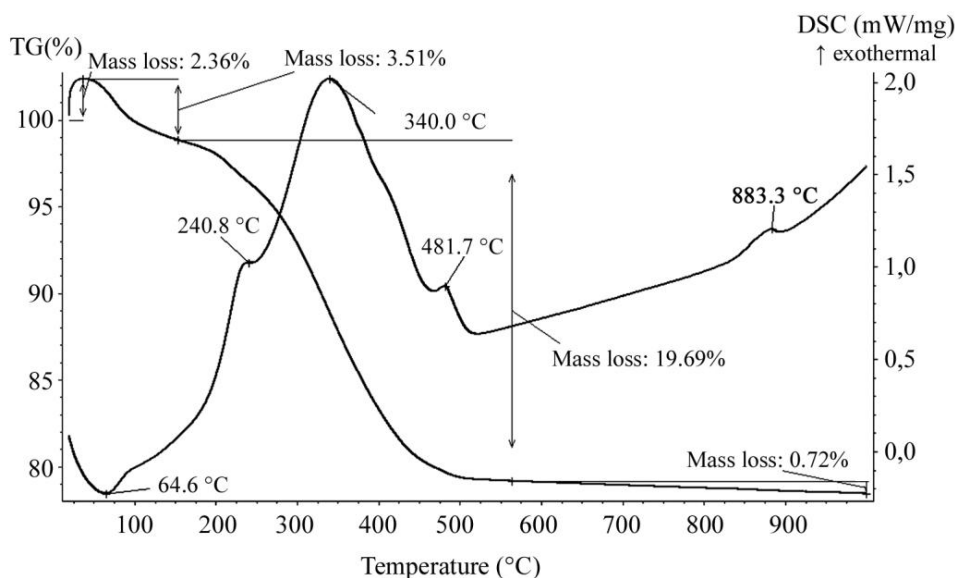


Fig. 1. Thermogravimetric curves of the sorbent modified by HA and PHMG.

There are five peaks on the thermogram of the sorbent with polymer anchored. The first peak at the temperature of 64.5°C is endothermal. Peaks at the temperatures of 240°C, 340°C, and 481°C are connected with

polymer burning out from the surface. The peak at 883°C is attributed to crystallization water. Complete burning occurs at 600°C with 21.56% mass loss.

Thermo-gravimetric curves of the sorbent samples obtained were relatively identical and were corresponding with literature data<sup>1, 7, 9</sup>. They revealed that sorbents can be used within certain temperature range up to 160°C. These thermogravimetric data corroborate the increase in stability of HA, when anchored onto the for modified silicas surface.

### 3.2. Infrared spectroscopy

In order to confirm the immobilization of HA on modified surfaces, infrared spectra of the materials were obtained. The spectra performed in KBr pellets for silica gell, HA samples and humic sorbent are shown in Figure 2. Infrared spectra were explained considering literature data<sup>1, 6-9</sup>.

It can be seen that the adsorption spectra of HA and HS display readily identifiable peaks at 2923 and 2853  $\text{cm}^{-1}$ , which are characteristic of -CH-group symmetric and anti-symmetric stretching vibrations. We can see bands at 807, 1100, and 3450  $\text{cm}^{-1}$  on the infrared spectrum of the initial matrix (silica gel). A large broad band at 3450  $\text{cm}^{-1}$ , which is attributed to the presence of O-H stretching frequency of silanol groups and also to the remaining adsorbed water; the intense band related to siloxane stretching ( $\nu$ -Si-O-Si) of these groups at 1100  $\text{cm}^{-1}$ ; a band assigned to Si-OH stretching frequency for silanol groups at 807  $\text{cm}^{-1}$  and the band around 1650  $\text{cm}^{-1}$ , assigned to angular vibration of water molecules.

Furthermore, the HS presented a characteristic peak at 2950  $\text{cm}^{-1}$ , assigned to C-H stretching of the tetrahedral carbon, which confirms the attachment of the organic molecule onto silica surface. In the infrared spectrum of the PHMG-modified silica gel we can see bands near 1600  $\text{cm}^{-1}$ , which were classified as belonging to the benzene ring; a peak at 1661  $\text{cm}^{-1}$  of C-N bond fluctuating, peaks at 3300 and 3415  $\text{cm}^{-1}$  of -OH group and N-H bond of PHMG-amino group.

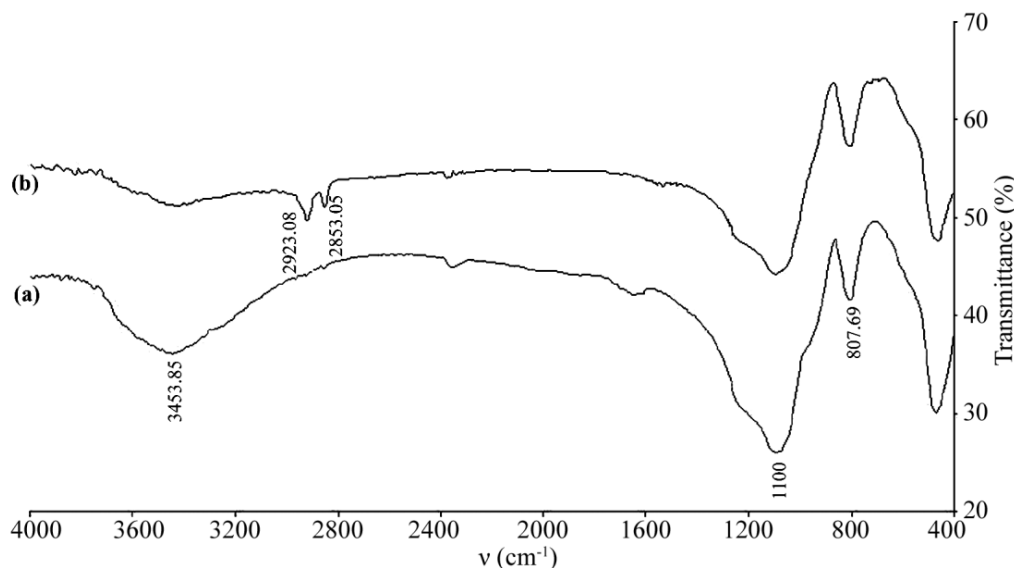


Fig. 2. Infrared spectra of silica gel (a) and HA (b).

Having analyzed the infrared spectra, we can conclude that there is strong interaction between the silica gel

surface and PHMG as well as between PHMG and HA. The dominating peaks of HS are almost the same as that of HA fraction, which proves that humic acids were grafted to silica matrices successfully.

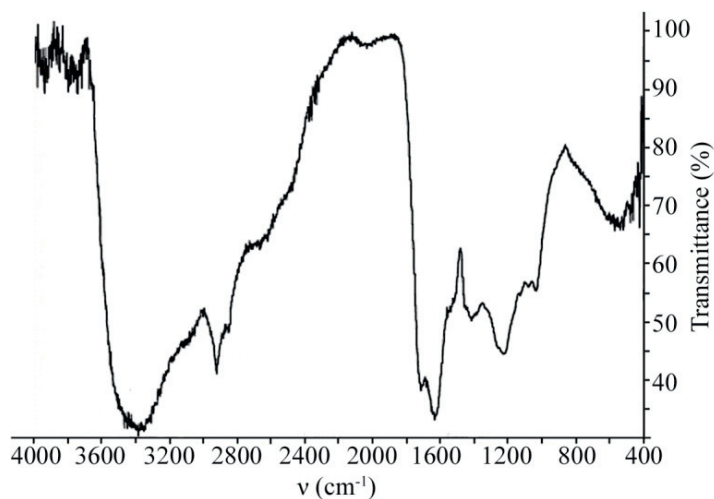


Fig. 3. Infrared spectrum of humic sorbent.

### 3.3. Model of surface structure of humic sorbent

Structural model of humic sorbent was proposed based on the obtained results see Fig. 4.

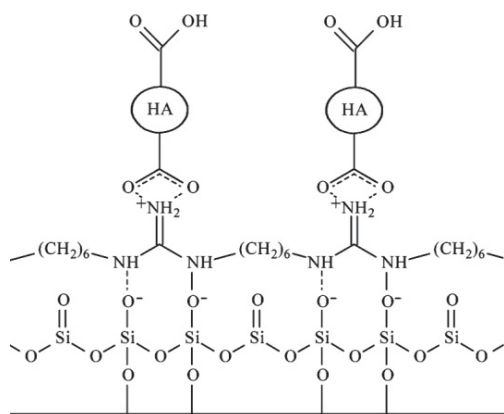


Fig. 4. Model of surface structure of silica gel matrix PHMG-modified with grafted HA.

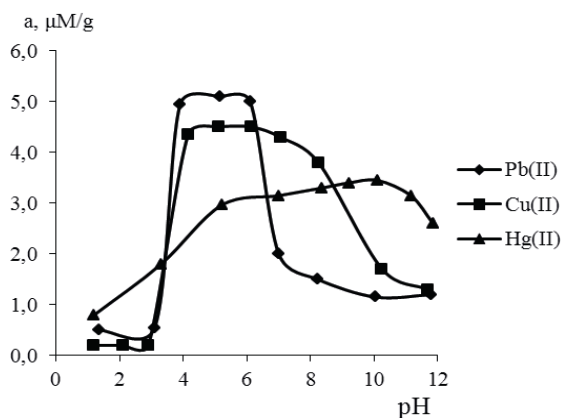


Fig. 5. Correlation of sorption of Cu (II) – (1), Pb (II) – (2), Hg (II) - (3) with HA and the pH level of the solution.

### 3.4. Sorption behaviour

It is noted that HA with metals ions in a certain pH range forms chelated salts due to various functional groups. If there is a range of metals ions in water solution with a certain pH value, the sorbent reacts with these

metals forming complexes with a different degree of stability.

In the present work the effect of solution pH on their interacting with HA immobilized on silica gel were studied to determine optimal pH ranges for sorption of metal ions and their complexation with HS see Fig. 5.

It is known from literature data that HA are not selective complexing agents, because they interact with a large number of ions. Depending on solutions acidity some metals take part in complexing reactions while other do not react in these conditions. The relation of Cu (II), Pb (II) and Hg(II) to HA immobilized on silica gel is studied as the number of sorbed metal ions as function of solution pH see Fig 5 to the determined optimal pH ranges of interaction.

From the given figure, we can see that the maximum sorption of metals ions is seen within the following pH range: 4-8 for copper (II), 4-6 for lead (II) and 5-11 for mercury (II). Sorption of Cu (II) and Pb (II) begins only with pH 4, which is likely to be due to the change in the composition of HA functional groups with depression of acidity in the pH range lower than 4. Sorption decreases with  $\text{pH} > 6$  for lead (II) and  $\text{pH} > 8$  for copper (II), which is due to hydrolysis. Mercury (II) in this pH range sorbs. As it is noted in the literature, the pH range or acidity of aqueous solutions, in which reactions of complexation are possible, is primarily determined by the inclination of elements to form stable compounds with this functional group and their formation rate, but not by the dissociation rate of complexes in acidic medium.

The ability of HS to adsorb metal ions from water was evaluated by measuring the sorption isotherms of divalent lead, copper and mercury in optimal conditions of metals interaction (for lead (II) and copper (II) at pH 4 and for mercury (II) at pH 4).

Mercury (II) reacts with the formation of disubstituted complex of mercury (II) at pH 0-3 and monosubstituted complex at pH 5-10. Copper (II) reacts with HA forming monosubstituted complex of copper (II) at pH 4-10.

Sorption isotherms of lead (II), copper (II) and mercury (II) obtained in optimal conditions of metals sorption are in figures 5 and 6. They belong to L-type, which demonstrates the intense interactions between HA and metal ions.

Copper (II) has a larger degree of affinity to the sorption layer if compared to mercury (II) because the initial section of the isotherm of copper (II) is in bent relative to the axis of concentrations. This means that there is high adsorption with low metal concentration in the solution. As is evident from figure 6, sorption isotherm of mercury (II) has Henry region, which means that the value of adsorption is directly proportional to the metal concentration in the solution. This indicates that there is possible equivalence of sorption sites in this range of concentrations and that the number of involved adsorption sites is much lower than the number of free ones, i.e. sorption occurs in the conditions which correspond to approximation of ideal solutions.

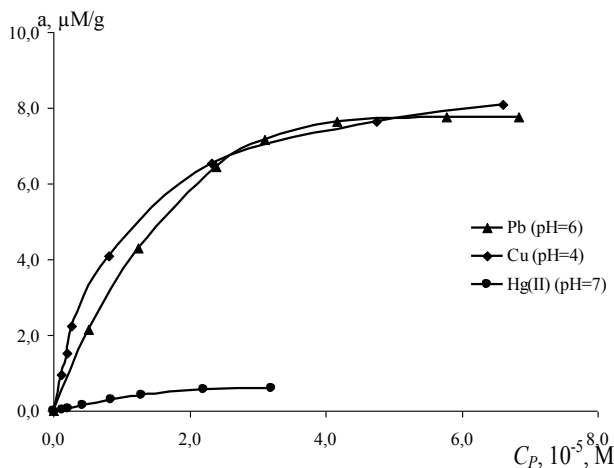


Fig. 6. Isotherms of Pb (II) ( $t=30$  min), Hg (II) and Cu (II) ( $t=120$  min) sorption by humic sorbent ( $\text{SiO}_2\text{-PHMG-HA}$ ) ( $V=50\text{ml}$ )

### 3.5. Models of sorption

Sorption isotherm of lead (II) can be used to demonstrate the model of sorption according to Langmuir equation (1).

$$\frac{[C]}{a} = \frac{1}{a_m K} + \frac{1}{a_m} [C] \quad (1)$$

The isotherm is defined by the equation (1) and looks like common adsorption of monomolecular layer. This means that  $Pb^{2+}$  ions are chemically adsorbed on humic sorbent due to coordinate bonds with the formation of monomolecular layer.

Sorption isotherms of copper (II) and mercury (II) are described well by the Freundlich equation (2).

$$\lg a = b + n \lg [C] \quad (2)$$

This means that apart from chemical sorption of  $Cu^{2+}$  and  $Hg^{2+}$  by humic sorbent there is also physical adsorption by the sorbent pores and there are certain ensembles formed on the surface of the sorbent.

## 4. Conclusion

Using the developed methods of controlled chemical modification, humic acids of peat were fixed on the surface of silica gel through the layer of polyhexamethylguanidine. Attachment of HA to a solid support prevents the solubilization of these compounds in solvents. Thermogravimetry and the infrared spectroscopy have confirmed the success of the attachment of the humic acids onto modified silica surface.

Model of surface structure of humic sorbent was proposed based on the obtained results.

Humic sorbent has high affinity to bind the main toxicants of aqueous solutions (ions of  $Pb^{2+}$ ,  $Hg^{2+}$  and  $Cu^{2+}$ ), the concentration of which needs to be regularly monitored. Depending on the interaction of ions with the surface of humic sorbent, maximal sorption is reached in the pH range: 4-6 for lead (II), 4-8 for copper (II) and 5-11 for mercury (II).

Thus, we can conclude that this new humic sorbent can be applied in analytic chemistry as solid-phase sorbent for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Hg^{2+}$  ions preconcentration from water for their further analysis carried out using different methods and also for removal of contaminants from aqueous solutions.

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