NOVEL SUPRAMOLECULAR HUMIC SORBENT FOR PRECONCENTRATION OF Pb2+, Cu2+ AND Hg2+ IONS FROM AQUEOUS SOLUTION

1OLGA V. VETROVA, 2KONSTANTIN B. KONOVALOY, 3MICHAEL A. GAVRILENKO

1Institute of Monitoring of Climatic and Ecological Systems of the Siberian Branch of the Russian Academy of Sciences, 10/3 Academichesky ave, Tomsk 634055, Russian Federation,
2National Research Tomsk Polytechnic University, 30 Lenin ave, Tomsk 634050, Russian Federation,
3National Research Tomsk State University, 36 Lenin ave, Tomsk 634050, Russian Federation
E-mail: vetrovao.v@mail.ru, konoko@tpu.ru, dce@mail.ru

Abstract- In this study, humic sorbent was synthesized and characterized by infrared spectroscopy and thermogravimetric analyses. Silica gel was respectively modified with humic acids extracted from peat, after treatment of silica gel by humic acids. This way is characterized by not strong enough fixation of the reagents on the silica gel surface. The immobilized humic acid for removing metal ions from aqueous solution, such as wastewaters.

Keywords- Sorption, Humic Sorbent, Preconcentration, Polyhexamethylene Guanidine

I. INTRODUCTION

Groundwater contamination by metal ions has become an issue of worldwide concerns because of its threats to human health. 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. Pb(II), Cu(II) and Hg(II) ions are among the most common heavy metal ions in industry effluents.

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 concentrations. Sorption is widely used for preconcentration of the elements. It demands less organic solvents and can remove interferences and preconcentrate the objective simultaneously.

Since the discovery of surfactant-templated synthesis of ordered mesoporous materials, the research on the preparation and characterization of these novel supramolecular sorbents has been expanded very fast. 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). This way is characterized by not strong enough fixation of the reagents on the silica gel surface. The attachment of HA, which are a specific class of natural organic complex agents that are often polydispersive structured polyelectrolytes of an amphiphilic nature, can lead to novel supramolecular materials with interesting properties. HA are formed by a mixture of weak-acid polyelectrolytes, 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 supramolecular 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 solubilization. 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 polyanines, 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.

The aim of this work is to test novel supramolecular HS prepared by sequential treatment of silica gel by polyhexamethylene guanidine of linear structure and humic acids as sorbent for previously concentration of Cu (II), Pb (II) and Hg (II) ions in aqueous matrixes and removing this ions from water.

II. EXPERIMENTAL

A. Materials and methods
Silica gel - silochrome C-80 (100–230 mesh, specific surface area of 80 m² g⁻¹, 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...

The manner of silica gel modification was as described in. 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 (SiO₂–PHMG) and the mixture was stirred at ambient temperature. Prepared sorbent (SiO₂–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.

B. 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⁻¹. Infrared spectra of all samples were performed in KBr pellets in the 4000–500 cm⁻¹ region with a resolution of 4 cm⁻¹, by using a Nicolette 3700 spectrophotometer.

C. Adsorption experiments with HS
The sorption behaviors of metal ions (Pb²⁺, Cu²⁺ and Hg²⁺) were analyzed by using Freundlich and Langmuir adsorption isotherms, which were analyzed by using 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 cm³ of aqueous solution with divalent metal ions concentration (Pb²⁺, Cu²⁺ and Hg²⁺), 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...

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

III. RESULTS AND DISCUSSION

During sequential treatment by PHMG and NRS 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 NRS, which can interact with extractable metal ions under appropriate conditions.

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

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

There are five peaks on the thermogramm of the sorbent with polymer anchored. The first peak at the temperature of 64.5°C is endothermic. 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 of 600°C with 21.56% mass loss. Thermo-gravimetric curves of the sorbent samples obtained were relatively identical and were corresponds with literature data. 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 modified silicas surface.

B. 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 gel, HA samples and humic sorbent are shown in Figure 2. Infrared spectra were explained considering literature data.

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

Furthermore, the HS presented a characteristic peak at 2950 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 cm$^{-1}$, which were classified as belonging to the benzene ring; a peak at 1661 cm$^{-1}$ of C–N bond fluctuating, peaks at 3300 and 3415 cm$^{-1}$ of –OH group and N–H bond of PHMG-amino group.

C. Structural model
Structural model of humic sorbent was proposed based on the obtained results.

D. Sorption behavior
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. 4. 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 4 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 pH > 6 for lead (II) and pH > 8 for copper (II), which is due to hydrolysis. Mercury
Novel Supramolecular Humic Sorbent for Preconcentration of Pb²⁺, Cu²⁺ and Hg²⁺ ions From Aqueous Solution

(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).

Figure 5 - Isotherms of Pb (II) (t=30 min) and Cu (II) (t=120 min) sorption by humic sorbent (SiO₂–PHMG–HA) (V=50ml)

Figure 6 - Isotherms of Hg (II) sorption by humic sorbent (SiO₂–PHMG–HA) (V=50ml, pH=7, t=120 min)

Mercury (II) reacts with the formation of direplaced complex of mercury (II) at pH 0-3 and monoreplaced complex at pH 5-10. Copper (II) reacts with HA forming monoreplaced 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 indent 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.

E. Models of sorption

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

\[
\frac{[C]}{a} = \frac{1}{a_K} \cdot \frac{1}{a_m} \cdot [C]
\]

The isotherm is defined by the equation (1) and looks like common adsorption of monomolecular layer. This means that Pb²⁺ 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).

\[
\log a = b + n \log [C]
\]

This means that apart from chemical sorption of Cu²⁺ and Hg²⁺ by humic sorbent there is also physical adsorption by the sorbent pores and there are certain ensembles formed on the surface of the sorbent.

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 polyhexamethyleneguanidine. Attachment of HA to a solid support avoids 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.

Structural model of humic sorbent was proposed based on the obtained results. Novel supramolecular humic sorbent has high affinity to bind the main toxicants of aqueous solutions (ions of Pb²⁺, Hg²⁺ and Cu²⁺), the concentration of which needs to be regularly monitored.

Depending on the interaction of ions with the surface of novel supramolecular 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 novel supramolecular humic sorbent can be applied in analytic chemistry as...
solid-phase sorbent for Pb2+, Cu2+ and Hg2+ ions preconcentration from water for their further analysis carried out using different methods and also for removal of contaminants from aqueous solutions.

REFERENCES


★★★