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OBTAINING OF NEW TYPES SORBENTS FOR THE EXTRACTION OF HEAVY METALS FROM AQUEOUS SOLUTIONS

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Purpose. Currently, the wastewater treatment plants are an urgent environmental problem. The most dangerous pollutants are heavy metals and organic substances. Several industrial wastewater streams may contain heavy metals such as: lead, chromium, cadmium, nickel, zinc, arsenic, mercury, copper, silver. With the aim of sewage treatment is widely used adsorbents of different chemical structure and different mechanism of action. The topical issue today is the search for effective and inexpensive sorbent that can purify water from heavy metal ions. Natural adsorbents, in particular chitosan, can be used for wastewater treatment. **Methodology.** In our work the sorption of ions of heavy metals: (Cu (II), Zn (II), Cr (VI), Cd (II), Pb (II)) on ChCS in static conditions were studied. We have applied the infrared spectra (IR) for determine the degree of deacetylation of sorbent. Modelling of chelating complex Pb(II) – ChCS was realized by the method of molecular mechanics in using of program HyperChem. **Results.** The objective of this work was to study of sorption properties of chitin- and chitosancontaining sorbents which were prepared from fungus mycelium of Aspergillus Niger – waste of biotechnological production of citric acid. These sorbents used for removing heavy metals (Cu (II), Zn (II), Cr (VI), Cd (II), Pb (II)) from the water solutions. The influencing degree of deacetylation (DD) and size of particles on sorption properties of ChCS and ChaCS was shown. Also proposed the use of a sorbent based on natural aluminosilicate, namely by modification of previously heat-treated zeolite aluminum silicate with chitosan. It is shown that the obtained granulated sorbents possess high adsorption characteristics in relation to heavy metals ions and organic dyes, and by creating on the surface of granular sorbents insoluble polysaccharide layers have good technological characteristics, namely high strength and filtering ability. **Originality.** For the first time we showed feasibility of using ChCS for sorption of heavy metal ions from aqueous solutions. For the first time, we have carried out the integrated research of the adsorption ability of ZCHC (zeolite/chitosan hybrid composite) as adsorbent. It is shown that the obtained granulated sorbents possess high adsorption characteristics in relation to heavy metals ions and organic dyes, and by creating on the surface of granular sorbents insoluble polysaccharide layers have good technological characteristics, namely high strength and filtering ability. **Practical value.** The sorbents from Aspergillus Niger can be alternative to animal chitin and chitosan for removal of metal ions from water solutions. It is shown that the obtained granulated sorbents possess high adsorption characteristics in relation to heavy metals ions and organic dyes. The experimental studies have confirmed that the obtained granulated sorbents can be used for wastewater treatment. References 11, tables 4, figures 1.

Key words: sorbents, water purification, chitin, chitosan, zeolite.

ОТРИМАННЯ НОВИХ ТИПІВ СОРБЕНТІВ ДЛЯ ВИЛУЧЕННЯ ВАЖКИХ МЕТАЛІВ ІЗ ВОДНИХ РОЗЧИНІВ

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Проведено дослідження впливу ступеня деацетилирования і розміру частинок на сорбційні властивості ХСС і ХанСС. Встановлено, хітин хітозанвмісні комплекси ефективно поглинають іони важких металів з водних розчинів; ступінь деацетилювання комплексів впливає на величину сорбції. Також нами пропонується сорбент на основі природного алюмосилікату – цеоліту модифікуваний хітозаном, котрий придатний для ефективного очищення водних розчинів від іонів важких металів і від домішок органічних речовин різної природи. Природні адсорбенти, зокрема хітозан, може бути використаний для очищення стічних вод. Показана ефективність використання хітинвмісних комплексів В результаті експерименту встановлено, що одержувані гранульовані сорбенти на основі цеоліту виявляють високі сорбційні властивості по відношенню до іонів важких металів та органічних речовин. Доведено, що за рахунок створення на поверхні сорбентів полісахаридного нерозчинного шару покращуються технологічні показники, тобто збільшується міцність і фільтрувальну здатність

Ключові слова: сорбенти, очистка, хітин, хітозан, цеоліт.

PROBLEM STATEMENT. Last years the attention of the scientists and contributors to chitin, chitosan and chitin containing compounds has increased. Chitosan is mainly obtained by deacetylation of chitin (poly-β-(1,4) acetyl glucosamine) from wastes of the seafood industry (crab and shrimp shells and squid pens) and presents all the advantages of a low-cost renewable raw material. Chitosan is an effective sorbent for metal species. More specifically, chitosan has been shown to be an effective sorbent for Cu(II) cations in aqueous solution [1-4].

The chitosan market is relatively large, as its ease of physical and chemical modification may be used in such fields as medicine and wastewater treatment.

Development on the basis of sorbents, due to its natural origin, detoxicant, safety for humans and the environment, is a very promising direction for addressing environmental and biomedical problems. Chitosan sorbents can be used for purification of aqueous solutions of medicinal substances, drinking water and beverages, technological solutions and soils and for removal the natural impurities of heavy metals, radionuclides, acid gases, organic pollutants and pesticides. It should be noted that chitosan sorbents have shown better performance of known sorbents, so as low ash content and biodegradable to minimize the amount of waste in their packaging and disposal.

The aim of our work was analysis of the physical and chemical characteristics of ChCS and also their sorbate properties to ions of heavy metals. In previous works based on the analysis of the elements was established, that ChCS, comprises 31% chitin, 65% glucan, of 2,5% melanin and 1,5% proteins [5, 6].

EXPERIMENTAL PART AND RESULTS OBTAINED. Insoluble chitin containing sorbents (ChCS) were obtained from waste during biotechnological production of a citric acid. The waste of biomasses of Aspergillus Niger was consecutively treated by hot (60^{o}C) 1 % water solution of NaOH for 90 minutes, then it was washed out by distilled water, by 1 M solution HCl and finally by organic solvent. The finished product was dried at 40^{o}C for one hour. The degree of deacetylation (DD) of ChCS is 0,8 %, grinded by the ball mill to the size of particles 100-200 meshes, were used as a raw material for obtaining the chitosancontaining sorbents (ChaCS) by well-known method [7]. This method includes the treatment of an initial raw material by 40 % water solution NaOH for 4 hours at temperature 118^{o}C. Such conditions of treatment were chosen as the most favorable for obtaining the chitosancontaining sorbents with good sorption characteristics and with degree of deacetylation 96 %. The degree of deacetylation was determined based on sorbent infrared spectra (IR) using the following equation [8]:

$$DD = \left[1 - \left(\frac{A_{1655}}{A_{3450}}\right)\frac{1}{1{,}33}\right]\cdot 100, \qquad (1)$$

where A_{1655} and A_{3450} are absorbency values at 1655 and 3450 cm^{-1} for the amide I band and hydroxyl band respectively.

Modelling of chelating complex Pb(II) - ChCS was realized by the method of molecular mechanics using the HyperChem program.

In our work the sorption of ions of heavy metals: (Cu(II), Zn(II), Cr(VI), Cd(II), Pb(II)) on ChCS in static conditions were studied. The static conditions: 0,02 g sorbent (ChCS or ChaCS) was mixed in 0,125 mM solution (100 ml) of the metals salts for 1 hr at 20^{0}C and pH 6,8. After filtration, the analysis was carried out by flame atomic absorption spectrometry. Capacity of sorption q (mg/g) was calculated as:

$$q = \frac{(C_{in} - C_{eq})\cdot V}{m}, \qquad (2)$$

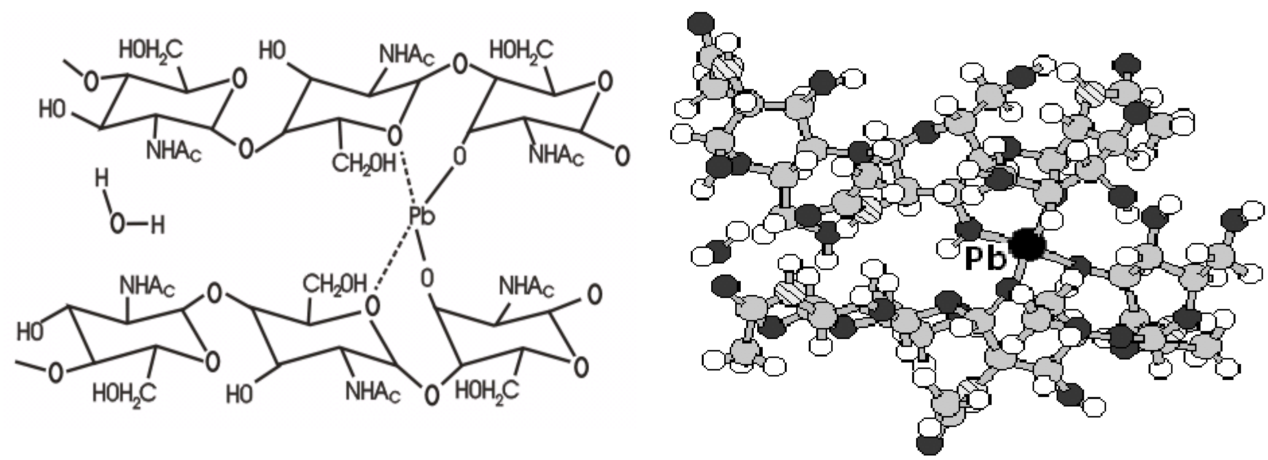
where C_{in} – initial metal concentration in solution (mg/l); C_{eq} – equilibrium concentration (mg/l); V – sample volume (l); m – sorbent weight (g).

For an estimation of selective sorbate ability ChCS and ChaCS the distribution factor was determined as:

$$K_d = \frac{(C_{in} - C_{eq})\cdot V}{C_{eq}\cdot m}, \qquad (3)$$

where C_{in} – initial metal concentration in solution (mg/l); C_{eq} – equilibrium concentration (mg/l); V – sample volume (l); m – sorbent weight (g).

It is known, that chitin can extract the ions of metals from water solutions, and where will form chelating complexes. However practically there is no information about functional groups which are implicated into this process. In our paper were involved the different atoms of oxygen and nitrogen from two chains of chitin, H_2O and Pb^{2+} in molecular modeling. Optimization was carried out for four possible structures. The most probable is chelating complex which consists of the plumbum ion between two chitin chains as well as in coordination Pb^{2+} participating the ring oxygen (O-5′) and the oxygen of C-3 hydroxyl (Fig. 1).



a) b)

Figure1 – Chelating complexes chitin- plumbum: a – before optimization; b – after optimization:
- Pb; - N; - C; - H; - O

This chelating complex is stable with the minimal energy of conformation. These data confirm results which were received on cell wall chitin-cadmium complexation in N. crassa grown under conditions of Cd-toxicity [8].

For a preliminary assessment of the selective adsorption capacity of the complexes was calculated from the distribution coefficient K_d (tab. 1), according to which the ranks of the selectivity of the complexes have the form:

For ChCS: Pb(II) = Cu(II) > Cd(II) > Zn(II) > Cr(VI);
For ChaCS: Cu(II) > Pb(II) > Cr(VI)> Cd(II)> Zn(II).

Presents ranks are similar to the ranks set for polyampholyte.

In our opinion, this fact is explained by the fact that the composition of the complexes as part of polyampholyte include amino, carboxyl and hydroxyl groups, which form stable chelates with ions.

Table 1– Coefficient of distribution for ChCS and ChaCS

Sorbent	K_d, ml/g				
	Cu(II)	Zn(II)	Cr(VI)	Cd(II)	Pb (II)
ChCS	2000	410	348	610	2000
ChaCS	49500	500	5750	816	9462

The sorption ability of the chitincontaining sorbents for Cu(II), Zn(II), Cr(VI), Cd(II) and Pb(II) ions are presented in Table 2, which were obtained with powders of sorbents with different size of particle after an 1-h contact.

The size of particles influences on the sorption ability of sorbents. The decrease of the particles size is accompanied with increasing sorption ability of sorbents for all metals which were studied. Established the increase in static exchange capacity with increasing dispersity of the complexes due to the higher active surface. Increasing *DD* of sorbents contributes increment of sorption ability of sorbents, and especially for Cr(VI) ions. These results can be explained by increasing of the quantity of pores in structure of sorbents in higher significances *DD* and larger access to amino groups. The values for Cr(VI) ions removal with ChaCS are higher because they considerably better, than other metals, chelating with amino groups.

Table 2 – Dependence sorption ability of sorbents from the size of particles and *DD*

Sorbent	*DD*,%	Particle size, µm	*q*, mg/g				
			Cu(II)	Zn(II)	Cr(VI)	Cd(II)	Pb(II)
ChCS	0,8	710-850	22,4	10,4	3,7	22,4	61,8
		355-500	25,6	13,6	5,1	26,9	80,3
		150-250	32,0	18,2	6,8	38,0	103,6
ChaCS	96	710-850	27,5	11,7	11,3	31,4	88,6
		355-500	30,4	15,6	12,8	35,3	107,1
		150-250	36,8	20,5	15,8	43,1	130,8

In recent decades, especially increased interest in composite materials based on chitosan, in particular the creation of sorbents based on it. It was established the possibility of its use as a matrix for spaces of the zeolite [9]. Studies have shown that chitosan-inorganic composites can find application in medicine, in the field of membrane separation and purification. Among all kinds of inorganic fillers, zeolites are especially appealing due to their thermal and chemical stability and great potential for the separation of ions by cation exchange. Zeolites are crystalline microporous aluminosilicates represented by the empirical formula $M^{n+}_{2/n}O_2{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}yH_2O$, where M is usually alkaline or alkaline earth cations [9–12]. Despite the attention given to the properties of composites, the way in which the preparation of mixed systems affects the properties of each component has been less deeply delved. The stability of the zeolites in the conditions of encapsulation is a main issue that is not always taken into account in the literature.

The use of a sorbent based on natural aluminosilicate is proposed, by modifying it with chitosan, which is suitable for efficient cleaning of water solutions from heavy metal ions and from the impurities of organic substances of different nature. For the preparation of the sorbent as the aluminosilicate framework was used natural aluminosilicate zeolite of the Cherkassy Deposit, characterized by the following composition (%wt.): SiO_2 – 70.21; Al_2O_3 – 12.27; Fe_2O_3 – 1.2; FeO – 0.55; TiO_2 – 0.14; MnO – 0.073; P_2O_5 – 0.033; K_2O – 3.05; Na_2O – 1.77; SO_3 – 0.10; CaO + MgO – 10.604.

For the preparation of the aluminosilicate basis the zeolite has been pre-heat treated and ground to a particle size up to 0,07–0,08 mm. For the treatment of the aluminosilicate basis was used a 3 % solution of chitosan in a 3 % aqueous solution of acetic acid.

For the production of sorbent the milled zeolite was mixed with 3 % solution of chitosan cetatenilor (mass ratio 1:1) for 30 minutes on a magnetic stirrer and added a 5 % solution of ammonia in an amount necessary to bring the pH of the solution above the sediment to 8–9. Then the excess of solution was drained, and the condensation doughy mass has been passsed through the filters with a diameter of 2 mm. Obtained granules were dried at room temperature until dry, and then kept them in a 10 % solution of humic acid for 4 hours. The pellets were separated from the solution and dried at a temperature of about 130 °C for 2,5 hours.

In the course of work was defined physico-chemical parameters obtained for the adsorbent, namely: moisture content, bulk density, ion exchange capacity, dispersion, pore size, mechanical strength for crushing (table 3).

Table 3 – Characteristics of the obtained sorbent

№	Characterization of the sorbent	Without processing humic acids	Processing humic acids
1	Specific gravity, g/cm3	1,10	1,07
2	Humidity, %	2,70	1,40
2	The size of the granules of the sorbent, mm	0,1-0,08	0,075
3	Specific surface, m2 /g	24,60	20,0
4	Static volumetric capacity, mg/g		
Cu^{2+}		3,42	4,90
Fe^{3+}		3,40	6,50
5	Mechanical crushing strength, kg/cm^2	10,50	10,90

Table 4 – The impurity content in the model solution

Mg, mg/l	Ca, mg/l	Fe, mg/l	Cu, mg/l	Zn, mg/l	Ni, mg/l	Mn, mg/l
4,3	12,8	1,9	0,5	1,8	0,8	0,5

For the purification of water were used the column, filled with sorbent of mass of 100 g. Through this filter layer were investigated missed water with the speed of the passing water at 0,,5 liter /hour. Samples for analysis were selected each 100 L, 500 L and 1000 L. Content of impurities has been determined by photocolorimetry method.

Moisture content and bulk density of the adsorbent are important factors that affect the speed and efficiency of wastewater treatment. The increase in the bulk density of the adsorbent reduces the amount of adsorbent used for water purification from impurities of organic nature, which affects production costs.

The sorbents obtained in this work were investigated in the purification process of water model solution with a content of ions close to the industrial waters. Characteristics of the solution are given in table 4.

Empirically it is shown that the obtained granulated sorbents possess high adsorption characteristics in relation to heavy metals ions and organic dyes. Creating on the surface of granular sorbents insoluble polysaccharide layers have good technological characteristics, namely high strength and filtering ability. The hybrid composite exhibits higher adsorption capacity and stronger chemical affinity than pristine zeolite and chitosan. The exchange capacity of zeolite as sorption-boosting charge in chitosan-zeolite composites has been preserved by controlling the encapsulation conditions. Modification of the sorbent by treatment of humic acid enhances the sorption capacity in relation to ions of copper and iron.

The experiment has found that the resulting granular sorbents show high sorption properties towards heavy metal ions and organic substances. It was proved that creating on the surface of the sorbents insoluble polysaccharide layer improved technological parameters, i.e. increased the strength and filtering ability.

In the future we plan a more detailed study of the sorption properties of the adsorbent and its modification.

CONCLUSIONS**.** In this paper has been shown, that biomasses of Aspergillus Niger fungus mycelium – waste received during the biotechnological production of a citric acid, may be used for reception chitincontaining sorbents and has been suggested by the authors of method. The sorbents from Aspergillus Niger can be alternative to animal chitin and chitosan for removal the metal ions from water solutions. It is known, that sorption of metals on chitin and chitosan is accompanied the chelating complexes formation. The modeling and quantum-chemical computations of these complexes was conducted, it showed, that the most probable is chelating complex which consists of the metal ion between two chains of chitin as well as in coordination Me^{2+} as a part of the ring oxygen (O-5′) and the oxygen of C-3 hydroxyl. The sorption ability of the sorbents for Cu(II), Zn(II), Cr(VI), Cd(II) and Pb(II) ions is dependent on *DD* and size of sorbents particles .

As shown in our earlier works ChCS and ChaCS are good petroleum and soluble dyes sorbents from water solutions. Economically and environmentally advantageous to use ChCS, as in the processing of biomass treated with chemical solutions of low concentration at a temperature of about 60°C. Investigated the adsorption ability of ZCHC (zeolite/chitosan hybrid composite) as adsorbent that was prepared by mixing zeolite and chitosan. Empirically it is shown that the obtained granulated sorbents possess high adsorption characteristics in relation to heavy metals ions and organic dyes, and by creating on the surface of granular sorbents insoluble polysaccharide layers have good technological characteristics, namely high strength and filtering ability.

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ПОЛУЧЕНИЕ НОВЫХ ТИПОВ СОРБЕНТОВ ДЛЯ ИЗВЛЕЧЕНИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ ИЗ ВОДНЫХ РАСТВОРОВ

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Проведено исследование влияния степени деацетилирования и размера частиц на сорбционные свойства ХСС и ХанСС. Установлено, хитин хитозансодержащие комплексы эффективно поглощают ионы тяжелых металлов из водных растворов; степень деацетилирования комплексов влияет на величину сорбции. Также нами предлагается сорбент на основе природного алюмосиликат - цеолита модификуваний хитозаном, который пригоден для эффективной очистки водных растворов от ионов тяжелых металлов и от примесей органических веществ различной природы. Природные адсорбенты, в частности хитозан, может быть использован для очистки сточных вод. Показана эффективность использования хитинвмисних комплексов. В результате эксперимента установлено, что получаемые гранулированные сорбенты на основе цеолита проявляют высокие сорбционные свойства по отношению к ионам тяжелых металлов и органических веществ. Доказано, что за счет создания на поверхности сорбентов полисахаридного нерастворимого слоя улучшаются технологические показатели, то есть увеличивается прочность и фильтровальную способность.

Ключевые слова: сорбенты, очистка, хитин, хитозан, цеолит.

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