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ECOLOGICAL SORBENTS FROM CHEMICALLY MODIFIED AND HEAT TREATED VEGETATIVE RAW MATERIALS

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This paper is devoted to a comparative estimation of selective properties of natural cellulose-containing biopolymers and their modified species at sorption of heavy metal ions from composite salt solutions modelling electrolyte composition of biological media of organism. The modification carried out is based on depolymerisation of macromolecules of cellulose-polysaccharide complexes under various physical and chemical effects, selective oxidizing of alcoholic groups up to carbonyl and carboxyl ones, obtaining esters with compounds containing additional groups with acidic properties. The results of modifying of the vegetative wastes for the purpose of selectivity improvement of sorption are revealed in extraction of heavy metal ions from salt solutions. The components of vegetative raw materials are cellulose and lignin, their fibrillar structure giving a chance to form a developed porous structure of certain type sorption materials.

INTRODUCTION

The modern ecological situation in Ukraine is characterized by a boosted pollution level of environment by heavy metal ions, and this causes arising occupation and ecologically dependent diseases as well as cutting average duration of the people's life. Thus, accordingly to data of the Ministry of Public Health of Ukraine, more than 80% of the national territory is essentially polluted by harmful and toxic products of technogenic character including heavy metal ions and radioactive isotopes. Among the measures on protection of the people's health, the modern and effective ones are carried out of therapy and prophylaxis with adsorbing preparations (enterosorbents) and special food additives of antidote and protective action. Therefore one of priority directions of developing the modern technology is the protection of the people against toxic and harmful substances by creation of new cheap and effective adsorbents.

Among a plenty of adsorbing preparations the appreciable part is presented by polymers of natural origin, in particular, polysaccharides. The resource for production of such materials can be a multitonnage solid wastage of food and processing industry – shell of nuts, apricot, peach or plum stones, vegetable, apple and grape spews, pulp, peels of grain cultures, basket and peel of sunflower, beer distiller's grain, coffee waste, seaweeds etc. The main structural components of such wastage are cellulose, pectin, alginates, and lignin tight in biopolymeric complexes. These components are evolved both as a refined view ones and complexes consisted from various polysaccharides.

EXPERIMENTAL

In the paper, the following methods of chemical and thermal modifying the vegetative wastes are used [1, 2]:

– phosphorilation, sulphation, carboxylation;
– carbonization, activation, oxidation;
– lignifications (enrichment by lignin), and delignification (enrichment by cellulose).

Phosphorilation. The crushed biomass is heated up at the temperature of 100°C in 20% solution of phosphoric acid during 3 h at a ratio of acid : biomass = 5:1; then a biomass is separated, washed out by distilled water to neutral reaction and dried up. The obtained product, which contains cellulose phosphate, has high static exchange capacity (more then 4 meq/g) and can be used for binding and removal of heavy metal ions from aqueous solutions due to the mechanism of ion exchange, complexing or adsorption.

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Sulphation. The crushed biomass heated up at the temperature of 100°C in 20% solution of sulfuric acid during 3 h at a ratio of acid : biomass = 5:1; then a biomass is separated, washed out by distilled water to neutral reaction and dried up. The obtained product, which contains both cellulose sulfate and carboxylic, aldehyde, and ketone oxygen-containing groups, has static exchange capacity above 2 meq/g and its appearance and properties are close to those of activated carbons.

Carboxylation. The crushed biomass is processed by mix concentrated nitric and sulfuric acids at the ratio 3:1 during 3 h at a ratio of reagent : biomass = 10:1 (at the temperature of 100°C); then the biomass is separated, washed out by distilled water to neutral reaction and dried up. At such a processing, there are deeper depolymerization of the carbohydrate complex and its partial oxidation due to dehydration and formation of carboxymethylcellulose. The high static exchange capacity of the product (~3.5 meq/g) makes it perspective material due to its adsorption ability in relation to heavy metal ions.

Carbonization. The crushed biomass (the size of particles of 0.2–0.5 mm) is heated up in a quartz reactor, placed into the hermetic furnace, up to temperature of 800°C in inert gas (argon) atmosphere and maintained for 1 h at this temperature. Thus take place, first, removal free as well connected moisture, and also other volatile compounds (at 100–170°C), and second, at the further increasing temperature up to 800°C occurs structural transforming the products of pyrolysis; the mass of a product thus decreases almost for 50%. Carbonized product obtained has good characteristics of specific total volume of the pores (~0.1 cm^3/g) and static exchange capacity (~1.3 meq/g).

Activation. The carbonized biomass obtained accordingly to a previous circuit is treated for activation at high temperature (800°C) steam during 20 min. Such an activation results in increasing specific surface area of material, total volume of pores ~0.35 cm^3/g, and static exchange capacity ~2 meq/g. The yield of the final activated carbon achieves 20–25% of initial mass of the crushed waste material. The carbon activated by steam contains both strong and weak carboxylic as well phenol groups and can be used for adsorption removal of heavy metal ions and their complex compounds.

Oxidation. The crushed biomass is processed by 30% solution of hydrogen peroxide during 20 h at a ratio of reagent : biomass = 10:1 (at room temperature); then the biomass is separated, washed out by distilled water to neutral reaction and dried up. The oxidized product obtained has rather high exchange capacity (2.8 meq/g), white color without a smell and acid taste. It can be used for adsorption of toxic substances and heavy metals in medical and ecological technologies.

Enrichment by lignin. Vegetative raw materials (nuts shell, grape and fruit stones, wheat and sunflower peel) are hydrolyzed by mineral or organic acid with concentration of 0.5–10% mass at the temperature of 80–200°C, hydromodule factor being 1 to 10, during 20–180 min and then we activate the adsorbent obtained by aqueous solution which contains alkaline metal hydroxide, carbonate or bicarbonate in concentrations of 0.5 to 15% mass (calculated for Me_2O, where Me – K, Na) at the temperature of solution of 70–110°C, hydromodule factor being 1 to 10, during 20–180 min and the residual alkaline is neutralized by aqueous solution of mineral or acetic acid or that of calcium chloride up to pH 5.5–7.5.

Enrichment by cellulose. The crushed biomass is processed by 15% solution of KOH during 24 h at the ratio of reagent : biomass = 10:1 (at the temperature of 20°C); then the biomass is separated, washed out by distilled water to neutral reaction and dried up.

RESULTS AND DISCUSSION

In various modes of processing the porous structure is formed and essentially the specific surface area of materials increases and also rather high surface density of the functional groups capable to ion-exchange and complexion is created on a surface.

The materials modified gain high reactivity, easily enter in reactions of joining and exchange and can serve as selective sorbents. Their properties are estimated in processes of sorption of some heavy and transition metal ions and organic dyes from aqueous solutions [3, 4].

In this work, the results of adsorption testing of the vegetative materials modified of cellulose-lignin type, obtained by us under laboratory conditions due to chemical modifying and heat treatment of vegetative waste products are described.

The study on adsorption capability of the modified materials have been executed under static conditions from solutions of salts of heavy metals (lead, cadmium, nickel, copper, zinc, cobalt, manganese, and strontium) within the initial concentration of 12.5–0.3 mM/L.

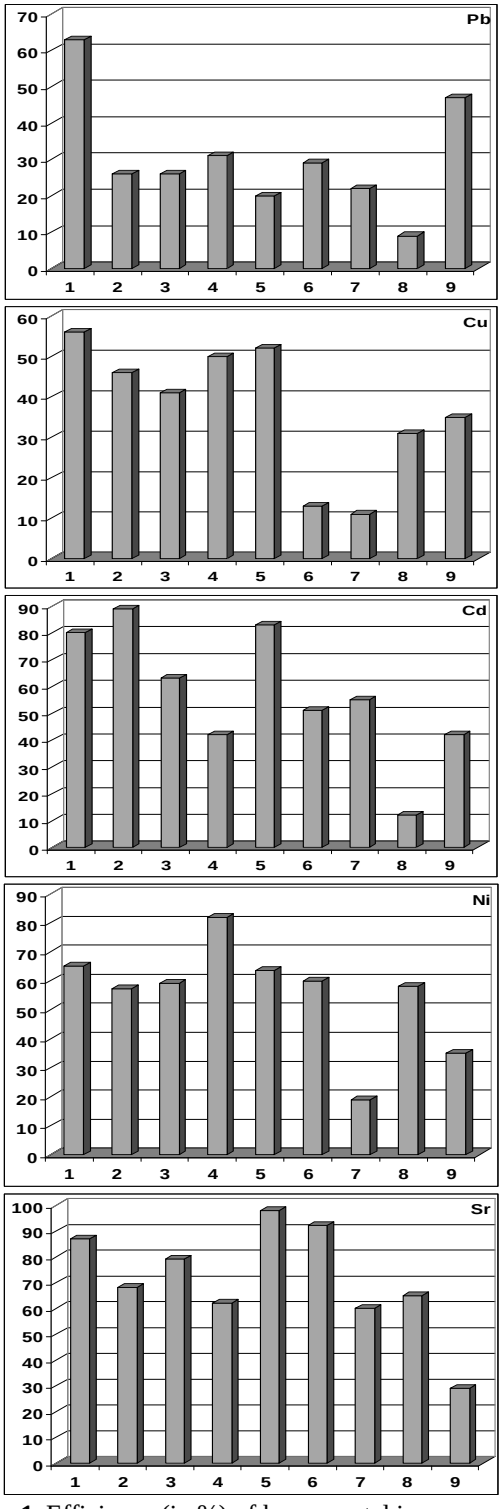

Fig. 1. Efficiency (in %) of heavy metal ions removal by different modified biosorbents obtained from waste products of corncobs: *1* – initial biomass; *2* – phosphorilated biomass; *3* – sulfated biomass; *4* – biomass processed by hydrogen peroxide; *5* – carboxylated biomass: *6* – carbonized biomass; *7* – activated carbonizing biomass; *8* – biomass enriched by cellulose; *9* – biosorbents enriched by lignin

Initial and equilibrium concentrations of heavy metal ions are found by the atomic-absorption spectroscopy method with a KAS-120.1 equipment (Selmi, Ukraine).

The magnitudes of the effect of binding of heavy metal ions under condition of their initial concentration of 0.1 g/L are resulted in the diagrams.

As the samples obtained have shown a high sorption capacity to various ions (Cu^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Sr^{2+}), it was interesting to study their sorption capability to mercury ions as the most hazardous industrial ecotoxicants.

In Fig. 2, diagrams of coefficients of distribution for mercury ions are presented at their extraction from aqueous solution by the modified biomass.

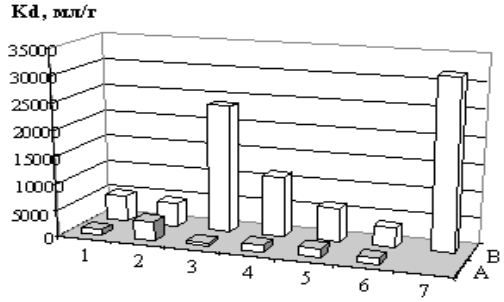

Fig. 2. Distribution coefficients for sorption of Hg^{2+} ions: *1* – beet marc; *2* – walnut shell; *3* – apricot stones shell; *4* – buckwheat peel; *5* – sunflower shuck; *6* – cherry stones shell; *7* – lignin medicine "Polyphepan" (for comparison). *A* – initial biomass; *B* – modified samples; (*1B* – marc modified by HCl; *2B–7B* – lignin materials

It is seen that for some samples, the coefficients of distribution increase for several orders and reach magnitudes of several thousand what testifies to perspectives of use of such materials as selective sorbents in order to purify waters from cationic forms of mercury.

CONCLUSIONS

On the basing analysis of chemical composition of a plant by-product of agriculture, alimentary and process industry, a possibility is shown of a wide spectrum of related sorbents with the raised selectivity concerning cations of transition and heavy metals

The analysis of the results obtained gives a chance to compare the capability of the prepared sorbents to bind various ions of toxic metals and to offer the composition of biological (food and fodder) additives, enterosorbents, and the combined preparations with expressed curative (detoxication and correction) activity.

The modified products obtained seem to be perspective for solving ecological problems of

treatment of sewage waters and technological solutions and also, apparently, problems of veterinary science and medicine on extraction from biologic media of harmful and toxic cations including heavy metals and radionuclides.

REFERENCES

1. *Pat. 76835* Ukraine, Int. Cl. A61K 36/87 Method of obtaining lignin-containing enterosorbents (variants) / V.O. Denisovych, A.A. Nikolaychuk, L.A. Kupchik, M.T. Kartel – Filed 15.09.2004, Publ. 15.09.2006. – 8 p. (in Ukrainian).
2. *Pat. 78108* Ukraine, Int. Cl. B01J 20/04 Method of obtaining sorption additive from processing wastes of vegetative raw materials / T.I. Myronyuk, A.A. Nikolaychuk, M.T. Kartel et al. – Filed 29.03.2005, Publ. 15.02.2007. – 3 p. (in Ukrainian).
3. *Kartel N.T., Kupchik L.A., Korostyatynets V.D.* Adsorption means on the base of solid complexones of natural hydrocolloid type // CERECO 2000: Proc. 3rd Intern. Conf. on Carpathian Euroregion Ecology (21–24 May, 2000, Miskolc-Lillafured, Hungary). – P 146–154.
4. *Kartel M.T., Nikolaychuk A.A.* Sorption means of cellulose-lignin type obtained from agricultural wastes // The Environment and Industry: Proc. Symp. INCD ECOIND SIMI (28–30 Oct., 2009, Bucharest, Romania). – V. 1. – P. 59–65.
5. *Nikolaichuk A.A., Kartel N.T., Kupchik L.A., Denisovich V.A.* Synthesis and properties of the biosorbents received on a basis of cellulose-lignin vegetative raw materials – agriculture wastes // Sorbtsionnye i khromatograficheskie protsessy. – 2007. – V. 7, N 3. – P. 489–498 (in Russian).
6. *Karmanov A.P., Kocheva L.S.* Cellulose and Lignin. Properties and Application. – Syktyvkar: Komi URO RAN, 2006. – 248 p. (in Russian).
7. *Karmanov A.P.* Self-organization and Structural Organization of Lignin. – Ekaterinburg: URO RAN, 2004. – 270 p. (in Russian).

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Екологічні сорбенти з хімічно модифікованої та термообробленої рослинної сировини

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В роботі дана порівняльна оцінка селективних властивостей целюлозовмісних рослинних біополімерів та їхніх модифікованих форм як сорбентів іонів важких металів з композитних сольових розчинів, що моделюють електролітний склад рідин організму людини. Проведена модифікація була заснована на деполімеризації макромолекул целюлозовмісних полісахаридних комплексів під впливом різних фізичних і хімічних факторів, селективному окисненні спиртових груп до карбонільних і карбоксильних, одержанні естерів з додатковим вмістом кислотних груп. В результаті модифікування рослинної сировини поліпшується її сорбційна селективність щодо іонів важких металів з сольових розчинів. Фібрилярна структура складових рослинної сировини – целюлози та лігніну – дає можливість сформувати розвинену пористу структуру сорбційних матеріалів певного типу.

Экологические сорбенты из химически модифицированного и термообработанного растительного сырья

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В работе дана сравнительная оценка селективных свойств целлюлозосодержащих растительных биополимеров и их модифицированных форм как сорбентов ионов тяжелых металлов из композитных солевых растворов, моделирующих электролитный состав биологических жидкостей организма. Осуществляемая модификация основана на деполимеризации макромолекул целлюлозосодержащих полисахаридных комплексов под влиянием различных физических и химических факторов, селективном окислении спиртовых групп до карбонильных и карбоксильных, образовании сложных эфиров с дополнительным содержанием кислотных групп. В результате модифицирования растительного сырья улучшается его сорбционная селективность к ионам тяжелых металлов из солевых растворов. Фибриллярная структура компонентов растительного сырья – целлюлозы и лигнина – позволяет сформировать развитую пористую структуру сорбционных материалов определенного типа.