FERROCYANIDE BIOSORBENTS BASED ON LIGNOCELLULOSE WASTE PRODUCTS FOR MULTIFUNCTIONAL PURPOSE

Mykola Kartel, Vita Galysh

O.O. Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, General Naumov 17, 03164 Kyiv-164, Ukraine, nikar@kartel.kiev.ua

Abstract

New composite biosorbents based on lignocellulose complex, derived from the waste of food industry – apricot pits, and ferrocyanides of d-metals were synthesized. An influence of pretreatment of initial apricot pits by acid-alkali scheme was established. It was found out that such pretreatment leads to an increase in the specific surface area of the lignocellulose material in two times and the total pore volume up to six times. The physical, chemical, structural properties of the obtained materials were investigated. The sorption behavior of initial materials and lignocellulose-inorganic samples toward cesium-137, heavy metals, Methylene blue, gelatin, vitamin B_{12} was studied. Comparative analysis of the sorption properties of obtained biosorbents based on different ferrocyanides towards different ecotoxicants was carried out. Obtained results allow to state that new composite biosorbents are universal materials for adsorption of radionuclides, heavy metals and organic pollutants from water solutions and can be used in radiochemistry, analytical chemistry, industry, medicine and veterinary.

Keywords*:* *biosorbent, cesium, heavy metals, ferrocyanide of d-metal, lignocellulose.*

1. Introduction

Contamination of water sources with pollutants of organic and inorganic nature, especially heavy metals and radionuclides, is a serious environmental and public health problem. Ions of heavy metals and radionuclides can get to human and animal body mainly through inhalation and orally with contaminated food and water. For example, the adsorption of soluble forms of nuclides by the body tissues is fast and reaches almost 100%. Such pollutants can cause severe intoxication, due to its ability to bind to sulfhydryl, phosphate, carboxyl groups of biomolecules, which reduces the enzyme activity and deterioration of many metabolic processes and cause cytolysis, hepatic-cell failure and others diseases [1-4].

Sorption methods with the application of different inorganic sorption materials are widespread used for removal of pollutants from aqueous wastes. For nowadays it is promising from an economic point of view to use the residues from agriculture and food industry as sorbents for environmental protection. It will not only help to solve the problem of its utilization, but also allows receiving useful products of multifunction purpose in large volumes. Apricot pits are multitonnage waste of food industry, a complex of organic lignocellulose (LC) polymers with valuable properties, including sorption ability. Selective sorption materials based on LC-materials can be produced by chemical modification of the initial polymer matrix. During the modification processes the fixing of ion exchange or complexing groups on the surface of the LC-matrix can take place. One way to obtain selective composite sorbents toward cesium ions is the impregnation of plant materials with the solutions of ferrocyanides of d-metals ([FC]M, where M – Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) [5-6] that characterized by high selectivity with respect to cesium [7] that considered as the most hazardous among all radionuclides due to relatively long half-life, high toxicity and migration properties. Such composite materials based on plant raw material can also be used as enterosorbents to prevent pollutant accumulation in human and animal body.

The aim of this study is characterization and comparative analysis of structural and sorption properties of lignocellulose-inorganic biosorbents.

2. Materials and Methods

Apricot pits were used as a raw material. The chemical composition of the initial and material were determined according to the TAPPI standards for the different components: T-222 for lignin, T-211 for ash, T-204 for ethanol-benzene extractives. The initial apricot pits were ground, sieved and the fraction with the diameter 0.12 mm was used for further processing.

Synthesis of LC-matrix was performed by acid-alkali scheme that involved the hydrolysis of initial raw material with 3.0 N solution and the following delignification of obtained product with 0.3 N solution of sodium carbonate. Both steps were carried out during 60 min at 90 ^{o}C and the ratio of solid to liquid phase was 4:1. Than LC-product was separated from the solution by filtration, washed with distilled water at 80 °C to achieve neutral medium, dehydrated and dried at 50 ^{o}C to constant moisture of 5–7%. Synthesis of combined sorbents of LC-[FC]M type were done by the method described in [8].To prepare LC-matrix and modifying solution of [FC]M such chemicals as hydrochloric acid (HCl), sodium carbonate ($Na_2CO_3{\cdot}10H_2O$), potassium hexacyanoferrate ($K_4[Fe(CN)_6]{\cdot}3H_2O$), iron sulphate ($Fe_2(SO_4)_3{\cdot}9H_2O$), nickel sulphate ($NiSO_4{\cdot}7H_2O$), cobalt sulphate ($CoSO_4{\cdot}7H_2O$), copper sulfate ($CuSO_4{\cdot}5H_2O$), and zinc sulphate ($ZnSO_4{\cdot}7H_2O$) of A.G. grades were used.

The sorption of ^{137}Cs on obtained materials was studied under static conditions according to the procedure described in [8] and evaluated by the values of parameters recovery rate (S, %) and distribution coefficient (Kd, cm^3/g). Methylene blue adsorption was carried out at the concentration 100 mg/L. Dye solutions were prepared in 0.15 M phosphate buffer with pH 6.0. Sorbent sample was 0.20 g, the volume of solution - 25 ml. Initial and equilibrium concentrations of dye were determined by spectrophotometric method with the application of Specord M40 ("Carl Zeiss", Germany), wavelength 664 nm. The sorption of metals ions were done in static conditions of model solutions with the concentration 50 mg/l. The mass sorbent - 0.2 g, the volume of the solution

- 50 ml, pH 6.0, duration - 24 h at the constant stirring. Vitamin B_{12} and gelatin sorption on biosorbents performed from the simulated solutions with pH 2.0 and 7.5 according to the procedure described in [9].

The IR spectra of samples were recorded on a Specord M80 ("Carl Zeiss", Germany) spectrophotometer in the range of 4000-300 cm^{-1}. The preparation of lignocellulose-inorganic materials for examination consisted in rubbing materials with KBr at the ratio 1:9 with the following pressing into tablets.

The specific surface area of the initial and modified materials was determined by nitrogen adsorption at 77 K using the analyzer NOVA 2200 ("Quantachrome", USA). The pore volume of the materials was determined by desiccators' method of adsorption of benzene vapor.

3. Results and Discussion

An analysis of the component composition of raw materials shows that plant tissue of apricot pits contains a significant amount of lignin and cellulose (Table 1) that indicating the feasibility of complex processing of these raw materials to obtain an efficient biosorbents.

Table 1. Characteristics of initial and modified by acid-alkali scheme LC-materials

Characteristic	Apricot pits	LC-matrix
Content of the main components, %:		
cellulose	40.3	29.0
lignin	50.7	66.9
ethanol-benzene extractives	7.0	3.1
ash	2.0	1.0
Specific surface, m^2/g	3.5	6.5
Pore volume, cm^3/g	0.03	0.19

Due to acid-alkali treatment an increase in the specific surface of the material in 2 times is observed because of the dissolving and removing resins, fats, waxes, inorganic compounds, low molecular hemicellulose, partially depolymerization of cellulose. At the same time the destruction of lignin-carbohydrate bonds take place. The pore volume LC-material thus increases in 6 times.

Modification of the LC-complex with [FC]M solutions under heating leads to the immobilization of inorganic phase on the organic surface with the formation of combined LC-[FC]M biosorbents. IR spectra of initial and modified materials (Fig. 1) indicate an appearance of the band of (CN)-groups (2085 – 2100 cm^{-1}) after immobilization of the [FC]-phase on LC-[FC]M.

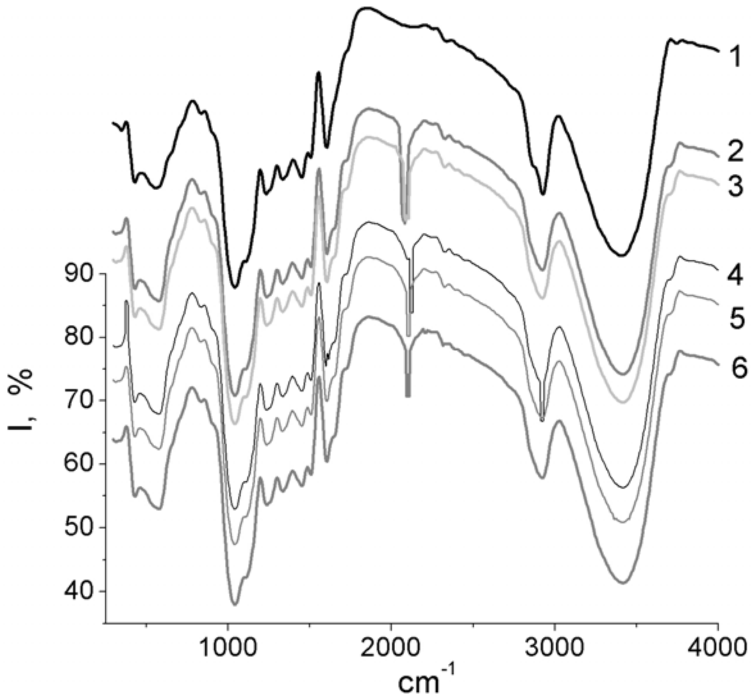
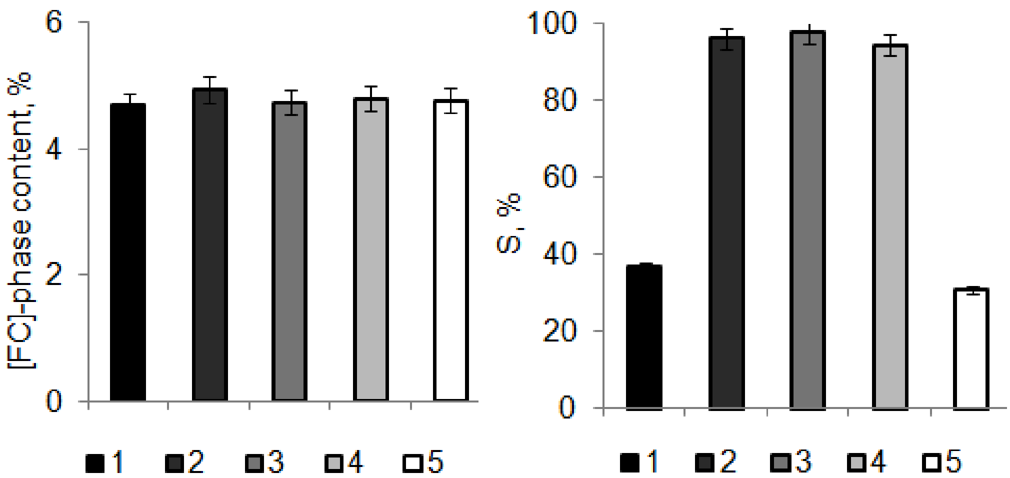


Figure 1. IR spectra of initial LC (1) modified with: 2 – $Fe_4([Fe(CN)_6])_3$; 3 – $K_2Ni[Fe(CN)_6]$; 4 – $K_2Co[Fe(CN)_6]$; 5 – $Cu_2[Fe(CN)_6]$; 6 – $Zn_2[Fe(CN)_6]$.

The broad peaks in the region 3000 – 3700 cm^{-1} indicate the presence of v(OH) of the groups involved in hydrogen bonds, while the band at 1636 cm^{-1} is attributed to δ(HOH) of absorbed water. Absorption band in the spectra in the interval 2800 - 3700 cm^{-1} corresponds to symmetric and asymmetric stretching v(C-H) in methyl and Methylene groups of lignin and polysaccharide. The absorption band at 1740 cm^{-1} corresponds to δ(C=O) vibrations. Skeletal v(C=C) vibrations of aromatic ring in structural unit of lignin are at 1440, 1508, 1604 cm^{-1}.

The properties of the resulting composite lignocellulose-inorganic sorbents are shown in Fig. 2.



a *b*

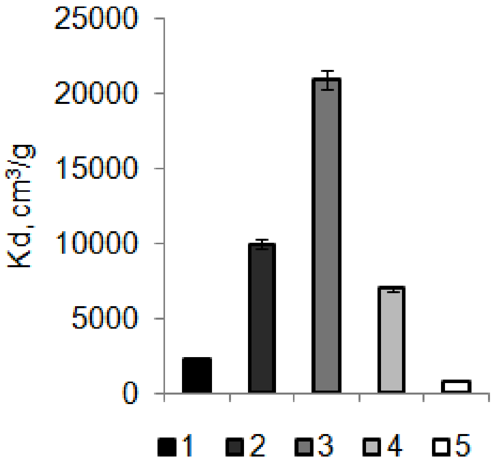


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Figure 2. Properties of obtained lignocellulose-inorganic biosorbents: *a* – content of [FC]-phase, *b* – recovery rate of ^{137}Cs; *c* – distribution coefficient of ^{137}Cs respectively for: *1* – LC-[FC]Fe; *2* – LC-[FC]K-Co; *3* – LC-[FC]K-No; *4* – LC-[FC]Cu; *5* – LC-[FC]Zn.

Comparison of the efficiency of the cesium sorption on various LC-[FC]M sorbents shows that despite approximately the same content of the inorganic component, biosorbents are characterized by different absorption properties. The maximum value of Kd corresponds to the sorption materials based on [FC]K-Ni and [FC]K-Co so indicating a high selectivity towards cesium ions. Obtained results show that the sorption capabilities of biosorbents with respect to cesium correspond to the following progression:

LC-[FC]K-Ni > LC-[FC]K-Co > LC-[FC]Cu > LC-[FC]Fe > LC-[FC]Zn.

The same sequence in the sorption properties of different [FC]M toward ^{137}Cs is observed [7] during the coprecipitation of microquantities cesium with individual [FC]M. In general, obtained results indicate a high sorption capacity of synthesized composite biosorbents for cesium at a low content of [FC]M in the bulk of LC-matrix.

Sorption properties of obtained materials towards organic toxicants are shown in Table 2. It was found out that modification of LC-matrix with [FC]M in all cases causes a decrease of the total volume of pores and adsorption capacity for methylene blue equally. According to [10] sorbents with specific surface 23-29 m^2/g based on hydrolytic lignin from soft wood characterized by sorption capacity for methylene blue about 100 mg/g. In this case the basic mechanism of organic dye binding is adsorption in the pores. In the case of LC-materials along with adsorption in the pores, is a chemical interaction of the organic cation with functional groups of cellulose and formation of compounds of clathrate type take place. Due to this, prepared lignocellulose-inorganic samples (specific surface about 7 m^2/g) characterized by high sorption capacity for Methylene blue.

Table 2. Sorption properties of obtained biosorbents towards organic toxicants

Biosorbent	Adsorption pore volume, cm^3/g	Sorption capacity, mg/g					
		Methylene blue	Vitamin B_{12}		Gelatin		
			pH 2.0	pH 7.5	pH 2.0	pH 7.5	
LC-matrix	0.19	47.5	1.9	2.6	0	19.7	
LC-[FC]Fe	0.14	39.7	1.3	2.3	0	19.6	
LC-[FC]K_2-Co		40.0	1.5	2.2	0	19.7	
LC-[FC]K_2-Ni		39.8	1.3	2.2	0	19.6	
LC-[FC]Cu		40.1	1.4	2.2	0	19.7	
LC-[FC]Zn		40.5	1.2	2.2	0	19.6	

Results also demonstrate that the most affinity to vitamin B_{12} ($M(C_{63}H_{88}CoN_{14}O_{14}P)=1355$ synthesized materials show in a slightly alkaline solution. Overall, obtained data indicates low absorptive capacity of biosorbents towards toxicants with middle molecular weight in comparison with activated carbon (sorption capacity for vitamin B_{12} at the same pH is 10.9 mg/g).
Gelatin was used as a marker for the determination of sorption activity of synthesized lignocellulose-inorganic materials towards toxins and pathogens of protein nature. It was found out that sorbents derived from plant materials do not show sorption activity for compounds of protein nature in acidic solutions. This is because the proteins belong to macromolecular amphoteric polyelectrolyte, which isoelectric point is observed at pH 4.8-5.0, i.e. at pH 2 proteins are positively charged and therefore at a pH of 7.5 - negatively, that causes its adsorption on charged surfaces. Sorption capacity of obtained materials towards toxin of protein nature in alkaline medium is 20 mg/g, which is 40% less than for sorbents based on hydrolytic lignin. And this difference can be explained by the content of polysaccharide component. LC-materials, which contain 28% of cellulose, have a partial negative charge in alkaline solution as the protein, so electrostatic repulsion occurs. In this case, sorption of gelatin on biosorbents takes place due to the presence active functional groups of different nature ($-NH_2$, -COOH, $-CONH_2$ etc) in the structure of the peptide chain. Such groups have affinity for oxygen-containing functional groups of lignin.
We also investigated the sorption capacity of biosorbents for ions of cadmium, lead, iron, copper and zinc from aqueous solutions, that characterized by toxic effects on human body. Investigation of sorption capacity obtained materials for metal ions indicate that previous chemical modification of apricot pits by acid-alkali scheme can significantly increase the sorption capacity of LC-matrix (Fig. 3). Adsorption capacity for metal ions of the resulting LC-material increases on average 2-3 times compared with the initial apricot pits due to increasing of specific surface area and accessibility of active functional groups of lignin and cellulose, which participate in sorption. However, loading [FC]-salts on a LC-carrier leads to reduction of sorption capacity for 15%.

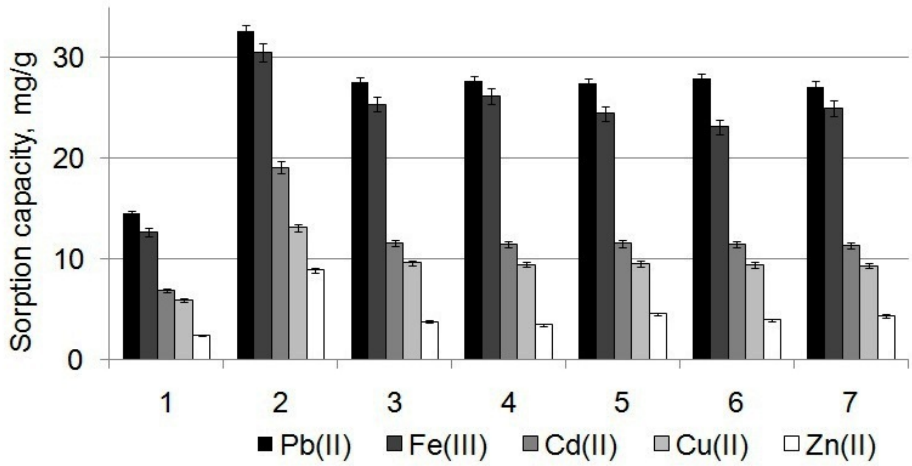

Figure 3. Sorption capacity of biosorbents towards metal ions:
1 – apricot pits; 2 – LC-complex; 3 – LC-[FC]Fe; 4 – LC-[FC]K-Co; 5 – LC-[FC]K-Ni;
6 – LC-[FC]Cu; 7 – LC-[FC]Zn.

The analysis of data shows that sorption ability of all studied LC-materials for metal ions decreases in the following: Pb^{2+} > Fe^{3+} > Cd^{2+} > Cu^{2+} > Zn^{2+}. Overall, the data of sorption capacity of LC- [FC]M sorbents for metal ions does not concede a value of mentioned parameter for sorbents based on hydrolytic lignin from waste products of agriculture and food industry [11].

4. Conclusions

Composite lignocellulose-inorganic biosorbents were synthesized based on apricot pits and ferrocyanides of d-metals. The study sorption ability has confirmed that obtained materials are characterized by high sorption properties with respect to cesium microquantities. The efficiency of ^{137}Cs removal from the simulated solutions with the composite sorbents decreases as follows: LC-[FC]K-Ni > LC-[FC]K-Co > LC-[FC]Cu > LC-[FC]Fe > LC-[FC]Zn. The regularities of sorption of metal cations, dyes, gelatine and vitamin B_{12} from aqueous solutions with composite materials were investigated. Sorption properties of LC-[FC]M samples towards ecotoxicants slightly decreasing in comparison with the LC-matrix but relatively high compared with the initial apricot pits.

Synthesized biosorbents can be used as materials of multifunctional purposes: as sorbents in radiochemistry and analytical chemistry for the concentration of cesium radionuclides for further research as well as in ecology - for effective removal of radionuclides from low-level radioactive solutions and water treatment; as enterosorbents with sorption, radioprotective and antioxidant properties for the application in medicine for the radionuclide injuries treatment; in veterinary as a feed additive that will reduce the adsorption of radionuclides in the gastrointestinal tract of animals with the aim to obtain normative pure products (meat, milk, etc.).

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