- CONFERENCES -

SYNTHESIS AND CHARACTERIZATION OF COMBINED SORBENTS BASED ON BLEACHED COTTON FIBERS AND COPPER-POTASSIUM FERROCYANIDES

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Combined sorbents based on cotton fiber and copper-potassium ferrocyanide were obtained. The influence of the main technological parameters of modification process on the inorganic component content in the final product and sorption properties was investigated. The sorption properties of new combined sorbents toward microamounts of ^{137}*Cs were found out. The structure of obtained sorbents was studied by methods of X-Ray diffraction and the decrease in degree of crystallinity of the modified sample was shown. A comparative analysis of the thermal characteristics of the initial and the modified fiber was done. It was found out that the thermal degradation of bleached cotton fiber modified by copper-potassium ferrocyanide occurs at higher activation energy than the initial fiber.*

Introduction

One of the sources of radionuclides contamination is a nuclear power station where a large quantity of low-level radioactive waste solutions that contain radioactive elements can be formed. Radioisotopes with half-lives to decades are the most dangerous for environment. To such radioisotope ^{137}Cs belongs. ^{137}Cs is the main dose-related radionuclide with a half-life 30.2 years which characterized by high migration ability [1]. Cesium radionuclides may adversely affect the human body because of their ability to accumulate in the tissues, causing a number of diseases [2-6]. All this leads to environmental problems and makes it necessary to find new ways to solve them.

The development of new selective sorption materials for removing of radioactive cesium from aqueous solutions with low and medium activity level is an urgent task. With this purpose various sorbents can be widely used: natural, synthetic, modified, complexing, etc. [7-11] The effectiveness of the sorbent and the character of the absorption process depend on the nature of the sorption material, the concentration of radioactive elements and the presence of contaminants of inorganic and organic nature.

Salts of polyvalent metals are characterized by high selectivity towards cesium, in particular ferrocyanides of transition metals ([FC]Me, where Me - metal cations) which characterized by high chemical and thermal stability [12]. Since [FC]Me are highly dispersed and microcrystalline substances to improve performance its immobilization should be carried out on support media [13-15]. As such a carrier bleached cotton fiber can be considered.

Experimental

Bleached cotton fibers (BCF) were used as the raw material for obtaining of combined [FC]-sorbents. Chemical composition of the fibers is shown in Table 1.

Table 1. Chemical composition of BCF

Components	Content, %
Cellulose	99.5
Lignin	0.45
Resins, fats, waxes	absent
Ash	0.05

Synthesis of combined sorbents was carried out by holding BCF in solutions of [FC]K-Cu at the following parameters of modification process: concentration [FC]K-Cu – 2…4 g/L; molar ration of $Cu^{2+}/[Fe(CN)_6]^{4-}$ – 1,5; pH – 2.6…11.5, duration – 2 h; temperature 70…90 °C. At the end of modification process the obtained combined sorbents were washed and dried at room temperature.

Sorption properties [FC]-sorbents toward to ^{137}Cs were studied in static conditions by continuously mixing 0.05 g of combined sorbents with 20 cm^3 of model solution which contain 1.0 mol/L of sodium nitrate and microamounts of radionuclide ^{137}Cs (~10^5 Bq/dm^3). After reaching equilibrium concentration the liquid and solid phases were separated by filtration through a paper filter "blue tape". The specific activity of the radionuclide ^{137}Cs in initial solutions and in solutions after sorption was determined using NRG-603 (Czech Republic) $\gamma-$ray analyzer. Sorption characteristics of the sorbents were evaluated by the values of distribution coefficient (C_d) and recovery rate (S), which are determined by the formulas 1 and 2, respectively:

$$C_d = \frac{A_0 - A_{eq}}{A_{eq}} \times \frac{V_L}{m_s} \qquad (1)$$

$$S = (1 - A_0 / A_{eq}) \times 100\% \ , \qquad (2)$$

where A_0, A_{eq} – respectively the initial and equilibrium specific activity of radionuclide ^{137}Cs, Bq/dm^3; V_L – volume of liquid phase, cm^3; m_s – sorbent mass, g.

Kinetic characteristics of the obtained materials were studied by intensive mixing of 200 cm^3 solution (100 Bq/cm^3) and 0.087 g of air-dried sorbent. At certain intervals sampling of was carried out and the specific activity of radionuclide ^{137}Cs was determined. By the results the value of the degree of equilibrium (F) at the time (τ) was calculated by formula (3):

$$F_\tau = E_\tau / E_\infty , \qquad (3)$$

where E_τ, E_∞ – sorbent capacity in time τ and at full saturation respectively, Bq/g. The value of E_∞ was determined in an independent experiment conducted under the same conditions at a contact time of 24 h.

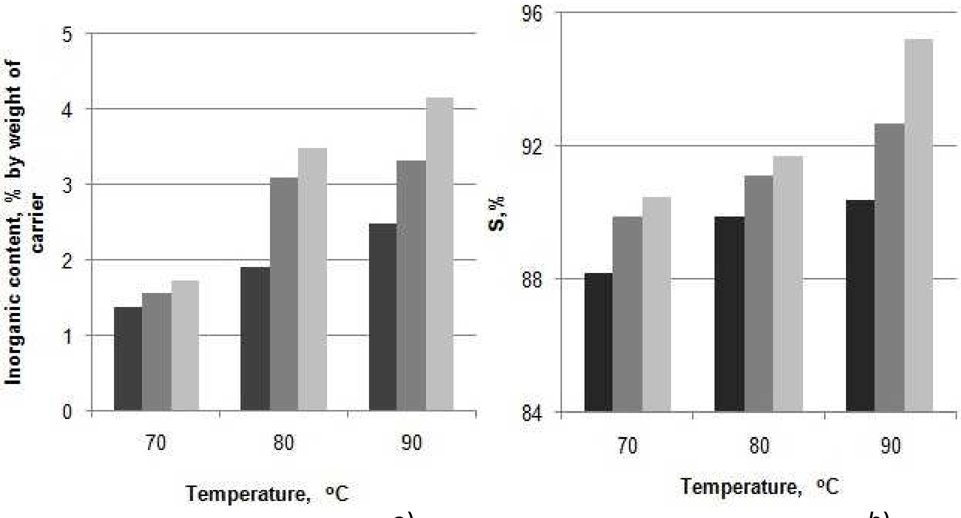
X-Ray diffraction: XRD patterns of the samples were recorded on a diffractometer DRON-4-07 in the filtered (Ni filter in the reflected beam) CuK$_\alpha$ radiation.

IR spectroscopy: To prepare the samples for IR spectroscopy cellulosic materials were triturated with KBr (2:90 ratio) and compressed into tablets. The spectra of the samples were recorded in the infrared region 4000 - 300 cm^{-1} with spectral resolution of 4 cm^{-1}.

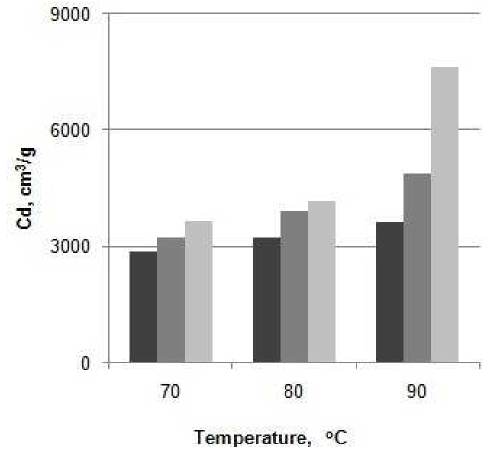
Differential thermal analysis (DTA): thermal degradation was studied using equipment Q-1500D with digital registration results. The cellulose samples of 30 mg were used for analysis, a heating rate 10 ^{o}C/h.

Results and discussion

The sorption properties of the combined [FC]-sorbents depend on the content of an inorganic component, which in turn depends on the process conditions. The influence of the basic technological parameters of modification process on the properties of the obtained sorbents is shown in Fig. 1.



a) b)



c)

Figure 1. The influences of the temperature of modification process on inorganic contents (*a*), recovery rates (*b*) and distribution coefficients (*c*) at the different [FC]K-Cu concentration : ■ – 2 g/L; ▩ – 3 g/L; □ – 4 g/L.

It was found out that increasing the concentration of [FC]K-Cu in the initial solution and increasing the modification process temperature leads to an increase of the inorganic component in the final product as a partial swelling of BCF take place thus appears access of the reagent to microfibrils of cellulose fibers. Furthermore, immobilization of [FC]-particles on the fiber surface occurs involving the maximum number of functional groups. As can be seen from the figure 1 the increase of the basic parameters is also leads to an increase in the sorption characteristics. The combined [FC]-sorbent obtained at the concentration of [FC]K-Cu in initial solution 4 g/L and the process temperature 90 ^{o}C characterized by maximum values of distribution coefficient (7700 cm^3/g) and recovery rate (95.2 %). Further increase in temperature over 90 ^{o}C is not advisable because the degradation of cellulose matrix take place which leads to decrease in mechanical properties of the carrier.

The kinetics of sorption is an important step in the study of the sorption properties of the sorbent, as it allows determining the mechanism of the process of absorption. Fig. 2 shows the dependence the degree of equilibrium from time during the sorption of microamounts of ^{137}Cs.

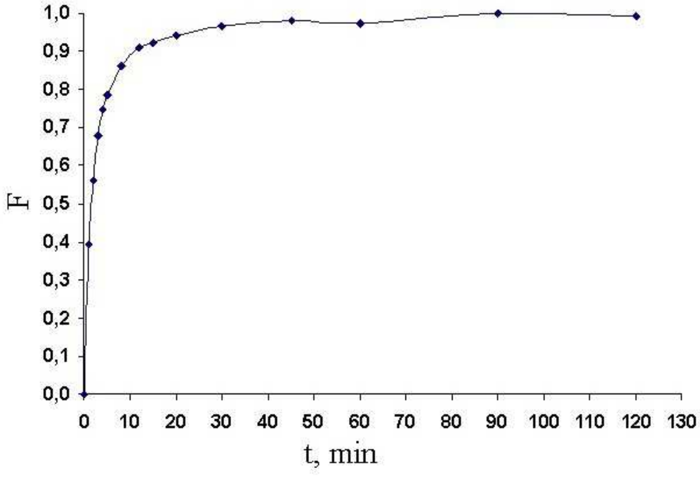


Figure 2. Dependence of the degree of equilibrium from time

The results indicate that the sorption equilibrium on the obtained sorbent is achieved after 30-40 minutes, indicating the high kinetic characteristics of [FC]-cellulose sorbent based on [FC]K-Cu. To determine the mechanism of cesium sorption the kinetic dependence of cesium sorption in coordinates $F-\tau^{1/2}$ was built (Fig. 2).

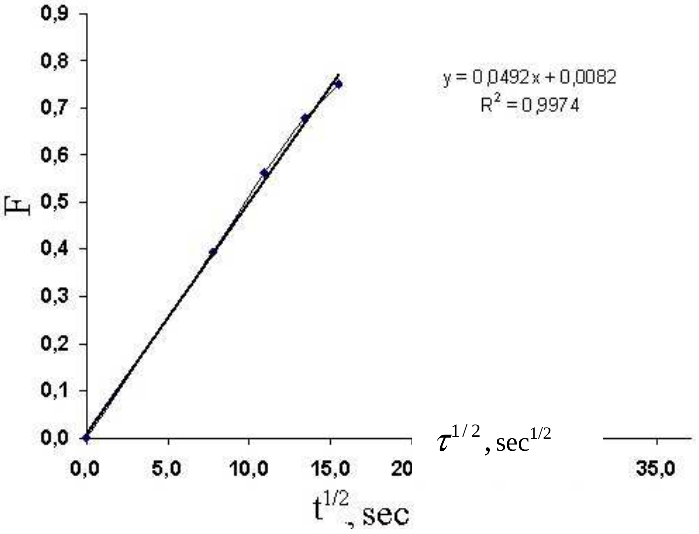


Figure 3. Kinetic dependence of sorption of ^{137}Cs in the coordinates $F-\tau^{1/2}$.

These results demonstrate that the kinetic dependence of sorption of 137Cs is well approximated by a straight line that indicates the internal diffusion mechanism of sorption.

Diffraction patterns of samples of the initial and modified BCF are presented in Figure 4. The peak positions correspond to X-ray reflections from the crystalline planes of the monoclinic grating of cellulose. The most intense peaks are observed at 2θ = 14.64^o, 16.13^o and 22.61^o refers to the plane of reflection (101), (10-1) and (002) respectively (Table 2). In the diffraction pattern of modified sample the peaks that refer the crystal structure of a modifier are not observed which is probably is caused by its highly dispersed position.

The intensity ratio of the diffraction peaks caused by the scattering of rays from crystalline regions and diffuse amorphous halo is used to estimate the degree of crystallinity - relative content of the crystalline portion in cellulose. The initial BCF characterized by degree of crystallinity at the level of 73%. Diffraction patterns of the modified sample is differ from the diffraction initial material by less intensity of the main diffraction peaks that indicates a change in the degree of crystallinity. This allows concluding that in the result of holding BCF in [FC]K-Cu solution partial destruction of highly oriented regions of cellulose occurs. The degree of crystallinity of the obtained combined sorbent is 69%

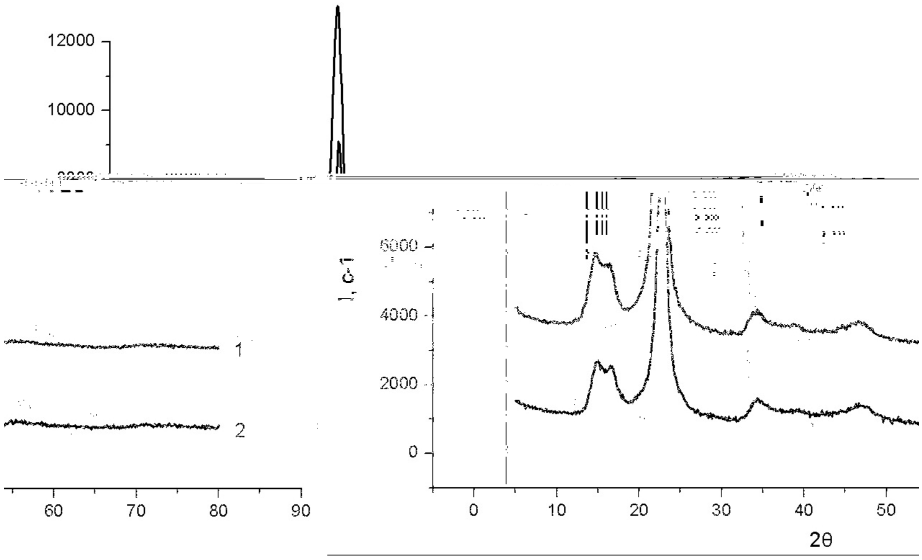


Figure 4. The diffraction patterns: 1 – BCF; 2 – BCF-[FC]K-Cu.

Table 2. Characteristics of the diffraction peaks of initial and modified BCF.

Material	2θ, degree	Interplanar spacing, A°	hkl	The half-width reflex, degree	The degree of crystallinity, %
BCF	14.64 16.13 22.61	6.05 5.50 3.93	(101) (10-1) (002)	3.1 3.4 1.7	73
BCF-[FC]K-Cu	14.95 16.52 22.78	5.93 5.37 3.90	(101) (10-1) (002)	3.2 3.4 1.6	69

IR-spectra of initial BCF and modified by [FC]K-Cu are presented in Figure 5, the assignment of the absorption bands was done and results are shown on Table 2. Analysis of the IR spectra of the original and modified BCF indicates the appearance in the spectra of the samples the band CN-groups (2144 cm^{-1}) after immobilization of [FC]-phase.

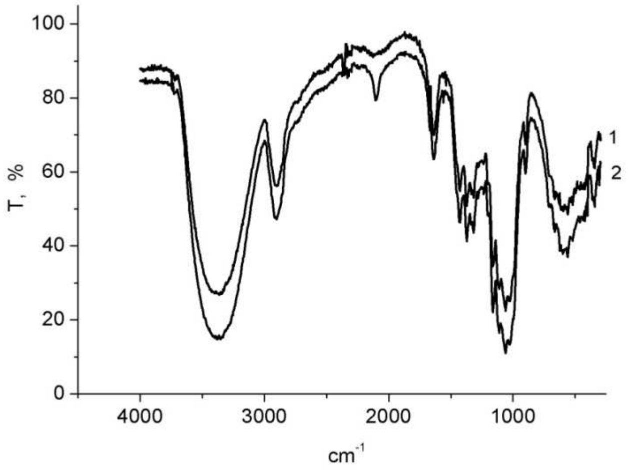


Figure 5. IR-spectra: 1 – BCF; 2 – BCF-[FC]K-Cu

IR-spectra of initial and modified BCF are characterized by the presence of absorption bands at 3600-3000 cm^{-1}, which correspond to the valence vibrations of free OH-groups. The broadening of these bands for modified sample indicates a partial disordering and the restructuring of the hydrogen bonds during modification process. The absorption bands in the region of vibrations of glucopyranose rings 1200-1000 cm^{-1} in the spectra of modified sample is not different from the same band in the spectrum of initial material. This shows the preservation of cyclic structure during chemical modification.

Table 2. The assignment of the absorption bands.

Region of the spectrum, cm^{-1}	Maximum of absorption band, cm^{-1}		Assignment of the bands
	BCF	BCF-[FC]K-Cu	
4000-3000	3650		VV* free OH-groups
	3500–2860		VV OH-groups involved in the intermolecular H-bonds
3000-2000	2940–2860		VV of the bounds in the groups of CH and CH_2
	-	2144	VV CN-groups
2000-1500	1636		DV** of the bounds in H-O-H
1500-1200	1430, 1370		DV of the groups CH_2
	1336, 1316		DV of O-H in CH_2OH
	1290, 1240		DV of CH_2 in CH_2OH
	1205		DV of OH
1200 - 1100	1165, 1112, 1060, 1040		VK of C-O
1000 - 800	900		DC of CH_2 (at C_1)

*VV - valence vibrations,

**DV - deformation vibrations.

Results of the thermal decomposition of the initial and modified BCF are shown in Fig. 6. The analysis of the data shows a stepped thermal conversion of cellulosic materials. In the temperature range to 277 °C dehydration of cellulosic samples occurs. This stage consists of two main processes: desorption of physically bound water (weight loss is 4.5 – 5.5%) with the following desorption of chemically bound water (weight loss is 0.8 - 1%).

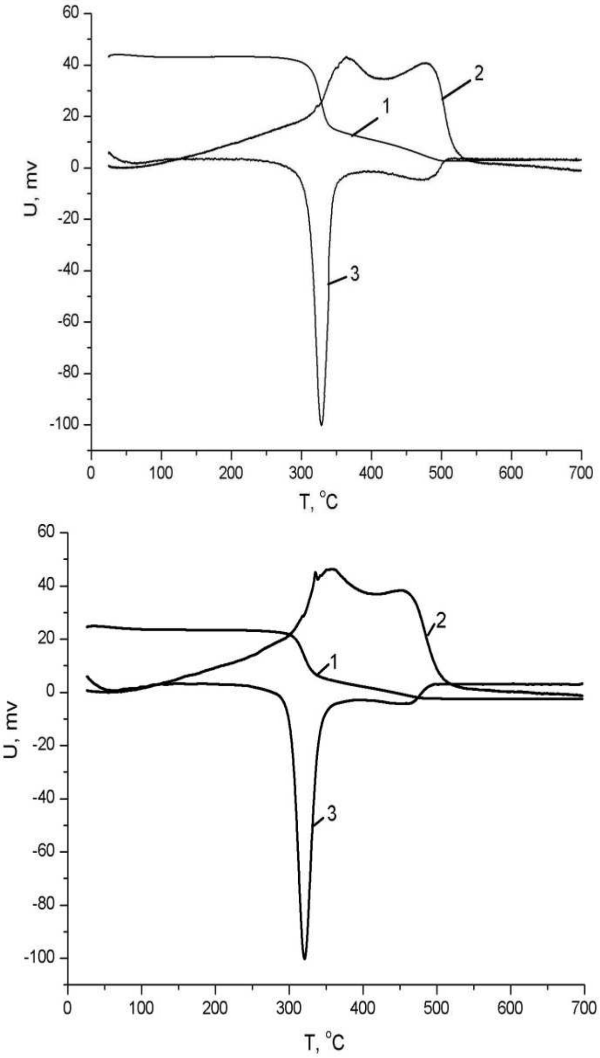


Figure 6. DTA results: A – BCF, B – BCF-[FC]K-Cu; 1 – TG, 2 – DTA, 3 – DTG.

Final temperature of dehydration process for BCF-[FC]K-Cu is 13 °C lower initial BCF that connected with high content of low molecular weight fraction, which is formed as a result of the modification process. For the dehydration process of cellulosic samples activation energies were calculated (Table 3). Data analysis indicates that activation energy for dehydration of BCF after modification of [FC]-phase is lower than the initial BCF.

Stage of thermal degradation of cellulosic materials is accompanied by a maximum weight loss which corresponds to clearly pronounced minimum on DTG curves for both samples. On DTA curves in the temperature range 300-530 °C the exothermic peaks indicate the formation and evaporation of gaseous products of cellulose degradation.

Table 3. Characteristics of thermal degradation for initial and modified BCF.

Material	Dehydration process		Thermal destruction	
	Activation energy of dehydration, kJ/mol	Temperature, ^{o}C	Temperature of exothermic effects, ^{o}C	The activation energy, kJ/mol
BCF	41,40	80 - 277	365 480	187 329
BCF-[FC]K-Cu	36,11	71 - 264	338 350 455	364 97 397

Appearance of exothermic peaks with maxima at 338 °C for modified sample correspond to the process of thermal degradation of [FC]-phase [16]. For BCF-[FC]K-Cu in the temperature range 300 - 530 °C the shift of exothermic peaks which belong to the thermal decomposition of the cellulose matrix to the region of lower temperatures are observed.

Conclusion

The method of obtaining new combined sorption materials based on bleached cotton fiber and copper-potassium ferrocyanide was developed. The influence of the concentration of the initial solution for modification and the process temperature on the sorption properties of final products was shown. It was found out that combined sorbents characterized by high kinetic characteristics and the internal diffusion mechanism of sorption.

Modification process of BCF accompanied by changes in the structure of the cellulose which results in the destruction of highly oriented regions causing a decrease in the degree of crystallinity. With a decrease in the modified samples crystalline areas the endothermic effect is shifted to a low-temperature region.

References

1. Vasilenko I.Y, Vasilenko O.I. Radioactive cesium // Energy: Economy, Technology, Ecology, 2001. - N7. - P. 16-22. (in Russian).
2. Lin W., Mota D.F., Zhang Q., Olsen K.W. Nuclear magnetic resonance and oxygen affinity study of cesium binding in human erythrocytes // Archives of biochemistry and biophysics, 1999. – Vol. 369, №1. – P. 78–88.
3. Leggett R.W., Wiliams L.R., Melo D.R., Lipsztein J.L. A physiologically based biokinetic model for cesium in the human body // The science of the total environment, 2003. – N317. – P. 235–255.

4. Racine R., Gradcolas L., Grison S., Gourmelon P., Gueguen Y., Veyssiere G., Souidi M. Molecular modification of cholesterol metabolism in the liver and the brain after chronic contamination with cesium-137 // Food and Chemical Toxicology, 2009. – N47. – P. 1642–1647.
5. Cardis E., Howe G., Ron E., Bebeshko V. at al. Cancer consequences of the Chernobyl accident: 20 years on // Journal of Radiological Protection, 2006. – 26. – P. 127–140.
6. Jacob P., Bogdanova T.I., Buglova E., Chepurniy M. Thyroid cancer risk in areas of Ukraine and Belarus affected by the Chernobyl accident // Radiation Research, 2006. – N165. – P. 1–8.
7. Ding D., Zhao Y., Yang S. et al. Adsorption of cesium from aqueous solution using agricultural residue – walnut shell: equilibrium, kinetic and thermodynamic modeling studies // Water Research, 2013. - N47. – P. 2563–2571.
8. Chmilivska E. Zeolites – materials of sustainable significance // Environment Protection Engineering, 2010. – Vol. 36, N4. – P. 127–135.
9. Ishikawa N.K. Radiocesium sorption behavior on illite, kaolinite, and their mixture // Radioprotection, 2009. – Vol. 44, N5. – P. 141–145.
10. Ildiz B., Erten H.N., Kis M. The sorption behavior of Cs^+ ion on clay minerals and zeolite in radioactive waste management: sorption kinetics and thermodynamics // Journal of Radioanalytical and Nuclear Chemistry. – 2011. – Vol. 288. – P. 475–483.
11. Sawhney B.L. Selective sorption and fixation of cations by clay minerals: a review // Clays and clay minerals. – 1972. – Vol. 20. – P. 93–100.
12. Milyutin V.V., Geis V.M., Klindukhov V.G., Obruchikov A.V. Coprecipitation of microamounts of Cs with ferrocyanides of various metals // Radiochemistry, 2004. – Vol. 46, N5. – P. 444–445.
13. Milonjic S., Bispo I., Fedoroff M., Loos-Neskovic C., Vidal-Madjar C. Sorption of cesium on copper hexacyanoferrate/polymer/silica composites in batch and dynamic conditions // Journal of Radioanalytical and Nuclear Chemistry, 2002. – Vol. 252, N3. – P. 497–501.
14. Panasyugin A.S., Goikova N.B., Strukova O.V. Concentrating of radiocesium with selective sorbents // Radiochemistry, - 2003. – Vol. 45, N3. – P. 290–292.
15. Orechovska J., Rajec P. Sorption of cesium on composite sorbents based on nickel ferrocyanide // Journal of Radioanalytical and Nuclear Chemistry, 1999. – Vo. 242, N2. – P. 387–390.
16. Feng X., Jing S., Wu Q., Chen J., Song C. Thermal decomposition of potassium titanium hexacyanoferrate (II) loaded with cesium in fixed bed calciner // Chinese Journal of Chemical Engineering, 2007. – N15(2) – P. 184–189.