

UDC 615.011:615.453.3

DOI: 10.15587/2519-4852.2018.128730

STUDYING THE INFLUENCE OF THE NATURAL ZEOLITE TABLETS MANUFACTURING TECHNOLOGY ON SORPTION KINETIC OF LONG-LIVING ^{90}Sr AND ^{137}Cs RADIONUCLIDES AND Pb^{2+} AND Hg^{2+} HEAVY METALS FROM WATER SOLUTION IN VITRO

© V. Rybachuk, O. Ruban, A. Krasnopyorova, G. Yuhno

Мета: Вивчити вплив технології отримання на адсорбційну активність таблеток цеоліту природного (кліноптилоліту) по відношенню до довгоживучих радіонуклідів ^{90}Sr і ^{137}Cs та важких металів Pb^{2+} і Hg^{2+} з водного розчину *in vitro*.

Методи: Таблетки готували прямим пресуванням та пресуванням з попередньою вологою грануляцією (зволожувач – 7 % крохмальний клейстер). Сорбційну здатність ентеросорбентів досліджували методом статичної сорбції при $\text{pH}=2-8$ температурі 37°C . Концентрацію свинцю в розчинах визначали методом атомно-абсорбційної спектроскопії на атомно-абсорбційному спектрофотометрі С-115 ПКС. Концентрацію ртуті визначали методом безполум'яної атомізації за допомогою ртутної приставки ПР-115. Вміст радіонуклідів визначали за радіоактивністю зразків за допомогою радіометру α - β -автомат NRR-610 "Tesla".

Результати: За результатами проведених досліджень вивчено адсорбційну активність модельних зразків ентеросорбентів на основі цеоліту природного в формі таблеток отриманих за технологією прямого пресування та пресування з попередньою вологою грануляцією. Виявлено, що сорбційні властивості зразків відносно важких металів та радіонуклідів в більшій мірі залежать від кислотності розчину ніж від технології отримання таблеток. Встановлено, що процес іонного обміну на дослідних зразках складається з двох стадій - швидкої і повільної. Цей факт пояснюється адсорбцією іонів в першу чергу всередині макро- і мезопор на поверхні матеріалу, а зменшення швидкості в подальшому – дифузії іонів всередині мікропористого простору, і ця стадія є лімітуючою в процесі адсорбції. Зіставлення отриманих даних щодо сорбційно-селективних властивостей зразків дозволило розташувати досліджені іони в порядку зменшення їх взаємодії з сорбентами $\text{Pb}^{2+} > \text{Hg}^{2+} > ^{137}\text{Cs} > ^{90}\text{Sr}$.

Висновки: Доведено, що технологія отримання таблеток не чинить суттєвого впливу на активність препарату *in vitro*. Результати експериментальних досліджень будуть використані у подальшому при розробці складу та технології таблеток, що містять цеоліт природний (кліноптилоліту), як основний діючий компонент

Ключові слова: цеоліт природний, таблетки, пряме пресування, волога грануляція, важкі метали, радіонукліди, адсорбція

1. Introduction

Pollution with heavy metals and radionuclides is one of the most harmful to the biosphere of the Earth, with the most diverse harmful consequences for both people's health and the life of living organisms. Along with pesticides, dioxins, petroleum products, phenols, phosphates and nitrates, heavy metals and radionuclides jeopardize the very existence of civilization. Increasing the scale of environmental pollution, as a result of rapid scientific and technological progress, is turning into an increase in genetic mutations, cancer, cardiovascular and occupational diseases, poisoning, dermatosis, and the decrease in immunity and related diseases [1].

2. Formulation of the problem in a general way, the relevance of the theme and its connection with important scientific and practical issues

In conditions of high anthropogenic pressure on the environment, a number of harmful substances, including heavy metals and radionuclides, enter the human body. The main sources of these substances in the body are potable water, atmospheric air and food. Accumulating in the body of heavy metals and radionuclides impede the normal development and functioning of the body, and in high doses cause irreversible changes [2].

One of the ways of solving this situation is enterosorption. Oral use of enterosorbent drugs over a period of time allows both to prevent the flow of these substances into the human body [3], and to ensure their gradual removal from the body [4]. However, drugs present in the arsenal of practitioners do not always meet the requirements of practitioners in combating the negative factors of the toxic load on the body. In this regard, the search and development of safe and effective means for the prevention and treatment of the negative effects of heavy metals and radionuclides on the human body is an important task of medicine and pharmacy.

3. Analysis of recent studies and publications in which a solution of the problem are described and to which the author refers

The development and introduction of zeolite preparations naturally at various times was carried out by V. I. Chueshov, D. V. Rybachuk, L. V. Yakovleva, T. V. Krutskich and others who studied the physico-chemical, technological and pharmacological properties of natural zeolite powder and granules based on it. In our previous studies, the conformity of substance to the requirements for medical sorbents was investigated, the kinetics of granulation was studied, the composition and technologi-

cal aspects of obtaining tablets were studied, the optimal type of packaging and the conditions of storage of the active substance and products on its basis were determined [5, 6].

4. The field of research considering the general problem, which is described in the article

To date, enterosorbents in the Ukrainian market are presented in different formulations [7]. These include carbon sorbents derived from natural or synthetic raw materials, natural and synthetic aluminosilicates, clay minerals, synthetic silicon-containing sorbents (organosiloxanes, aerosols), biopolymer-based sorbents, including natural organic fibers ("food fibers"), synthetic organic polymers (polyvinylpyrrolidone, cholestiramine, etc.), and combined medications [8]. However, unfortunately, there are no enterosorbents on the basis of natural zeolite (clinoptilolite) [9, 10]. Ukraine has huge reserves of this mineral, which is characterized by low cost. The development of pharmaceuticals with this substance will allow the introduction of a new effective drug on the basis of raw materials of domestic production.

5. Formulation of goals (tasks) of article

The purpose of the work was to study the effect of the technology of obtaining on the adsorption activity of natural zeolite tablets (clinoptilolite) in relation to long-lived radionuclides ^{90}Sr and ^{137}Cs and heavy metals Pb^{2+} and Hg^{2+} from an aqueous solution in vitro.

6. Presentation of the main research material (methods and objects) with the justification of the results

The subjects of the study were tablets containing enterosorbent on the basis of natural zeolite (clinoptilolite) obtained by direct compression (sample number 1) [6] and compression with pre-wet granulation (sample number 2), where 7 % starch paste was used as a moisturizer [7]. We used solutions of salts $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$; $\text{Pb}(\text{NO}_3)_2$ qualification "c.p." with initial concentrations of metal ions (C_0) 7.25 mg/l and 6.74 mg/l, respectively. The sorption capacity of enterosorbents for heavy metals of lead and mercury was investigated by the method of limited volume (static sorption) at $\text{pH}=2$ and $\text{pH}=6$ and at a temperature of 37°C . Under these conditions, the tablets (0.1 g) were actively stirred with a magnetic stirrer with 10 ml of metal salt solutions prior to disintegration and achieving a thermodynamic equilibrium. The acidity of the solutions was monitored using a pH meter and adjusted by adding HCl or NaOH solutions.

The concentration of lead in solutions was determined by atomic absorption spectroscopy at the atomic absorption spectrophotometer C-115 PCS. Measurement of the analytical signal of lead was carried out in a flame of acetylene-air at a wavelength $\lambda=283.3$ nm, a width of the monochromator slit – 0.4 nm, a current of a lamp – 3 mA.

The concentration of mercury in the investigated solutions was determined by the method of flame atomization with the help of mercury device PR-115. Measurement of the analytical signal of mercury was carried out at wavelength $\lambda = 253.7$ nm, width of the monochromator slit – 0.1 nm, current of the lamp – 5 mA. The maximum relative error of the determination of metal

ions by atomic absorption spectroscopy with a confidence probability of 0.95 and the number of measurements 6 was 3 %.

The sorption capacity of the samples relative to the radionuclides was studied using the static sorption method at 37°C and at pH values 2.0, 5.5 and 8.0. Radionuclide solutions ^{90}Sr ($1.8 \cdot 10^7$ Bq/dm³) and ^{137}Cs ($3.2 \cdot 10^7$ Bq/dm³) were used without carriers. Absorbents of 0.1 g were mixed with 10 ml of solutions containing radionuclides ^{90}Sr and ^{137}Cs , prior to the determination of sorption equilibrium. The activity of the model solutions before and after the determination of the sorption equilibrium was determined according to the standard method of activity of the dry residue of 0.2 ml of aliquot of the solution. The radioactivity of the dry residue was measured using a radiometer α - β -automaton NRR-610 "Tesla". The statistical error of experiments did not exceed 5 %.

In order to determine the time needed to achieve the sorption equilibrium, the kinetics of ion exchange on the sorbents studied was studied. The kinetic curves were obtained by the method of sequential determination of the concentration of ions in the interval of time 0.5, 1, 2, 3, 4 and 5 hours. The constancy of a certain concentration of heavy metal ions or the constancy of radioactivity of two consecutive samples was indicative of the sorption equilibrium in the system.

In conditions of established equilibrium, the solution-sorbent system determined the equilibrium concentration of metal ions (C_{eq}) and calculated the equilibrium sorption capacity of sorbents (A_{eq} , mg/g) for heavy metals:

$$A_{eq} = \frac{(C_0 - C_{eq}) \cdot V}{m} \quad (1)$$

The coefficient of sorption (K_s , %) and the coefficient of distribution of metal ions between sorbent and solution (K_d , l/g) were calculated by the formulas:

$$K_d = \frac{(C_0 - C_{eq}) \cdot V}{C_{eq} \cdot m} \quad (2)$$

$$K_s = \frac{(C_0 - C_{eq})}{C_0} \cdot 100 \quad (3)$$

where C_0 , C_p – initial and equilibrium concentration of solution, mg/l; V – total volume of solution, l; m – mass of sorbent, g.

For the quantitative characterization of the interaction of sorbents with radionuclides, the K_s and K_d indices were determined using formulas 2 and 3, in which, instead of concentration values, the values of the initial (I_0 , imp/s) and equilibrium (I_r , imp/s) radioactivity of solutions were used.

Adsorption of radionuclides and heavy metal ions on sorbents depends on many factors. Among them, the most important is the contact time of the solution with the sorbent. For the study of the dependence of the time of contact of the sorbent with the solution and the degree of removal of cations from the solution adsorption of

long-lived radionuclides ^{90}Sr and ^{137}Cs and Pb^{2+} and Hg^{2+} ions were carried out on samples of zeolite tablets (Fig. 1, 2). According to the obtained data, the highest activity in relation to all metals showed samples of tablets obtained by direct compression. The use of the pre-wet granulation slightly influenced the adsorption activity towards its reduction, which averaged 8–10 % in the acidic medium, and almost did not differ when pH increased, as shown by the lead ions, and is not significant in the context of a significant improvement in the technological properties of the tablet mass after granulation [7]. The values of sorption capacity of sorbents for mercury and lead are 0.54–0.675 mg/g, which corresponds to the degree of extraction of 80–97 %. Analysis of the kinetics of sorption of radionuclides showed that the highest sorption activity showed examples of tablets obtained using previous wet granulation. As can be seen from Figs. 1 and 2, the process of ion exchange consists of two stages – fast and slow. This fact is explained by the adsorption of ions especially in the macro- and mesopores on the surface of the material, and reducing the rate further – by diffusion of ions inside the microporous space, and this is a limiting step in the process of adsorption. The highest rate of adsorption samples showed in the first 30 minutes and achieve adsorption equilibrium in heterophase system within 30-60 minutes from the start

of the experiment, as evidenced by the character line diagrams. In the investigated metal cations case change of the selectivity samples of tablets is agreed with the order of increase of ion energy and hydration, and selectivity of radionuclides to a greater extent is dependent on the thermodynamic properties of ions (Table 1).

Sorption properties of samples relative to heavy metals and radionuclides are more dependent on the acidity of the solution, as can be seen from the example of Pb^{2+} ions and radionuclides ^{90}Sr and ^{137}Cs (Fig. 3, 4). The obtained K_d values, depending on the pH of the solution (Table 2, 3), show that sorption of ions in the investigated range increases with increasing pH. Sorption capacity of clinoptilolite (as the main component of the studied tablets) determines its structure, which depends on the nature of the exchange cation, its size and the energy of hydration. To penetrate zeolite channels, ions should be completely or partially dehydrated. The most complete of radionuclides is a slightly hydrated cesium ion, the strontium ion is much less absorbed (Table 3), which has high values of the thermodynamic characteristics of hydration (Table 1). This dependence of the sorption value on the pH of the solution confirms the literature data [11], that the zeolites are weakly acidic poly-functional ion exchanges, and sorption is carried out according to the mechanism of ion exchange.

Table 1
Ionic radii [11], electronic configuration and thermodynamic characteristics of the hydration of the ions Pb^{2+} , Hg^{2+} , Cs^+ and Sr^{2+} [12]

Ion	Electronic configuration	Ionic radii, nm	$-\Delta H^0_{\text{hydr}}$, kJ/mol	$-\Delta S^0_{\text{hydr}}$, kJ/(mol·K)	$-\Delta G^0_{\text{hydr}}$, kJ/mol
Pb^{2+}	$6p^2$	0.132	1514	125	1477
Hg^{2+}	$5d^{10}6s^2$	0.110	1853	171	1803
Cs^+	$6s^1$	0.167	280	10.03	275
Sr^{2+}	$4s^2$	0.127	1475	163.03	1425

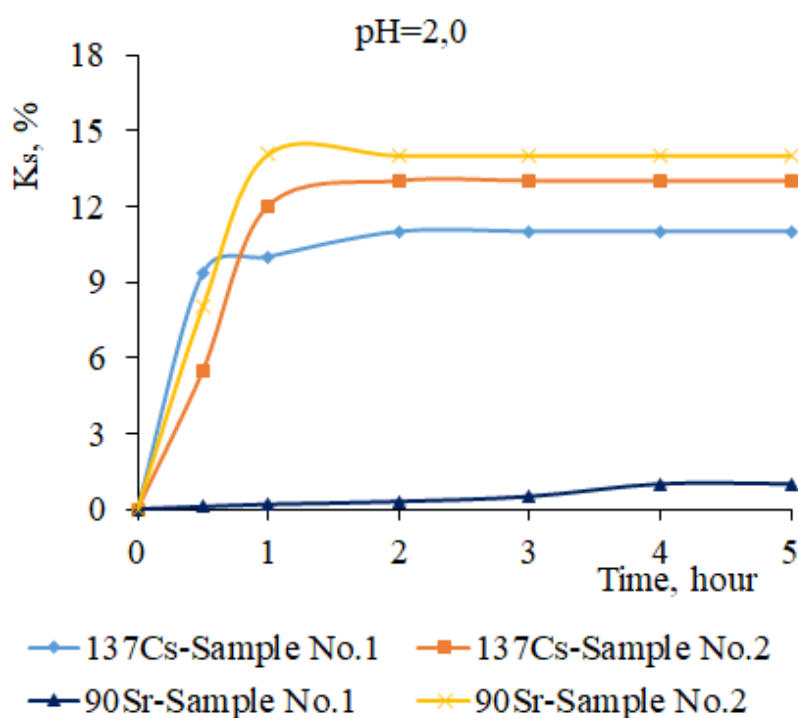


Fig. 1. Kinetics of sorption of radionuclides with model samples of enterosorbents

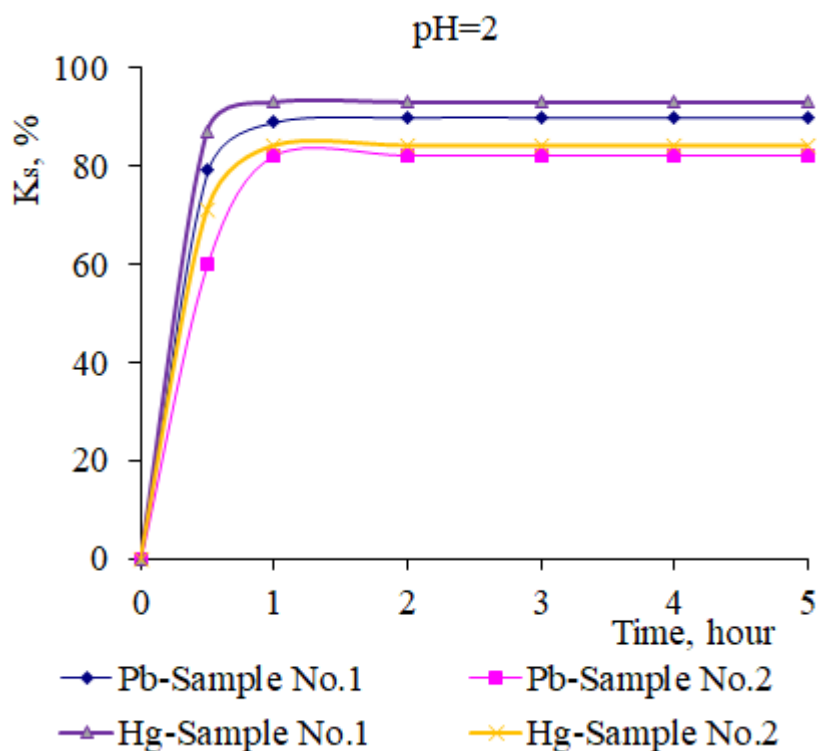


Fig. 2. Kinetics of sorption of lead ions and mercury by model samples of enterosorbents

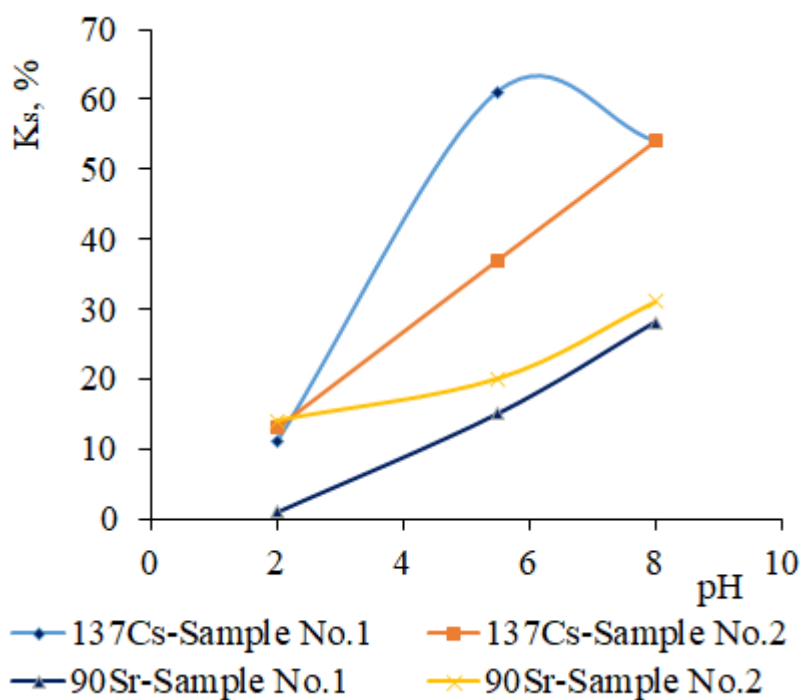


Fig. 3. Kinetics of sorption of radionuclides by model samples of enterosorbents at different pH values

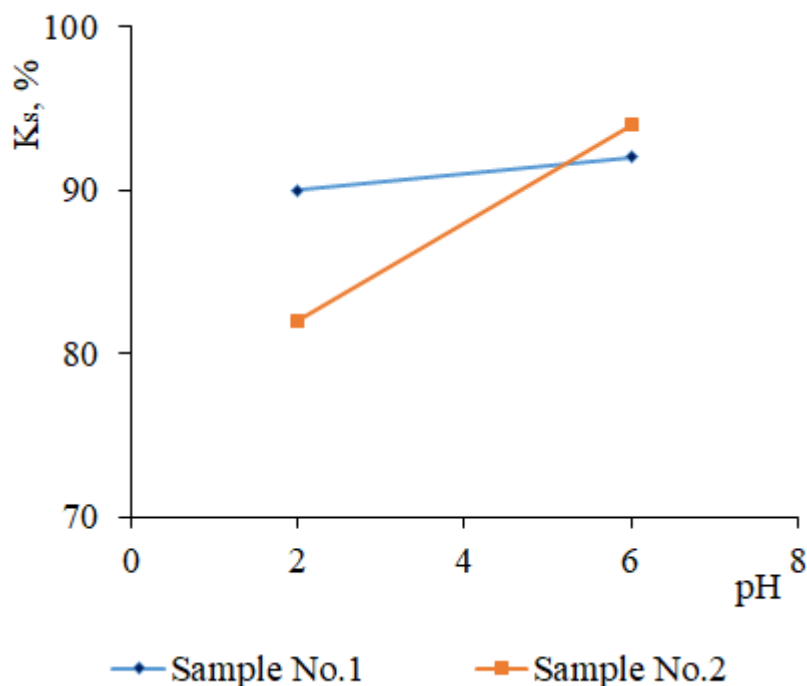


Fig. 4. Kineticsorption of ions Pb²⁺ model samples of enterosorbents at different pH values

Table 2

Sorption characteristics of the extraction of heavy metal ions

Sample №	Initial concentration (C ₀), mg/l	Equilibrium concentration (C _{eq}), mg/l	Equilibrium sorption capacity of sorbents (A _{eq}), mg/g	Degree of extraction (α), %	Distribution coefficient (K _d), l/g
Pb ²⁺ , pH=2.0					
1	6.74	0.56	0.618	91.7	1.10
2	6.74	1.32	0.542	80.0	0.41
Pb ²⁺ , pH=6.0					
1	6.74	0.337	0.640	95	1.90
2	6.74	0.202	0.654	97	3.23
Hg ²⁺ , pH=2.0					
1	7.25	0.50	0.675	93,1	1.35
2	7.25	1.16	0.609	83,7	0.52

Table 3

Distribution coefficients (K_d, l/h) ⁹⁰Sr and ¹³⁷Cs on combined sorbents 298.15 °K

Sorbent (squad number)	⁹⁰ Sr			¹³⁷ Cs		
	pH=2	pH=5.5	pH=8	pH=2	pH=5.5	pH=8
K _d , l/g						
1	0.012	0.017	0.040	0.028	0.160	0.117
2	0.015	0.024	0.046	0.016	0.060	0.115
K _s , %						
1	1	15	28	11	61	54
2	14	20	31	13	37	54

The values of the distribution coefficients (K_d, l/g) of heavy metals and radionuclides on the tablet samples, shown in tables 2 and 3, allow us to compare the sorption and selective properties of the samples and to determine the selectivity of the samples for the studied ions in the series Pb²⁺> Hg²⁺> ¹³⁷Cs> ⁹⁰Sr

Summing up the obtained data, it should be noted that the technology of obtaining natural zeolite tablets slightly affects its sorption properties of the studied

heavy metals and radionuclides, and its choice should be made primarily from the point of view of its influence on the technological properties of the liquid form and the needs of the production process.

7. Conclusions from the conducted research and prospects for further development of this field

The adsorption activity of model specimens of enterosorbents on the basis of natural zeolite in the form of

tablets obtained by direct compression and compression with pre-wet granulation was investigated. It is proved that the technology of obtaining tablets does not significantly affect the activity of the drug in vitro. The results

of experimental studies will be used in the further development of the composition and technology of tablets containing natural zeolite (clinoptilolite) as the main active ingredient.

Література

1. Effect of Toxic Metals on Human Health / Mudgal V. et al. // The Open Nutraceuticals Journal. 2010. Vol. 3, Issue 1. P. 94–99. doi: 10.2174/1876396001003010094
2. Suldina T. I. Soderzhanie tyazhelykh metallov v produktakh pitaniya i ikh vliyanie na organizm // Ratsional'noe pitanie, pishhevye dobavki i biostimulyatory. 2016. Issue 1. P. 136–140.
3. Tarasenko Yu. A., Gerashhenko I. I., Kartel N. T. Enterosorbtsiya kak metod vyvedeniya iz organizma tyazhelykh metallov i radionuklidov // Poverkhnost. 2014. Issue 6 (21). P. 110–121.
4. Yulish E. I., Krivushev B. I. Enterosorption method in the treatment of intoxication syndrome // Child's Health. 2011. Vol. 4, Issue 31. P. 25–28.
5. Rybachuk V. D., Rybachuk D. V. Vyvchennia vplyvu dopomizhnykh rehovyn na presuiemist poroshku tseolitu pryrodnoho // Visnyk farmatsii. 2010. Issue 3. P. 11–14.
6. Rybachuk V. D. Vyvchennia kinetyky utvorennia hranul tseolitu pryrodnoho pry riznykh sposobakh hranuliuvannia // Annals of Mechnikov Institute. 2016. Issue 4. P. 88–96.
7. Kompendium 2014 – lekarstvennye preparaty / ed. by Kovalenko V. N. Kyiv: MORION, 2014. 2448 p.
8. Nikolaev V. G., Gurina N. I. Sorbtsionnye materialy i mekhanizmy deystviya // Klinicheskaya efferentologiya. 2010. Issue 4. URL: <http://kiulong.com.ua/content/view/66/1/>
9. Campos V. The sorption of toxic elements onto natural zeolite, synthetic goethite and modified powdered block carbon // Environmental Earth Sciences. 2009. Vol. 59, Issue 4. P. 737–744. doi: 10.1007/s12665-009-0069-6
10. Natural Zeolites as Potential Materials for Decontamination of Radioactive Cesium / Johan E. et. al. // Procedia Environmental Sciences. 2015. Vol. 28. P. 52–56. doi: 10.1016/j.proenv.2015.07.008
11. Lurie Yu. Yu. Spravochnik po analiticheskoy khimii. Moscow: Nauka, 1979. 480 p.
12. Sienko M., Pley R., Khester R. Strukturnaya neorganicheskaya khimiya. Moscow: Mir, 1968. 344 p.

Дата надходження рукопису 27.03.2018

Vasiliy Rybachuk, PhD, Associate Professor, Department of Industrial Technology of Drugs, National University of Pharmacy, Pushkinska str., 53, Kharkiv, Ukraine, 61002,
E-mail: v.d.rybachuk@gmail.com

Olena Ruban, Doctor of Pharmacy, Professor, Head of Department, Department of Industrial Technology of Drugs, National University of Pharmacy, Pushkinska str., 53, Kharkiv, Ukraine, 61002

Alla Krasnopyorova, PhD, Senior Researcher, Head of Department, Department of Radiochemistry and Radioecology, Research Institute of Chemistry of V. N. Karazin Kharkiv National University, Svobody sq., 4, Kharkiv, Ukraine, 61022

Galina Yuhno, PhD, Senior Researcher, Department of Radiochemistry and Radioecology, Research Institute of Chemistry of V. N. Karazin Kharkiv National University, Svobody sq., 4, Kharkiv, Ukraine, 61022