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**STUDY OF THE INFLUENCE OF A GEL FORMER  
(THICKENER) TYPE ON THE SORPTION  
KINETIC OF LONG-LIVING RADIONUCLIDES  
AND HEAVY METALS BY NATURAL ZEOLITE  
PASTE FROM AN AQUEOUS SOLUTION IN  
VITRO**

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**Introduction**

The deterioration of the population health, due to the chemicalization of many aspects of life, requires the development and introduction of new medicinal technologies. To address this issue, various means of efferent therapy are used, among which a large role is given to sorption methods. One of the modern areas of efferent therapy is the oral administration of sorbents, the main part of which are medicines in granule, tablet and capsule form [1-2]. Having numerous beneficial properties inherent to these dosage forms, they are not suitable for use by patients who are unconscious or have swallowing problems. An alternative to solid dosage forms, in these kinds of cases, is using enterosorbents in paste form, because the latter, due to its soft consistency and ability to flow, can easily be introduced into the patient's body by means of a probe [3-4]. But in the Ukrainian pharmaceutical market the range of such medicines has only several positions, and therefore their development is relevant [5].

Among the promising sources for the creation of medicines with enterosorbitive activity in paste form the natural zeolite should be noted. Recent researches have shown that, due to its unique crystalline structure, zeolite is a good detoxifier that does not interact directly with vitamins, amino acids, proteins and other complex organic compounds and does not prevent the normal absorption of organic matter [6-7].

It is known from literature that technological aspects as well as composition of the dosage form predetermine the activity of the final product and require a rigorous and well-founded study at the preclinical stage of the medicine development [3]. Thus, the aim of our study was to investigate the influence of a gel former (thickener) type on the sorption kinetics of long-living  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  radionuclides and  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  heavy metals by natural zeolite paste from an aqueous solution in vitro.

**Materials and methods**

As objects for the study we used experimental pastes containing 25% natural zeolite each and different gel formers: 7% silicon dioxide (sample №1), 3% apple pectin (sample №2) and 0.5% sodium alginate (sample №3) [8-9]. For sorption, we used solutions of chemically pure salts  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and  $\text{Pb}(\text{NO}_3)_2$  at initial

concentrations ( $C_0$ ) of 7.25 mg/l and 6.74 mg/l respectively. The sorption capacity of heavy metals on enterosorbents was investigated by a limited volume method (static sorption) at pH = 2 and pH = 6 and at a temperature of 37°C. Under these conditions, sorbents (0.1 g) were actively mixed with 10 ml of solutions to achieve 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 by the use of atomic absorption spectrophotometer C-115 PCS. Measurement of the analytical signal was carried out in an acetylene-air flame (a wavelength  $\lambda = 283.3$  nm, a width of the monochromator slit - 0.4 nm, a flux of a lamp - 3 mA). The concentration of mercury was determined by the flame atomization method with the help of mercury device PR-115. (a wavelength  $\lambda = 253.7$  nm, a width of the monochromator gap - 0.1 nm, flux of the lamp - 5 mA). The sorption capacity radionuclides on samples also was studied by the static sorption method at 37°C and pH values 2.0, 5.5 and 8.0.  $^{90}\text{Sr}$  ( $1.8 \times 10^7$  Bq/dm<sup>3</sup>) and  $^{137}\text{Cs}$  ( $3.2 \times 10^7$  Bq/dm<sup>3</sup>) radionuclide solutions without carriers were used. 0.1 g of absorbents were mixed with 10 ml of solutions, containing  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  radionuclides, prior to achieve sorption equilibrium. The initial ( $I_0$ ) and equilibrium ( $I_{eq.}$ ) radioactivity were measured by a radiometer  $\alpha$ - $\beta$ -automaton NRR-610 "Tesla". The statistical error of experiments did not exceed 5%.

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

After established equilibrium in the solution-sorbent system, we determined the equilibrium concentration of metal ions ( $C_{eq.}$ ) and calculated the equilibrium capacity of sorbents ( $A_{eq.}$ , mg/g), the coefficient of sorption ( $K_s, \%$ ) and the coefficient of distribution ( $K_d$ , l/g) by the formulas:

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

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

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

where  $C_0$ ,  $C_{eq.}$  – an initial and an equilibrium concentration of solution, mg/l;  $V$  – a total volume of solution, l;  $m$  – a mass of sorbent, g.

For the quantitative characterization of the interaction between sorbents and radionuclides, the  $K_s$

and  $K_d$  indices were also calculated by formulas 2 and 3, in which the values of the initial ( $I_0$ , imp/s) and equilibrium ( $I_{eq}$ , imp/s) radioactivity were used instead of the concentration values.

### Results and discussion

Analysing obtained sorption kinetic curves, we can conclude that the process of sorption exchange includes two main stages – fast and slow. The first stage is responsible for the saturation of microcrystals by the

metal ions on the surface of the sorbent, which takes place in a rather short period of time. The second stage, which corresponds to a certain "straightening", indicates the complete saturation of sorbent surface by the metal ions and the subsequent slow diffusion ions inside the sorbent. For the most of the investigated objects, the achievement of the adsorption equilibrium in the heterophasic system took place within first 30-60 minutes of the experiment, which is evident from the character of the diagram lines (Fig. 1-2).

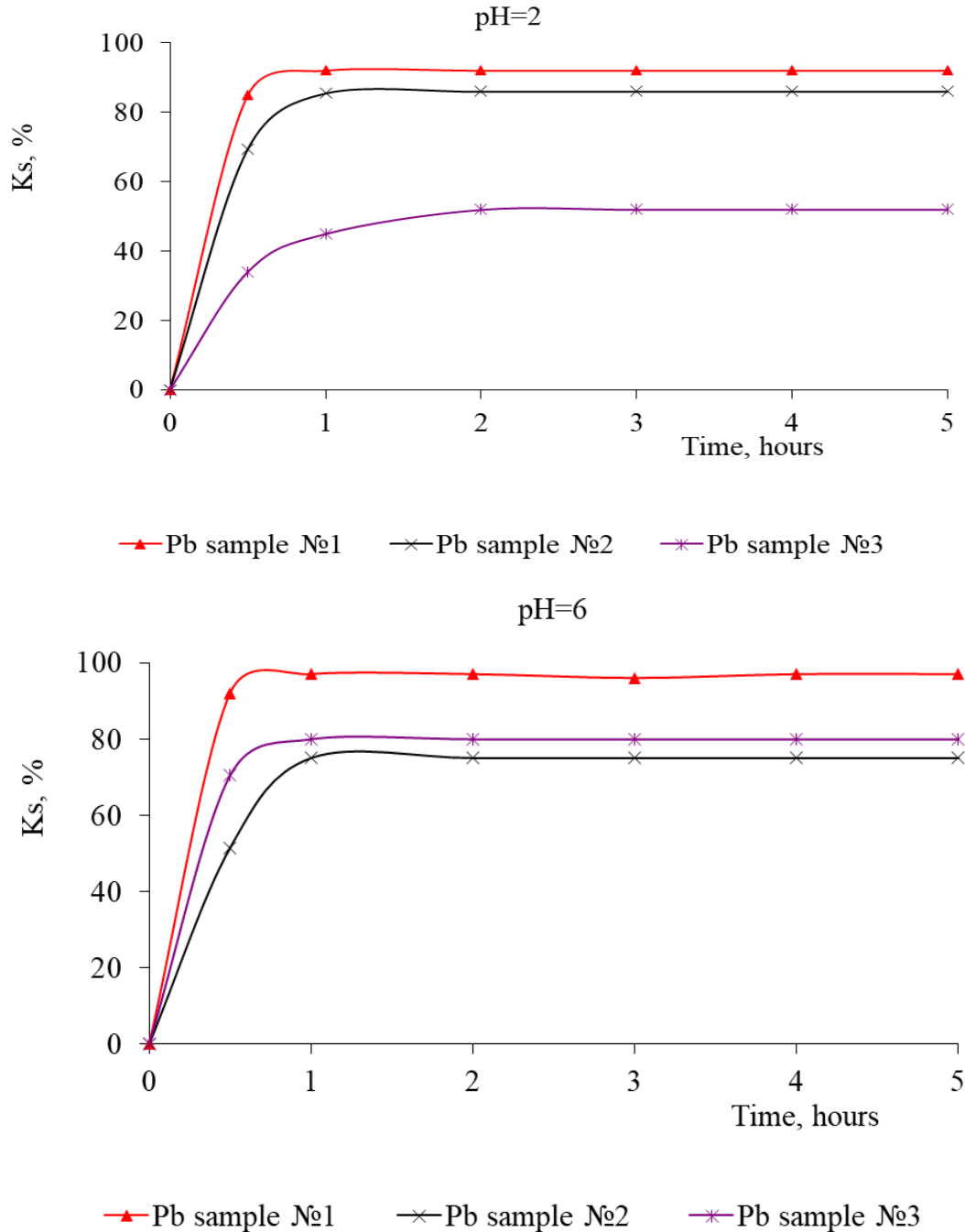
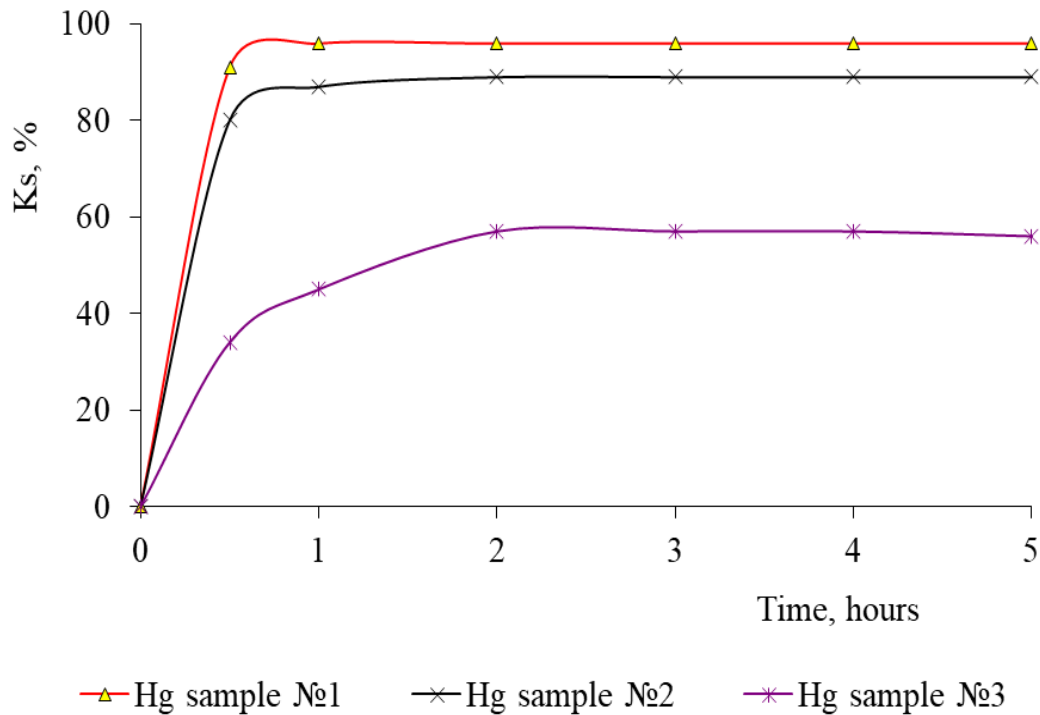


Fig. 1. Kinetics of sorption of lead ions at different pH values



**Fig. 2. Kinetics of sorption of mercury ions at pH = 2.0**

According to the obtained data (Table 1), the sorption activity of samples against the heavy metals ( $Hg^{2+}$  and  $Pb^{2+}$ ) varies widely and depends on a number of factors, such as the type of gel formers, pH value, nature and physico-chemical properties of ions.

Among the explored experimental samples of pastes, the greatest activity against all metals showed the composition of the paste containing silicon dioxide as a thickener. The sorption coefficient for lead and mercury ions was 93.2-99% and 95.8% respectively. The obtained values of the  $K_d$  and  $A_{eq}$  at different pH showed (Table 1) that the sorptive ability against heavy metal ions

increases with increasing pH values for compositions with silicon dioxide and sodium alginate, and decreases for samples containing apple pectin. This indicates that the main mechanism of sorption is ion exchange. However, the ion exchange mechanism is not unique. The value of sorption is also affected by the presence of auxiliary substances that contain OH-groups (silicon dioxide, pectinates, alginates), in which the formation of chelates with metal ions occurs.

**Table 1. Sorption characteristics of heavy metals on samples**

Number of sample	The initial concentration ( $C_0$ ) mg/l	The equilibrium concentration ( $C_{eq}$ ), mg/l	The equilibrium capacity of sorbents ( $A_{eq}$ ), mg/g	The coefficient of sorption ( $K_s$ ), %	The distribution coefficient ( $K_d$ ), l/g
$Pb^{2+}$ , pH=2,0					
1	6,74	0,46	0,628	93,2	1.37
2	6,74	0,93	0,581	86,2	0.62
3	6,74	3,25	0,349	51,7	0.11
$Pb^{2+}$ , pH=6,0					
1	6,74	0,07	0,667	99	9,52
2	6,74	1,61	0,513	76	0,51
3	6,74	1,35	0,539	80	0,40
$Hg^{2+}$ , pH=2,0					
1	7.25	0.30	0.695	95,8	2.32
2	7,25	0.80	0.645	88,9	0,81
3	7,25	3.19	0.406	56,0	0.13

The  $K_d$  value of studied samples against heavy metals, which are given in Table 1, allows us to compare the sorption and selective properties of samples and arrange the metal ions in order of decreasing their relative affinity to sorbents as  $Hg^{2+} > Pb^{2+}$ . This difference in selectivity can be explained by the difference in an electronic configuration, as well as by a radius and a value of hydration energy of ions (Table 2).

The study of the sorption activity of pastes against radionuclides showed that their sorption ability also depends on the pH value of the solution, the nature and physico-chemical properties of the ions. And the sorption activity changes in character and intensity with replacing the thickener in the experimental samples (Fig. 3-5; Table 3).

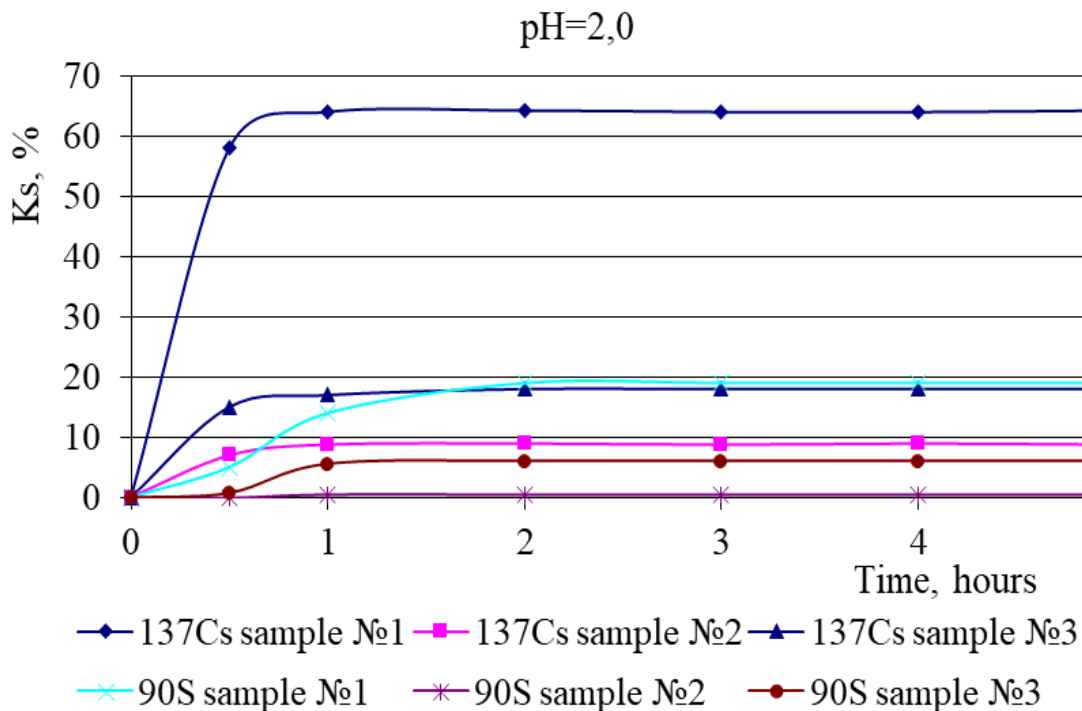
**Table 2. The ionic radius [10], the electronic configuration and the thermodynamic characteristics of ions  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cs^{+}$  and  $Sr^{2+}$  [11]**

Ion	The electronic configuration	The ionic radius, nm	$-\Delta H^0_{hydr.}$ , kJ/mol	$-\Delta S^0_{hydr.}$ , kJ/(mol · K)	$-\Delta G^0_{hydr.}$ , 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

The analysis of radionuclide sorption kinetic curves at different pH values (Fig. 3-5) showed that the equilibrium in radionuclide-sorbent systems interaction appears within first 60 minutes of the experiments. Significant influence on the sorption of radionuclides gives the pH value of the solution: the minimum sorption capacity is observed in acidic medium at  $pH = 2,0$  ( $K_s=9-64\%$ ), and it sharply increases with pH increasing and becomes maximal at  $pH = 5.5$  ( $K_s=54-91\%$ ) for all studied compositions, but decreases with further pH increasing. The dependents of radionuclides sorption from pH value indicates that they are in the ionic state in the solution. The complex nature of this dependence may be explained by the influence of the solution acidity on the

physico-chemical properties and the structure of the sorbents, as well as on their sorption-active centers [12]. In this connection, it can be assumed that under other equal conditions, the exchange capacity of the studied sorbents in the stomach environment will be minimal, and will grow in the moderately alkaline environment of different parts of the intestine.

The obtained  $K_d$  and  $K_s$  (Table 3) showed that samples better absorb  $^{137}Cs$  radionuclide at all pH values. The sorption characteristics of  $^{90}Sr$  are much lower, but they increase sharply with increasing pH values. The highest affinity with respect to  $^{137}Cs$  and  $^{90}Sr$  radionuclides was demonstrated by samples with silicon dioxide as a gel former.



**Fig. 3. Sorption kinetic curves of  $^{90}Sr$  and  $^{137}Cs$  radionuclides on pastes at  $pH = 2.0$**

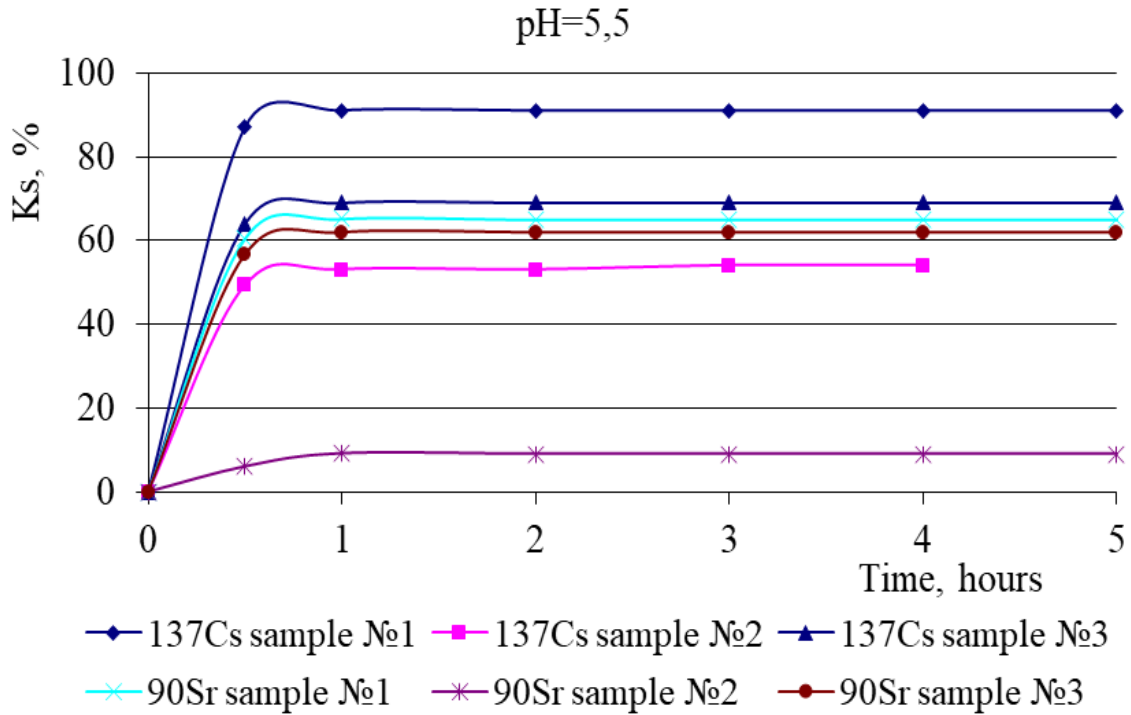


Fig. 4. Sorption kinetic curves of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  radionuclides on pastes at pH = 5.5.

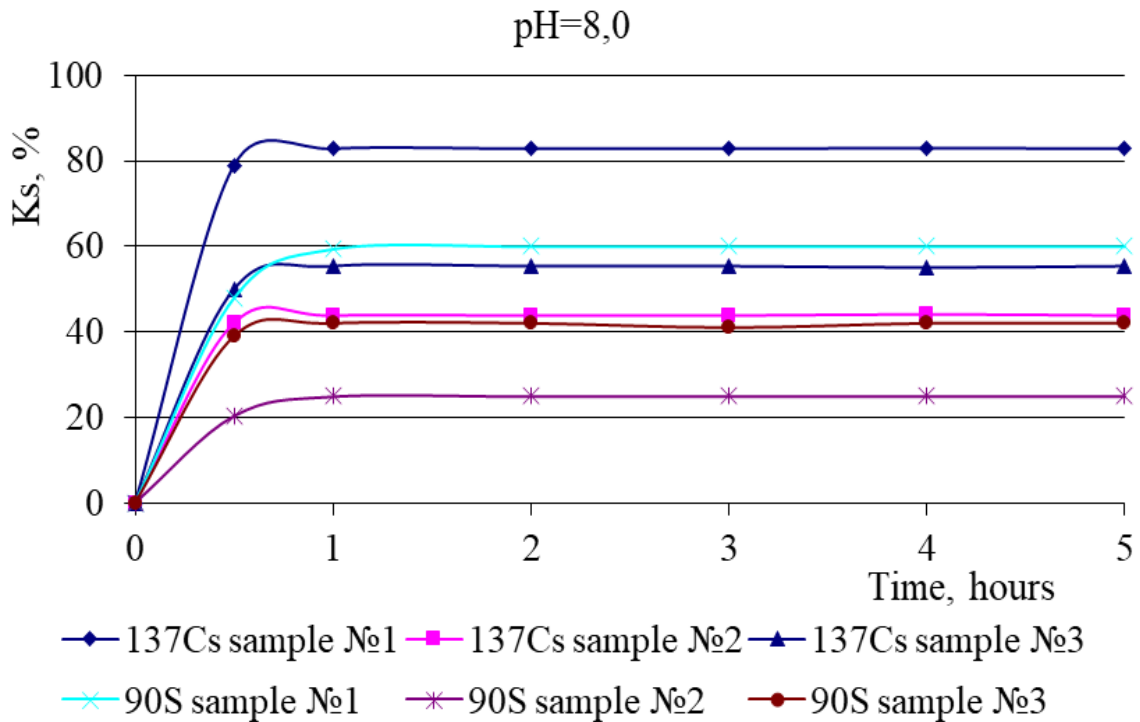


Fig. 5. Sorption kinetic curves of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  radionuclides on pastes at pH=8,0.

As noted above, the sorption capacity of ions strongly depends on the radius of the ion and the hydration energy of ions. Ions of equal energy but greater radius exhibit greater sorption ability as they are more strongly polarized and better attracted to the charged surface of the sorbent, and ions of smaller radius are more prone to hydration and the formation of a hydrated shell that reduces such electrostatic interactions. The radius of the ion of cesium is 0.167 nm, and the radius of the

strontium ion is 0.127 nm, therefore, the sorption capacity of the sorbents with respect to the cesium ions should be higher than with respect to the strontium ions, which is confirmed by experimental data (Table 3). Thus, based on the obtained results, silicon dioxide may be recommended as the best gelling agent for the preparation of medicines with natural zeolite (clinoptilolite) in the form of a paste for the removal of heavy metals and radionuclides from the human body.

**Table 3. Sorption characteristics of radionuclides on pastes**

Number of sample	<sup>137</sup> Cs			<sup>90</sup> Sr		
	pH=2	pH=5.5	pH=8	pH=2	pH=5,5	pH=8
	K <sub>d</sub> , l/g					
1	0,181	0,966	0,483	0,037	0,287	0,146
2	0,009	0,114	0,078	0,187	0,010	0,024
3	0,022	0,217	0,123	0,146	0,211	0,066
K <sub>s</sub> , %						
1	64	91	83	19	65	60
2	9	54	44	0,5	9	25
3	18	69	55	6	62	40

**Conclusions**

The influence of the type of gel former (thickener) on sorption kinetics of long-living <sup>90</sup>Sr and <sup>137</sup>Cs radionuclides as well as Pb<sup>2+</sup> and Hg<sup>2+</sup> heavy metals by natural zeolite paste (clinoptilolite) from an aqueous solution in vitro was studied. It was found that the studied sorbents have a sufficient absorption capacity for heavy metals and radionuclides at different pH values, but the best results have been demonstrated by samples containing silicon dioxide. The obtained results will be taken into account in the further development of medicines with natural zeolite (clinoptilolite) in the form of oral paste.

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**STUDY OF THE INFLUENCE OF A GEL FORMER (THICKENER) TYPE ON THE SORPTION KINETIC OF LONG-LIVING RADIONUCLIDES AND HEAVY METALS BY NATURAL ZEOLITE PASTE FROM AN AQUEOUS SOLUTION IN VITRO**

**Rybachuk V.D., Krasnopyorova A.P., Yuhno G.D.**

**Introduction.** The deterioration of the population health, due to the chemicalization of many aspects of life, requires the development and introduction of new healing technologies. One of the modern areas of efferent therapy is the oral administration of sorbents. An alternative to solid dosage forms, in some acute cases, is using enterosorbents in the form of paste, but in the Ukrainian pharmaceutical market, the range of such medicines has only several positions. The promising sources for the creation of such medicines is the natural zeolite. The aim of our study was to investigate the influence of a gel former (thickener) type on the sorption kinetics of long-living <sup>90</sup>Sr and <sup>137</sup>Cs radionuclides and Pb<sup>2+</sup> and Hg<sup>2+</sup> heavy metals by natural zeolite paste from an aqueous solution in vitro. **Materials and methods.** As objects for the study we used experimental pastes containing 25% natural zeolite each and different gel formers: 7% silicon dioxide, 3% apple pectin and 0.5% sodium alginate. As sorption medium, we used solutions 7.25 mg/l Hg(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O and 6.74 mg/l Pb(NO<sub>3</sub>)<sub>2</sub> and radionuclide solutions <sup>90</sup>Sr (1.8 × 10<sup>7</sup> Bq/dm<sup>3</sup>) and <sup>137</sup>Cs (3.2 × 10<sup>7</sup> Bq/dm<sup>3</sup>). The sorption capacity for heavy metals was investigated by a limited volume method at pH = 2 and pH = 6. The concentration of lead was determined by atomic absorption spectroscopy (atomic absorption spectrophotometer C-115 PCS) in a flame of acetylene-air (λ = 283.3 nm). The concentration of mercury was determined by the flame atomization method using mercury device PR-115 (λ = 253.7 nm). The sorption

capacity of the samples against radionuclides was studied by the static sorption method at pH values 2.0, 5.5 and 8.0. The radioactivity were measured by a  $\alpha$ - $\beta$ -automaton NRR-610 "Tesla" radiometer. Concentration of ions and radioactivity of solutions were controlled after 0.5, 1, 2, 3, 4 and 5 hours of experiment. The equilibrium capacity of sorbents coefficient ( $A_{eq}$ , mg/g), the coefficient of sorption ( $K_s$ , %) and the coefficient of distribution of ( $K_d$ , l/g) were calculated for evaluation the process. **Results and discussion.** The process of sorption includes two main stages – fast and slow. The first stage is responsible for the process of saturation of microcrystals by ions on the surface of the sorbent. The second stage, which indicates the complete saturation of sorbent surface by the ions with the subsequent slow diffusion ions inside the sorbent. For most of the investigated objects, the achievement of the adsorption equilibrium in the heterophasic system took place within first 30-60 minutes of the experiment. The sorption activity of samples against heavy metals and radionuclides varied widely and depended on a number of factors, such as the type of gel formers, pH of the solution, nature and physico-chemical properties of the ions (hydration energies, charge and radius of the ions). Significant influence on the sorption gave the pH value of the solutions. The complex nature of this dependence we explain by the influence of the acidity of the solution on the physico-chemical properties and the structure of the sorbents, as well as on their sorption-active centres. In this connection, it can be assumed that under other equal conditions, the exchange capacity of the studied sorbents in the stomach environment will be minimal, and will grow in the moderately alkaline environment of different parts of the intestine. The  $K_d$  value of studied samples against heavy metals allowed us to compare the sorption and selective properties of samples and arrange the metal ions in order of decreasing their relative affinity to sorbents as  $Hg^{2+} > Pb^{2+}$ . This difference in selectivity can be explained by the difference in an electronic configuration, as well as by a radius and a value of hydration energy of ions. The obtained  $K_d$  and  $K_s$  of radionuclides showed that samples better absorb  $^{137}Cs$  radionuclide at all pH values. The sorption characteristics of  $^{90}Sr$  are much lower, but they increase sharply with increasing pH values. The highest affinity with respect to  $^{137}Cs$  and  $^{90}Sr$  radionuclides was demonstrated by samples with silicon dioxide as a gel former. The greatest activity against all metals also showed the composition of the paste containing silicon dioxide as a gel former. Its sorption coefficient for lead and mercury ions were 93.2-99% and 95.8% respectively, and for  $^{90}Sr$  and  $^{137}Cs$  radionuclides were 19-65% and 64-91% respectively. **Conclusions.** The influence of the type of gel formers (thickeners) on the sorption kinetics of long-living radionuclides and heavy metals by natural zeolite paste (clinoptilolite) from an aqueous solution in vitro was studied. The best results samples with silicon dioxide have demonstrated. The obtained results will be taken into account in the further development of medicines with natural zeolite (clinoptilolite) in the paste form.

**Keywords:** natural zeolite, paste, sorption, radionuclides, heavy metals, gelling agents