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USE OF MATHEMATICAL MODELING FOR A COMPARATIVE ASSESSMENT OF THE SORPTION PROPERTIES OF NATURAL AND SYNTHETIC ZEOLITES TO COBALT

Comparison of the sorption capacity of natural zeolite (clinoptilolite) and synthetic zeolites (NaX and NaA) in relation to cobalt ions is done under dynamic conditions. The sorption capacity of zeolites in relation to cobalt was: for clinoptilolite - 59.00 mg/g; for zeolite NaX - 87.03 mg/g; for zeolite NaA - 73.00 mg/g. Based on the data obtained, mathematical modeling of sorption isotherms was carried out using the Langmuir equation, Chebyshev criterion, and the criterion of the least-squares method. The performed correlation of the factual and model results indicates that the considered models adequately reflect the sorption processes taking place in zeolites. The results obtained make it possible to use the considered models for prognostication of the behavior of zeolites with respect to cobalt.

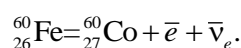
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1. Introduction

The development of technogenic modern society leads to an increasing influence of the products of technogenic production on the human body. These products include unstable isotopes, whose share in the environment has increased with the development of nuclear power. Dangerous isotopes include trace elements that are included in the human biological cycle. The appearance of these microelements in the form of unstable isotopes has a significant effect on the human body, despite the presence of microelements in quantities allowable for the body.

Cobalt rightfully belongs to such trace elements. Cobalt is one of the important elements for normal human life, it is part of one of the most essential vitamins for humans - B12 (cobalamin). Cobalt is involved in the processes of blood formation, the normal functioning of the nervous system, liver, and the formation of enzymatic reactions of the body. The human body's need for cobalt is up to 0.015 mg per day. It has been established that an excess of cobalt is harmful to the human body. In nature, there is a stable isotope of cobalt-59 and 22 more isotopes of cobalt. One of the most dangerous is cobalt-60, which is formed during the explosion of thermonuclear or nuclear weapons.

Cobalt-60 can also be formed during the operation of nuclear power plants. This is due to the activation of elements of construction. Cobalt-60 is a daughter product of β -decay of ^{60}Fe nuclide



The half-life of cobalt-60 is 5.2 yrs.

Cobalt-60 is widely used in medicine for the diagnosis and treatment of cancer [1, 2]. The availability of medical equipment containing cobalt-60 has led to a number of tragedies in the world, resulting in human casualties (Turkey - 1998, Thailand - 2000, Mexico - 2013). According to IAEA data, 10 thousand therapeutic devices with cobalt-60 are used in the world [3, 4].

The study of sorption and desorption of cobalt is an actual issue for the development of modern science and energy [5 - 11].

Nowadays, the interest has increased in the use of modified natural zeolites (by dealumination, forced introduction of the one exchangeable ion) for the sorption of the cobalt [12]. The great interest is shown in synthetic zeolites that can efficiently adsorb ^{60}Co , which is present in solution in the form of Co^{2+} ions [13].

In the work that was published earlier, the main attention was paid to the determination of the sorption coefficient [14].

Considering that the sorption coefficient is a relative indicator, it is advisable to use exchange capacity for quantification of sorption properties of zeolites. The use of an exchange capacity allows us to carry out mathematical modeling of sorption processes based on the Langmuir equation.

Earlier, similar mathematical processing of sorption processes on zeolites for cesium was carried out [15], therefore this work is a continuation of studies of the sorption properties of zeolites for their effective use in nuclear power.

The purpose of these studies was the comparison of the sorption capacity of natural and synthetic zeolites (clinoptilolite and synthetic - NaX zeolite and

NaA zeolite) in relation to cobalt and the construction of mathematical models to characterize these sorption processes. As a result of the research, a comparison between the actual data and the data obtained by the mathematical model of Langmuir was done.

2. Methods and objects of research

2.1. Objects of research

During the research natural zeolite clinoptilolite ($(K_2Na_2Ca) \times Al_2Si_7O_{18} \times 6H_2O$) and synthetic zeolites (NaX, NaA) were used. The natural zeolite clinoptilolite (Sokyrnitsky deposit, Transcarpathian region, Ukraine) refers to high-silicon zeolites. Ukraine has a large clinoptilolite deposit. Synthetic zeolites NaX and NaA refer to low-silicon zeolites.

2.2. Dynamic sorption of cobalt

For determination, an aqueous solution of cobalt sulfate - $CoSO_4$ was used (stable isotope of cobalt ^{59}Co , solvent - distilled water). The concentration of $CoSO_4$ in the solution was 0.0004 g/ml. The volume of the solution for pumping through the plant was 500 ml. For modeling of dynamic conditions of sorption, installation [16] was used. The installation consists of: pump, sorption column with cartridge, reservoir, measuring tank. Dimensions of the sorption cartridge: diameter 8 mm, height 25 mm. The mass of zeolites placed in the sorption plant was 2.0 g.

This construction of the sorption facility was optimal for the use of sorbents with a particle size of 3 - 5 mm. The pump was located in front of the sorption column, as a result of which the liquid repeatedly passed through the sorbent. Determination of sorption abilities of zeolites in dynamic conditions was carried out as a result of repeated circulation of a solution of cobalt sulfate by a sorption facility. Sampling for the determination of sorption equilibrium was conducted periodically. 80 cycles of sorption were held for the evaluation of completeness of the zeolites sorption processes. The duration of one cycle of sorption is 3 minutes [16].

The determinations of dynamic sorption were carried out at a constant temperature $t = 24$ °C.

2.3. Analytical part.

Quantitative determination of cobalt

The analytical part of the work was carried out on the analytical nuclear-physical complex "Sokol". The targets from a dry residue of a solution on a carbon substrate were used for measurements. Activation of cobalt was carried out by a beam of protons with energy $E_p \approx 1600$ keV, average current $I_r \approx 150$ nA. Registration of the exciting characteris-

tic X-ray emission of K-series of cobalt atoms was carried out using a Si-pin detector with a resolution of 155 eV at line 6.4 keV. The detector was placed at a distance of 7 cm from the target, at an angle of 135° to the proton beam. The Si-pin detector was equipped with a collimator Ø2.5 mm and a polyvinylchloride absorber 150 µm thick. The relative error of the measurements was 3 % [14 - 17].

Based on the results obtained, a quantitative assessment was carried out.

As a quantitative characteristic of the interaction of sorbents with cobalt, the sorption capacity of zeolites (q_c , mg/g) was used

$$q_c = \frac{(C_0 - C_p) \cdot V}{m}, \quad (1)$$

where C_0 and C_p are the initial and equilibrium concentrations of the solution, mg/ml; V - the volume of solution passed through the installation, ml; m - the mass of sorbent, g.

3. Results and discussion

The determination of the equilibrium concentration was carried out experimentally during the sorption process. The equilibrium concentration of cobalt for zeolites is presented in Table 1.

Table 1. Values of the equilibrium concentration of cobalt for zeolites in dynamic conditions

Sorption cycle	The equilibrium concentration of cobalt, mg/l		
	Clinoptilolite	Zeolite NaX	Zeolite NaA
20	0.10	0.41	0.07
60	0.30	1.23	0.47
80	0.40	1.64	0.50

The obtained values of the sorption capacity of zeolites to cobalt depending on the sorption cycle are presented in Table 2.

Table 2. Sorption capacity of zeolites in relation to cobalt in dynamic conditions

Sorption cycle	q_c , mg/g		
	Clinoptilolite	Zeolite NaX	Zeolite NaA
20	26.0 ± 1.3	60.1 ± 3.0	18.0 ± 0.9
60	55.0 ± 2.8	86.8 ± 4.3	69.0 ± 3.5
80	59.0 ± 3.0	87.0 ± 4.4	73.0 ± 3.7

The sorption capacity of synthetic zeolites is greater than that of the clinoptilolite, this is due to the structural features of zeolites. Synthetic zeolites belong to the group of low-silicon zeolites with a high content of Al^+ ions, which significantly increases the number of exchange centers (Zeolite

NaX (Si/Al) - 1.00 - 1.50; Zeolite NaA (Si/Al) - 0.70 - 1.20). The clinoptilolite belongs to high-silica zeolites (Si/Al - 4.25 - 5.25), which significantly increases the strength of the crystal structure, but reduces the number of exchange centers.

When conducting a comparative analysis of the sorption capacity of zeolites in relation to cobalt, the actual results were compared with the data of mathematical models. Adsorption is a process of spontaneous redistribution of system components between the surface layer of the sorbent and the liquid phase. The adsorption process is expressed by an isotherm characterized by the functional dependence of the amount of a substance absorbed by a surface from the pressure or concentration of this substance in another phase at a constant temperature. There is no unified theory describing all types of adsorption processes. Therefore, considering the sorption properties of zeolites and their interaction with the liquid phase, the Langmuir isotherm most reliably simulates the adsorption processes. The Langmuir isotherm model is applied to monolayer adsorption because this model assumes that adsorbate ions are uniformly distributed between adsorption centers. The Langmuir model is based on the following principles:

adsorption is localized in certain centers and is caused by chemical forces;

adsorption does not occur on the entire surface of the adsorbent, but in certain active centers that are characterized by the presence of free valences;

each active center is only able to interact with one molecule of adsorbate and on the surface of the adsorbent, only one layer of adsorbed molecules can be formed [18, 19].

The Langmuir model is described by the equation:

$$q_e = \frac{K_l \cdot q_m \cdot C_e}{1 + K_l \cdot C_e}, \tag{2}$$

where q_e is the equilibrium amount of adsorption, mg/g; C_e - equilibrium concentration in solution, mg/l; K_l - Langmuir constant, l/mg; q_m is the maximum adsorption capacity, mg/g.

To evaluate the reliability of the obtained results, mathematical modeling based on the principle of best approximation was used. The mathematical modeling allows determining the criteria for agreement. The most common are the following criteria: least square method; Chebyshev's criterion.

The criterion of the method of least squares involves minimizing the sum of error squares at the node points

$$J = \sum_{i=1}^n (F(x_i) - y_i)^2, \tag{3}$$

where y_i is the value of the initial function at the point x_i (tabular value); $F(x_i)$ is the value of the approximating function.

The criterion of the method of least squares allows one to obtain a smoothing of the curve, provides an opportunity to separate data, which do not require additional information about interference.

The minimal Chebyshev criterion is determined by the formula

$$J = \max |F(x_i) - y_i|, \tag{4}$$

where y_i is the value of the initial function at the point x_i (tabular value); $F(x_i)$ is the value of the approximating function.

The Chebyshev criterion reduces the extreme maximum error. The Chebyshev criterion is used when it is necessary to avoid large errors when approximating.

The calculation of the constants using the Langmuir equation, the Chebyshev criterion, and the least-squares test was carried out using the computer program "Langmuir", which is freely available.

The results obtained for all zeolites considered in the work are presented below (Tables 3 - 5, Figs. 1 - 3).

Table 3. Sorption capacity of clinoptilolite in relation to the cobalt (mg/g) (according to the "Langmuir" program)

Actual sorption capacity	Sorption capacity, calculated from the Langmuir isotherm	Sorption capacity, calculated by the Chebyshev criterion	Sorption capacity, calculated by the method of least squares
26.0 ± 1.3	26.00	26.00	26.80
55.0 ± 2.8	53.00	52.90	52.80
59.0 ± 3.0	61.20	61.00	60.50

Table 4. Sorption capacity of NaX zeolite in relation to the cobalt (mg/g) (according to the "Langmuir" program)

Actual sorption capacity	Sorption capacity, calculated from the Langmuir isotherm	Sorption capacity, calculated by the Chebyshev criterion	Sorption capacity, calculated by the method of least squares
60.1 ± 3.0	60.05	60.05	60.27
86.8 ± 4.3	84.68	84.57	84.46
87.0 ± 4.4	89.01	88.90	88.68

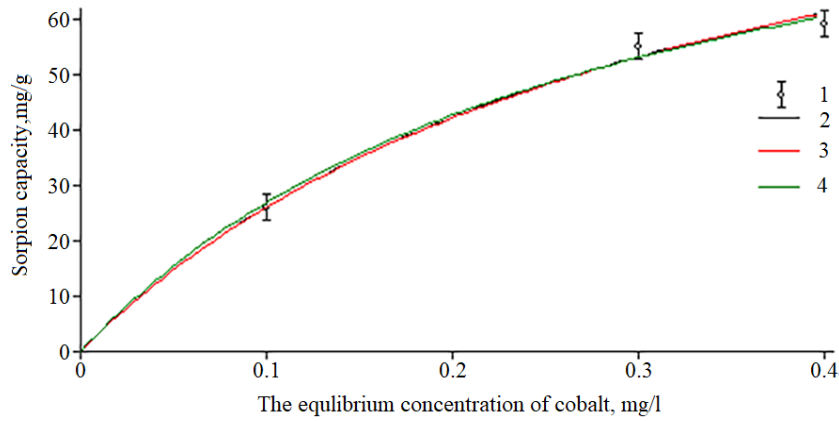


Fig. 1. Isotherms of cobalt sorption by clinoptilolite: 1 - actual results with allowable deviation interval; 2 - isotherm by the Langmuir curve; 3 - isotherm constructed according to the Chebyshev criterion; 4 - isotherm constructed by the method of least squares. (See color Figure on the journal website.)

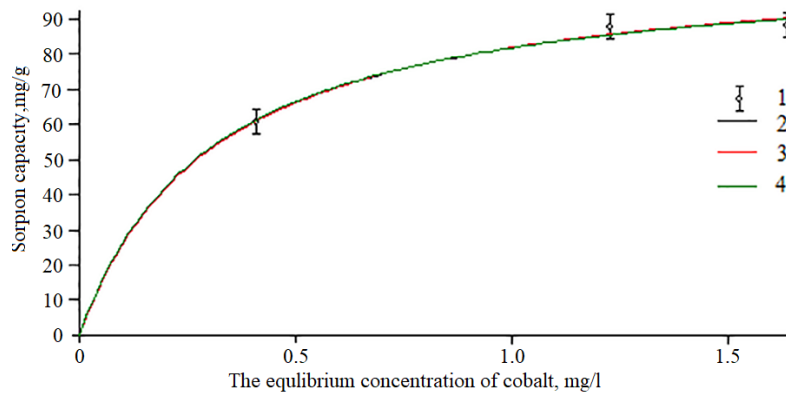


Fig. 2. Isotherms of cobalt sorption by zeolite NaX: 1 - actual results with allowable deviation interval; 2 - isotherm by the Langmuir curve; 3 - isotherm constructed according to the Chebyshev criterion; 4 - isotherm constructed by the method of least squares. (See color Figure on the journal website.)

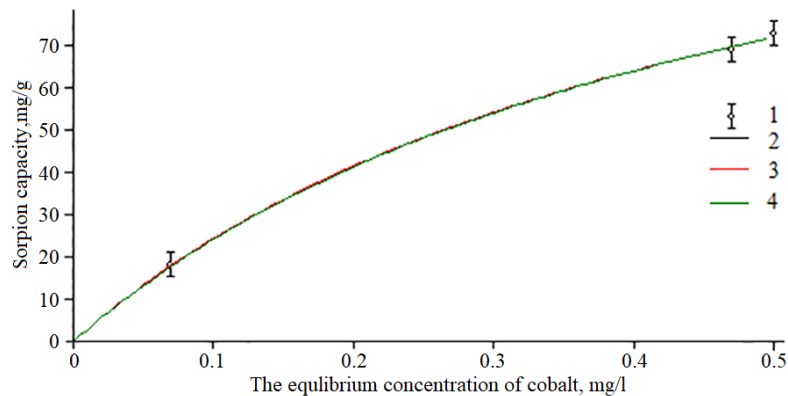


Fig. 3. Isotherms of cobalt sorption by zeolite NaA: 1 - actual results with allowable deviation interval; 2 - isotherm by the Langmuir curve; 3 - isotherm constructed according to the Chebyshev criterion; 4 - isotherm constructed by the method of least squares. (See color Figure on the journal website.)

The obtained results based on the Langmuir equation, and also with the Chebyshev criterion and the least-squares test, can be compared with the experimentally obtained results and the determination of the linear correlation coefficient for each of the sorbents. The correlation coefficient makes it possible to determine the linear relationship in the pair represented by the actual results and the calculated data obtained. The correlation coefficient was calculated by the formula

$$R_{X,Y} = \frac{\sum_{i=1}^m (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^m (X_i - \bar{X})^2 \sum_{i=1}^m (Y_i - \bar{Y})^2}}, \quad (5)$$

where \bar{X} , \bar{Y} - sample mean values; X_m - results of actual zeolite sorption and Y_m - model values of zeolite sorption.

Table 5. Sorption capacity of NaA zeolite in relation to the cobalt (mg/g) (according to the “Langmuir” program)

Actual sorption capacity	Sorption capacity, calculated from the Langmuir isotherm	Sorption capacity, calculated by the Chebyshev criterion	Sorption capacity, calculated by the method of least squares
18.0 ± 0.9	18.00	18.00	17.98
69.0 ± 3.5	70.40	70.40	70.40
73.0 ± 3.7	72.70	72.70	72.70

When considering the correlation coefficient, it is necessary to take into account that the closer the value of the coefficient to 1, then the greater the functional connections in the considered pair of actual and model results. If the value of the coefficient is closer to 0, then the connection is weak or absent. The results of determining the correlation coefficient are presented in Table 6. For clinoptilolite, the correlation coefficient varies from 0.9936 to 0.9941, for NaX zeolite - from 0.9914 to 0.9916, for NaA zeolite - 0.9996.

Table 6. Determination of the correlation coefficient for the considered sorbents of the actual results of sorption of cobalt and mathematical models

Mathematical models	Zeolites		
	Clinoptilolite	NaX	NaA
Langmuir isotherm	0.9936	0.9915	0.9996
Chebyshev criterion	0.9938	0.9914	0.9996
The criterion of the method of least squares	0.9941	0.9916	0.9996

The considered mathematical models make it possible to adequately assess the interaction of cobalt ions with clinoptilolite and synthetic zeolites. Comparing the results of modeling the sorption processes of cobalt by zeolites with the previously published results of modeling the sorption of cesium by zeolites [15], the following conclusions can be drawn. Mathematical models showed great agreement with the actual results despite the significant difference in the characteristics of isotopes which were sorbed (the radius of the atom, the charge of the ion of the isotope, the ionization energy). This makes it possible to construct mathematical models for describing sorption processes on zeolites of the natural and synthetic groups in the future.

4. Conclusions

When comparing the sorption capacities of clinoptilolite and synthetic zeolites (NaX zeolite and NaA zeolite) in relation to cobalt in dynamic conditions, it has been established that the highest sorption capacity in relation to cobalt is shown by synthetic zeolites (zeolite NaX $q_c = 87.03$ mg/g; zeolite NaA $q_c = 73.00$ mg/g), which exceeds the sorption capacity of clinoptilolite ($q_c = 59.00$ mg/g).

Using the “Langmuir” program of simulating cobalt sorption isotherms by zeolites in accordance with the Langmuir equation, the Chebyshev criterion and the least-squares test confirmed the experimental values of the sorption capacity. The correlation of the results indicates the correct choice of mathematical models.

The results obtained confirm that the passage of sorption processes on zeolites is described by the Langmuir equation. It can be concluded that the considered mathematical models can be suitable for describing the sorption of ions with different charges on natural and synthetic zeolites, comparing with the results of studies that were carried out earlier.

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ВИКОРИСТАННЯ МАТЕМАТИЧНОГО МОДЕЛЮВАННЯ ДЛЯ ПОРІВНЯЛЬНОЇ ОЦІНКИ СОРБЦІЙНИХ ВЛАСТИВОСТЕЙ ПРИРОДНОГО І СИНТЕТИЧНИХ ЦЕОЛІТІВ ДО КОБАЛЬТУ

Наведено порівняння сорбційної ємкості природного цеоліту (кліноптілоліту) і синтетичних цеолітів (NaX і NaA) по відношенню до іонів кобальту в динамічних умовах. На підставі отриманих даних було проведено математичне моделювання сорбційних ізотерм з використанням рівняння Ленгмюра, критерію Чебишева і критерію методу найменших квадратів. Проведена кореляція фактичних і модельних результатів свідчить про те, що розглянуті моделі адекватно відображають сорбційні процеси, що проходять у цеолітах, що дає змогу використовувати розглянуті моделі для прогнозування поведінки цеолітів щодо кобальту.

Ключові слова: кобальт, природний та синтетичний цеоліти, сорбція, математичне моделювання.

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