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EFFECT OF STRUCTURE-FORMING ADDITIVES ON ION-EXCHANGE PROPERTIES OF FERROCYANIDE-ALUMINOSILICATE SORBENTS

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The removal of radioactive cesium from aqueous solutions using clinoptilolite modified by various modifiers (ferrocyanides Ni, Cu, Fe and H_3BO_3) was carried out. The influence of chemical composition of solution, concentration of components in solution and ratio of solution volume and amount of adsorbent on the sorption process was studied. We showed high selectivity towards 137Cs (Kd = 4.38×103 – 3.1×104 ml/g). The mechanism of increasing the selectivity with respect to 137Cs when using H_3BO_3 as a structure-forming additive was considered.

The use of radioactive materials for medical, scientific and industrial purposes produces large amounts of low- and intermediate-level radioactive waste. Cesium-137 is one of the most dangerous radionuclides because of its long half-life and high compound solubility. Natural aluminosilicate materials, particularly clinoptilolite, are widely used to remove cesium from radioactive solutions [1]. Clinoptilolite is a natural zeolite. It has a low cost and is readily available. The spent solutions have a complex composition. This imposes stringent requirements for the selectivity of adsorbents. Natural ion-exchange materials are characterized by sufficiently high exchange capacity, but low selectivity.

It is well known that ferrocyanides possess high selectivity towards cesium [2-8]. The aim of the present study was to increase the selectivity of clinoptilolite. For this purpose, various additives (nickel, iron, and copper ferrocyanides and boric acid as a structure-forming agent) were applied to the surface of clinoptilolite. The ability of the synthesized composite ion-exchangers to absorb cesium from active solutions was investigated depending on the chemical composition of the solutions, the concentration of the components in the solution, and the ratio between the solution volume and the sample amount.

All reagents used were brands pure for analysis. Clinoptilolite from the Sokirnitsa deposit (Ukraine) was chosen as a matrix. The chemical composition of clinoptilolite is as follows:
SiO_2 – 68.64%; Al_2O_3 – 11.50%; Fe_2O_3 – 1.57%; MgO – 0.89%; CaO – 2.38%; Na_2O – 0.79%; K_2O – 2.98%; H_2O – 4.12%; SiO_2/Al_2O_3 – 10.13%.

The clinoptilolite samples were crushed, ground, and sieved to a particle size in the range of 250-1000 μm. The samples were then converted to sodium form by shaking in 1 M sodium chloride solution for 24 hours, then filtered, washed with distilled water, and air dried.

Clinoptilolite modified with nickel, iron, and copper ferrocyanides was synthesized as follows. First, Na^+-clinoptilolite was converted to the Met^+-form ($Met^+ = Ni^{2+}, Fe^{3+}, Cu^{2+}$) by adding solutions of salts of the corresponding metals. After 2 hours of exposure, the mixture was filtered off and washed with distilled water. Then 0.1 M solution of $K_4[Fe(CN)_6]$ was added to clinoptilolite treated with the corresponding cation. Then samples were filtered, washed and dried for two days at room temperature.

Ferrocyanide-containing samples were synthesized in the presence of boric acid using structure-forming additives. The clinoptilolite, which was in Fe-, Cu-, or Ni-form, was treated with a 10% boric acid solution before the stage of treatment with potassium ferricyanide. Then the obtained samples were washed with water to remove BO_3^{3+} ions. Completeness of washing was checked by infrared spectroscopy by the absence of characteristic lines corresponding to borate ions (1200 cm^-).

The details of preparation of composite ion-exchangers based on clinoptilolite were described in previous works [5,6].

Adsorption of ^{137}Cs long-lived isotopes was performed under static conditions on model solutions containing calcium, magnesium, sodium and chlorine ions as salt background at their weight ratio of Na:Ca:Mg:Cl=1:5:5:25. The total content of background salt ions was 360 mg/l, which corresponds to the chemical composition of drinking water in Minsk (Belarus).

In experiments with radioactive solutions, 10 ml of a solution containing ^{137}Cs was added to batches of 0.1 g of test samples. The suspensions were shaken for 24 hours at 25 ºC. After separating the solid sample from the liquid phase, the activity of the solution was measured. The initial activity of ^{137}Cs in the solutions was 4.44-102 Bq l^{-1}. Activity of solutions before and after establishment of equilibrium was measured by means of multichannel radiometer RUS-91 equipped with spectrometric scintillation detectors. Activity of radionuclide ^{137}Cs was determined by measuring intensity of gamma radiation.

Cesium removal experiments were performed under dynamic conditions. ^{137}Cs. The experiments were carried out in a glass column with a diameter of 10 mm at a filtration rate of 8-10 column volumes per hour. The height and volume of the adsorbent layer were 60 - 65 mm and 5.5 - 6.0 cm^3, respectively.

According to the experimental values of the activity of the solution before and after passing through the sorbent, the purification factor (Koch.) and the degree of sorption (S, %) were determined.

The data presented in Fig. 1 and Table 1 show different effects of the modification on the ion-exchange properties of clinoptilolite. Thus, the exchange capacity (E.C.) for cesium ions of ferrocyanide samples synthesized in the absence of H_3BO_3 did not change significantly. We observed only a slight increase in its value for the sample containing iron ferrocyanide, which, at first sight, contradicts the literature data [7] indicating an increase in the exchange capacity of individual ferrocyanides in the series FCNi > FCu > FCFe. However, it should be taken into account that the E.C. of the individual ferrocyanides essentially depends on the method, the conditions of their production, and, as a consequence, on the crystal structure being formed.

The deposition of ferrocyanides on the external and internal surfaces of the aluminosilicate is accompanied, as in the case of adsorption of alkali metals on individual ferrocyanides [2], by the distortion of their crystal structure, especially under the conditions of the limited intracrystalline space of the zeolite. This circumstance determines to a greater extent the changes in the E.C. values for cesium of ferrocyanide-alumosilicate samples that we have established.

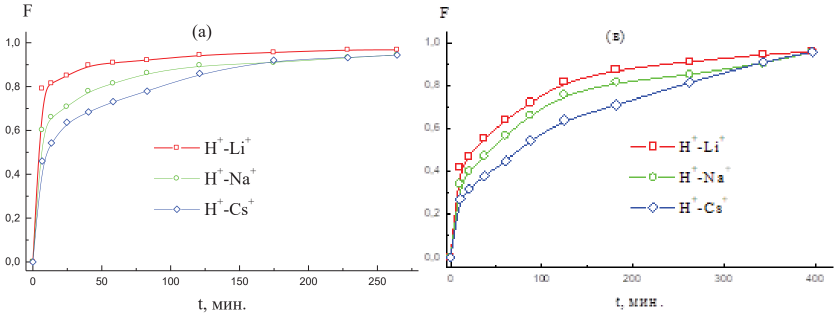

Fig.1. Kinetic curves of alkali metals exchange, where a - clinoptilolite modified with Cu ferricyanide, b - clinoptilolite modified with Cu ferricyanide and H_3BO_3, $F = Q_\tau/Q_\infty$ - absorption degree of incoming cation

Table 1. Ion-exchange characteristics with respect to cesium of ferricyanide-alumosilicate sorbents depending on the nature of ferricyanide and structure-forming additive

Sample + structure-forming additive	**S, %**	**K_{och}**	**K_d , mg/g**	**Exchange capacity, by Cs^+, mg-eq/g**
Initial clinoptilolite	97.9	46.9	4.59×10^3	1.51
Ferrocyanide Fe	98.1	54.1	5.0×10^3	1.6
Ferrocyanide Fe + H_3BO_3	98.8	84.4	8.3×10^3	1.49
Ferrocyanide Cu	99.2	142	1.4×10^4	1.51
Ferrocyanide Cu + H_3BO_3	99.7	309	3.1×10^4	1.46
Ferrocyanide Ni	98.8	88.0	8.7×10^3	1.55
Ferrocyanide Ni + H_3BO_3	99.4	162	1.6×10^4	1.33

The modification of clinoptilolite with ferricyanides in the presence of boric acid causes an increase in the selectivity of the samples, which is associated with the increasing manifestation of their ionocyte properties due to the features of the forming structure. In spite of the fact that the presence of BO33+ ions in the modified samples was not detected by X-ray diffraction analysis and IR spectroscopy (which testifies to the absence of their interaction with exchangeable zeolite cations and ferrocyanide anions), they nevertheless play the role of a structure-forming additive, which forms, after their removal in the synthesis process, intercrystalline cavities similar in size to hydrated cesium ions (rCs^+ = 3.1 Å и rBO_3^{3+} = 2.96 Å) preventing for steric reasons the adsorption of mineral background ions.

The influence of the steric factor on the process of alkali metal ions exchange can be confirmed by the kinetic curves of exchange on clinoptilolite modified with copper ferricyanide (Fig. 1), which was chosen as the object of study due to its highest selectivity to Cs as compared to the original zeolite. To quantify the exchange rate and determine its limiting stage, kinetic parameters of exchange were calculated. Comparison of the rate constants of the external diffusion process (R) with the exchange constant of the intradiffusion process (B) shows that at a given solution concentration the exchange rate of H -Li and H -Na is mainly determined by the intradiffusion process (Table 2), because R>>B. It should be noted that the values of the rates of the external and intra-diffusion processes, as well as the effective diffusion coefficient D' increase with decreasing counterion size. Consequently, the mobility of alkaline cations in the modified samples decreases, as for the original clinoptilolite (7), in the series Li > Na > Cs , which is the reverse of the selectivity series. From the kinetic curves of H -Li , H -Na, and H -Cs ion exchange on clinoptilolite modified with copper ferricyanide (Fig. 1) it is seen that up to 80%, 65%, and 55%, respectively, of the exchange capacity is realized by the external diffusion mechanism.

Table 2. Dependence of kinetic parameters of exchange of monovalent cations on clinoptilolite on the nature of structure-forming additive (t=^{0}C; fraction 1.5-2.5 mm; C_{MeOH} = 0.1 n)

Structure-forming additive	**Ex-change ions**	**External diffusion region**		**Intradiffusion region**	
		dQ/dτ, mg-eq/g c	**R, c-**	**D′, cm^2/c**	**B, c-**
Ferro-cyanide Cu	H+- Li+	0.003	8.04×10^{-3}	4.08×10^{-8}	1.0×10^{-5}
	H+-Na+	0.0028	6.11×10^{-4}	5.14×10^{-8}	1.27×10^{-5}
	H+-Cs+	0.041	3.43×10^{-4}	6.15×10^{-8}	1.52×10^{-5}
Ferro-cyanide Cu + H_3BO_3	H+- Li+	0.0017	5.16×10^{-3}	1.54×10^{-8}	3.79×10^{-6}
	H+-Na+	0.0018	3.50×10^{-4}	2.43×10^{-8}	6.00×10^{-6}
	H+-Cs+	0.0097	8.00×10^{-5}	5.04×10^{-8}	1.24×10^{-5}

For the samples modified by copper ferricyanide in the presence of boric acid (Fig.1, Table 2), a decrease in almost all kinetic parameters of ion exchange is observed. From the data of Fig.1 it is clear that in the case of H -Cs exchange by the fast external diffusion mechanism, only 30% of the exchange capacity is realized. The remaining 60-70% of the exchange capacity can be realized by the slow intradiffusion process. Thus, the introduction of boric acid changes the ratio between the rates of external and intradiffusion processes, causing the course of H -Cs exchange by the mixed mechanism.

From the data in Table 2 it can be concluded that the introduction of structure-forming additive in clinoptilolite significantly affects the rate constant (B) of the intradiffusion process. Thus, when hydrogen ions are exchanged for lithium ions, the B value decreases from 1.0×10 s to 3.79×10 s, i.e. by 2.7 times. For the exchange of H-Na, it is observed to decrease 2.1 times. In case of exchange for cesium ions, the value of the rate constant of the intradiffusion process decreases only by 20%. This character of the change in the B constant indicates a slowing down of the exchange rate of Na and Li ions on ferrocyanide samples modified in the presence of boric acid, and, as a consequence, an increase in their selectivity in relation to cesium. The data in Table 3 confirm the above, since the samples modified with ferricyanides in the presence of H_3BO_3 possess the distribution (Kd) and purification (Koch) ratios 1.8-6.7 times higher compa-red to the initial clinoptilolite and 1.5-2.2 times higher compared to the sorbents synthesized without the structure-forming additive.

Table 3. Influence of the structure-forming additive (H_3BO_3) on the values of distribution coefficients of ^{137}Cs

Sample	K_d, ml/g
Na-clynoptylolite	4.38×10^3
Clynoptylolite + Cu ferrocyanide	1.4×10^4
Clynoptylolite + Cu ferrocyanide + H_3BO_3	3.1×10^4

Thus, comparative tests on removal of cesium-137 by means of initial clinoptilolite and modified clinoptilolite modification by copper ferricyanide and boric acid as a structure-forming agent have been performed. It was found that modification of the clinoptilolite surface with a structure-forming additive leads to a 1.5-2.2-fold increase in selectivity. As a result of dynamic experiments, it was found that a column filled with clinoptilolite, a ferrocyanide Cu exchanger, allows the deactivation of ^{137}Cs from approximately 900 column volumes of solution with an initial activity of 4.44-102 Bq l^{-1}.

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ВЛИЯНИЕ СТРУКТУРООБРАЗУЮЩИХ ДОБАВОК НА ИОНООБМЕННЫЕ СВОЙСТВА ФЕРРОЦИАНИД-АЛЮМОСИЛИКАТНЫХ СОРБЕНТОВ

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Проведено удаление радиоактивного цезия из водных растворов с использованием клиноптилолита, модифицированного различными модификаторами (ферроцианидами Ni, Cu, Fe и H_3BO_3). Изучено влияние химического состава раствора, концентрации компонентов в растворе и соотношения объема раствора и количества адсорбента на процесс сорбции. Показана высокая селективность по отношению к 137Cs (Kd = 4,38×103 - 3,1×104 мл/г). Рассмотрен механизм увеличения селективности по отношению к 137Cs при использовании H_3BO_3 как структурообразующей добавки.