Organomineral sorbents based on clinoptilolite-containing tuffs
1. Preparation of organomineral anion exchangers using polyhexamethyleneguanidine

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A practically nonswelling sorbent with anion-exchange properties based on clinoptilolite-containing tuffs and polyhexamethyleneguanidine has been obtained. Its total anion-exchange capacity has been studied as a function of the ratio of the modifier and cross-linker concentrations, the deposit of the clinoptilolite-containing tuff, and pretreatment of its surface. The anion-exchange capacity of the sorbents reaches 0.22 meq. mL^{-1}. The conditions for the synthesis of the sorbent have been chosen, and the elemental composition of the samples obtained has been determined.

Key words: zeolites, clinoptilolite-containing tuff, organomineral sorbent; anion-exchange properties, ion-exchange capacity.

The increasing industrial demands for ion-exchange materials have stimulated the intense study of properties of natural zeolites as cheap ion-exchange sorbents.[1] Presently, the main directions of the efficient use of natural zeolites, in particular, clinoptilolite-containing tuffs (CT), as ion-exchange materials are: purification of drinking water from strontium and cesium radionuclides, excess stable strontium and some heavy metals; purification of industrial sewage from ammonium ions; deactivation of waste waters of nuclear power stations;[2] as well as applications in agriculture and livestock management. However, the list of areas where natural zeolites can be used as ion-exchangers could be considerably enlarged if they were subjected to chemical modifications resulting in the appearance of additional valuable properties of zeolites.

Much literature concerns methods for modifying the surface of an inorganic carrier. In particular, a new type of ion-exchanger, *viz.*, porous mineral carriers to whose surface organic, inorganic, or metallocomplex compounds are grafted, has been described.[3,4] Silica, silica gels, and oxides[3—5] are most often used as the carriers. The purpose of the present work is to prepare materials by modification of CT, which retain the properties of the carrier (in the given case, cation-exchange properties) and acquire additional properties, for example, anion-exchange properties.

Experimental

A natural zeolite, clinoptilolite-containing tuff, whose deposits are found in many regions of Russia, was chosen as the mineral carrier. The composition of its elementary cell may be presented by the formula $(\mathrm{K_2,Na_2,Ca})_3[\mathrm{Al_6Si_{30}O_{72}}]\cdot 24\mathrm{H_2O}$. Polyhexamethyleneguanidine chloride (metacide (MC)), which is an available polymeric compound containing amino groups, served as the modifier.

The modification was performed in the following way. Clinoptilolite-containing tuff washed off from a dust-like fraction was impregnated with a MC solution, vigorously stirred, left for 24 h, and then linked with epichlorohydrin (ECH). The quality of the prepared ion-exchange material was evaluated from a combination of characteristics, *viz.*, total exchange capacity (which was determined under static and dynamic conditions), sorption kinetics, and swelling.[6]

Results and Discussion

In developing a procedure for modifying CT, we considered the influence of various factors on the value of the anion-exchange capacity. The anion-exchange capacity of an unit volume (mL) of a swelled sorbent was a criterion for the choice of the sorbent. The concentration of the modifier and the ratio of the modifier and the cross-linker are two of the most important modification factors. The effects of the matrix, the

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deposit of CT, the grain size, the initial cation-exchange form of CT (natural or hydrogen), pretreatment of the matrix surface (boiling with water), and duration of the impregnation by the modifying solution (from 15 min to 1 day) were also studied.

The characteristics of the modified clinoptilolites (exchange capacities and swelling) as a function of the ratio ECH : MC are presented in Table 1.

As can be seen from these data, all of the CT samples treated with MC and ECH at the initial MC concentration of 33 % acquire anion-exchange capacity ranging from 0.13 to 0.22 meq. mL^{-1} (up to 0.88 meq. g^{-1}). Increasing the ECH content results in the enhancement of the capacity of the sorbent per 1 g, but not per unit volume, because swelling is noticeably changed. The swelling of the sorbents increases as the ECH content increases probably due to the increase in the total organic mass in the sample. For example, swelling of the sorbent reaches 230—300 % for ECH/MC = 0.4, whereas it is only 5 % when ECH/MC = 0.15. For the final choice of the modification conditions one must take into account that strongly swelling sorbents are inconvenient for practical use and their capacity calculated per unit volume may be comparable with the capacity of weakly swelling samples or may be even lower.

The kinetics of sorption by modified clinoptilolite-containing tuffs was studied for the sorption of bromide ions from a 0.005 *N* KBr solution. The breackthrough curves for the sorption of Br$^-$ on CT modified by a 33 % MC solution with different contents of ECH are presented in Fig. 1. Curves *1—3* were obtained for modified CT with a granulation of 0.5—1.0 mm and ECH/MC ratios equal to 0.2, 0.25, and 0.4, respec-

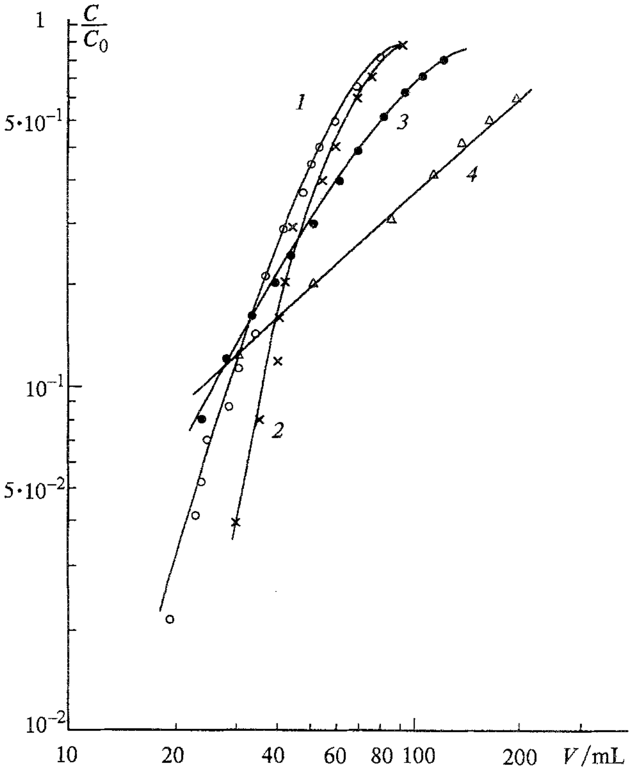

Fig. 1. Breackthrough curves of bromide ion from a 0.005 *N* KBr solution for the samples of modified CT depending on the ECH content: (*1*) ECH/MC = 0.20, granulation (*d*) is 0.5 to 1.0 mm, the height of the loading layer (*h*) is 2.7 cm, flow rate (v) is 0.8 mL min^{-1}; (*2*) ECH/MC = 0.25, d = 0.5 to 1.0 mm, h = 4.0 cm, v = 1.0 mL min^{-1}; (*3*) ECH/MC = 0.40, d = 0.5 to 1.0 mm, h = 4.2 cm, v = 1.0 mL min^{-1}; (*4*) ECH/MC = 0.40, d = 0.10 to 0.50 mm, h = 5.2 cm, v = 0.7 mL min^{-1}.

Table 1. Anion-exchange capacity and swelling of modified clinoptilolite-containing tuffs from different deposits depending on the ECH/MC ratio (initial concentration of MC is 33 %)

Deposit	Content* of clinoptilolite (%)	ECH/MC	Anion-exchange capacity**		Swelling (%)
			meq. mL^{-1}	meq. g^{-1}	
Bryanskoe	23	0.40	0.13	0.52	230
Kholinskoe	47	0.26	0.15	0.27	42
		0.40	0.16	0.37	130
Fokinskoe	14	0.20	0.17	0.23	—
		0.10	0.16	0.37	—
Tedzami	50	0.10	0.19	0.21	—
		0.15	0.15	0.19	5
		0.20	0.22	0.31	40
		0.40	0.20	0.82	300

* Content of clinoptilolite in the rock was determined at the Central Scientific Research Institute "GeoInerud", Kazan' (for CT from the Bryanskoe deposit) and at the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry of the RAS by S. S. Meshalkin (for other CT).

** In the range of changes in the exchange capacity from 0.12 to 0.32 meq. mL^{-1}, the determination error (Δx) was ±0.02 meq. mL^{-1} with relative standard deviation, S_r = 0.3 and confidence probability, P = 0.9, and n = 26.

Table 2. The effect of the MC concentration on the anion-exchange capacity of modified CT

Deposit	[MC] (%)	ECH/MC	Anion-exchange capacity /meq. mL^{-1}	Swelling (%)
Bryanskoe	1	1.0	0.07	8
	10	1.0	0.04	8
	33	0.4	0.13	230
Tedzami	25	0.2	0.17	40
	33	0.2	0.16	—
	40	0.2	0.19	
Tedzami	Nontreated		0.01	0

Table 3. Anion-exchange capacity of modified CT depending on granulation (*d*)

d/mm	Anion-exchange capacity/meq. mL^{-1}	Swelling (%)
0.10—0.25	0.16	12
0.25—0.50	0.14	8
0.50—1.00	0.14	4.8
1.00—1.60	0.15	1.9

Note. Granulation of air-dry samples is presented.

Table 4. Anion-exchange capacities of modified CT from different deposits (the initial form is hydrogen form)

Deposit	*d*/mm	Volume of 1 g of sorbent/mL		Capacity /meq. mL^{-1}
		H_2O	1 *N* NaCl	
Tedzami	0.5—1.0	1.2	1.16	0.14
Kholinskoe	0.25—0.5	1.2	1.0	0.14—0.16

tively. Curve *4* was obtained for the finer CT with ECH/MC = 0.4. It can be seen that the shape of the breackthrough curves from the sorbents with a low content of a cross-linker (see Fig. 1, curves *1* and *2*) is characteristic of filmdiffusional retardation, whereas for the sorbents with an elevated ECH content (see Fig. 1, curves *3* and *4*) the breackthrough curves flatten, and the exchange is less effective, which indicates a noticeable contribution from intradiffusional retardation. The data obtained make it possible to draw the conclusion that it is reasonable to use ECH solutions with a concentration ≤ 0.2 mol L^{-1}.

The influence of the MC content on the anion-exchange capacity of sorbents was considered for modified CT from the Bryanskoe and Tedzami (Georgia) deposits. The results are presented in Table 2.

It can be seen that for MC concentrations equal to 1 and 10 % the anion-exchange capacity is very small and is comparable with that obtained for the unmodified CT. Only at MC concentration equal to 25 % does the anion-exchange capacity reach 0.17—0.18 meq. mL^{-1}. A further increase in the MC concentration has almost no effect on the anion-exchange capacity.

The data on the influence of granulation on the capacity obtained for CT of the Tedzami deposit modified by 33 % MC at ECH/MC = 0.2 are presented in Table 3. It should be mentioned that all of the fractions were modified simultaneously under the same conditions. The anion-exchange capacity was determined for each fraction after sieving the modified sorbent.

As the data in Table 3 show, the anion-exchange capacity calculated per unit volume of the sorbent is almost independent of the size of the CT grain, which is probably associated with the differences in swelling of different fractions of modified CT (fine fractions swell more after modification than large fractions).

The possibility of replacing the cross-linker ECH with formaline, which is widely used in the synthesis of organic ion-exchangers, was studied for CT of the Kholinskoe deposit (Eastern Siberia) modified by 33 % MC. The sorbent obtained with the use of formaline is characterized by high swelling, and the capacity per unit volume of the sorbent is close to the corresponding value for the sorbent prepared with the use of ECH. It seems that the conditions of the cross-linking of metacide with

Table 5. Elemental composition of modified CT samples (33 % MC)

Deposit (*d*/mm)	ECH/MC	Content (%)			N_{exp}/N_{theor}	C_{exp}/C_{theor}	H_{exp}/H_{theor}
		N	C	H			
Tedzami							
(0.2—0.5)	0.2	1.04	2.23	0.20	0.24	0.24	0.10
(1.0—1.6)	0.2	0.91	1.86	0.17	0.21	0.20	0.10
Kholinskoe							
(0.5—1.0)	0.2	0.93	2.31	0.13	0.22	0.25	0.10
Tedzami							
(0.5—1.0)	0.4	4.29	11.6	1.68	1.00	1.00	1.00

Note. N_{exp}, C_{exp}, and H_{exp} are contents of N, C, and H (mg-at.) per unit mass of the modified CT; N_{theor}, C_{theor}, and H_{theor} are contents of N, C, and H in an elementary cell of MC cross-linked with the corresponding amount of ECH.

formaline need to be studied in more detail to prepare sorbents with lower swelling.

It is known that in some cases modification of inorganic surfaces (for example, silica) occurs more efficiently after acid treatment. In this connection, we modified CT, which had been preliminary treated with hydrochloric acid, *i.e.,* the hydrogen form of zeolites was modified. The results of this study are presented in Table 4.

As can be seen from the data in Tables 1 and 4, CT from various deposits may be used for preparing modified zeolites, and the use of hydrogen forms does not enhance the anion-exchange capacity.

Pretreatment of the matrix surface by boiling in water for 2 h and increasing the duration of the impregnation of zeolite with MC from 15 min to 24 h also do not affect the anion-exchange capacity of modified zeolites. A procedure for the preparation of sorbents with anion-exchange properties was developed based on the obtained results.

Elemental analysis of the modified samples was performed for the quantification of C, H, and N. The elemental composition of samples modified under the same conditions is relatively stable (Table 5) and, except for H, correlates well with the elemental composition of metacide cross-linked with ECH. Increasing the ECH/MC ratio (0.4) results in the stabilization of the composition of the modified CT in H as well.

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