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Effect of the acidic treatment on the adsorption and structural properties of the natural mineral sorbent $M_{45}C_{20}$

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Adsorption and structural properties of the initial natural mineral sorbent $M_{45}C_{20}$ and the sorbent treated with 2.33 M H_2SO_4 were studied. The sorbent mainly consists of montmorillonite and clinoptilolite. Aluminum, calcium, magnesium, sodium, and potassium ions are removed from the structure under the action of the acid. The specific surface, porosity of the sorbent, and pore size increase during this process. The sorption of ammonium ions in the natural samples predominantly follows the ion-exchange mechanism (exchange to calcium, magnesium, sodium, and potassium ions). The acid treatment changes the composition of the cation-exchange complex and results in an increase in the sorption capacity to ammonium ions by a factor of ~1.3.

Key words: natural mineral sorbent, acid activation, exchange sites, ammonium ions.

Fresh-water reservoirs receive agricultural runoff enriched in nitrogen fertilizers. Excessive levels of ammonial nitrogen cause pollution of the hydrosphere: entrophication of reservoirs, violation of ecological equilibrium, and water-quality problems. This situation is characteristic of regions, where fields are heavily fertilized to enhance the crop.[1] Various methods are used for the removal of ammonium ions from water: sorption, ion exchange, oxidation, biofiltration, and reverse osmosis.[2] Sorption and ion exchange on natural minerals are very promising processes, because the minerals are widely abundant in nature, they are highly selective to ammonium ions, and fairly cheap.[2—6] One of substantial drawbacks of the natural mineral sorbents is a reduced sorption capacity compared to that of the synthetic sorbents. The sorption capacity of the natural sorbents can be enhanced by the acid treatment,[3—9] and the highest sorption capacity is achieved by the treatment with sulfuric acid.[7,8,10] Many publications deal with the study of such natural sorbents as montmorillonite and clinoptilolite.[3—7,9—12] In this work, we described the effect of the acid treatment on the adsorption and structural properties of the natural and mineral sorbent $M_{45}C_{20}$. This sorbent consists of two main mineral components, *viz*., montmorillonite and clinoptilolite, and is considered to be a promising sorbent for the removal of ammonium nitrogen from waste waters.

Experimental

The object of the study is the natural mineral sorbent $M_{45}C_{20}$ from the Sokirnitsa deposit (Ukraine). The sorbent is polycomponent and consists of the clay and zeolite components: montmorillonite (M, 45%) and clinoptilolite (C, 20%), respectively. The sorbent sample also includes goethite (10%), illite (15%), and calcite (10%).[13]

Montmorillonite is a layered silicate mineral of the 2 : 1 structure, in which one layer of the octahedra with cations Al^{3+}, Fe^{3+}, or Mg^{2+} in the center, is linked with two layers of silicon—oxygen tetrahedra.[12] The structure of montmorillonite is shown in Fig. 1.[14]

Montmorillonite is characterized by the isomorphous substitution of aluminum by magnesium in the octahedral positions and of silicon by aluminum in the tetrahedral structures.[12] A residual negative charge of the layers is balanced by the hydrated cations Na^+, Ca^{2+}, Mg^{2+}, and, more rarely, K^+ situated in the interlayer space and capable of exchanging with ions from the solution. The structure of montmorillonite can contain active sites of the following types: coordinatively unsaturated ions Al^{3+} and Mg^{2+}, hydroxyl groups of the acidic and basic character, and oxygen atoms.[12]

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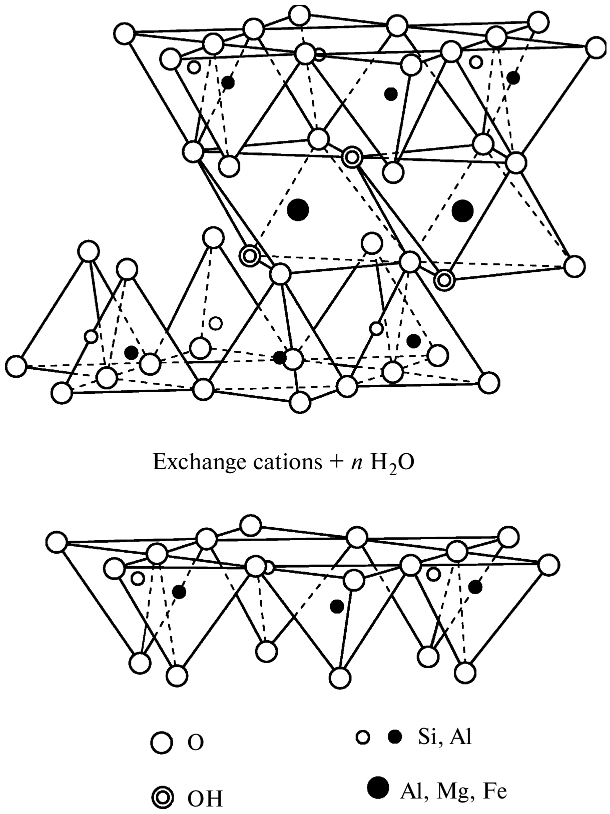


Fig. 1. Structure of montmorillonite.

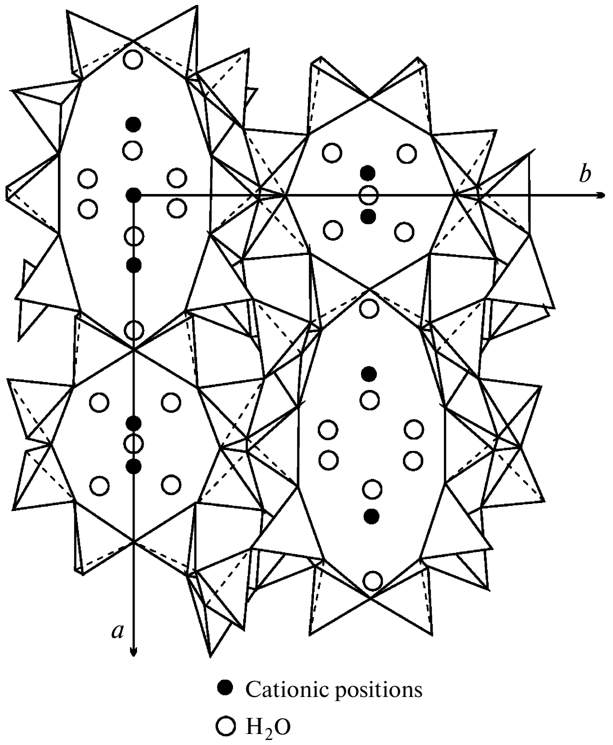


Fig. 2. Structure of clinoptilolite.

Clinoptilolite is classified as a framework zeolite. A specific feature of the framework structure of clinoptilolite is the existence of channels of various diameters formed by ten- and eight-membered rings of linked tetrahedra oriented in three directions and the nonstoichiometric substitution of aluminum for silicon in the tetrahedra. These structural features determine the molecular-sieve and ion-exchange properties of clinoptilolite (Fig. 2).[15] The alkaline and alkaline-earth metal cations surrounded by the water molecules are located in the intracrystalline channels of clinoptilolite.[12]

The natural sorbent (fractions <0.25 mm) were activated with 2.33 M H_2SO_4 in the ratio solid phase : acid = 1 : 3.4 with continuous stirring at 371 K for 6 h. The obtained pulp was filtered with a vacuum pump through a filter of synthetic fiber. The precipitate on the filter was washed with distilled water to pH = 4 and dried to a constant weight.[9]

The content of SiO_2 in the natural mineral sorbent (MCn) and in the sorbent treated with the acid (MCa) was determined by graviphotometric analysis, and the contents of Al_2O_3, Fe_2O_3, CaO, and MgO were determined by complexonometric titration. The relative determination inaccuracy for SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO was 0.7, 0.3, 0.1 0.3, and 0.1%, respectively.

The exchange capacity was estimated from the sum of cations K^+, Na^+, Ca^{2+}, and Mg^{2+} displaced from the cationic sites of the mineral sorbent $M_{45}C_{20}$ by the NH_4^+ ion. The contents of K^+ and Na^+ in the filtrate were determined by the method of flame photometry,[16] and those of the Ca^{2+} and Mg^{2+} ions were determined by complexonometric titration.[17] The amount of the NH_4^+ ions adsorbed by the sorbent phase was determined from the change in the concentration of NH_4^+ in the external solution during sorption by the ionometric method using the NH_4-selective electrode.[18] The cation-exchange capacity of the samples was determined by the treatment with a solution of 0.5 M NH_4Cl at 295 K.

The distribution constant (K) of the exchange cations was calculated as the ratio of the concentration of the cation in the sorbent phase to its concentration in the liquid phase.

In addition to standard adsorptives (nitrogen or benzene), water can be used for the determination of the specific surface and porous structure of the adsorbent.[19,20] The value of specific surface of the samples was calculated from the capacity of the monomolecular layer of water, and the latter was determined by the sorption isotherm of water vapor.[21] The true, imaginary, and bulk densities of the adsorbents were determined using a known procedure.[22] The total pore volume, total porosity, and average pore diameter were calculated using a procedure described earlier.[23] The data obtained are listed in Table 1.

The components of the sample after the acidic treatment were identified by X-ray diffraction analysis on a Dron 4-07 diffractometer (automatic mode, increment 0.1°, exposure time in each point 1 s, Co-Kα radiation).

To examine changes in the surfaces of MCn and MCa, we performed their microscopic studies on a JSM-6380 LV scanning electron microscope equipped with an INCA Energy-250 energy-dispersive attachment for elemental analysis.

Structural changes in the treated sorbent were monitored by IR spectroscopy. The spectra of the studied samples before and after adsorption of ammonium ions were recorded on a Vertex 70 spectrometer in the frequency range 400—4000 cm^{-1}.

Table 1. Adsorption structural characteristics of the sorbent $M_{45}C_{20}$

Sample	Density/kg m^{-3}			Porosity (%)	Total pore volume/m^3 kg^{-1}	Average pore diameter/nm	Specific surface to water vapors/m^2 g^{-1}
	bulk	imaginary	true				
MCn	1.17	2.75	4.30	36.05	0.1	2.6	197
MCa	1.09	2.18	4.08	46.57	0.2	3.2	260

Results and Discussion

The results of the analysis (Table 2) indicate that the acidic treatment considerably changes the chemical composition of the sorbent. A considerable part of iron (90.8%), calcium (76.3%), magnesium (36.4%), and aluminum oxides (33.3%) is dissolved upon the acidic treatment, resulting in a significant increase in the content of silica in the MCa from 56.75 to 80.90%. The dissolution of Fe_2O_3 is almost complete, since iron predominantly enters the foreign mineral goethite, which is easily dissolved in the acid, and a part of iron is present in the structure of montmorillonite that is less resistant to the action of acid than clinoptilolite. According to the results of determination of the content of Al_2O_3 and Fe_2O_3 in the MCn and MCa samples, the Fe-containing octahedra are mainly subjected to destruction, because the Fe—O bond is weaker than the Al—O bond.[5] The amount of CaO decreased by 76.3% due to the dissolution of calcite in the acid and the substitution of the Ca^{2+} ions for the H^+ ions. Thus, the acidic treatment increases the effective surface and the number of accessible active sites due to the removal of foreign impurities from the sorbent.

It was found by the X-ray diffraction analysis results (Fig. 3) that after the treatment with an H_2SO_4 solution the sample contained almost only clinoptilolite and the amorphous phase, whose existence is evidenced by the halo in the 2θ range 16—32°. This fact confirms a higher resistance of clinoptilotite to acid compared to that of montmorillonite. The amorphization of the clay mineral can be explained by the removal of the cations arranged in the surface octahedra of montmorillonite, due to which the silicon—oxygen networks are polymerized to form silica gel as an independent phase.[11]

The type and capacity of the exchange complex are among the most important adsorption characteristics of the natural sorbent determining the nature of the surface of its particles. The acidic treatment primarily results in the substitution of alkaline and alkaline-earth metal ions by hydrogen ions and, therefore, in the change in the nature of exchange sites of the sorbent.[5—7,12]

The data given in Table 3 suggest that the cation-exchange positions of the natural mineral sorbent $M_{45}C_{20}$ are occupied by the Ca^{2+}, Mg^{2+}, Na^+, and K^+ ions.

The highest contribution to the value of ion-exchange capacity of MCn is made by the Ca^{2+} (1.18 mg-equiv. g^{-1}) and Mg^{2+} ions (0.51 mg-equiv. g^{-1}). The exchange capacity for Ca^{2+} is considerably lower than its total content in the MCn sample (see Table 2). This is due to the fact that the sorbent includes Ca^{2+}-containing calcite incapa-

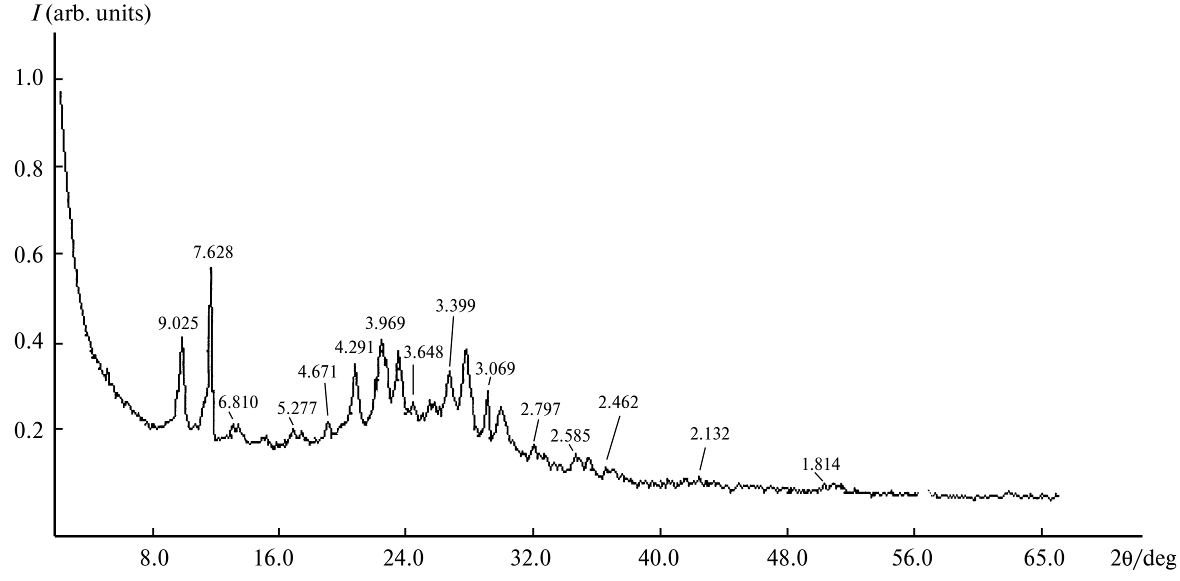


Fig. 3. Diffraction pattern of the MCa samples.

Table 2. Chemical composition of the sorbent $M_{45}C_{20}$

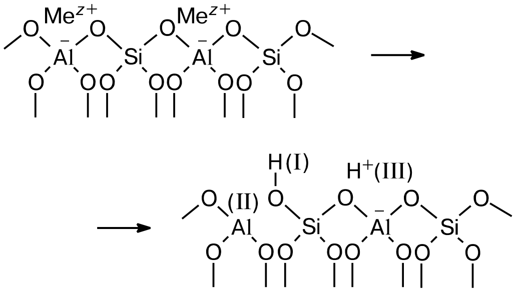
Sample	Chemical composition (wt.%)					SiO_2/R_2O_3
	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	
MCn	56.75	14.02	11.20	2.47	9.84	2.37
MCa	80.82	9.34	2.66	1.57	0.90	7.89

ble of ion exchanging. In addition, the nature of the sorbate itself affects the process of ion-exchange sorption. Probably, the size of the large complex ion NH_4^+ makes the incorporation of the NH_4^+ ions into the interchannel space of the mineral difficult. Therefore, a portion of the Ca^{2+} ions located near the sorbent surface are predominantly displaced upon the exchange. An analysis of the data in Table 3 shows that the total amount of the displaced cations is nearly equal to that of the NH_4^+ ions consumed by the sorbent. It can be therefore inferred that the sorption capacity of the MCn sample depends mainly on the presence of exchange cations. The contribution of other ions, which are in the composition of the active sites (coordinatively unsaturated ions Al^{3+}, hydroxyl groups, and oxygen atoms) to the overall ion-exchange adsorption of the NH_4^+ ions is insignificant (<1%).

The amount and composition of the cation-exchange complex change substantially due to the removal of cations from the sorbent structure under the action of the acidic treatment. The amount of the Ca^{2+} cations removed from MCn sample is the lowest (19.6%), whereas the amounts of the Mg^{2+} (81.7%), Na^+ (68.8%), and K^+ (54.8%) cations are the highest. The decrease in the amount of alkaline and alkaline-earth metal cations capable of exchanging is confirmed by the elemental analysis results (Table 4).

Of the set of exchange cations remained after the acidic treatment, the Ca^{2+} cations contribute maximally to the value of exchange capacity (0.95 mg-equiv. g^{-1}). In spite of the decrease in the amount of exchange cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+), the phase of the MCa sorbent adsorbs a considerably greater amount of the NH_4^+ ions than MCn (see Table 3), which coincides with the literature data.[3,4] This can be due to the change in the nature of the exchange complex: not only the Ca^{2+} cations become the main exchange ions, but also the hydrogen ions that appear due to the replacement of cations in the sorbent phase by the H^+ ions from a solution, which facilitates the adsorption process.[24] The decationization results in the cleavage of the Si—O—Al bond and formation of active sorption sites: silanol groups (I), three-coordinated aluminum atoms (II), and Brönsted sites (III) (Scheme 1).[12]

Scheme 1



Me^{z+} are metal cations

Hydrogen ions can substitute not only alkaline and alkaline-earth metal cations but also iron and aluminum ions,[11] which is confirmed by a decrease in the amounts of Fe_2O_3 and Al_2O_3 (see Table 2).

The behavior of the sodium, potassium, calcium, and magnesium cations that are exchanged by ammonium cat-

Table 3. Cation-exchange capacity of the sorbent $M_{45}C_{20}$*

Sample	Cation-exchange capacity				$\Sigma(Na^+, K^+, Ca^{2+}, Mg^{2+})$	$Q_{NH_4^+}$ in sorbent phase
	Na^+	K^+	Ca^{2+}	Mg^{2+}		
MCn	0.170	0.042	1.180	0.509	1.90	1.92
MCa	0.053	0.019	0.949	0.093	1.11	2.43

* All values are given in mg-equiv. g^{-1}.

Table 4. Elemental composition of the sorbent $M_{45}C_{20}$

Sample	Content of main elements (wt.%)									
	O	Na	Mg	Al	Si	K	Ca	Ti	Fe	Cu
MCn	54.43	0.63	1.64	6.88	23.37	2.31	5.11	0.45	4.18	1.01
MCa	55.60	0.39	0.27	2.74	30.84	1.57	3.03	0.36	0.58	1.94

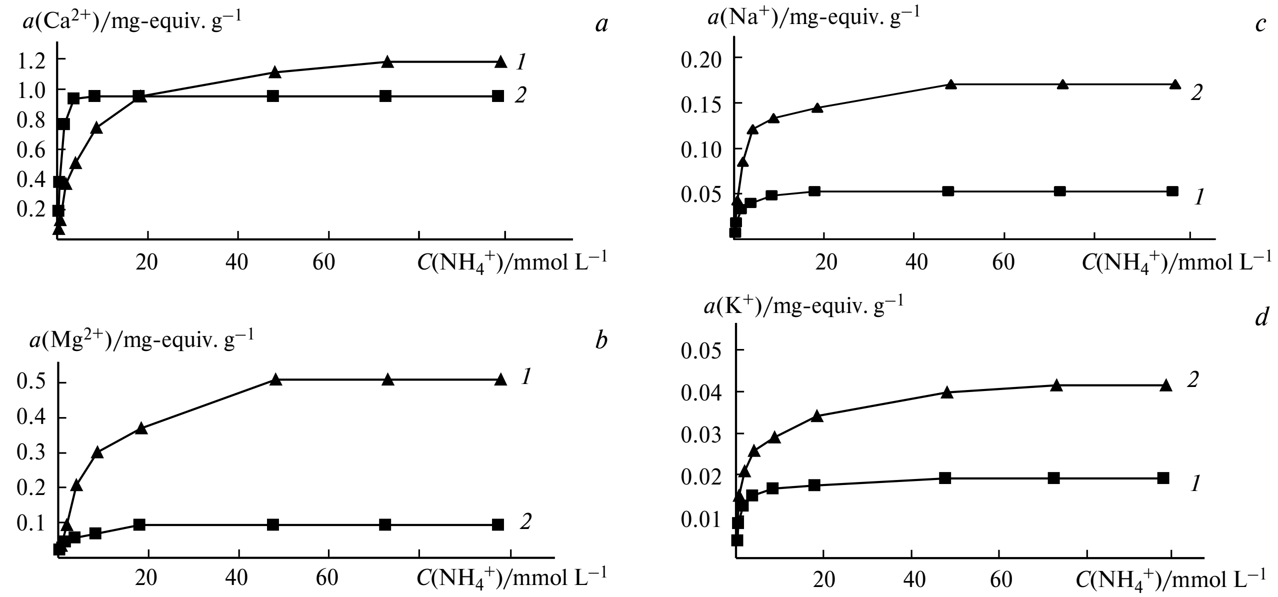


Fig. 4. Amount of desorbed cations Ca^{2+} (*a*), Mg^{2+} (*b*), Na^+ (*c*), and K^+ (*d*) as a function of the equilibrium concentration of NH_4^+ for sorption on MCn (*1*) and MCa (*2*).

ions was estimated from the curves of the dependence of the amount of desorbed cations on the concentration of an NH_4Cl solution during the sorption of the NH_4^+ ions (Fig. 4).

The desorption curves of the cations are similar in shape and can be described by the Langmuir equation[22]

$$1/a = 1/a_{\max} + 1/(a_{\max}K_dC), \quad (1)$$

where a is the amount of the desorbed exchange cation per weight unit of the sorbent at equilibrium, mmol g^{-1}; $a_{\max}$ is the maximum amount of the desorbed exchange cation per weight unit of the sorbent, mmol g^{-1}; C is the equilibrium concentration of the sorbate in the aqueous phase, mmol L^{-1}; and K_d is the desorption equilibrium constant.

The parameters of Eq. (1) determined graphically from the experimental data on the basis of the dependence $1/a$—$1/C$ are presented in Table 5.

An analysis of the experimental data (see Fig. 4) shows that with an increase in the NH_4^+ concentration the ion exchange proceeds differently on the initial sample and on the sample treated with the acid.

Table 5. Parameters of the Langmuir equation

Cation	MCn		MCa	
	K_d	$a_{\max}$	K_d	$a_{\max}$
Ca^{2+}	0.149	1.353	0.751	1.333
Mg^{2+}	0.137	0.463	1.384	0.082
Na^+	0.362	0.188	0.485	0.065
K^+	0.805	0.037	1.022	0.020

Unlike the natural sample, the sample treated with the acid can exchange metal cations for ammonium ions in large amounts already at low concentrations. The ion exchange of the NH_4^+ ions by Ca^{2+} ions is especially interesting. On the MCa sample this process is considerably more intensive, and the maximum amount of the NH_4^+ ions is adsorbed at a concentration of the external solution of NH_4Cl of 10 mmol L^{-1}, whereas on the MCn sample the equilibrium is achieved at $C = 75$ mmol L^{-1}. The maximum exchange for the Mg^{2+}, K^+, and Na^+ cations on the MCa sample is observed at the concentration of an NH_4Cl solution equal to 20 mmol L^{-1}, while for the MCn sample the maximum exchange is observed at 50 mmol L^{-1}. The dependences of the distribution constant (K_d) of the Ca^{2+} cation on the equilibrium concentration of NH_4^+ upon sorption on the MCn and MCa samples are shown in Fig. 5. The value of K for the MCa and MCn samples decreases with an increase in the concentration of the NH_4^+ ions. For the concentration of the NH_4^+ ions $>$ $>$ 10 mmol L^{-1}, the value of K of the sample treated with the acid attains a minimum value, which is lower than the constant determined for the exchange on the initial sample (see Fig. 5).

The consideration of the regularities of absorption in the IR spectral range of the natural mineral acid-activated sorbent $M_{45}C_{20}$ and the samples after the sorption of the NH_4^+ ions suggests that the ammonium ions are sorbed on the studied sorbent according to two mechanisms: donor-acceptor and ion-exchange. The ion-exchange mechanism is confirmed by the appearance of the spectra (Fig. 6) of the characteristic, strong absorption bands at 3144 and 1396 cm^{-1} reflecting stretching and bending vibrations of

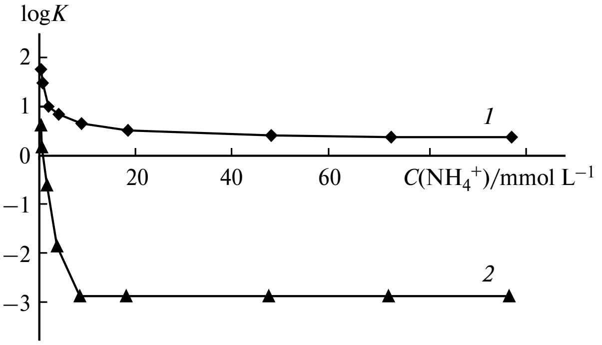


Fig. 5. Distribution constant of the Ca^{2+} cation (K) as a function of the concentration of the NH_4^+ ion for sorption on MCn (*1*) and MCa (*2*).

the N—H bonds in the structure of NH_4^+. The donor-acceptor interaction is evidenced by the appearance in the corresponding regions (3300—3200 cm^{-1}) of stretching vibrations of the N—H bonds involved in intermolecular interactions and bending vibrations at 1580 cm^{-1}. These characteristic vibrations are detected as absorption bands of lower intensity, which suggests an insignificant contribution of this type of adsorption to the adsorption process.

The acidic treatment of the natural mineral sorbent $M_{45}C_{20}$ induces a series of complicated reactions changing the nature of exchange cations and the site of localization of exchange cations in the aluminosilicon—oxygen layer and in the framework of the minerals. The active sites in the treated sample become more accessible for exchange in the adsorption and structural properties, such as an increase in the specific surface (by a factor of 1.3), porosity (by a factor of 1.3), and average pore size (by a factor of 1.2) (see Table 1). These changes are confirmed by the analysis of the morphological features of the surface (Fig. 7).

As can be seen from the presented images of the surface (see Fig. 7), the acid-treated sorbent is characterized by a higher degree of dispersion due to the destruction of the montmorillonite structure and amorphization of the sample. Surface heterogeneity of the MCa sample can also be conceived by considering an increase in the number of secondary pores compared to the natural sorbent.

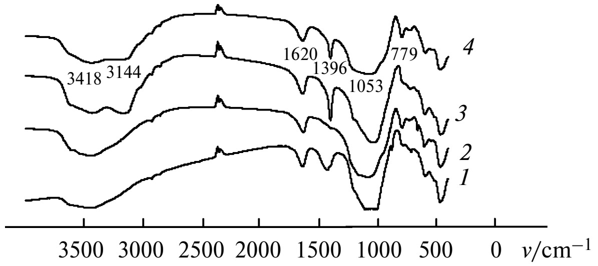


Fig. 6. IR spectra of the samples MCn (*1*) and MCa (*2*) and the same samples saturated with the NH_4^+ ions (*3* and *4*, respectively).

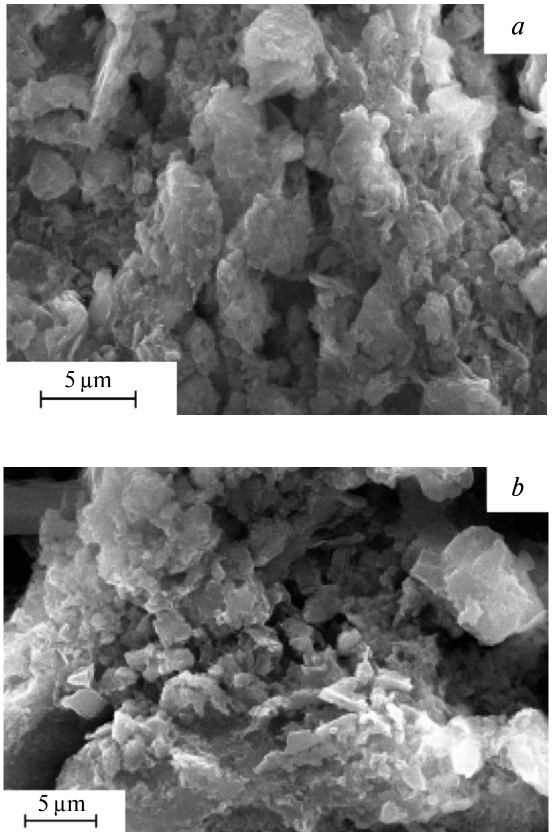


Fig. 7. Morphology of the surface of MCn (*a*) and MCa (*b*) (magnification 4500).

Thus, it was shown on the basis of chemical and IR spectrometric analyses that the treatment of the natural mineral sorbent $M_{45}C_{20}$ with 2.33 M H_2SO_4 was accompanied by complicated chemical processes. The main process is the activation of sorption sites due to decationization, cleavage of the Si—O—Al bond, and formation of the hydrogen bond of the sorbent. The destruction of the clay component (montmorillonite) and the appearance of the amorphous phase were established by X-ray diffraction analysis and confirmed by the result of electron microscopic analysis. It was shown that the acidic treatment of the studied sorbent changed its adsorption structural properties compared to the untreated sorbent. The specific surface, porosity, and pore size of the sorbent increase due to the dissolution and removal of iron, aluminum, calcium, magnesium, sodium, and potassium ions from the structure of the minerals, which facilitates the enhancement of the adsorption capacity for ammonium ions by a factor of 1.3.

References

1. O. A. Alekin, *Osnovy gidrokhimii* [*Foundations of Hydrochemistry*], Gidrometeoizdat, Leningrad, 1970, 280 pp. (in Russian).

2. G. A. Samburskii, *Vestnik MITKhT* [*Bulletin of the Moscow Institute of Fine Chemical Technology*], 2010, **5**, No. 5, 106 (in Russian).
3. M. Sprynskyy, M. Lebedynets, R. Zbytniewski, J. Namiesnik, *Separation and Purification Technology*, 2005, **46**, No. 3, 155.
4. M. Rozic, S. Cerjan-Stefanovic, S. Kurajica, V. Vancina, E. Hodzic, *Water Research*, 2000, **34**, 3675.
5. Yu. I. Tarasevich, *Prirodnye sorbenty v protsessakh ochistki vody* [*Natural Sorbents in Water Purification Processes*], Naukova Dumka, Kiev, 1981, 208 pp. (in Russian).
6. Yu. I. Tarasevich, F. D. Ovcharenko, *Adsorbtsiya na glinistykh mineralakh* [*Adsorption on Clay Minerals*], Naukova Dumka, Kiev, 1975, 352 pp. (in Russian).
7. Yu. I. Tarasevich, *Stroenie i khimiya poverkhnosti sloistykh silikatov* [*Structure and Chemistry of the Surface of Layered Silicates*], Naukova Dumka, Kiev, 1988, 248 pp. (in Russian).
8. L. I. Bel´chinskaya, L. A. Novikova, F. Ressner, *Sorbtsionnye i khromatograficheskie protsessy* [*Sorption and Chromatographic Processes*], 2005, **5**, 799 (in Russian).
9. L. I. Bel´chinskaya, K. A. Kozlov, A. V. Bondarenko, G. A. Petukhova, M. L. Gubkina, *Sorbtsionnye i khromatograficheskie protsessy* [*Sorption and Chromatographic Processes*], 2007, **7**, 572 (in Russian).
10. L. I. Bel´chinskaya, O. A. Tkacheva, I. A. Sakhokiya, *Khim. Khim. Tekhnol.* [*Chemistry and Chemical Technology*], 1996, **39**, No. 6, 56 (in Russian).
11. E. G. Kukovskii, *Osobennosti stroeniya i fiziko-khimicheskie svoistva glinistykh mineralov* [*Specific Features of the Structure and Physicochemical Properties of Clay Minerals*], Naukova Dumka, Kiev, 1966, 132 pp. (in Russian).
12. O. M. Mdivnishvili, *Kristallokhimicheskie osnovy regulirovaniya svoistv prirodnykh sorbentov* [*Crystal Chemical Foundations for Control of the Properties of Natural Sorbents*], Metsniereba, Tbilisi, 1978, 268 pp. (in Russian).
13. L. I. Bel´chinskaya, N. A. Khodosova, L. A. Bityutskaya, *Fiziko-khimiya poverkhnosti i zashchita materialov* [*Physicochemistry of Surface and Protection of Materials*], 2009, **45**, No. 2, 218 (in Russian).
14. R. E. Grim, *Applied Clay Mineralogy*, McGraw—Hill, New York, 1962, 422 pp.
15. N. F. Chelishchev, B. G. Berenshtein, V. F. Volodin, *Tseolity — novyi tip mineral´nogo syr´ya* [*Zeolites As a New Type of Mineral Raw Materials*], Nedra, Moscow, 1987, 176 pp. (in Russian).
16. A. N. Zyablov, *Analiticheskaya khimiya: Uchebno-metodicheskoe posobie* [*Analytical Chemistry: Educational Methodical Manual*], LOP VGU, Voronezh, 2006, 75 pp. (in Russian).
17. T. V. Eliseeva, L. V. Zolotareva, V. F. Selemenev, *Prakticheskie raboty po analiticheskoi khimii. Kompleksonometriya. Okislitel´no-vosstanovitel´noe titrovanie: Uchebno-metodicheskoe posobie* [*Practical Works on Analytical Chemistry. Complexonometry. Redox Titration: Educational Methodical Manual*], IPTs VGU, Voronezh, 2008, 54 pp. (in Russian).
18. RD 52.24.394-95 *Metodicheskie ukazaniya. Opredelenie ionov ammoniya v vodakh s ispol´zovaniem ionoselektivnogo elektroda* [*Methodical Instructions. Determination of Ammonia Ions in Waters Using an Ion-Selective Electrode*], GKhI, Rostov-on-Don, 1995, 9 pp. (in Russian).
19. V. V. Gur´yanov, G. A. Petukhova, L. A. Dubinina, *Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 40 [*Russ. Chem. Bull.*, *Int. Ed.*, 2007, 40].
20. V. V. Gur´yanov, G. A. Petukhova, N. S. Polyakov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 2636 [*Russ. Chem. Bull.*, *Int. Ed.*, 2005, **54**, 2726].
21. I. A. Kirovskaya, *Adsorbtsionnye protsessy* [*Adsorption Processes*], Izd-vo Irkutsk Univ., Irkutsk, 1995, 304 pp. (in Russian).
22. N. V. Kel´tsev, *Osnovy adsorbtsionnoi tekhniki* [*Foundations of Adsorption Technique*], Khimiya, Moscow, 1984, 592 pp. (in Russian).
23. F. D. Ovcharenko, *Gidrofil´nost´ glin i glinistykh mineralov* [*Hydrophilicity of Clays and Clay Minerals*], Akad. Nauk UkrSSR, Kiev, 1961, 292 pp. (in Russian).
24. G. N. Al´tshuler, E. V. Ostapova, L. A. Sapozhnikova, O. G. Al´tshuler, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 2560 [*Russ. Chem. Bull.*, *Int. Ed.*, 2004, **53**, 2670].

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