

## Research Article

# Contribution of Ion-Exchange and Non-Ion-Exchange Reactions to Sorption of Ammonium Ions by Natural and Activated Aluminosilicate Sorbent

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The effect of acid and alkaline activation of complex natural aluminosilicate sorbent on its chemical composition, surface properties, and adsorption capacity towards ammonium ions was studied. An increase in specific surface area of the sorbent by 1.3 times after acid treatment and by 1.5 times after alkaline activation was shown. The change of ion-exchange complex of sorbent as a result of activation was observed. Sorption isotherms of ammonium ions on natural and activated samples were obtained and were satisfactorily described by the Langmuir equation. The evaluation and comparison of desorbed cations of alkali and alkaline earth metals were carried out. It was confirmed that ion-exchange processes primarily contributed to sorption of ammonium ions by natural and acid-activated silica-alumina, in contrast to alkali-activated one, for which absorption of nonexchangeable ammonium ions increased adsorption capacity of ammonium ions by 1.5 times.

## 1. Introduction

Use of natural aluminosilicates in sorption purification processes [1, 2] and catalytic conversion of various substances [3] is currently receiving increasing interest due to their unique properties already available in their natural state, as well as new properties acquired during modifying and activation of aluminosilicates [4]. Natural aluminosilicates have good adsorption and ion-exchange properties; they widely occur in nature and have low cost. The structure of these materials can be represented by a variety of components, for example, a layered clayey (montmorillonite), a framework zeolite structure (clinoptilolite), and so forth.

Usually montmorillonite and clinoptilolite containing clays are activated by various methods of treatment, such as thermal treatment [5], ion exchange [6, 7], and treatment with acids [8, 9] and alkali [10, 11]. By activation the chemical composition of minerals is selectively modified that results in an increase in specific surface area, specific pore surface and thermostability, changes in the surface pH, and so forth.

Currently, montmorillonite minerals are often modified in such processes as grafting [12], silylation [13], and intercalation [14, 15] due to inclined swelling capacity. At the same time, the materials based on natural zeolites are valuable as catalysts and supports owing to their rigid frame structure.

Due to specificity of crystal structure and chemical composition, montmorillonite and clinoptilolite reveal high ability to ion-exchange reactions of movable cations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ , which mostly equivalently contribute to adsorption processes on these materials. However, depending on physical and chemical properties of molecules being adsorbed, sorption processes may proceed via several other pathways, so-called non-ion-exchange reactions, which may include hydrogen bonding, Van der Waals interaction, complexation reaction, or even irreversible chemisorption.

Present study was aimed at investigation of sorption of ammonium ions on natural and activated complex aluminosilicate sorbents with clayey and zeolite components and assessment of contribution of ion-exchange and non-ion-exchange reactions to sorption processes.

TABLE 1: Chemical composition of natural and activated sorbent  $M_{45}C_{20}$ .

Sorbent	Content (% per absolutely dry sample)								Silicate module, $SiO_2/Al_2O_3$
	$SiO_2$	$Al_2O_3$	$Fe_2O_3$	CaO	MgO	$Na_2O$	$K_2O$	Loss on ignition	
MCN	56.65	14.32	7.03	8.12	1.62	0.79	2.78	7.9	2.65
MCAc	80.71	9.14	0.70	1.86	1.04	0.24	1.32	7.3	8.20
MCAIk	50.72	15.50	8.13	8.79	0.55	5.32	2.80	7.3	2.14

Note: MCN: natural sorbent  $M_{45}C_{20}$ ; MCAc and MCAIk are  $M_{45}C_{20}$  sorbent treated with acid and alkali, respectively.

## 2. Materials and Methods

Natural mineral sorbent  $M_{45}C_{20}$  from the Sokirnitza deposit (Ukraine), which has nanosized pores (average pore diameter ~3 nm), was studied. The sorbent is a multicomponent porous system consisting of the clayey component (montmorillonite (M): 45%) and the zeolite component (clinoptilolite (C): 20%). In addition, such minerals as goethite (10%), illite (15%), and calcite (10%) were present in the sample [16]. Fractions of natural sorbent of 0.25 mm particle size were activated by treating with solutions of 2.33 M  $H_2SO_4$  and 2 M NaOH following the procedure described in [9, 17].

The following methods were used to determine the chemical composition of natural and alkali-treated sorbent according to the "State Standard 2642.297–2642.1197": photometry and gravimetric analysis ( $SiO_2$ ), complexometric titration ( $Al_2O_3$ ,  $Fe_2O_3$ , MgO, and CaO), flame spectrometry ( $Na_2O$  and  $K_2O$ ), and photometry and gravimetric analysis ( $TiO_2$ ).

Cation-exchange capacity of the samples was determined by measuring the content of the exchange cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ ) replaced by  $NH_4Cl$  solution [18].  $K^+$  and  $Na^+$  content was determined by flame photometry;  $Ca^{2+}$  and  $Mg^{2+}$  content was determined by complexometric titration.

The specific surface area of the samples was calculated from isopiestic isotherms of water vapors sorption [19]. The true and apparent densities of the adsorbents were determined using the procedures previously described in [19].

Sorption isotherms of ammonium ions for aluminosilicate samples under study were obtained at 295 K under static conditions by technique of variable concentrations [20]. For this, 0.2 g of air-dried natural or activated samples was placed in 200  $cm^3$  of  $NH_4Cl$  solution, the concentration of which ranged from 2.5 to 200  $mmol/dm^3$ . The flasks were shaken for 3 h to reach sorption equilibrium. After that, the equilibrium solutions of  $NH_4Cl$  were separated from the sorbent particles by filtration, and concentrations of  $NH_4^+$  ions were determined using an  $NH_4^+$ -selective electrode [20] and the ionomer "Expert-001."

Quantity of ammonium ions absorbed by  $M_{45}C_{20}$  sorbent under equilibrium at a given concentration of external solution was calculated according to

$$q = \frac{(C_0 - C_{\text{equil.}}) \cdot V}{m}, \quad (1)$$

where  $C_0$  and  $C_{\text{equil.}}$  are initial and equilibrium concentration of  $NH_4Cl$  solution,  $mmol/dm^3$ ;  $V$  is volume of  $NH_4Cl$  solution,  $dm^3$ ;  $m$  is mass of sorbent charge, g.

## 3. Results and Discussion

*3.1. Influence of Acid and Alkaline Treatment on Chemical Composition of  $M_{45}C_{20}$  Aluminosilicate Sorbent.* The chemical composition of natural and alkali-treated nanoporous mineral sorbent  $M_{45}C_{20}$  is specified in Table 1.

It follows from Table 1 that the value of silica module of the natural sample is equal to 2.65 due to the fact that clay components (montmorillonite and illite) predominate over zeolite (clinoptilolite) content. Moreover, an increased content of calcium and iron oxides is typical of the mineral under study, which is caused by the presence of calcite impurity (10%) and goethite (10%). Content of  $Na_2O$  is insignificant (less than 1%).

The chemical composition of natural sorbent  $M_{45}C_{20}$  was significantly altered by acid activation (Table 1). Acid treatment led to dissolution from 30 to 90% of  $Al_2O_3$ ,  $Fe_2O_3$ , CaO, MgO,  $Na_2O$ , and  $K_2O$  oxides dissolved. Consequently, content of silica in the MCAc sample significantly increased from 56.65% to 80.71%.  $Fe_2O_3$  almost entirely dissolved (90%) since iron enters mainly in the crystal structure of montmorillonite, which is unstable to acids. Also,  $Fe^{+3}$  ions are components of goethite, the related impurity of the investigated mineral, which easily dissolves in acid forming sulfates.

Comparison of  $Al_2O_3$  and  $Fe_2O_3$  contents in the samples of the MCN and the MCAc indicates a preferential destruction of Fe-containing octahedra, due to a weaker bond Fe–O compared to the Al–O bond [21]. The amount of CaO was reduced by 76.3% due to the substitution of  $Ca^{2+}$  for  $H^+$  ions and calcite dissolution in acid to form calcium sulfate.

Usually, acid activation involves three steps: removal of exchangeable cations (decaionating), dealumination of framework, and formation of amorphous silicon-oxygen phase. The sequence and intensity of the steps are determined by treatment conditions and specific characteristics of minerals [22, 23]. According to [22, 23], the process of decaionating for montmorillonite and clinoptilolite can be represented by the following scheme.

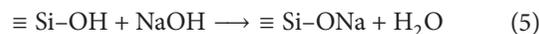


In addition to decationating and dealumination processes, there is an acid decomposition of impurities contained in sorbent, leading to opening of blocked active sites and, therefore, to an increase in effective surface, which is the reason for changes in sorption properties of sorbent [24].

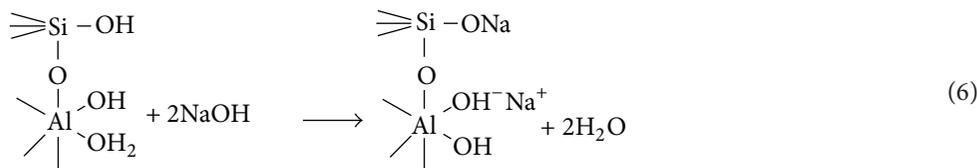
As can be seen from the data in Table 1, by the treatment of natural sample with NaOH solution, SiO<sub>2</sub> underwent the most significant changes. The SiO<sub>2</sub> content decreased by 6%. The decrease in Na<sub>2</sub>O content is caused by its dissolution in the alkali, which is accompanied by a decrease in the silica ratio from 2.65 for the natural sample to 2.14 for the treated sample. Meanwhile, the Na<sub>2</sub>O content increases abruptly (by a factor of 6.7). The changes in contents of the remaining

oxides are insignificant, with the exception of MgO, the content of which decreases approximately threefold.

The change in the chemical composition being observed may be attributed to the fact that alkali influence on clay materials and zeolites results in Na<sup>+</sup> being exchanged for H<sup>+</sup> ions of hydroxyl groups bound to silicon atoms at the boundaries of the silicon-oxygen layer of clinoptilolite [22]:

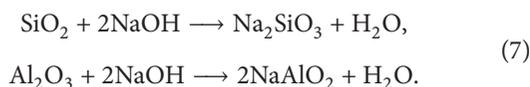


In case of montmorillonite, Na<sup>+</sup> ions can be exchanged for H<sup>+</sup> ions of hydroxyl groups bound to aluminum atoms at the boundaries of the octahedral layer [22]:



Therefore, Na<sub>2</sub>O content in the treated sample strongly increases due to adsorption of Na<sup>+</sup> from the solution according to the above described schemes. Moreover, Na<sup>+</sup> ions are accumulated in the structure of the MCalk due to the exchange reaction with Mg<sup>2+</sup>, which explains the fact that MgO content decreases after the alkaline treatment (Table 1).

Meanwhile, dissolution of aluminum silicate takes place during alkaline treatment yielding sodium silicate and sodium aluminate in accordance with the following schemes [25]:



As aluminate and silicate are accumulated in the alkaline medium, the polycondensation reaction is likely to occur between aluminate and silicate ions yielding an amorphous aluminosilicate followed by partial crystallization of the amorphous phase in NaOH solution. This process was determined by the ratios between the mole numbers of silicate, aluminate, and water [25, 26].

The processes occurring during alkaline and acid treatment also lead to a change in the surface characteristics of material by increasing its surface area and porosity.

Investigation of water vapor adsorption on the surface of natural and activated M<sub>45</sub>C<sub>20</sub> sorbent by an isopiestic method showed that the S-shaped isotherms were obtained, indicating the multilayer adsorption of water. Using the BET equation, the adsorption capacity of a monolayer (*qm*) as well as sorbent specific surface area (SSA) was determined (Table 2).

The data in Table 2 indicate that acid or alkaline activation of natural sorbent M<sub>45</sub>C<sub>20</sub> increased its surface area by 1.3 and 1.5 times, respectively. The rise of surface properties values of activated sorbents is a result of formation of new micro-

TABLE 2: Adsorption capacity and specific surface area of natural and activated M<sub>45</sub>C<sub>20</sub> sorbent.

Sorbent	<i>q<sub>m</sub></i> , mmol/g	SSA, m <sup>2</sup> /g
MCN	2.55	197
MCAc	3.38	261
MCalk	3.77	297

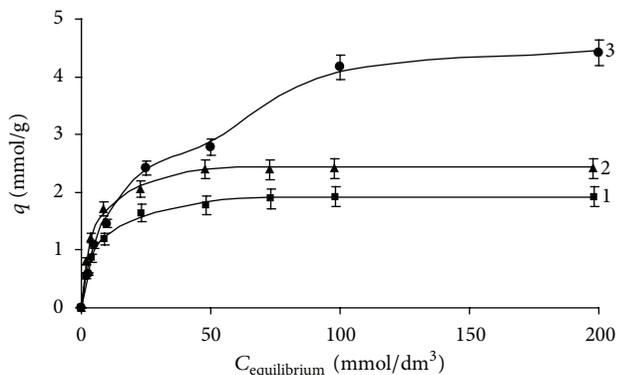


FIGURE 1: Isotherms of NH<sub>4</sub><sup>+</sup>-ions sorption on natural (1), acid-treated (2), and alkali-treated (3) M<sub>45</sub>C<sub>20</sub> sorbent.

and mesopores in its structure due to decationating and dealumination processes, dissolution of impurities, and possible transformation of the lamellar structure of montmorillonite in a rigid framework structure of zeolite [27].

3.2. Sorption Equilibrium in System M<sub>45</sub>C<sub>20</sub> Sorbent-NH<sub>4</sub><sup>+</sup>. Isotherms of NH<sub>4</sub><sup>+</sup> sorption on natural and activated samples of M<sub>45</sub>C<sub>20</sub> sorbent are given in Figure 1.

It follows from Figure 1 that natural sorbent M<sub>45</sub>C<sub>20</sub> revealed sorption activity for ammonium ions, showing

the maximum adsorption capacity of 1.90 mmol/g. This value corresponds to ion-exchange capacities of ammonium ions for various natural zeolites, which ranges from 1 to 2.7 mmol/g [28] and exceeds that one for montmorillonite, for which exchange capacity for  $\text{NH}_4^+$  lies within 0.8–1.5 mmol/g [29, 30]. High values of sorption capacity obtained for  $\text{M}_{45}\text{C}_{20}$  sorbent are caused by the mixed nature of its structural components, both layered and zeolite-like, the small grains size used (0,25 mm), and a high value of specific surface.

Sorption isotherms of ammonium ions on activated samples indicate that acid- and alkali-treated samples improved adsorption capacity, which increases in the row  $\text{MCN} < \text{MCAc} < \text{MCAlk}$ . The reason for this is the processes considered in the previous section, leading to a change in the composition of cation-exchange complex and the nature of sorption centers and increasing the specific surface area, porosity, and phase composition of natural  $\text{M}_{45}\text{C}_{20}$  sorbent during acidic and alkaline activation.

Sorption isotherms of ammonium ions on natural and activated samples were described using the Langmuir equation in the following form [31]:

$$q = q_{\max} \frac{K_a \cdot C_{\text{equilib.}}}{1 + K_a \cdot C_{\text{equilib.}}}, \quad (8)$$

where  $q$  is quantity of the sorbate per mass unit of sorbent under equilibrium, mmol/g;  $q_{\max}$  is maximal sorption capacity of sorbent, mmol/g;  $C_{\text{equilib.}}$  is equilibrium concentration of sorbate in aqueous phase, mmol/dm<sup>3</sup>;  $K_a$  is constant of adsorption equilibrium, dm<sup>3</sup>/mmol.

Parameters of Langmuir equation were found by its linearization and building linear  $1/q - 1/C_{\text{equilib.}}$  dependences. The resulting values of parameters are represented in Table 3 for the values of correlation coefficients of at least 0.97.

It results from Table 3 that maximum adsorption capacity for ammonium ion, calculated by the Langmuir model, exceeds capacity of natural sorbent by 1.3 times after acid and by 2.2 times after alkaline activation. The lowest value of adsorption equilibrium constant for alkali-treated sample, in our opinion, was caused by the fact that a large amount of ammonium ions was absorbed over nonexchange mechanism.

The equilibrium distribution coefficient, which determines selectivity of the  $\text{M}_{45}\text{C}_{20}$  sorbent to ammonium ions in the entire range of concentration of external solution, was calculated by

$$K_d = \frac{q'_{\infty}}{C_{\text{equilib.}}}, \quad (9)$$

where  $K_d$  is distribution coefficient;  $q'_{\infty}$  is a desorption value per unit of sorbent volume, mmol/cm<sup>3</sup>.

Value of sorption  $q'_{\infty}$  is related to sorption value  $q_{\infty}$ , attributed to unit of sorbent mass, by a ratio

$$q'_{\infty} = (1 - \varepsilon) q_{\infty}, \quad (10)$$

TABLE 3: Parameters of Langmuir equation by sorption of ammonium ions on  $\text{M}_{45}\text{C}_{20}$  sorbent.

Sorbent	$q_m$ , mmol/g	$K_a$ , dm <sup>3</sup> /mmol
MCN	1.92	0.21
MCAc	2.42	0.33
MCAlk	4.15	0.09

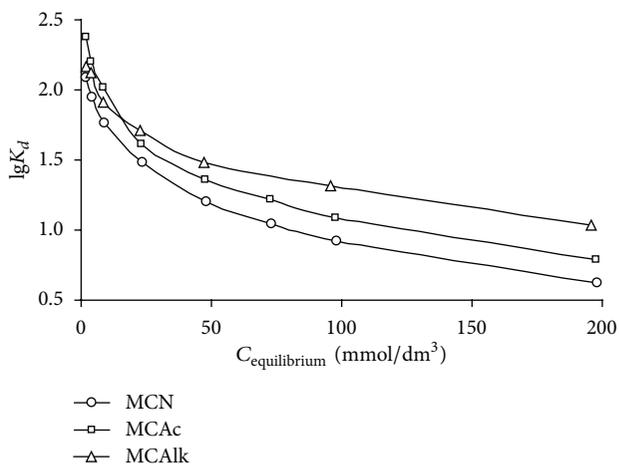


FIGURE 2: Dependence of logarithm of distribution coefficient of  $\text{NH}_4^+$  from equilibrium solution concentration.

where  $\varepsilon$  is porosity of sorbent layer, defined by a formula [32]:

$$\varepsilon = 1 - \left( \frac{\rho_b}{\rho_a} \right), \quad (11)$$

where  $\rho_b$  and  $\rho_a$  are bulk and apparent density of sorbent, respectively, g/cm<sup>3</sup>.

For samples of MCN, MCAc, and MCAlk, the porosity came to the values  $\varepsilon = 0.57, 0.50,$  and  $0.52$ , respectively.

Taking into account (8) and (9), the distribution coefficient is expressed in a view

$$K_d = \frac{(1 - \varepsilon) q_{\infty}}{C_{\text{equilib.}}}. \quad (12)$$

Dependence of logarithm of distribution coefficient of  $\text{NH}_4^+$  from their equilibrium concentration in solution is shown in Figure 2.

For natural and activated samples of  $\text{M}_{45}\text{C}_{20}$  sorbent, a decrease of distribution coefficient with increasing concentration of ammonium ions in solution was observed (Figure 2). It should be noted that at low concentrations ( $C_0 < 10$  mmol/dm<sup>3</sup>) the highest value of  $K_d$  for MCAc sample was found. This fact testifies that the high intensity  $\text{H}^+ - \text{NH}_4^+$  ion-exchange makes major contribution to the sorption process on acidly treated sorbent. On the other hand, ion-exchange of  $\text{Na}^+$  for  $\text{NH}_4^+$  takes place predominantly on alkali-treated sample.

At concentrations  $C_0 > 10$  mmol/dm<sup>3</sup>, an increase in  $K_d$  for MCAlk is observed compared to the MCAc through its greater exchange capacity and a significant contribution of nonexchange absorption.

TABLE 4: Quantity of exchangeable cations desorbed from natural  $M_{45}C_{20}$  sorbent by sorption of  $NH_4^+$ -ions.

$C_{\text{equilb.}} (NH_4^+)$ , mmol/dm <sup>3</sup>	Quantity of desorbed cations, mmol/g				$\sum Na^+, K^+, Ca^{2+}, Mg^{2+}$ , mmol/g	$C_{NH_4^+}$ in sorbent phase, mmol/g
	$Na^+$	$K^+$	$Ca^{2+}$	$Mg^{2+}$		
1.950	0.085	0.020	0.370	0.092	0.567	0.550
4.143	0.115	0.025	0.481	0.208	0.829	0.857
8.806	0.134	0.029	0.741	0.301	1.207	1.194
23.363	0.154	0.035	0.952	0.395	1.536	1.637
48.228	0.160	0.039	1.105	0.453	1.757	1.772
73.108	0.170	0.041	1.180	0.509	1.901	1.892
98.076	0.170	0.041	1.180	0.509	1.901	1.924

TABLE 5: Quantity of exchangeable cations desorbed from acidly treated  $M_{45}C_{20}$  sorbent by sorption of  $NH_4^+$ -ions.

$C_{\text{equilb.}} (NH_4^+)$ , mmol/dm <sup>3</sup>	Quantity of desorbed cations, mmol/g				$\sum Na^+, K^+, Ca^{2+}, Mg^{2+}$ , mmol/g	$C_{NH_4^+}$ in sorbent phase, mmol/g
	$Na^+$	$K^+$	$Ca^{2+}$	$Mg^{2+}$		
1.695	0.029	0.013	0.504	0.036	0.581	0.805
3.787	0.040	0.015	0.677	0.058	0.790	1.213
8.288	0.048	0.017	0.909	0.071	1.046	1.712
22.951	0.053	0.017	0.949	0.093	1.112	2.049
47.607	0.053	0.019	0.949	0.093	1.113	2.393
72.592	0.053	0.019	0.949	0.093	1.113	2.408
97.589	0.053	0.019	0.949	0.093	1.113	2.411

3.3. Influence of Activation of Natural  $M_{45}C_{20}$  Sorbent on Ratio between Ion-Exchange and Non-Ion-Exchange Sorption of  $NH_4^+$ -Ions. To assess contributions of ion-exchange and non-ion-exchange sorption of ammonia ions by investigated aluminosilicate samples, quantities of displaced exchangeable cations of  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  were determined (Table 4).

It is seen from Table 4 that the total number of displaced exchangeable cations was almost equal to the amount of absorbed  $NH_4^+$ -ions on natural sorbent in the whole range of external solution concentration. This fact, as was indicated earlier, suggests that the uptake of ammonium ions by natural sorbent was due to the exchange reaction between the ammonium ions in aqueous solution and exchangeable cations in the sorbent phase. The intensity of  $NH_4^+$ -ions

exchange for cations decreases in the sequence  $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ .

As shown in Table 5, the amount of  $NH_4^+$ -ions adsorbed by acid-activated samples MCAc exceeds about twice the total amount of desorbed cations  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ . This can be related, firstly, to the transition of natural sorbent into  $H^+$ -form by the acid treatment. As a result, the composition of cation-exchange complex of MCAc, to a greater extent, was determined by exchange hydronium ions, whose quantity was 0.79 mmol/g, and was estimated as difference in the amount of desorbed cations by sorption on MCN and MCAc-samples. In addition, protons of silanol groups, located next to three-coordinated aluminum atoms as well as on the surface of the sorbent, were also involved in the exchange reaction [33]

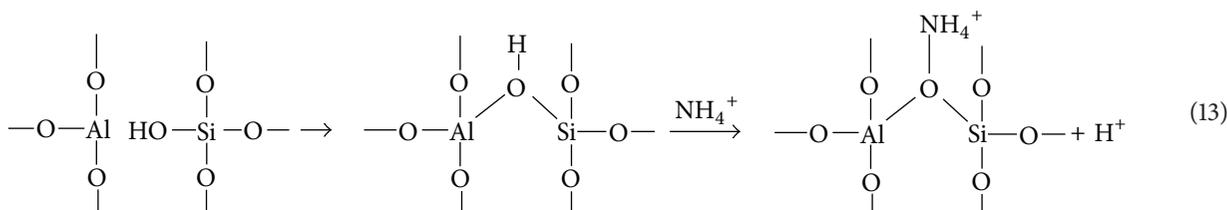


Table 6 shows that the total cation-exchange capacity of aluminosilicate MCAc was increased by 1.5 times due to an increase in proportion of  $Na^+$ -ions in the interlayer space as a result of alkali treatment. Therefore, ion-exchange mechanism of sorption of  $NH_4^+$ -ions implies their exchange

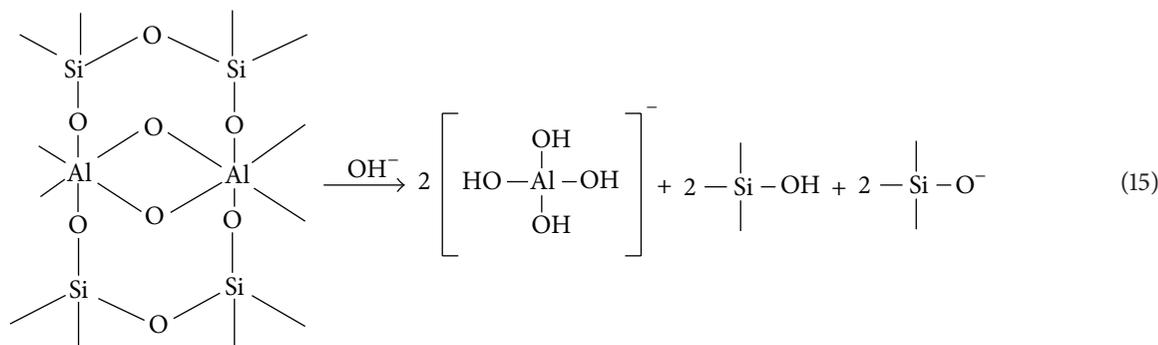
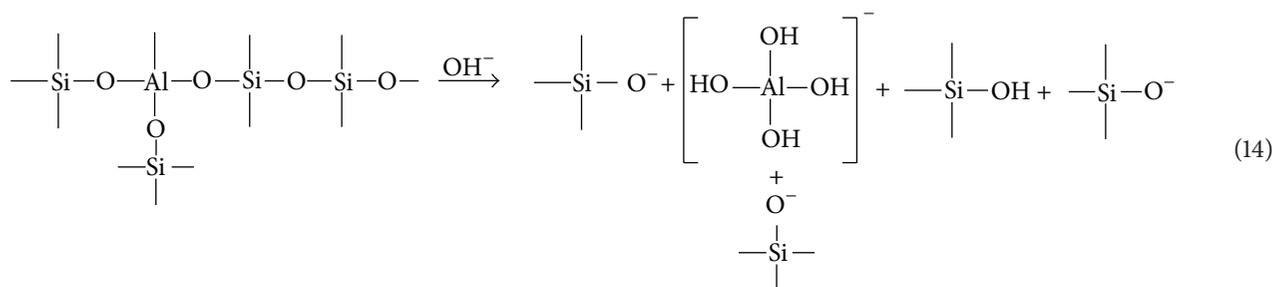
interaction mainly with  $Na^+$ -ions. However, despite this, the quantity of adsorbed ammonium ions was about 1.5 times higher than the number of desorbed exchange cations for alkaline-activated sorbent. The increased amount of adsorbed  $NH_4^+$ -ions by MCAc sorbent phase compared to the amount

TABLE 6: Quantity of exchangeable cations desorbed from alkali-treated  $M_{45}C_{20}$  sorbent by sorption of  $NH_4^+$  -ions.

$C_{\text{equilb.}}(NH_4^+)$ , mmol/dm <sup>3</sup>	Quantity of desorbed cations, mmol/g				$\sum Na^+, K^+, Ca^{2+}, Mg^{2+}$ , mmol/g	$C_{NH_4^+}$ in sorbent phase, mmol/g
	$Na^+$	$K^+$	$Ca^{2+}$	$Mg^{2+}$		
1.915	0.397	0.018	0.351	0.052	0.817	0.585
3.916	0.554	0.024	0.521	0.096	1.195	1.084
8.545	0.773	0.029	0.721	0.166	1.690	1.455
22.579	0.923	0.034	0.994	0.209	2.160	2.421
47.213	1.202	0.041	1.061	0.223	2.524	2.787
95.831	1.260	0.042	1.204	0.250	2.782	4.169
195.580	1.291	0.042	1.202	0.265	2.797	4.420

of desorbed exchangeable cations most likely testifies to a significant contribution of nonexchange sorption mechanism. In this case, the transformation of the layered clay structure of the original  $M_{45}C_{20}$  aluminosilicate into the zeolite one with the formation of new zeolite phase, heulandite, should be considered. Under the action of NaOH solution, there

was a destruction of silicon skeleton of clinoptilolite and aluminosilicate frame of montmorillonite via  $-Si-O-Si-$ ,  $-Si-O-Al-$ , and  $-Al-O-Al-$  bonds with formation of low polymeric aluminate and silicate anions and the anions of silicon acids [34] according to scheme (13) for clinoptilolite and (14) for montmorillonite:



Expanding the size of entry channels of aluminosilicate, providing occurrence of ammonium ions in the internal cavity and additional hydroxylation of surface, contributed to the sorption of ammonium ions in micropores of the sorbent due to additional interaction, leading to formation of a weak electrolyte  $NH_4OH$  in the sorbent phase.

#### 4. Conclusion

Sorption capacity for  $NH_4^+$  ions of natural complex  $M_{45}C_{20}$  sorbent was carried out applying its acid and alkali treatment.

As a result of acid activation, the composition of ion-exchange complex of MCAc sorbent was provided mainly by

hydronium ions; the specific surface area and porosity were increased due to decationating and dealumination processes as well as dissolution of impurities.

In case of alkaline activation, mainly  $Na^+$  and  $Ca^{2+}$  ions constituted the ion-exchange complex of sorbent and the contribution of the zeolite-like structural component of the aluminosilicate was increased.

The preferential exchange of  $H^+$  for  $NH_4^+$  ions was typical for acid-treated sample, while for alkali-activated one, there was a significant contribution of nonexchange  $NH_4^+$  ions absorption resulting from additional interaction with newly formed silanol groups, leading to formation of a weak electrolyte  $NH_4OH$  in the sorbent phase.

## Symbols

$M_{45}C_{20}$ : Natural sorbent containing 45% of montmorillonite and 25% of clinoptilolite

MCN: Natural sorbent

MCAC: Acid-treated sorbent

MCAk: Alkali-treated sorbent

$q$ : Quantity of the sorbate per mass unit of sorbent under equilibrium, mmol/g

$q_m$ : Monolayer adsorption, mmol/g

$q_{co}$ : Maximal sorption capacity of sorbent, mmol/g

$q'_{co}$ : Adsorption value per unit of sorbent volume, mmol/cm<sup>3</sup>

$C_0$ : Initial concentration of NH<sub>4</sub>Cl solution, mmol/dm<sup>3</sup>

$C_{equil}$ : Equilibrium concentration of NH<sub>4</sub>Cl solution, mmol/dm<sup>3</sup>

$V$ : Volume of NH<sub>4</sub>Cl solution, dm<sup>3</sup>

$m$ : Mass of sorbent charge, g

SSA: Specific surface area, cm<sup>2</sup>/g

$K_a$ : Constant of adsorption equilibrium, dm<sup>3</sup>/mmol

$K_d$ : Distribution coefficient

$\epsilon$ : Porosity of sorbent layer

$\rho_b$ : Bulk density of sorbent, respectively, g/cm<sup>3</sup>

$\rho_a$ : Apparent density of sorbent, respectively, g/cm<sup>3</sup>.

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