Adsorption modification of the zeolite surface with chitosan

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In order to modify the surface, thermal acid activation of the zeolite of the Chankanai deposit was conducted. It was found that the treatment of the mineral with acid at high temperature leads to a decrease in the content of Ca, Al and Sr in its composition. Adsorption of chitosan on the surface of thermoacid-activated zeolite was also studied. Processing of the adsorption isotherms according to Langmuir and Freundlich models showed that the maximum adsorption of chitosan on the zeolite surface is 30.1 mg/g and the Freundlich constant 1/n is 0.75. On the IR-spectra of chitosan-modified zeolite, a certain shift to the higher frequencies of the peak was found at the oscillation frequency of 1638 cm^{-1}, which can be explained by the contribution of amino groups adsorbed on the surface of the mineral. The shift to the left of the peak at 581 cm^{-1}, typical for aluminosilicate groups, is also an evidence of their interactions with chitosan. When studying the effect of chitosan concentration on the wetting of the modified zeolite powder, it was found that at concentration of $2\cdot10^{-3}$ base mol/L, an increase in the wetting angle from 10° to 47° occurs due to surface overcharging. According to the data of adsorption, IR spectroscopy and wetting of the surface, the main mechanism for binding chitosan to the zeolite surface was due to the electrostatic interaction of polymer amino groups with silicate and aluminosilicate groups of the mineral, stabilized by hydrogen bonds between the OH-groups of the polymer and ≡Si-O-groups of the solid phase.

Keywords: zeolite; chitosan; modification; adsorption; thermal acid activation.

Цеолит бетін хитозанмен адсорбциялық өңдеу

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Бетті өңдеу мақсатында Шаңқанай кен орнының цеолитін термоқышқылдық активациялау жүргізілді. Жоғары температурада минералды қышқылмен өңдеу оның құрамындағы Ca, Al және Sr үлесінің төмендеуіне апаратындығы анықталды. Термоқышқылды белсендірілген цеолит бетінде хитозанның адсорбциясы зерттелді. Адсорбция мәліметтерін Ленгмюр және Фрейндлих модельдері бойынша өңдеу цеолит бетіндегі хитозанның максималды адсорбциясының мәні 30,1 мг/г, ал 1/n константасының 0,75-ке жететіндігін көрсетті. Хитозанмен өңделген цеолиттің ИҚ-спектрінде 1638 $см^{-1}$ тербеліс жиілігіндегі шыңның жоғары жиілігі анықталды, бұл жайт минерал бетінде адсорбцияланған амин топтарының үлесімен негізделді. Алюмосиликатты топтарға тән 581 $см^{-1}$ аймағындағы шыңның да сол жаққа ығысуы олардың хитозанмен өзара әрекеттесуінің дәлелі болып табылады. Хитозан концентрациясының цеолит ұнтағына су тамшыларының жұғуына әсерін зерттеу барысында полимердің $2\cdot10^{-3}$ негіз-моль/л концентрациясында жұғу бұрышының 10°-тан 47°-қа дейін артуы байқалды және бұл өзгерістер беттің теріс зарядының оң зарядқа ауысуымен негізделді. Адсорбция, ИҚ-спектроскопия, сканерлеуші электрондық микроскопия және жұғу мәліметтері бойынша хитозан макромолекулаларының цеолит бетімен байланысуының негізгі механизмі полимердің амин топтарының минералдың силикаттық және алюмосиликаттық топтарымен электростатикалық әрекеттесуі болып табылады, бұл әрекеттесу полимердің ОН-топтары мен қатты фазаның ≡Si-O- топтары арасындағы Н-байланыстармен тұрақтандырылған.

Түйін сөздер: цеолит; хитозан; өңдеу; адсорбция; термоқышқылдық активация.

Адсорбционная модификация поверхности цеолита хитозаном

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С целью модификации поверхности проведена термокислотная активация цеолита Чанканайского месторождения. Установлено, что обработка минерала кислотой при повышенной температуре приводит к снижению содержания Ca, Sr и Al в его составе. Изучена адсорбция хитозана на поверхности термокислотно-активированного цеолита. Обработка данных адсорбции по Ленгмюру и Фрейндлиху показала, что значение максимальной адсорбции хитозана на поверхности цеолита составляет 30,1 мг/г, а константы 1/n - 0,75. На ИК-спектрах модифицированного хитозаном цеолита обнаружено некоторое смещение влево пика при частоте колебаний 1638 $см^{-1}$, что объяснено вкладом аминогрупп, адсорбированных на поверхности минерала. Смещение влево пика при 581 $см^{-1}$, характерного для алюмосиликатных групп, также является свидетельством их взаимодействия с хитозаном. При изучении влияния концентрации хитозана на смачивание порошка цеолита установлено, что при концентрации $2\cdot10^{-3}$ осново-моль/л происходит увеличение угла смачивания от 10° до 47°, обусловленное перезарядкой поверхности. На основании данных адсорбции, ИК-спектроскопии и смачивания поверхности сделано заключение, что основным механизмом связывания хитозана с поверхностью цеолита является электростатическое взаимодействие аминогрупп полимера с силикатными и алюмосиликатными группами минерала, стабилизированное Н-связями между ОН-группами полимера и ≡Si-O- группами твердой фазы.

Ключевые слова: цеолит; хитозан; модификация; адсорбция; термо-кислотная активация.

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1. Introduction

Clay minerals are the most widely used natural raw materials, ranging from building materials to enterosorbents [1-5]. Among them, zeolites, so-called “molecular sieves”, are particularly distinguished, due to their ability to adsorb molecules smaller than 10 Å. Along with high adsorption capacity, they also have ions-exchange properties [6-8]. The use of zeolites for purification of gases was also reported [9]. The high porosity and the ability to control particle size by dispersion determine the prospects for using this mineral in the development of composite materials: in construction chemistry by combining with other minerals, in biotechnology as carriers of enzymes, microorganism cells to create selective biosorbents and biocatalysts. However, as natural minerals, zeolites have a negative charge on their surface. Most microbial cells are also negatively charged. For combination with other minerals and microbial cells, the modification of the zeolite surface with positively charged polymers and surfactants is needed. The well-known cationic polymers and surfactants such as polydimethyldiallylammonium chloride, polyvinylpyridinium chloride, cetylpyridinium bromide and chloride can have toxic effects on enzymes and microbial cells. Among cationic polymers, chitosan obtained from chitin is most harmless to living organisms and environment [10,11]. However, there is no information in the literature about the use of chitosan to regulate the surface properties of clay minerals. In this regard, the aim of this study was to modify the surface of the zeolite using chitosan.

2. Experiment

Zeolites of Chankhanai deposit (Almaty region) were used. Zeolite samples were crushed to particle size of 10-30 µm, then washed twice with distilled water and dried at 200°C. However, zeolite particles with long-term exposure in the aqueous medium increased the optical density of suspensions due to leaching of fine particles of impurities, which complicated their analysis. In this respect, the method of treatment with mineral acid and high temperature was used, which is widely used for purification of clays from impurities [12, 13]. 50 g of zeolite were mixed with 250 mL of 15% (w/w) H_2SO_4, boiled for 4 h at 100°C on a water bath. Then the mineral was washed with distilled water, pH of which was brought to 7 by 0.1 M NaOH. The purified zeolite was dried at 200°C for 2 h.

Zeolite composition was determined using X-ray fluorescence spectrometer Focus 2M (Russia) using Fe-radiation in the range from 2 V to 37 V with a measurement accuracy 3%. The intensity of the diffraction maxima was estimated by an analytical method in a tetragonal singoniya. Experiments were carried out at 25±0.2°C**.**

Chitosan purchased from Sigma Aldrich (USA) was used for the modification of zeolite. The concentration of chitosan was varied in the range of $(0.1\text{-}1.0)\cdot10^{-2}$ base mol/L. For this purpose, 100 mL of a solution containing 0.16 g of chitosan was prepared. Then 1 mL of the solution was mixed with 9 mL of distilled water. Other solutions were prepared in a similar way. For modification of the zeolite surface, 1 g of mineral sample was put in 20 mL chitosan solution with a concentration of $(0.1\text{-}1.0)\cdot10^{-2}$ base mol/L for 2 h. Adsorption of chitosan on the zeolite surface was calculated by the formula: $A=(C_1-C_2)\cdot V/m$, where C_1 and C_2 – initial and equilibrium concentrations of chitosan, base mol/L; V – solution volume, L; m – zeolite mass, g.

Determination of chitosan concentration was performed using UV–7504 (Shanghai, China) spectrophotometer with a measurement accuracy ±2%. Analysis was based on the dependence of the optical density of polymer solutions on the concentration. Experiment was carried out in cuvettes with an absorbing layer thickness of 1 cm. The dependence of the optical density of the chitosan solution with concentration of $1 \cdot 10^{-2}$ base mol/L on a wavelength in the range of 200-800 nm in 10 nm increments was obtained. The maximum optical density corresponded to a wavelength of 210 nm. Then, at this wavelength, a concentration dependence of the optical density of chitosan was obtained. Range of polymer concentration from 10^{-3} base mol/L to 10^{-2} base mol/L was used. For analysis, the linear range of the curve was used.

FTIR-spectroscopy studies were performed using the Fourier-transform infrared spectrometer Avatar 370-CsI (Thermo Nicolet, USA) in tablets with KBr. For this, the samples of thermal-acid-activated zeolite, chitosan powder, and zeolite treated with $1 \cdot 10^{-2}$ base mol/L concentration solution of chitosan were used. Each of them was individually pressed with KBr at the ratio 2:250 (mg/mg). Studies were conducted in the frequency range from 400 to 4000 cm^{-1}.

KBr with quality "pure for analysis" (ChemPlus, Russia) was used during FTIR analysis for the preparation of tablets. Dried sample of KBr was used.

The wetting angle was determined by applying water droplets to the powder of zeolite samples modified with chitosan solution with concentration from $0.1 \cdot 10^{-2}$ to $1.0 \cdot 10^{-2}$ base mol/L, and drawing the tangents to the images of droplets.

3. Results and discussion

There are two large zeolite deposits in Kazakhstan: Tayzhuzgen (East Kazakhstan Region) and Chankanay (Almaty Region). The zeolites of the Chankanay deposit are smaller than the Tayzhuzgen ones. In addition, the latter contain quartz in their composition, which compicates their grinding. Thermal-acid treatment improves the quality of clay sorbents, however, it significantly changes their composition. It was found that thermal-acid treatment of the Chankanay deposit zeolite results in the decrease of the amount of Ca, Al, Ti, Mn and Sr in the composition of the mineral, and the decrease in the content of Ca, Al and Sr is particularly observable (Figure 1, Table 1). The Ca content in the initial sample decreased from 8.9 wt% to 1.8 wt% after treatment; the Sr content decreased from 2.1 wt% to 0.5 wt%. In the case of Al, a decrease of content from 24.3 to 16.6 wt% was observed. At the same time, there is a significant increase in the amount of silicon and iron. This change in the composition of zeolite indicates that Ca, Mn, and Sr compounds in the composition of the mineral are presented as impurities, which can be easily removed by thermal-acid treatment. The decrease of Al content can be explained by specific decomposition of mineral structure. An increase in the amount of Si and Fe can be associated with an increase in their specific contribution to the mass of zeolite upon dissolution of other elements. It also follows from these data that Ca, Al, Ti, Mn and Sr ions play the role of exchange cations, and atoms of Si and Fe, being the main components of the crystal lattice of the mineral, will play a decisive role in the adsorption of other substances on the zeolite surface.

Table 1 – Effect of thermal-acid activation on the composition of the zeolite

Base elements	Mass content, %	
	Natural zeolite	Thermal-acid activated zeolite
K	4.7	5.0
Ca	8.9	1.8
Si	18.4	29.1
Fe	40.0	45.8
Al	24.3	16.6
Ti	1.1	0.9
Mn	0.5	0.3
Sr	2.1	0.5

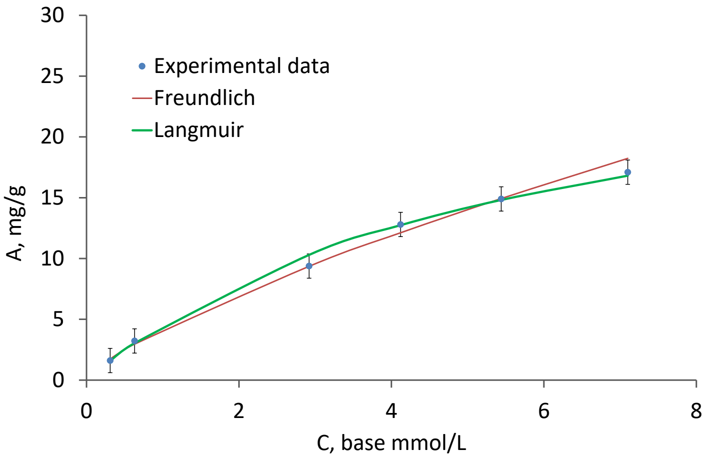

Figure 1 – Adsorption isotherm of chitosan on the surface of thermal-acid activated zeolite, T=25°C

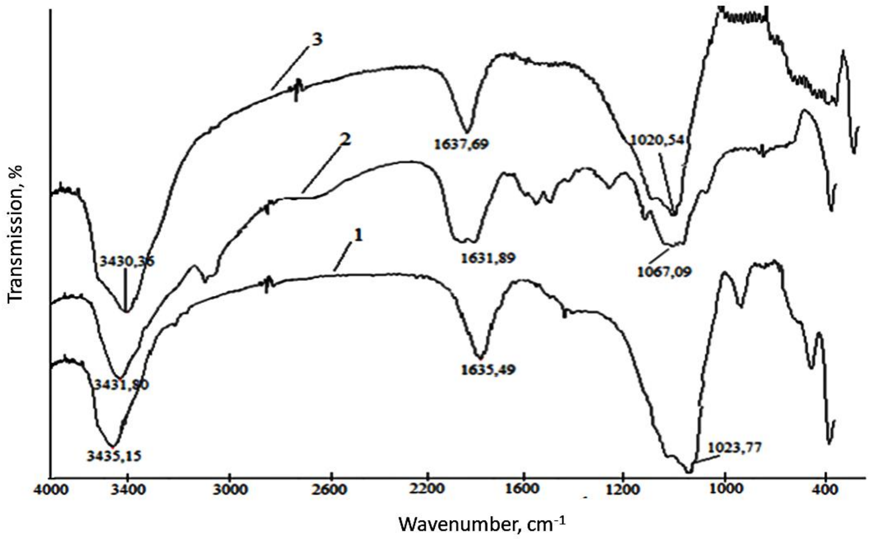

Figure 2 – FTIR spectrum of thermal-acid activated zeolite (1), chitosan (2) and zeolite-chitosan system (3)

Studies on the surface modification of zeolite particles after thermal-acid treatment were aimed at determining the optimal concentration of the modifying agent (Figure 1). The isotherm of chitosan adsorption on zeolite has the form of a rising curve. The data of adsorption were described using Langmuir and Freundlich models [14]. To do this, Langmuir's equation was transformed into the straight-line equation:

$$\frac{C}{A} = \frac{1}{A_{max} \cdot K} + \frac{C}{A_{max}} \quad (1)$$

The intercept was equal to $\frac{1}{A_{max} \cdot K}$, and the slope was equal to $1/A_{max}$. The value of maximum adsorption of chitosan on the surface of zeolite according to Langmuir model was 30.1 mg/g, which is close to the values of adsorption of low-molecular surfactants on the surface of clays [15]. To calculate the Freundlich constants, the adsorption data $A=K_F \cdot C^{1/n}$ were represented graphically as a function of $lgA=f(lg\,C)$. The intercept was equal to lgK_F, and the slope was equal to $1/n$. The value of constant K_F indicates the adsorption capacity of adsorbent, and $1/n$ indicates the affinity of the adsorbed substance to the adsorbent, i.e. the intensity of interaction of an adsorbate-adsorbent. If the value of $1/n$ is in the range of 0.6-0.8, the adsorbent is considered favorable for adsorption [16,17]. In the case of chitosan adsorption on zeolite, $1/n$ was equal to 0.75 meaning that it is within this interval.

The adsorption isotherms constructed using Langmuir and Freundlich constants coincide with the isotherms obtained from experimental data. The values of the determination coefficient R^2 were 0.98 for the Langmuir model and 0.99 for the Freundlich model (Table 2). It follows that both models satisfactorily describe the process of adsorption of chitosan on the zeolite surface.

FTIR-spectroscopic studies were conducted to obtain information on the mechanism of zeolite-chitosan interaction. The data of FTIR-spectroscopic measurements of zeolite before and after chitosan modification are shown in Figure 2. In the case of the initial zeolite, the greatest adsorption bands were recorded at the frequencies of vibration of 3435 cm^{-1}, 2488 cm^{-1}, 1635 cm^{-1}, 1024 cm^{-1}, 856 cm^{-1} and 581 cm^{-1}. Fluctuations in the range from 1600 to 3600 cm^{-1} can be caused by deformation vibrations of OH-groups of water molecules and SiOH-groups of mineral. The peak at 1024 cm^{-1} can be provided with deformation vibrations of Si-O-Si groups, and the peak at 581 cm^{-1} is due to the presence of Si-O-Si and Al-O-Si groups in the zeolite [18,21].

In the FTIR-spectrum of chitosan, the peak at 3432 cm^{-1} can be due to OH-groups of water molecules. In addition, it can be attributed to the NH_2-groups of the polymer. The adsorption band at 2881 cm^{-1}can be attributed to the vibrations of C-H bonds of the hydrocarbon chains of chitosan, and band at 1632 cm^{-1} is caused by NH_2- groups. The wide adsorption band at the 1067 cm^{-1} frequency can be explained by the skeletal vibrations of the C-O groups [19,20].

Table 2 – The comparison of models of chitosan adsorption on the surface of zeolite

System	Temperature, °C	Langmuir model			Freundlich model		
		K_L, L/mg	A_{max}, mg/g	R^2	1/n	K_F, mg/g	R^2
Zeolite-chitosan	25	0.18	30.1	0.98	0.75	4.18	0.99

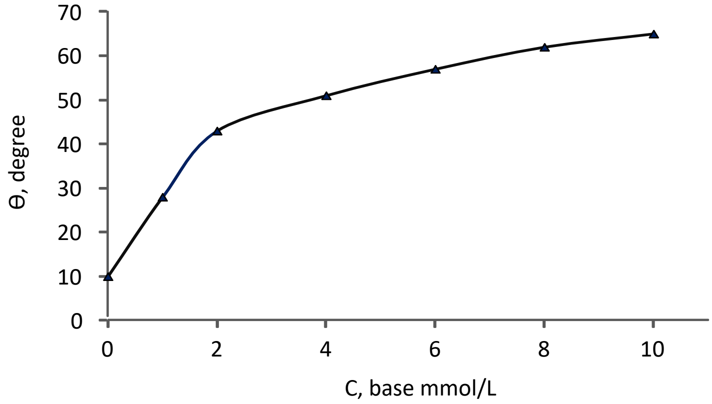

Figure 3 – Effect of chitosan concentration on the wetting of zeolite particles surface

In the FTIR-spectrum of the modified zeolite, all characteristic bands of the initial zeolite were observed (Figure 3). Some shifts to the higher frequencies of the peak at 1638 cm^{-1} can be explained by the contribution of amino groups adsorbed on the surface of the mineral. The shift to the left of the peak at 581 cm^{-1}, typical for aluminosilicate groups, is also evidence of their interaction with chitosan. Vibrations at 856 cm^{-1} and 921 cm^{-1} can be assigned to Si-O-Si bonds [21, 22].

Based on the FTIR-spectroscopy data it can be assumed that the adsorption of chitosan on the zeolite surface takes place due to the electrostatic interaction of amino groups of the polymer with the silicate and aluminosilicate groups of the zeolite, stabilized by hydrogen bonds between the OH, NH_2-groups of chitosan and the oxygen atoms of the silicate groups.

Studies of the wettability of the surface of mineral particles were also conducted to confirm the fact of modification of the zeolite surface with chitosan solution (Figure 3). Water droplets instantly spread on the surface of the initial mineral with a wetting angle of 10°. After modification, there is a sharp increase in the wetting angle due to the adsorption of macromolecules of the cationic polymer on the zeolite surface. At concentration of $2{\cdot}10^{-3}$ base-mol/L, the contact angle increased to 47°. When changing the polymer concentration from $4{\cdot}10^{-3}$ to $1{\cdot}10^{-2}$ base-mol/L, the contact angle values were within 60° indicating the high hydrophilicity of the zeolite surface [23]. The hydrophilicity of the mineral surface covered with the polymer can be caused by the presence of OH-groups along the macromolecules of chitosan. In addition, some of the polymer amino groups can remain free, without participating in electrostatic interaction with the zeolite surface. Such phenomenon takes place in the case of excessive amount of polymer in the system in relation to the solid surface. In fact, electron micrographs of zeolite after modification show a tendency to increase the particle size (Figure 4), which can result from the flocculating action of the adsorbed polymer. Thus, the polymer adsorption leads to a recharge of the surface or change of the charge from negative to positive.

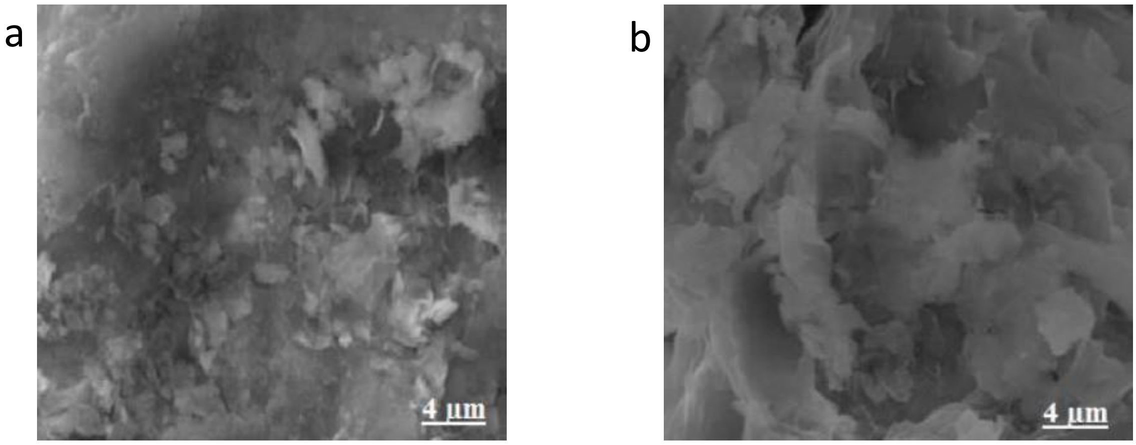

Figure 4 – Electron microscopic images of the thermal-acid activated zeolite before (a) and after modification (b) by chitosan (x 30000)

4. Conclusions

Thus, using the adsorption of chitosan on the surface of thermal acid-activated zeolite, the modification of its surface was conducted. It was shown that the surface modification leads to a change of the negative charge of the mineral to positive. The main forces responsible for the adsorption of chitosan are electrostatic interactions and hydrogen bonds.

In order to increase the adsorption capacity of the zeolite, thermal-acid activation has been proposed. Modification of thermal-acidactivated zeolite surface with a negative charge by adsorption of cationic polymer chitosan conducted, and the maximum adsorption of chitosan on the zeolite surface was found to be 30.1 mg/g. Modification was proved using FTIR analysis. It was found that the modification of the surface leads to change of negative charge of the mineral to a positive. Shift of the frequencies from 1635 cm^{-1} to 1638 cm^{-1} is the evidence of presence of positive charged amino groups of the zeolite surface. Changing of the peak at 581 cm^{-1}, characterizing aluminosilicate groups, is also evidence of their interaction with chitosan.

The main forces responsible for the adsorption of chitosan on the zeolite surface are electrostatic interactions and hydrogen bonds. Studies of the wettability of the surface of mineral particles showed that the contact angle was increasing with the increase of concentration of the polymer and the maintenance of the high hydrophilicity of the surface of zeolite.

These results can be used for sorbents preparation in sewage treatment, for the development of effective biocatalysts and biosorbents in biotechnology, for targeted changing of built materials hydrophilicity in construction.

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