STUDY OF THE ADSORPTION OF WATER , BENZENE VAPORS OF NATURAL AND MODIFIED MONTMORILLONITE

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Received 26.02.2026
Reviewed 28.03.2026
Accepted 30.04.2026

To produce effective adsorbents and catalysts based on natural aluminosilicates, it is necessary to control their porous structure and parameters depending on various factors. The pore-structural characteristics of natural and modified montmorillonite samples were studied based on their adsorption of water and benzene vapor, and their kinetic properties were also examined.

The textural properties of the modified montmorillonite samples were analyzed using adsorption isotherms of benzene and water molecules, which determined the radial distribution of pore volume. The results showed that the specific pore volume and effective pore diameter of montmorillonite increase with increasing pressure. This indicates the presence of a more developed mesoporous structure in this sorbent. A study of the adsorption and structural properties of natural and modified montmorillonite revealed that after treatment with aqueous solutions of various metal salts, its specific surface area and total pore volume increase.

***Keywords**: montmorillonite, benzene, sorbent, isotherm, adsorption, specific surface area, pore volume.*

https://doi.org/10.59849/0005-2531.2026.3.95

Introduction

Clay minerals with a layered structure and variable interlayer space, such as montmorillonite and vermiculite, are of considerable interest as adsorbents due to their developed porous structure and ion exchange capacity. The peculiarities of their structure determine their high sensitivity to the nature of the adsorbed substances, especially polar compounds such as water, alcohols and amines. It has been established that in the interlayer space of montmorillonite, adsorbed water molecules are coordinated by exchange cations, simultaneously forming hydrogen bonds both with the surface oxygen atoms of the crystal lattice and with each other. The interaction of water molecules with the mineral surface is determined by a combination of ion-dipole, hydrogen, and van der Waals interactions. The influence of exchangeable cations, particularly transition metal ions, manifests itself in a significant distortion of the electronic structure of the adsorbed molecules, allowing them to be considered aprotic Lewis acid sites with pronounced electron-withdrawing capacity. Adsorption processes on montmorillonite are usually described by the polymolecular adsorption model, in particular the BET equation, which allows one to estimate the specific surface area and parameters of the porous structure of the material. Natural montmorillonite is characterized by pronounced hydrophilicity, but its modification with metal salts leads to a significant change in surface properties, including an increase in the specific surface area, pore volume, and a shift in equilibrium towards hydrophobicity, which

increases its adsorption capacity in relation to organic compounds such as benzene.

It should be noted that traditional criteria for assessing hydrophilicity, such as specific heat of wetting, are not always applicable to microporous systems due to the difficulty of correctly determining their specific surface area. In this regard, the study of the adsorption-structural characteristics of montmorillonite based on adsorption-desorption isotherms of various substances is of particular relevance.

Our Republic has significant reserves of natural aluminosilicates, in particular montmorillonite from the Ag-Dere deposit, which opens up broad prospects for their practical use as adsorbents and catalysts. For the effective use of this raw material, a detailed study of its porous structure and the study of adsorption patterns depending on various factors is necessary.

The aim of the work is to study the porous-structural characteristics of natural and modified montmorillonite based on the analysis of adsorption-desorption isotherms of water vapor and benzene, as well as to establish the influence of exchange cations on their adsorption properties. The structure of the pore space of natural montmorillonite from the Ag-Dere deposit was studied, and the adsorption-desorption isotherms of water vapor and benzene were also studied. The specific surface area and total pore volume were determined using the BET method, the kinetics of adsorption processes were analyzed, and the effect of modification on the hydrophilic-hydrophobic properties of the material was revealed [1-3].

As a result of the study of the adsorption-structural properties of natural and modified forms of montmorillonite, it was shown that after treating montmorillonite with aqueous solutions of salts of various metals, the specific surface area and total pore volume of montmorillonite increase. It has been shown that chemical and structural modification makes it possible to change the physicochemical properties of montmorillonite and significantly expand the areas of their possible application. The study of the chemistry and texture of the surface of sorbents is of particular interest due to the fact that it is this surface that serves as the interface between the adsorbent and the liquid or gaseous phases. It should be noted that all sorption processes of gases and vapors begin with the act of adsorption on the outer surface of sorbents and catalysts, which is of great importance [4–6]. At very low relative vapor pressures, equilibrium, especially in the case of strong adsorption on adsorbents with a non-uniform surface, is usually established very slowly.

Experimental part

For the experimental study, natural montmorillonite, collected from the Ag-Dere deposit (Republic of Azerbaijan), was used. The montmorillonite content in the samples was about 75%, the remainder was represented by quartz, feldspar and calcite. When studying the geometric structure of sorbents obtained on the basis of natural aluminosilicates, it is necessary to use adsorption isotherms of vapors of various substances for quantitative analysis and comparative study of intermolecular interactions of adsorbent–adsorbate and adsorbate–adsorbate, as well as to evaluate changes in the physicochemical properties of the sorbent surface depending on various factors. The Co^{2+} form of montmorillonite was obtained by ion exchange treatment with aqueous solutions of cobalt salts using a well-known technique described in the literature [7-9]. The adsorption of Co^{2+} ions on thermally treated bentonite was characterized using scanning electron microscopy. Based on the conducted studies, it was established that when modified with cobalt salts, the Na+, K+, Ca^{2+} cations located in the interlayer space of bentonite were exchanged for Co^{2+} ions. (Fig. 1)

Mg K	1.47	1.28	2.43	MgO
Al K	6.49	5.09	12.26	Al_2O_3
Si K	34.19	25.78	73.15	SiO_2
Cl K	0.00	0.00	0.00	-
K K	1.09	0.59	1.31	K_2O
Ca K	1.13	0.60	1.59	CaO
Fe K	1.68	0.64	2.16	FeO
Co K	5.58	2.00	7.09	CoO
O	48.37	64.02		
Results	100.00			

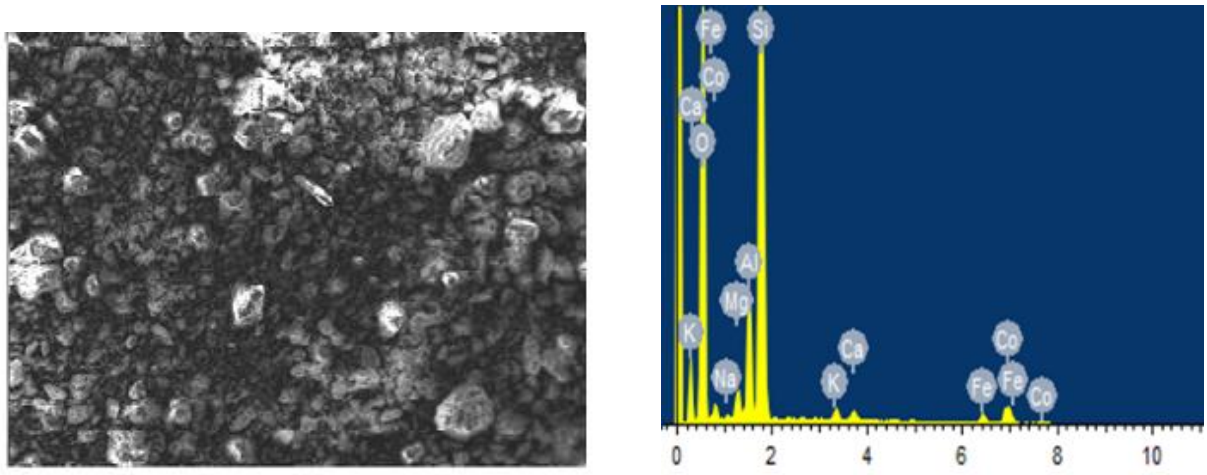

Fig. 1. Elemental analysis of the Co^{2+} form of montmorillonite using a scanning microscope

The study of the distribution of pore volume by radii of sorbents obtained on the basis of montmorillonite when using them as catalysts and adsorbents in various branches of petrochemical-chemical processes has important theoretical and practical significance. Using the vapor adsorption isotherm, one can gain insight into the structural characteristics of sorbents. The adsorption-desorption isotherms of adsorbents have an S-shape, caused by the sequential filling of the pores of sorbents obtained from natural crystalline aluminosilicates. The study focused on determining the porous-structural characteristics of montmorillonites based on benzene and water vapor adsorption using the BET method and derivatography. Adsorption-desorption isotherms of water and benzene vapor on sorbent samples were measured using a vacuum setup with a McBean-Bakr quartz balance. Using adsorption-desorption isotherms, we determined the monolayer capacity, the fraction of undesorbed adsorbate, the total pore volume, and the specific surface area of the adsorbent for benzene vapor. To measure the specific surface area using the BET method, adsorption to a relative pressure of 0.3-0.4 mmHg is sufficient. The rate at which adsorption equilibrium is established depends on the nature of the adsorbent. The sorbents were pre-evacuated for 6 hours at 20°C. Adsorption-desorption isotherms of benzene and water on natural montmorillonite. Polar molecules with small diameters, like water, easily penetrate the mesopores of natural montmorillonite due to ion-dipole interactions with exchangeable cations located in the montmorillonite mesopores.

In Fig. 2 the adsorption isotherms of water vapor at a temperature of 20°C by natural montmorillonite are presented. As can be seen from Fig. 2, polar molecules with small

diameters (like water) easily penetrate into the micropores of natural montmorillonite due to ion-dipole interaction with exchange cations located on the micropores of montmorillonite. This process corresponds to a circular rise in the water adsorption isotherm in the region of relatively low pressures at P/Ps=0.30-0.40. At this stage, water adsorption occurs due to the filling of the remaining unoccupied space of the micropores of the sorbent with the adsorbate. Up to P/Ps = 0.9, adsorbed water molecules form hydrogen bonds between themselves and exchange cations from the first coordination sphere of the sorbent, while the adsorption curve of the Co^{+2}-form of montmorillonite rises sharply to P/Ps = 0.9. Thisndicates the presence in the sorbent there are more developed secondary transition pores.

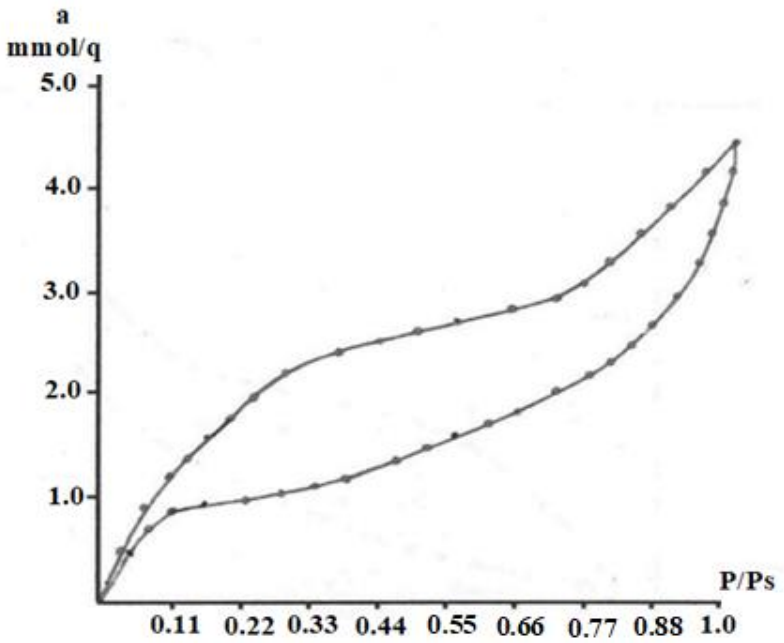

Fig. 2. Isotherms of adsorption- desorption of water vapor for natural montmorillonites.

From the water vapor adsorption isotherm, one can get an idea of the structural characteristics of the adsorbent [10].

Fig. 3 shows the adsorption-desorption isotherms of water vapor on the Co^{+2}- form of montmorillonite.

As a result, a comparison of the adsorption-desorption isotherms of water vapor on natural and its Co^{+2}- form montmorillonite shows that after treating bentonite with cobalt salt, the shape of the isotherm changes, which indicates an increase in the adsorption capacity of the sample with respect to water molecules.

Figure 4. shows the kinetic curve of the adsorption of water vapor on natural montmorillonite and Co^{+2}- forms at P = 18 mm Hg. It follows from the figure that within 60 minutes about 80% of the micropore volume is filled with water molecules, the sorbent is saturated water, and then the curve runs parallel to the x-axis. From a comparison of the kinetic curves of vapor adsorption on natural and Co^{+2}-form montmorillonite, it can be seen that the adsorption capacity of water vapor on Co^{+2}-form is greater than on natural montmorillonite. Within 40 minutes it occurs filling the total volume of micropores with Co^{+2}-form of montmorillonite by 85-70%, respectively.

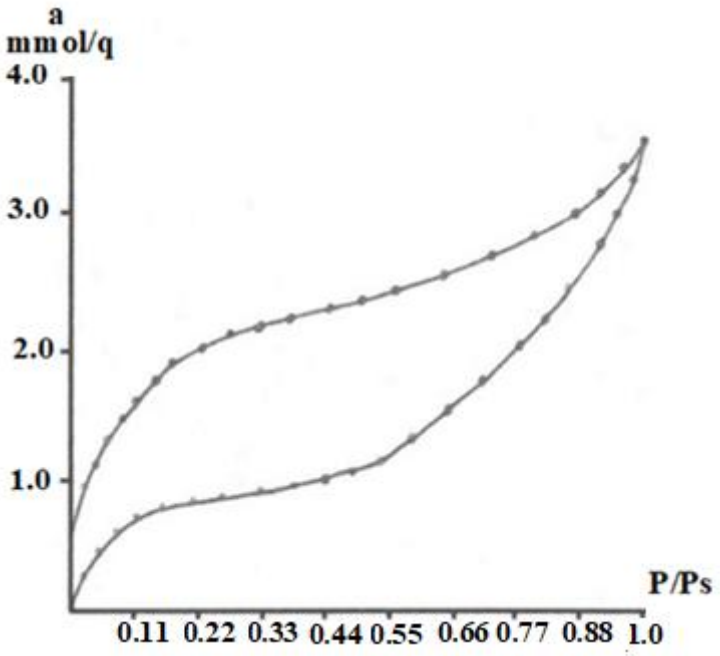

Fig. 3. Isotherms of adsorption-desorption of water vapor with Co^{+2} form of montmorillonites

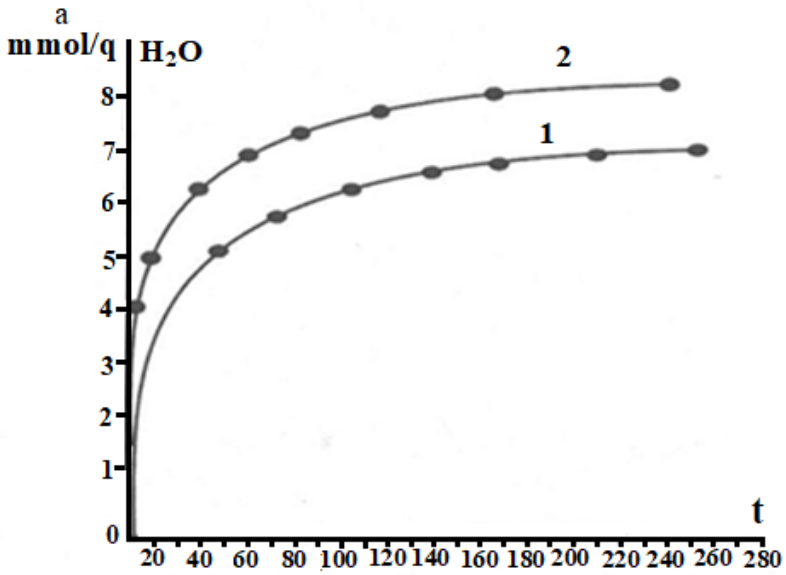

Fig. 4. Kinetic curve of vapor adsorption on Co^{+2}-forms (2) and natural montmorillonites (1)

Fig. 5. shows the adsorption-desorption isotherms of benzene at a temperature of 20°C on samples of montmorillonite taken from the Agdere region's deposits. As can be seen from the isotherms and critical curves of adsorption-desorption at P/Ps=0.8, the isotherm rises higher, which shows that there is a developed mesopore in the porous structure of montmorillonite [11-13].

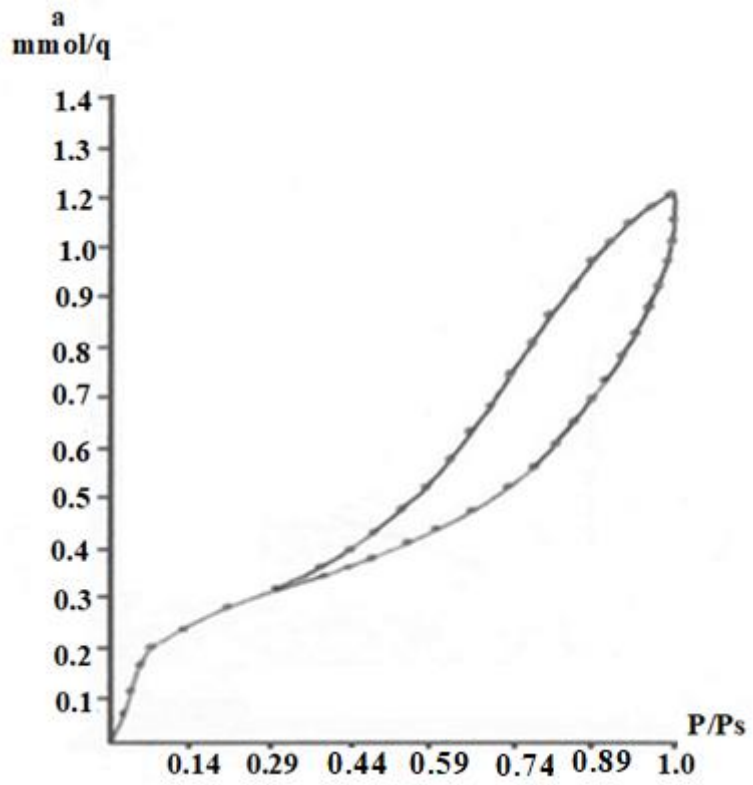

Fig. 5. Isotherm of benzene adsorption on natural montmorillonite.

From the adsorption-desorption isotherm of benzene vapor on the Co^{2+} form of montmorillonite presented in Fig. 6, it follows that when the partial pressure of benzene is increased to P/Ps = 0.20-25, the formation of a monolayer with a low-energy surface is completed. On the adsorption-desorption isotherms of benzene vapor Co^{2+}-montmorillonite exhibits a sharp increase in sorption at P/Ps close to 1. This can be explained by the fact that on the secondary porous structure of montmorillonite there are quite large pores in which benzene vapors condense [14-18].

Benzene molecules do not penetrate into the interpacket space of the Co^{+2} form of montmorillonite; their adsorption occurs on the outer surface of the sample and is adsorbed only in the secondary porous space of its crystals [19-22]. From the isotherms and critical curves of adsorption-desorption at P/Ps=0.8, the isotherm rises higher, which shows that there are mesopores developed in the porous structure of montmorillonite.

The parameters calculated from the differential adsorption isotherm curve for benzene are presented in Table 1.

Table 1 indicates that with increasing pressure system, the specific pore volume in bentonite and the effective pore diameters increase. A study of the textural properties of bentonite samples revealed that the modified samples achieve maximum textural properties compared to natural montmorillonite

Table 2. presents the values of specific surface area (S, m^2/g) and total pore volume ($V_{\Sigma}cm^3/g$) determined in the study of montmorillonite samples for benzene adsorption using the . The determination method is described in the literature (23-25).

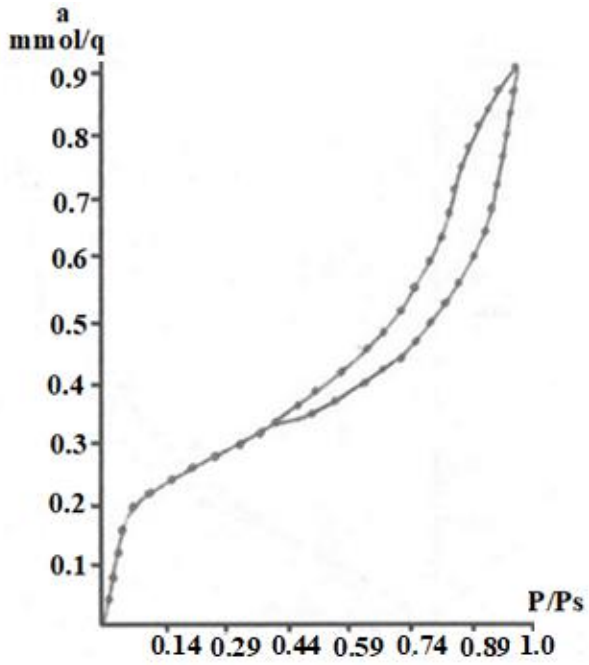

Fig. 6. Isotherm of benzene adsorption on Co^{+2} forms of montmorillonite.

Table. 1 Calculation parameters of sorbent pores based on the desorption branch of the benzene isotherm

P	P/P_s	a, mmol/q	$\ln(P_sP)$	d,A
0	-	-	-	-
5	0.07	0.43	2.640	15.96
10	0.14	0.51	1.946	21.7
15	0.20	0.616	1.541	27.35
20	0.30	0.616	1.2528	33.62
30	0.43	0.643	0.8473	50
40	0.59	1.0	0.560	75.3
50	0.70	1.07	0.337	125.2
60	0.85	1.30	0.1542	273
65	0.93	1.34	0.0742	568
70	1.0	-	-	-

Table 2. Values of specific surface area (S, m^2/g) and total pore volume (V_Σ, cm^3/g) of modified montmorillonite samples for benzene

Samples	$S,m^2/q$	$V_{\Sigma,}sm^3/q$
Natural bentonite	10.42	0.075
Co^{2+}- bentonite	41.32	9.49
Ni^{2+}- bentonite	12.87	2.95

As can be seen from the tabular data, depending on the change in the ionic radius of the exchange cations (from 0.66 A to 0.80 A), specific surface area and pore volume, the studied bentonite samples are arranged as follows:

Co^{2+}-mont> Ni^{2+}-mont> natural.mont.

Results

A study of the adsorption and structural characteristics of natural and modified montmorillonite revealed that treating the mineral with aqueous solutions of various metal salts increases its specific surface area and total pore volume. Modifying montmorillonite with Co^{2+} ions and other transition metals has been shown to significantly alter its structure and surface properties, manifesting itself in the development of a porous structure and an increase in the available adsorption surface area. Ion exchange has been found to be an effective method for targeted regulation of the material's hydrophilic-hydrophobic balance, significantly expanding its range of practical applications. Thus, natural montmorillonite and its modified forms represent promising adsorption materials suitable for use in environmental cleanup, catalysis, and the petrochemical industry.

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TƏBİİ VƏ MODİFİKASİYA OLUNMUŞ MONTMORİLLONİTDƏ SU, BENZOL BUXARLARININ ADSORBSİYASININ TƏDQİQİ

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Təbib alümosilikatlar əsasında effektiv adsorbentlərin və katalizatorların hazırlanması ücün müxtəlif faktorlardan asılı olaraq onların məsaməli qurluşlarını və parametrlərinin tənzimləmək vacibdir. Təbii və modifikasiya olunmuş montmorilonit nümunələrinin məsaməli quruluş xüsusiyyətləri su və benzol buxarlarının adsorbsiyası vasitısi ilə tədqiq edilmiş, kinetik xüsusiyyətləri də öyrənilmişdi. Modifikasiya olunmuş montmorillonit nümunələrinin tekstur göstəriciləri benzol və su molekullarının adsorbsiyası izotermlərinə əsasən tədqiq edilərək, onların məsamələrinin həcminin radiusa görə paylanması müəyyən edilmişdir. Alinan nəticələrə əsasən təztiq artdıdca monmorillonitdəki məsamələrin xüsusi həcmi və məsamələrin effektiv diametri artır. Bu sorbentdə daha çox inkişaf etmiş mezoməsamələrin möcud oldugunu göstərir. Təbii və modifikasiya olunmuş montmorillonitin adsorbsiya-struktur xüsusiyyətlərinin tədqiqi nəticəsində məlum olmuşdur ki,monmorilloniti müxtəlif metalların duzlarının sulu məhlulları ilə işlədikdən sonra monmorillonitin xüsusi səth sahəsi və ümumi məsamə həcmi artır.

Açar sözlər: *montmorillonit, benzol, sorbent, izoterm, adsorbsiya, xüsusi səth, tutum həcmi.*