

NATURAL ZEOLITE-CLINOPTILOLITE CHARACTERISTICS DETERMINATION AND MODIFICATION

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The article is devoted to the preparation of adsorbents for polymer adsorption on their surface. Adsorption of polymers on the surface of adsorbents from a solution has been widely developed and received a great deal of attention in research works, which prove the topicality of its use in development of new composite materials and solve many problems concerning the polymers characteristics and properties. The adsorbents drawbacks, i.e. small specific surface area, diameter of the primary pores and their amount have been determined. In addition to chemical and mineral composition of the natural adsorbents, texture and structural characteristics are essential for studying and developing of adsorbents that take part in different adsorption processes. The material under study is a natural zeolite –clinoptilolite (Sokyrnytsia deposit, Zakarpattia region, Ukraine). The reported physical-and-chemical characteristics have been given.

Key words: adsorption, zeolite, modification, nitric acid, specific surface area, porosity, cation.

Розглянуто підготовку сорбентів для адсорбції полімерів на їх поверхні. Їх модифікація в розчинах поширена на практиці та популярна у наукових роботах, що свідчить про актуальність і доцільність цього методу для створення нових композиційних матеріалів, зокрема полімерних. Визначено недоліки адсорбентів як сорбентів для пластмас, а саме малу площу питомої поверхні, діаметр вхідних пор та їх кількість відносно поверхні. Поряд з хімічним та мінеральним складом природних сорбентів, текстурні та структурні властивості є одними з основних під час дослідження та покращення властивостей сорбентів, щоб їх можна було використовувати у спеціальних адсорбційних процесах. Вихідним матеріалом, який досліджується у роботі, є вітчизняний природний цеоліт – клиноптилоліт (Сокирницьке родовище Закарпатської області, Україна).

Ключові слова: адсорбція, цеоліт, модифікація, азотна кислота, питома поверхня, пористість, катіони.

Introduction

At present, the role of natural adsorbents in many industrial applications and research has been growing. The polymer adsorption from solution on the surface of adsorbents received a great deal of attention in scientific research and has been specifically thoroughly studied. This fact clarifies the topicality of their proper use to create new composite materials and solves many problems connected with properties and characteristics of polymers. However, not all of the adsorbents have sufficient adsorptive capacity in the natural state.

The adsorbents drawbacks, i.e. small specific surface area, diameter of the primary pores and their amount, have been determined. In addition to chemical and mineral composition of the natural adsorbents, texture and structural characteristics are essential for studying and developing of adsorbents that take part in different adsorption processes. The adsorption properties are basically predefined by the chemical structure of their surface, pore size and distribution of pore volume according to the radii. The process is facilitated by a certain pore structure. Successful solving of many theoretical and practical problems is connected with selection of adsorbents with the pore structure relevant for this process [1, 2].

Different conditions are assigned to the adsorbents, i.e. high adsorptive capacity, good selectivity, easy regeneration, mechanical strength of particles, filtration capacity and catalytic activity.

To acquire the appropriate physical-and-chemical, catalytic and adsorptive properties the natural adsorbents are activated or modified. The following activation methods have found wide application: thermal and hydrothermal treatment, treatment with inorganic and organic substances etc. [3]

The natural mineral adsorbents can be singled out from the wide range of adsorbents. Nowadays zeolites are widely used. They are referred to as the adsorbents with microporous cage structure and possess high adsorptive and molecular-sieve activity. The adsorptive properties of zeolite are determined by its internal crystalline space. These adsorbents are acid-resistant (disruption of the mineral structure at pH less than 1), heat-resistant (600 C and higher), non-carcinogenic (zeolite content in the mineral does not exceed 0,001 mg/g). The main constituents of the zeolite cage are silicon-oxygen and aluminum-oxygen tetrahedral and octahedral elements. Their cage contains channels and interconnected spaces, where the metal cations and water molecules are stored. The cations are mobile and can be exchanged to a certain extent by other cations [4].

Experimental procedure

The natural zeolite – clinoptilolite (Sokyrnytsia deposit, Zakarpattia region) has been studied. Zeolite extracted from Sokyrnytsia deposit is a natural mineral that belongs to the class of microporous aluminosilicates containing in their internal crystalline cage the exchange metal cations and water molecules.

Zeolites of this class are based on the open tetrahedral cage, with a system of channels which size is determined by the content of silicon. The cage of the structure is formed with a network of eight-membered (channel B) and ten-membered rings (channel A), located in *ab* plane, and eight-membered rings (channel C), located in *bc* plane (Fig. 1b).

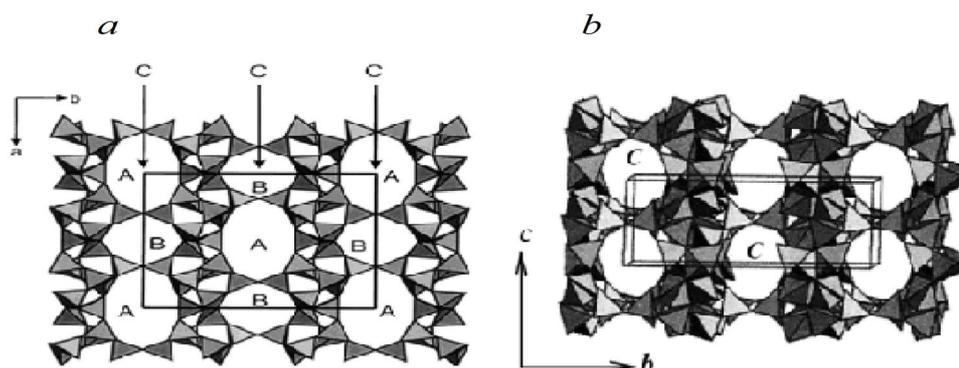


Fig. 1. a) Tetrahedral model of clinoptilolite, indicating 10-membered A and 8-membered B channels that are bridged with 8-membered C channels (projection along *c* axis); b) parallel channel C formed with the ellipsoidal 8-membered rings [5].

The channels in the structure are filled with the cations, which are located in the positions M1(Na), M2(Ca), M3(K) and M4(Mg), and water molecules. Water is included into the structure forming the hydrated film around the exchange cations in the channels.

In clinoptilolite the mole Si/Al ratio reaches 4,25-5,25 according to its chemical composition. It is referred to the group 7 ($T_{10}O_{20}$); typical content of the elemental cell is $(Na, K)_6[Al_6Si_{30}O_{72}] \cdot 24H_2O$.

The parameters value of the clinoptilolite elemental cell, which are given in literature, nm: $a = 1,767$, $b = 1,791$, $c = 7,410$, $\beta = 116,37^\circ$, space group of symmetry $C2/m$ [5, 6].

Some research results of physical and chemical characteristics of clinoptilolite activated by different acids are given in [7-9].

The aim of the paper is to investigate the alteration of the specific surface area, pore size and volume, elemental cell dimensions under treatment of zeolite clinoptilolite with the solutions of 1, 3, 6, 8 moles of nitric acid.

Chemical composition of clinoptilolite has been examined using emission spectrometer with inductively coupled plasma ICAP-6500, applying the ICP OES method, which consists in measuring

radiation emitted by the sample elements inserted in the inductively coupled plasma. The samples were dried and then turned into solution by dissolving in hydrochloric, nitric and hydrofluoric acids. The process of dissolution was carried out in the hermetically sealed containers in the microwave oven under controlled temperature and pressure.

Subsequently, the clinoptilolite samples were modified in the following procedure: 50 g of natural zeolite of a certain fraction (0-0,63 mcm) were treated with 1, 3, 6, 8 mol nitric acid. The flask content was being boiled for 6 hours at 110°C. After boiling the samples were washed with distilled water to pH=5 [10]. Then the samples were dried to the constant weight.

Parameters of specific surface area, pore distribution according to their volume and diameter were identified applying the BET method using the specific surface area analyzer NOVA 2200e Quantachrome Instruments, which consists in adsorption and desorption of liquid nitrogen at 77°K. The X-ray structural analysis was carried out using the X-ray diffractometer Rigaku Ultima IV.

Experimental results and discussion

The elemental content of the natural zeolite – clinoptilolite has been identified (table 1). The quantitative composition of the main metal oxides, constituting the rock, has been calculated (table 2). It has been established that the value of Si/Al = 4,0 is assumed to be the conventional distinction point between heulandites and clinoptilolite [5]. Minerals with the ratio of $Si/Al \leq 4,0$ are referred to as the heulandite, and the clinoptilolite has the ratio of $Si/Al \geq 4,0$. In this research work $Si/Al=4,9$, which proves it to be the clinoptilolite. The weight loss of a sample on drying constitutes 18,51%.

Table 1.

Elemental composition of the clinoptilolite

Element	Wave length, nm	Amount, % mass.	Element	Wave length, nm	Amount, % mass.
Ag	328.0	0.0007	In	230.6	<0.0003
Al	396.1	7.03	K	766.4	3.09
B	208.9	<0.0003	Li	670.7	0.0010
Ba	455.4	0.0797	Mg	279.0	0.2395
Bi	223.0	<0.0003	Mn	257.6	0/0245
Ca	315.8	1.92	Na	589.5	1/93
Cd	214.4	<0.0003	Ni	231.6	0.0003
Co	230.7	<0.0003	Pb	220.3	0.0018
Cr	267.7	0.0003	Si	251.6	34.50
Cu	324.7	0.0004	Sr	421.5	0.0310
Fe	259.8	1.45	Ti	334.3	0.1260
Ga	417.2	0.0012	Zn	206.2	0.0037

Table 2.

Calculation of the elements in the metal oxides of the main elements (forming the rock)

Metal oxide	Amount, % mass.
Al ₂ O ₃	13.23
CaO	2.68
Fe ₂ O ₃	2.07
K ₂ O	3.72
MgO	0.40
Na ₂ O	2.60
SiO ₂	73.90

As Figure 2 shows, after being modified with acid the clinoptilolite specific surface area grows reaching its maximum value when treated with 3 moles of nitric acid in comparison with the primary non-modified samples. This fact shows that the lattice structure has changed, namely distance between

the hollow spaces, porosity, adsorptive capacity and the amount of active centers on the surface have increased.

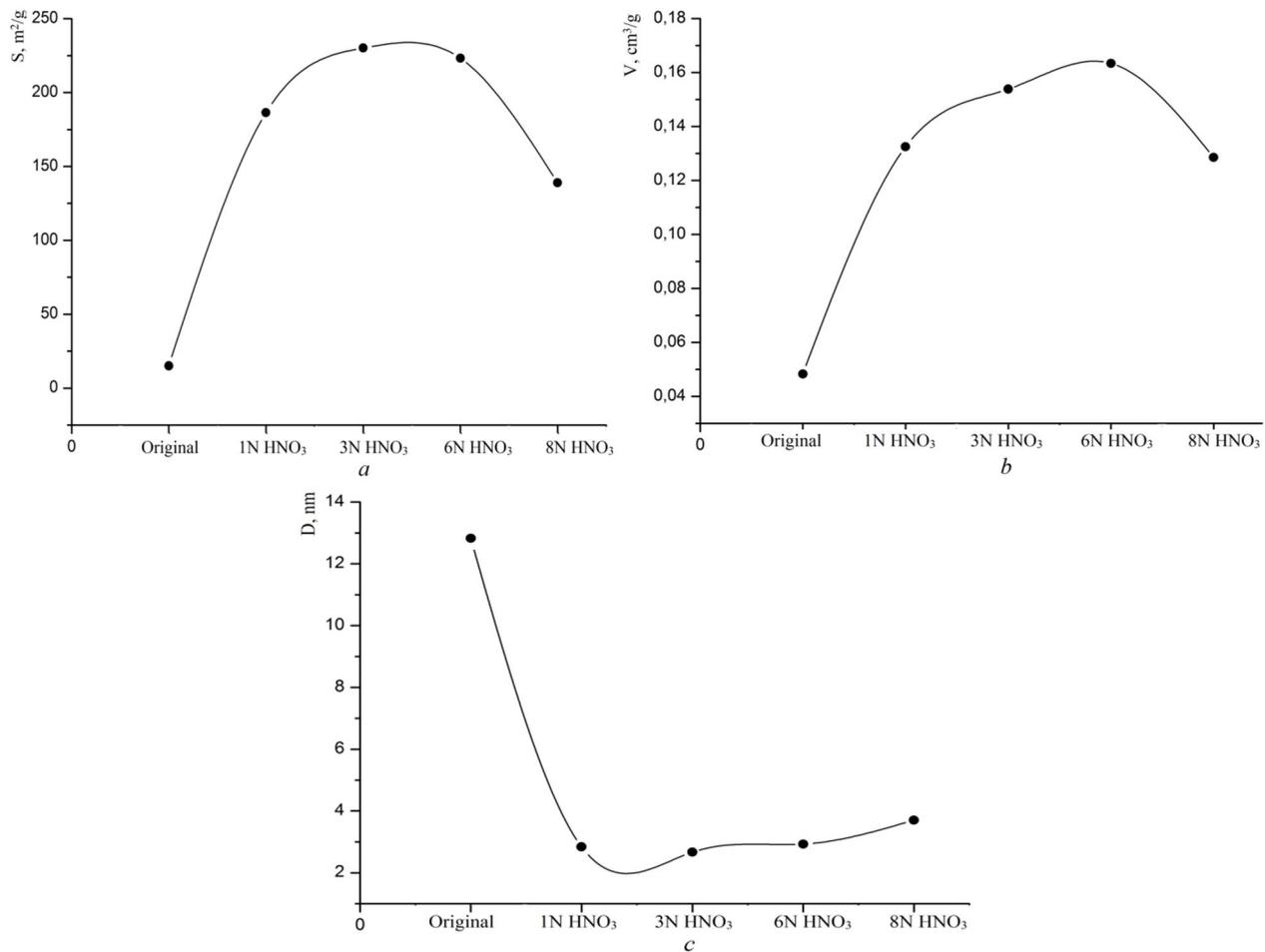


Fig. 2. Graphs of alteration: a) specific surface area; b) bulk volume of pores; c) average pore diameter of the primary and modified clinoptilolite samples

When the concentration of acid grows (6 and 8 moles of acid), the decrease in specific surface area size is observed. This phenomenon can be clarified by the fact that the acid influences the mineral more actively; therefore, the structural cations elution occurs more intensively in the following succession $Mg^{2+} > Fe^{2+} > Fe^{3+} > Al^{3+}$. Considering the alteration of the bulk volume and the average pore diameter, it should be noted that when zeolite is treated of with 1 mole of acid, the average pore diameter reduces and the bulk volume increases. The reason why this change occurs is that the micro-pores transform into meso-pores, and meso-pores, in their turn, evolve into macro-pores; this is shown in Figure 3, that is, the profound chemical changes take place.

With further increase of concentration up to 6 moles of acid, even more active elution occurs. As a result, the bulk volume and average diameter of pores is increased. Considering a sample modified with 8 moles of acid, it can be noted that the specific surface area is reduced greatly, the average diameter grows and the bulk volume is decreased. It demonstrates the action of acid, which actively elutes pores forming large hollow spaces and disrupting the structure.

The modification process consists in decationation and dealumination, leading to displacement of the exchange metal cations by the hydrogen ions; as a result, H-zeolite forms, and $-Si-O-Al-$, $-Al-O-Al-$ bonds are broken, creating new active centers with three coordinated aluminum atoms and hydroxyl groups. The protons from the hydroxyl groups increase the amount of active centers.

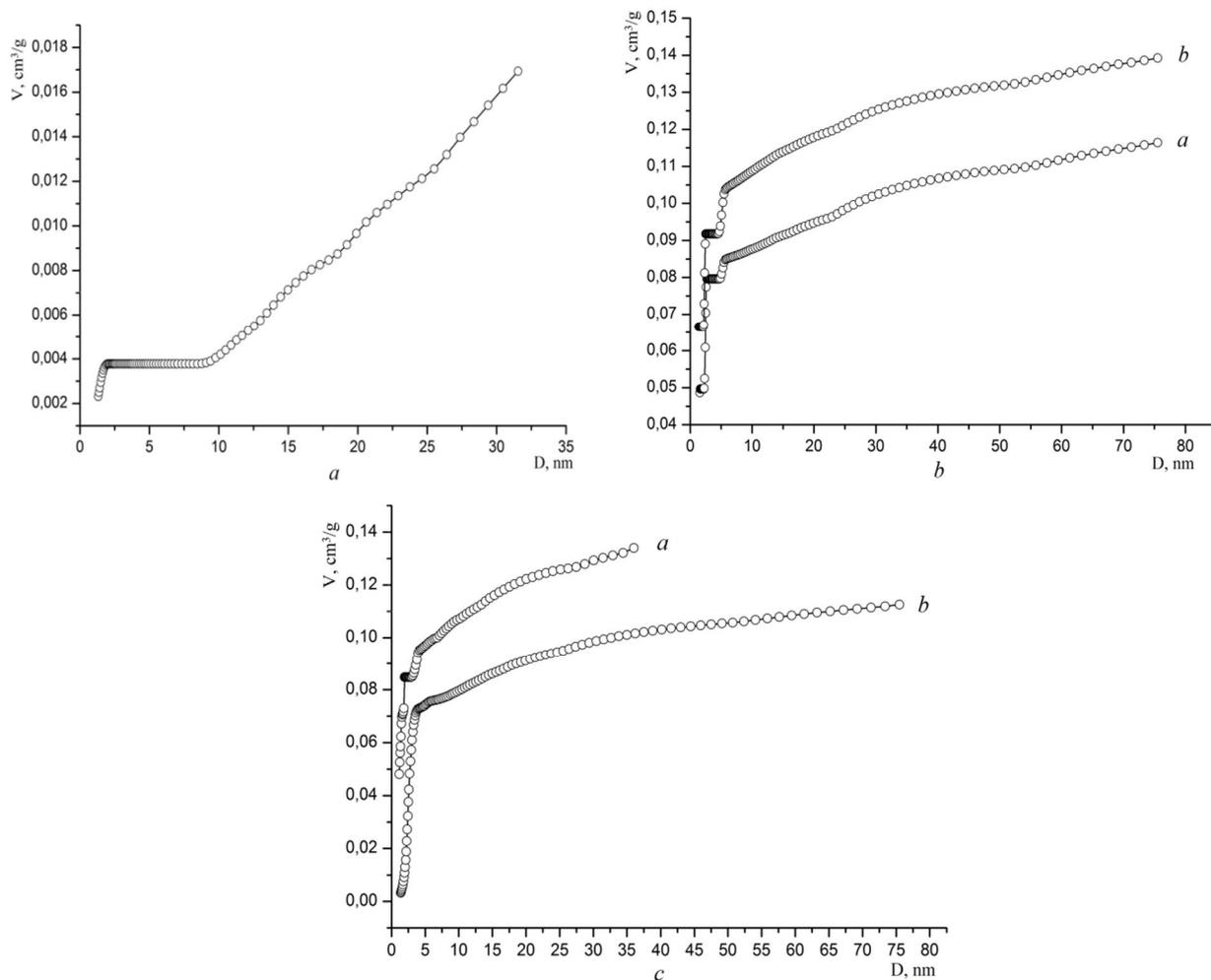


Fig. 3. Graph of pore distribution according to the size: a) primary sample; b) modified: a – 1 and b – 3 moles of nitric acid; c) modified: a – 6 and b-8 moles of nitric acid

Considering the graph that indicates the changes in the characteristic values of elemental cell of the clinoptilolite sample (Fig. 4), it could be noticed that the volume of the elemental cell is decreased with the acid concentration. Therefore, as a result of acid activation of a sample, the oxides Al_2O_3 , Fe_2O_3 , CaO and MgO , as well as hydrated water are removed from its crystal lattice, this leads to the increase of the SiO content. This is accompanied by the lattice structure changes: distances between hollow spaces, porosity, adsorptive capacity and amount of active centers on the inner surface grow.

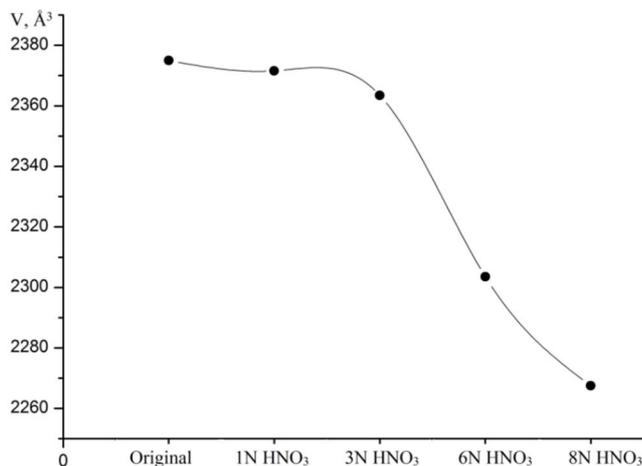


Fig. 4. Graph of size alteration of the samples' elemental cell

Conclusion

Alteration of porosity, specific surface area, pore diameter and volume of the primary and modified clinoptilolite has been envisaged. Consistent structural changes were observed, when a sample was treated by 1 mole of nitric acid, its specific surface area and pore volume grew, the increase continued under treatment by 3 moles of nitric acid. The active influence of acid causes the specific surface area and volume decrease and pore diameter increase after being treated with 6 and 8 moles of acid, because it leads to greater elution of the metal cations and formation of bigger channels and hollow spaces. Due to this fact strength of zeolite is reduced, which leads to its disruption when being used. The acid treatment gives more active adsorptive centers; this enhances adsorption of substances.

1. Mykhajlova O. *Teksturnye y strukturnye svojstva pryrodnykh y modyficirovannykh dispersnykh system* / O. Mykhajlova, T. Lyghyna, V. Ghrevcev, F. Aukhadeev // *Struktura y dynamyka molekulyarnykh system*. – 2007. - №1. – S. 360 – 363. 2. Nejmark Yzraylj Evseevych *Syntetycheskiye myneraljnye adsorbenty y nosytely katalyзаторov* / Y.E. Nejmark. – Kyev: Nauk. dumka, 1982. – 216s. 3. Агуров Э.А. *Прыродные мyneraljные sorbенты, ykh акtyвyрование y модыficирование* / Э.А. Агуров.: yzd. “FAN” – Tashkent, 1970. – 252s. 4. Oshakbaev M. *Yspolzovanie pryrodnykh aljmosylykatnykh ghlyn dlja ochystky fosfornoj kysloty* / M. Oshakbaev // *Khymycheskyj zhurnal Kazakhstan*. – 2009. - №1. – S. 13-19. 5. Ghrechanovskaja E. *Мetryka элементарной jачейкы y Si/Al – v ceolytakh rjada ghejlandyt – klynoptylolyt sokyrnyckogho mestorozhdenyja (Zakarpatj'e, Украйна)* / E. Ghrechanovskaja // *Mineraljnyj zhurnal*. – 2010. – 32. – №4. – S. 12 – 22. ISSN 0204 – 3548. 6. Brek D. *Ceolytové molekulyarnye syta* / D. Brek; per. s anghl. A. Kljachko, Y. Myshyna, V. Jakersona – Moskva: yzd. Myr, 1976. – 768s. 7. Arcoya A. *Physicochemical and catalytic properties of modified natural clinoptilolite* / A. Arcoya, J.A. Gonzalez, N. Travieso and X.L/ Seoane // *Clay Minerals*. – 1994. - №29. – P. 123 – 131. 8. Kowalczyk P. *Porous structure of natural and modified clinoptilolites* / P. Kowalczyk, M. Sprynskyy, A. Terzyk, M. Lebedynets, J. Namiesnik. B. Buszewski // *Journal of Colloid and Interface Science*. – 2006. – P. 77 – 85. 9. Wani P. *Heavy metal adsorption by clinoptilolite from aqueous solutions* / P. Wani, S. Thorat // *Current World Environment*. – 2008. –V.3. - №1. –P. 135 – 141. 10. Rakytskaya T. *Adsorption of water vapour by natural and chemically modified clinoptilolite and mordenite samples* / T. Rakytskaya. T. Kiose, A. Truba, A. Ennan, R. Dlubovskiy, V. Volkova // *Chemistry, Physics and Technology of Surface*. – 2012. – V.3. – №4. – P. 455 – 462.