

L.G. Eprikashvili, G.P. Tsintskaladze, T.N. Kordzakhia, M.G. Zautashvili,  
N.V. Pirtskhalava, M.A. Dzagania, T.M. Sharashenidze

## EFFECT OF ACID MODIFICATION OF NATURAL ZEOLITES ON THE ADSORPTION OF SOME PHARMACOPOLLUTANTS

*Petre Melikishvili Institute of Physical and Organic Chemistry of the Iv. Javakhishvili Tbilisi State University  
31 A. Politkovskaia Str., Tbilisi, 0186, Georgia (Saqartvelo), E-mail: luba.eprikashvili@tsu.ge*

Wastewater and natural waters contain various pollutants of both natural and artificial origin. Treatment of these waters is carried out comprehensively by various methods, which significantly increases costs. Currently, the problem of a large amount of drugs entering the wastewater is very relevant. Drugs, unchanged or in the form of metabolites, enter the wastewater together with the waste products of a living organism. To solve urgent practical problems of water purification, a possibility of using natural zeolite materials as sorbents has been recently considered.

Being a natural aluminosilicates of frame-type structure, these minerals have a number of unique adsorption properties that can be used in water treatment processes. Treatment with acid solutions (alkalis, salt solutions and some organic compounds) allows to improve significantly their sorption characteristics for decision of a particular problem. Zeolites, being chemically stable minerals, are capable to withstand the effects of chemically active medium without destruction of the crystal lattice.

The effect of boiling acid (HCl) on natural zeolites from Georgian deposits (mordenite and clinoptilolite) and the possibility of their use for adsorption treatment of wastewater were studied in this work. Identification of modified zeolites was carried out on the basis of X-ray diffractograms and IR-spectra. It has been shown that natural clinoptilolites (mordenite and zeolite) are characterized by high thermostability and acid resistance even after acid-modification, and the resulting hydrogen forms are distinguished by high concentration of active centers; the efficiency of adsorption method for wastewater treatment from some pharmacopollutants when using acid-modified natural zeolites has been also shown. This method will solve the problem of entering the environment of drugs with lower costs.

**Keywords:** natural zeolites, clinoptilolite, mordenite, drugs, wastewater treatment

### INTRODUCTION

Analysis of scientific studies in recent years shows that the presence of medicaments in surface- and wastewater, as well as in drinking water is a global environmental threat. Until quite recently, the fight against these substances was not provided worldwide [1–4]. Drugs currently being developed have high biological activity, are highly resistant in the environment and enter living organisms as a combination of different drugs and their effect on the body is not predictable.

One of the most promising methods of deep treatment of wastewater and surface water is the sorption method. The advantages of the sorption method include: the capability to remove contaminants of a wide range to almost any residual concentration regardless of their chemical stability, the absence of secondary contaminants, cost-effectiveness associated with the repeated use of the sorbent and process controllability.

The adsorption method of removing organic pollutants from water is based on the difference in energies of van der Waals interaction between dissolved substance and solvent molecules with the surface of a solid adsorbent. The formation of chemical bonds between the dissolved substance and the surface groups of adsorbents is also possible [5]. The possibility of porous structure materials adsorption is also associated with a developed adsorption surface and its availability [6]. The competition of the processes of water binding and adsorption in aqueous solutions is due to the distinction and selection of adsorbents for the removal of organic and inorganic substances from water [7].

### MATERIALS AND METHODS

In recent years available natural sorbents, in particular natural zeolites (Mordenite – MOR, Clinoptilolite – Cl, etc.) as well as their modified forms are used in the processes of wastewater treatment from various contaminants of organic and mineral origin.

World experience shows that the transportation of zeolite raw materials over long distances is not profitable, as a result of which each of the regions creates its own raw material base to solve the corresponding technological problems [8–16]. The use of these minerals as sorbents is determined by their high sorption properties, micro-mesoporous structure, and the availability of pores for the penetration of large organic molecules to the functional groups of the sorbent.

In scientific works [1–4], the possibilities of using mordenite (Bolnisi-Ratevani locality, Georgia) and clinoptilolite (Kaspi-Khandaki locality, Georgia) as adsorbents of the  $\beta$ -lactam antibiotic ceftriaxone (CEF –  $C_{18}H_{18}N_8O_7S_3$ ) from the group of cephalosporins and some fluoroquinolones: norfloxacin (NOR– $C_{16}H_{18}FN_3O_3$ ), moxifloxacin (MOX– $C_{21}H_{24}FN_3O_4$ ), as well as the development of a technique for their analysis in model solutions using HPLC was studied. The chromatographic analysis was performed using a LC-20AD Prominence Shimadzu HPLC System (Japan) and a HPLC column - Agilent SB-C18 4.6×250 mm, 5  $\mu$ m (USA). To prepare model analytical standards of antibiotics, “Aqua FX” water purification system, analytical balances – a LEX-

210 (USA) and a Hanna Instruments HI 2211 pH-meter (USA) were used. All the measuring equipment has been properly calibrated and certified.

The HPLC methods have been tested for reliability (stability of the standard solution, compatibility test of the PVDF membrane filter, study of the influence of critical factors using the experiment plan - DoE), system suitability test (SST), specificity, linearity range, accuracy, detection limits (LOD) and quantitative determination (LOQ) in accordance with the methodologies [17–21] and ICH Q2 guidelines [22, 23].

One way to change the hydrophilic-hydrophobic properties and structural characteristics of these zeolites is acid activation.

The adsorption capacity of the above natural zeolites and their acid-modified forms was studied both under static and dynamic conditions on a specially designed flow-through unit. As a result of the experiments carried out, basic information on operation of the sorbent layer under different process parameters was obtained.

Table 1 presents data on the use of the degree of sorbent layer equilibrium activity ( $\eta$  %) of the adsorption column with various fillers for the tested drugs under dynamic conditions.

**Table 1.** Degrees of equilibrium activity of the adsorption column sorbent layer ( $\eta$  %) with various fillers for the tested drugs under dynamic conditions

Antibiotic	Degree of utilization of sorbent layer equilibrium activity, $\eta$ , %					
	Cl. initial	HCl. 2 N	HCl. 5 N	MOR initial	HMOR 2 N	HMOR 5 N
Moxifloxacin (MOX- $C_{21}H_{24}FN_3O_4$ )	14.10	25.71	32.64	40.31	62.83	76.92
Norfloxacin (NOR- $C_{16}H_{18}FN_3O_3$ )	16.46	48.78	53.91	30.71	58.73	70.59
Ceftriaxone (CEF- $C_{18}H_{18}N_8O_7S_3$ )	–	20.69	25.80	29.20	30.31	33.33

As can be seen from the table, the degree of use of equilibrium activity of the sorbent layer in the adsorption column increases with increasing concentration of the modifying acid. Adsorption of various molecules of the studied zeolite samples is accompanied by strong heterogeneity of the internal field of its channels. As the narrow channels get filled, the adsorbed molecules, probably, interact with each other in a complex way.

## RESULTS AND DISCUSSION

Development of scientific basis for the preparation and application of effective adsorbents

based on natural zeolites makes it necessary to study the nature of active centers, the nature of exchangeable cations and free porosity of their adsorption space structures, elucidation these factors in adsorption processes as well as establishing the relationship between physical and chemical properties.

An important characteristics of zeolites are chemical stability, the capability to withstand to chemically active medium without destruction of the crystal lattice. Modification of zeolites by treatment with various substances, in particular with aqueous acid solutions, makes it possible to

significantly improve their characteristics and expand their range of use. During the process of ion exchange of compensating cations for a proton ( $H^+$ ) or a hydronium ion ( $H_3O^+$ ), the hydrogen form of the zeolite is partially formed. The possibility of destruction of zeolite structure by strong acid depends on the number of aluminum atoms located in tetrahedra of frame, because, presumably, they are the sites of acid attack during hydrolysis [24].

The interaction of adsorbed molecules with the adsorbent matrix is determined by the presence of Lewis and Brønsted acidic sites. When producing H-forms of such zeolites, their treatment with mineral acids is accompanied by parallel decationization and dealumination processes while maintaining the crystal structure of the mineral. Dependent on the nature of the sorbed molecules, sorption can be carried out both by ion exchange mechanism or by non-exchange absorption due to different types of interaction [24, 25].

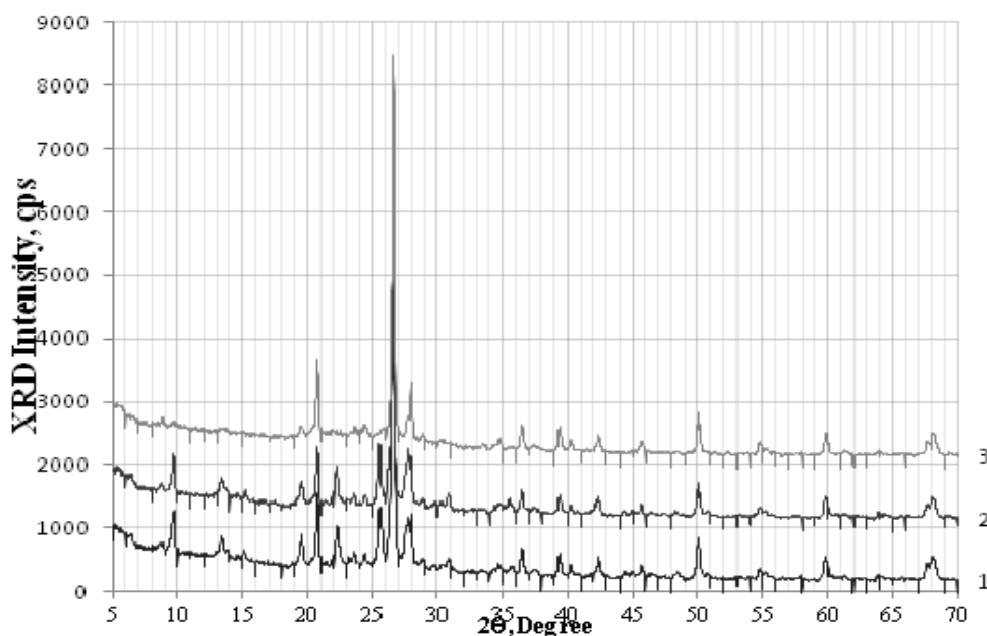
Zeolite identification was based on X-ray diffractograms and IR-spectra. The analysis of the chemical composition of mordenite and clinoptilolite study samples was carried out on a device Spectroscout XEP-04. The diffractograms

were taken on a Drone-4 device. Infrared spectroscopic studies were performed on an Agilent Cary 630 FTIR Spectrometer in the region of  $350\text{--}1300\text{ cm}^{-1}$ .

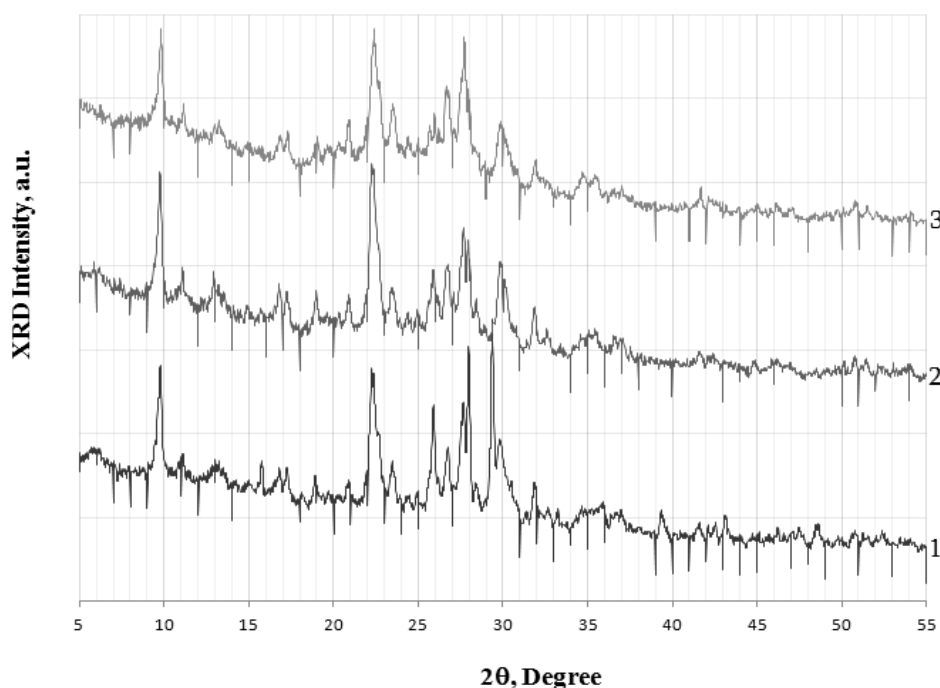
Zeolite phase content ranged between 50–55 % for clinoptilolite and between 50–60 % for mordenite. Initial forms of the zeolite samples used were only washed with distilled water and dried in a thermostat without pre-treatment. Modification was carried out with hydrochloric acid of various concentrations (2N and 5N) by boiling under reflux. After treatment, the samples were washed with distilled water to  $pH = 7$ , dried in a thermostat at  $100\text{--}150\text{ }^\circ\text{C}$  within 3 h.

The chemical composition of mordenite varies within a narrow limits, the Si/Al ratio ranges from 4.5 to 5.5.

The exchange cations of mordenite are represented by calcium and sodium; potassium and magnesium are present in smaller quantities. Chemical modification provides ample opportunities for regulating the molecular-sieve properties of mordenite. The high value of the silicate module (Si/Al) makes the mineral highly resistant to heat and acid.



**Fig. 1.** X-ray diffractograms: 1– Initial MOR; 2– Modified MOR (with 5N solution of HCl); 3– Modified MOR (with 10N solution of HCl)



**Fig. 2.** X-ray diffractograms: 1– Initial Cl; 2– Modified Cl (with 2N solution of HCl); 3– Modified Cl (with 5N solution of HCl)

Figs. 1–2 show X-ray diffractograms of the studied samples of mordenite and clinoptilolite (initial and acid-modified).

Diffractograms of initial natural mordenite treated with boiling acids of various concentrations show that despite the changes in chemical composition, the zeolite crystal lattice remains unchanged after acid treatment. The diffractogram of natural and treated with 5 N boiling acid (HCl) zeolite is similar to the diffractogram of original mordenite. The acid leaching of zeolites is characterized by the fact that the acid exposes a mineral framework, which preserves in such event the zeolite architecture. At the same time, the value of silicate modulus (Si/Al) is also increased. Treatment of mordenite with 10 N acid this value increases to 24.45, but the diffractogram of this sample indicates partial destruction of crystal structure.

Diffractograms of Clinoptilolite, both natural and acid-treated (with 2 N and 5 N solution of HCl) samples differ slightly from the initial one. However, changes in the chemical nature of the active centers and porosity of clinoptilolite after modification lead to an increase in its sorption activity. Increasing the pore size of clinoptilolite by unlocking the channels of aluminosilicate

frame contributes to a greater accessibility of sorbate molecules to the active centers.

Nanomodification of zeolites by chemical or thermal methods contributes to the appearance of various active centers in their structure. Both Brønsted and Lewis acid sites may be present in zeolites. The active centers of zeolites are one of the most important factors causing their widespread use in various processes. By means of IR-spectroscopy several types of hydroxyl groups were detected on zeolite surfaces [26–28]. They can be found on the zeolite crystal surface or in places of crystal lattice defects, as well as on the surface of amorphous silica phase present in zeolites as impurities [26–28]. In addition, there are acid OH-groups in zeolites associated with the lattice three-coordinate aluminum atoms Si(Al)–OH, which are obtained during zeolite decationation. These OH-groups serve as Brønsted acid sites and are responsible for the catalytic activity of zeolites [29]. Brønsted acidic groups are mainly localized in large cavities formed by channel crossing.

Table 2 and 3 show the IR-spectra of the initial and acid-modified samples of mordenite and clinoptilolite. Comparison of the IR-spectra of natural mordenite with an acid-treated (5 N) sample showed the presence of all characteristic

**Table 2.** Vibrational assignment of the IR-spectrum of studied samples mordenite

Vibrational assignment	Initial MOR	Modified MOR (with 5N solution of HCl)	Modified MOR (with 10N solution of HCl)
V <sub>def.</sub> - deformational vibration	471	463	473
V <sub>inter-def.</sub> - Deformation vibration between tetrahedra	621 691	-	-
V <sub>intra-sim</sub> - Internal tetrahedral symmetric valence vibration	728	796	796
V <sub>intra-as</sub> - Inner tetrahedral asymmetric valence vibration	1048 1065	1078	1096
V <sub>inter-as</sub> - Asymmetric valence vibration between tetrahedra	1165	1163	1163

**Table 3.** Vibrational assignment of the IR-spectrum of studied samples clinoptilolite

Vibrational assignment	Initial Cl	Modified Cl (with 2N solution of HCl)	Modified Cl (with 5N solution of HCl)
V <sub>def.</sub> - deformational vibration	465	472	469
V <sub>inter-def.</sub> - Deformation vibration between tetrahedra	520 593	522 593	520 588
V <sub>intra-sim</sub> - Internal tetrahedral symmetric valence vibration	712 774	778	793
V <sub>intra-as</sub> - Inner tetrahedral asymmetric valence vibration	1040	1052	1065

absorption bands in the area of the aluminum-silicon-oxygen framework of zeolite [30]. A slightly different spectral pattern was observed for the sample modified by 10 N acid. There are no deformation vibrations in the spectrum at 621 and 694  $\text{cm}^{-1}$ ; frequencies of intratetrahedral valence vibrations change in the frequency band from 1085 to 1095  $\text{cm}^{-1}$ , indicating an increase in the silicate module – Si/Al. There is also a low-intensity band at 940  $\text{cm}^{-1}$ , which is characteristic of the anion  $\text{Si-O}^-$ , indicating the break of the long chain of zeolite structure [5, 31].

After treatment of the clinoptilolite sample with 2 N acid solution (HCl), various clay impurities are removed and the structure is improved. At that, the dealumination of the zeolite begins. This is indicated by the change in

the frequency intensity spectrum of Si–O–Si(A1) of intertetrahedral vibrations from 603 to 588  $\text{cm}^{-1}$ . The treatment of zeolite with 5 N acid (HCl) solution the bands of intertetrahedral vibrations at 520, 602, 669  $\text{cm}^{-1}$  significantly decreased and, accordingly, the frequency of Si–O–Si(A1) intratetrahedral valence vibrations increased from 1058 to 1065  $\text{cm}^{-1}$ , which indicates an increase of Si/Al modulus in zeolite. Thus, acid treatment of zeolite slightly destroys the zeolite structure. As acid concentration increases, the number of acid centers increases both in places of zeolite structure defects and on its surface. At the same time, the number of Brønsted acid centers in the zeolite porous system decreases [32].

In the study and development of sorbents involved in various adsorption processes, along

with the chemical and mineral compositions of natural zeolites, textural and structural characteristics are fundamental. Nanomodification of natural zeolites with solutions of hydrochloric acid (or alkali) leads to a significant increase in the values of physical, mechanical and textural characteristics: the specific surface of the zeolite increases on average up to five times, and the total pore volume doubles. Changes in the texture parameters of the studied samples (specific surface area, mesopore volume and total pore volume, pore size distribution) were determined by the method of low-temperature nitrogen adsorption/desorption at 77.2 K using an ASAP 2020 Plus (Nitrogen) Physisorption Analyzer (BASIS MODEL). The obtained isotherms were processed by the Barret-Joyner-Hallenda (BJH) method [33, 34].

Among the studied samples of mordenite and clinoptilolite, natural (initial) samples are characterized by the lowest specific surface area, density, porosity and total pore volume. Studies have shown that acid treatment of zeolites leads to an increase in the number and size of mesopores, as well as the volume of micropores. Nanomodification of samples with acid is accompanied by an increase in the specific surface by an average of 30–70 %  $\text{m}^2/\text{g}$ , volumes – by an average of 20–50 %  $\text{cm}^3/\text{g}$  and pore

diameters, porosity and decrease in true density. The most significant changes in the structure of mordenite occurred when it was treated with 10 N boiling acid. Thus, by varying the type of modifying agent, it is possible to form a porous structure at the micro-, meso- and macropore-levels.

The possibility of modifying natural zeolites without insignificant crystal lattice disturbance makes it possible to change the hydrophilic-hydrophobic properties, the chemical nature of the reaction centers and the textural characteristics of the sorbent, and expands their scope of application.

## CONCLUSION

Studies have shown that natural zeolites – mordenite and clinoptilolite are characterized by high thermal stability and acid resistance even after acid modification, and the obtained hydrogen forms differ from others by a high concentration of active centers.

Natural zeolites are a potentially industrial type of mineral raw materials, and their comprehensive assessment allows to make better use of the mineral wealth and increases their investment prospects [10–12, 33–38] for creating of new nanoporous materials which can be used in various technological processes.

## Вплив кислотної модифікації природних цеолітів на адсорбцію деяких фармакополітантів

Л.Г. Епрікашвілі, Г.П. Цінцкаладзе, Т.Н. Кордзахія, М.Г. Заугашвілі,  
Н.В. Пірцхалава, М.А. Дзаганія, Т.М. Шарашенідзе

*Інститут фізичної та органічної хімії ім. П. Мелікішвілі Тбіліського державного університету ім. І. Джавахішвілі  
вул. Г. Політковської, 31, Тбілісі, 0186, Грузія, luba.eprikashvili@tsu.ge*

*Стічні та природні води містять різні забруднюючі речовини як природного, так і штучного походження. Очищення цих вод здійснюється комплексно різними методами, що значно збільшує витрати. В даний час дуже актуальною є проблема потрапляння великої кількості ліків у стічні води. Ліки в незміненому вигляді або у вигляді метаболітів потрапляють у стічні води разом із продуктами життєдіяльності живого організму. Для вирішення актуальних практичних завдань очищення води останнім часом розглядається можливість використання природних цеолітних матеріалів як сорбентів. Будучи природними алюмосилікатами каркасної структури, ці мінерали мають низку унікальних адсорбційних властивостей, які можуть бути використані в процесах водопідготовки. Обробка кислотними розчинами (лугами, розчинами солей і деяких органічних сполук) дозволяє значно полішити їх сорбційні характеристики для вирішення конкретної задачі. Цеоліти, будучи хімічно стійкими мінералами, здатні протистояти впливу хімічно активного середовища без руйнування кристалічної ґратки. У роботі досліджено вплив соляної кислоти (HCl) на природні цеоліти грузинських родовищ (морденіт і*

кліноптилоліт) та можливість їхнього використання для адсорбційного очищення стічних вод. Ідентифікацію модифікованих цеолітів проводили на основі рентгенівських дифрактограм та ІЧ-спектрів. Показано, що природні кліноптилоліти (морденіт і цеоліт) навіть після кислотної модифікації характеризуються високою термостабільністю і кислотостійкістю, а отримані Н-форми відрізняються високою концентрацією активних центрів; також показано ефективність адсорбційного методу очищення стічних вод від деяких фармакополітантів при використанні кисло-модифікованих природних цеолітів. Цей метод дозволить вирішити проблему надходження в середовище препаратів з меншими витратами.

**Ключові слова:** природні цеоліти, кліноптилоліт, морденіт, очищення стічних вод

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