

RESEARCH ARTICLE

FEASIBILITY STUDY FOR THE USE OF NATURAL MORDENITE IN PURIFICATION PROCESSES OF WASTEWATERS FROM PHARMACEUTICAL POLLUTANTS

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

Iv. Javakhishvili Tbilisi State University; P. Melikishvili Institute of Physical and Organic Chemistry.

.....

Manuscript Info

Abstract

Manuscript History Received: 20 January 2021 Final Accepted: 24 February 2021 Published: March 2021

*Key words:-*Mordenite, Zeolite, Adsorption, Pharmaceutical Pollutants, Water Purification

..... The present research concerns the possibility of adsorptive removal of the frequently used antibiotics - moxifloxacin and norfloxacin on natural zeolites - mordenite and its acid-modified form from aqueous solutions. The adsorption of the above-mentioned antibiotics on the selected natural zeolite samples was investigated under static and dynamic conditions. Adsorption experiment under dynamic conditions carried out using the specially constructed dynamic type of laboratory equipment. Based on the data of chemical, IR spectroscopic, X-ray diffraction analyses, it has shown that when the zeolite adsorbent is treated with an acid, an equivalent exchange of extra framework cations for a hydrogen ion and dealumination occurs and silanol groups are formed at the same time. The increase in the adsorption activity of mordenite as a result of its treatment with acid is associated with an increase in the pore size due to the unblocking of the adsorbent aluminosilicate framework channels during dealumination.

Copy Right, IJAR, 2021,. All rights reserved.

Introduction:-

Modern rates pace of development of various industries, which play a leading role in the global fuel and energy balance, leads to sharply increasing man-made loads on all objects of the natural environment. The urgency of the global problem of health and environmental protection contributed to the high interest of the world scientific community in zeolites. Natural zeolites and zeolite-containing rocks, being a widespread and cheap mineral raw material, have a unique spectrum of physical, physicochemical and adsorption properties, due to which they have found wide application in the practice of cleaning various objects, in particular natural and wastewaters [1].

Adsorption systems, adsorbents aimed at reducing environmental risk, reducing energy intensity of processes, refusal of special sorbents, etc., should be attributed to compliance with the principles of "green economy" [2,3]. This approach implies a high degree of minimization of expenses during water purification from toxic and harmful components. Economic aspects of this process play a very relevant role, allowing the purification and additional treatment of wastewater, thus, reducing the anthropogenic load on water bodies.

At present, 15 varieties of zeolite minerals have been identified in Georgia, but among them industrial significance may have only: analcime, clinoptilolite-heulandite, phillipsite, laumontite and mordenite (MOR). The presence of large reserves of natural zeolites in Georgia contributed to the study of adsorption properties of both initial and nano-modified samples in order to create adsorption materials effective for the extraction of certain pharmaceutical ingredients namely fluoroquinolones (FQs) – moxifloxacin (MOX) ($C_{21}H_{24}FN_3O_4$) and norfloxacin (NOR)

Corresponding Author:- L.G. Eprikashvili

Address:- Iv.Javakhishvili Tbilisi State University; P.Melikishvili Institute of Physical and Organic Chemistry.

 $(C_{16}H_{18}FN_3O_3)$ from wastewaters, as well as the study of adsorption process mechanisms of pharmaceutical substances [4,5].

Fluoroquinolone antibiotics are synthetic antibacterial drugs with a 4-quinolone basic structure (Figure 1) which can inhibit the proliferation of many Gram-negative and Gram-positive bacteria [4,5].



The presence of fluorine atoms is a critical factor for high activity; the activity of this antibiotic increased by approximately tenfold. So, they have been widely used in medical and veterinary practice. However, as a result of antibiotic overuse, public concern about FQs has significantly been increasing in the past decades. The environmental concern of FQ antibiotics residues in the aquatic environments is not only on their potential to increase antibiotic resistance but also on their unfavourable ecotoxicity profile [6]. The presence of FQs residues in effluents from households, hospitals, and pharmaceutical industries is a significant cause of acute and chronic toxicity, as well as the emergence of resistant bacteria. Consequently, removal of FQ residues from the environment is a crucial issue [7,8].

Adsorption method is a well-controlled process that allows to removing various contaminants up to almost any residual concentration, regardless of the chemical stability of pollutants, the absence of secondary contaminants, and the cost efficiency associated with the repeated use of the sorbent [9].

The adsorption method for removal of organic pollutants from wastewaters is based on the difference variety in energies of Van der Waals interaction of dissolved substance molecules and solvent with solid adsorbent surface or on formation of chemical bonds between dissolved substance and surface groups of adsorbent. The possibility of adsorption of porous structure materials is also associated with the developed adsorption surface and its availability. The competition of water binding and adsorption processes in aqueous solutions is caused by differentiation and selection of adsorbents for removal of organic and inorganic substances from wastewaters [10].

Natural mordenite is a mineral with the formula of typical oxide $- Na_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 6H_2O$. Idealized composition of elementary cell is $Na_8[(AlO_2)_8(SiO_2)_{40}] \cdot 24H_2O$. Depending on geological conditions of deposits, sodium cations can be partially replaced by potassium, calcium or magnesium cations. The ratio of SiO_2/Al_2O_3 in mordenite zeolites varies between 8.3-10.7. Mordenite has a tetrahedral structure in which a silicon or aluminum atom is surrounded by four oxygen atoms. Tetrahedrons are grouped in chains (Figure 2). Inside the chains, there are adsorption cavities [11,12].





Figure 3:-Projection of the mordenite structure direction the main channels.

Mordenite structure is penetrated by a two-dimensional system of 8- and 12-membered channels. Some cations are localized in eight-membered channels, and some - in large channels. Cations block narrow 8-membered channels, and only large channels with diameter of 0.67 nm are open for the diffusion of molecules; Na-, Ca-mordenites are unblocked after treatment with hot hydrochloric acid. Chemical modification provides ample opportunities for regulating the molecular sieve and catalytic properties of mordenite. The limiting adsorption volume of both narrow-porous and wide-porous mordenite varies between 0.076-0.09 cm³ g⁻¹. The difference in the molecular-sieve properties caused by the different arrangement of sodium cations, which in narrow-pore mordenite are located in large twelve-membered channels (0.59-0.47 nm) and thus, narrow their effective diameter. In wide-pore ones they are localized in the depths of niches composed double eight-membered rings (0.39-0.47 nm) and do not prevent the penetration of large molecules into large channels [11-15]. The projection of the mordenite structure in the direction of the main channels is shown in Figure 3.

Experimental:-

Natural mordenite with zeolite-phase content of 50-60% from Bolnisi-Ratevani deposit (Georgia) was used in this study. The chemical composition of mordenite varies within narrow range, the ratio of Si/Al is within 4.5-5.5. Chemical composition of the studied samples of mordenite is presented in Table 1. The analysis of the chemical composition of natural and treated mordenite samples was carried out using Spectroscout XEP-04 (Germany).

	Concentration		
Oxides, %	Initial MOR	Modified MOR (with 5N	Modified MOR (with
		solution of HCl)	10N solution of HCl)
SiO_2	71.64	76.18	88.53
Al ₂ O ₃	9.955	9.828	3.184
CaO	4.137	2.257	0.3999
Fe ₂ O ₃	2.614	2.577	1.631
Na ₂ O	1.66	1.179	0.1353
K_2O	1.313	1.47	1.247
MgO	1.109	0.8912	0.4318
TiO ₂	0.3012	0.3296	0.236
P_2O_5	0.06694	0.02415	0.0006924
MnO	0.05198	0.03122	0.008663
SO_3	0.03272	0.002502	0.002502
Si/Al	6.34	6.84	24.45
$\Sigma H_2 O$	7.12	4.95	4.19

Table 1:- Chemical composition of natural mordenite from Bolnisi-Ratevani deposit (Georgia) and acid-modified samples.

Exchange cations are represented by calcium and sodium; potassium and magnesium are present in smaller quantities. Chemical modification provides ample opportunities to regulate the molecular-sieve properties of mordenite. The high value of the silicate module (Si/AI) determines the high thermal- and acid-resistance of the mineral.

The X-ray diffraction analysis of the studied samples of mordenite (initial and acid-modified) was carried out using X-ray diffractometer - Drone-4 (Russia). The obtained diffractograms are presented in Figure 4. The diffractogram of the initial natural mordenite treated by boiling acids of different concentrations show that despite of changes in the chemical composition, the crystal lattice of zeolite remains unchanged after acid treatment. The diffractogram of natural (native) and treated boiling 5N solution of hydrochloric acid (HC1) zeolite is similar to the diffractogram of original mordenite.



Figure 4:- X-rEay diffractograms of initial MOR (a), modified MOR with 5N HCl (b) and modified MOR with 10N HCl (c).

Leaching of zeolites with acids is characterized by the fact that acid exposes the mineral frame, which preserves the architecture of the zeolite. At the same time, the value of the silicate module increases. It should be noted that treatment of mordenite with 10N HC1 increases this value to 24.45 (Figure 4), but the diffractogram of this sample indicates the destruction of the crystal structure and the mordenite lattice becomes more defective, which is probably a consequence of leaching.

Figure 5 presents IR spectra of mordenites – initial and acid-modified with 5N HC1 and 10N HCl. IR-spectrometric study was performed using Agilent Cary 630 FTIR Spectrometer (USA) in the range of 350-1300 cm⁻¹. Comparison of the IR spectra of natural mordenite with an acid-treated sample (5N HCl) showed the presence of all characteristic absorption bands of the aluminosilicon-oxygen framework of the zeolite. A somewhat different spectrum is observed for the sample modified with 10N HCl, which is probably caused by the deformation of the zeolite structure [13].



Figure 5:- IR spectra of initial MOR (a), modified MOR with 5N HCl (b) and modified MOR with 10N HCl (c).



Along with the chemical and mineral compositions of natural zeolites, textural and structural characteristics are fundamental in the study and development of adsorbents involved in various adsorption processes. Nano-modification 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 area of the zeolite increases on average up to five times, and the total pore volume doubles. To characterize the texture parameters of the studied samples (specific surface area, volume of mesopores and total pore volume, pore-size distribution), the method of low-temperature adsorption-desorption of nitrogen at 77.2 K was used. The procedure was carried out on the equipment – Micromeritics Asap 2020 Plus Physisorption Analyzer (USA). The obtained isotherms were processed by the Barrett-Joyner-Hallend (BJH) method [16, 17].

Among the studied mordenite samples, the natural mordenite sample is characterized by the lowest specific surface area, density, porosity and total pore volume. Nano-modification of samples with acid solution is accompanied by an increase in specific surface area (to 70.84 from 162.33 m^2/g), volumes (to 0.086 from 0.097 cm³ g⁻¹), pore diameters, porosity and a decrease in true density. The most significant changes in the structure of the zeolite occurred during its treatment with 10N boiling acid solution. By varying the type of modifying agent, it is possible to form a porous structure at the level of micro-, meso- and macro-pores.

The adsorption capacity of zeolites was studied under static and dynamic conditions. Adsorption capacity of mordenite samples by water vapour was studied by excitation (desiccant) method (pre-activation temperature 400 $^{\circ}$ C) (Table 2). As it is obvious from the above data, modification of natural mordenite with 5N acid solution increases its adsorption capacity by 7.3%, while treatment with 10N acid solution leads to its decrease (Figure 6) [18-20].

 Table 2:- Adsorption capacity by water vapour on mordenite samples at 18 °C.

Sample	Adsorption a, mmol / g
Initial MOR	3.363

Modified MOR (with 5N solution of HCl)	3.608
Modified MOR (with 10N solution of HCl)	3.069

Investigation of adsorption properties of natural and modified samples of mordenite in relation to selected FQ antibiotics was carried out under dynamic conditions on the specially designed dynamic type equipment. The change of FQ antibiotic sorbate concentration at the outlet of adsorption column was determined by the validated HPLC method [5]. The HPLC analysis was performed using LC-20AD Prominence Shimadzu HPLC System (Japan) and HPLC column – Agilent SB-C18 4.6×250 mm, 5 μ m (USA). To prepare model aqueous test solutions of each FQ antibiotic – moxifloxacin and norfloxacin, the analytical standards (MilliporeSigma) and "Aqua FX" water purification system, analytical balance – LEX-210 were used. All the measuring equipment have been properly calibrated.

Figure 6:- Modification of the initial mordenite with HCl [19].



The concentration of the sorbate (FQ antibiotic) in the adsorbent before the start of the process is zero, the concentration of the sorbate in the input stream is constant.

The dynamics of sorption processes considers the spatio-temporal distribution of components between the phases of the system (one of which is solid), which occurs when these phases move relative to each other.

Experimental study of adsorption dynamics usually has two purposes: to check the adequacy of the model of the experiment and to obtain information from the output curves of adsorption needed to select adsorbents, their sizes and design. Adsorption process is characterized by probabilistic functions of particle distribution between mobile and solid phases, on the basis of which concentration distribution curves are found. For practical calculation of adsorption processes, a number of generally accepted simplifications were used in the work: 1) only one component of the flow is adsorbed; 2) The mobile phase is incompressible, and the concentration of adsorbed substance is so low that changes in flux density due to adsorption loss can be ignored; 3) The flow is moving in one direction at a constant flow rate [11,14].

The dynamic characteristics of the adsorption process were studied using the above-mentioned equipment which consists of three parts: 1) a glass adsorption column, 2) a cylindrical electric furnace, 3) a high-pressure pump. In dynamic condition through the prepared zeolite samples placed in a glass adsorption column, the studied FQ antibiotic sorbate solution at a concentration of 1.0 mg mL⁻¹ was passed. The experiment was carried out at room temperature (22 ± 3 °C), with the flow rate of 1.0 mL min⁻¹. When analysing the results obtained with the experiment, approximate test solutions for problems of equilibrium and non-equilibrium frontal dynamics of adsorption were used.

Results And Discussion:-

On the basis of experimental data, adsorption output curves describing the dependencies of adsorbed sorbate concentration growth behind the zeolite layer in time were constructed (the ratio of effluent concentration to influent concentration of the sorbate - C/C_0 versus time) which are shown in Figure 7.

The experiment was carried out until the adsorption capacity of the zeolite layer was fully worked out, i.e. until the sorbate concentration equal to its concentration in the initial solution (influent solution) appeared at the outlet of the adsorption column. The dynamic characteristics of adsorption of moxifloxacin and norfloxacin calculated from experimental data are summarized in Table 3, 4.



Figure 7:- Output adsorption curves of NOR on initial mordenite (a), on mordenite activated with 5N HCl (b), on mordenite activated with 10N HCl (c) and MOX on initial mordenite (d), on mordenite activated with 5N HCl (e), on mordenite activated with 10N HCl (f)

The dynamic adsorption capacity of the adsorbent layer (a_d) characterizes the amount of substance absorbed before the moment of "breakthrough" (τ_b) and attributed to the mass of loading of the entire adsorbent. From the "moment of breakthrough", extracted substance appears in the outgoing stream and its concentration begins to increase progressively. Between the time of protective action of the sorbent layer and the length of the adsorbent (L) there is a dependence determined by the formula of N. A. Shilov [11]: $\tau_b = K \times L - \tau_o$ A.1

where K is coefficient of the protective action, showing the time taken by the 1 cm high adsorbent layer retains the absorbed substance in a stationary mode, cm, τ_0 is time loss of protective action associated with the initial period of formation of the sorbate distribution curve, min; L is height of loading of the adsorbent layer (in this case 24 cm).

The equilibrium adsorption capacity of the sorbent layer depends on the nature of the sorbate and adsorbent (a_{eq}) and was calculated by the formula [11]:

 $a_{eq} = W \times \tau_b \times C_o + W \times \Delta \tau \times C_o \times \varphi / V$ A.2

where, W is the volumetric flow rate of the sorbate influent solution, cm³ min⁻¹; τ_b is time of protective actions of the sorbent layer, min; C_o – initial concentration of pollutant (influent concentration), mg mL⁻¹; $\Delta \tau$ is the difference in sorbent layer performance time to complete saturation - τ_{eq} , i.e., the time of occurrence of the maximum (equilibrium) concentration and breakthrough concentration - τ_b through the sorbent layer, min; ϕ is the coefficient of the symmetry of the output curves or the distribution curves, V – the mass of the loaded adsorbent.

The height of the working layer - L_o , determined from the output curves reflecting pollutant concentration rises behind the adsorbent layer with time, is an important characteristic of the dynamics of the adsorption process. The value of L_o , the length of the mass-transfer zone, was determined on the basis of the obtained output curves according to the equation reported in the papers. The efficiency equilibrium adsorption capacity of the adsorbent layer (the degree of utilization of the adsorbent) – η , % is determined by the ratio of the dynamic adsorption capacity of the layer to the equilibrium adsorption capacity of the sorbent layer (Table 3, 4) [4, 11].

Table 3:- The dynamic characteristics of NOR adsorption on initial and modified MOR.

Some	dynamic	characteristics	of	Antibiotic - norfloxacin

antibiotics adsorbtion	Initial MOR	Modified MOR (with 5N solution of HCl)	Modified MOR (with 10N solution of HCl)
Height of working sorbent layer – L _o , cm	39.84	30.00	47.59
Dynamic adsorption activity of sorbent layer to antibiotic $-a_d$, mg/g	0.14	0.17	0.09
Equilibrium adsorption activity of sorbent layer to antibiotic – a _{equi.} , mg/g	00.9	0.12	0.05
Degree of utilization of the sorbent $-\eta$, %	64.29	70.59	60.00

Table 4:- The dynamic characteristics of MOX adsorption on the initial and modified MOR.

Some dynamic characteristics of	Antibiotic - moxifloxacin		
antibiotics adsorbtion	Initial MOR	Modified MOR (with	Modified MOR (with 10N
		5N solution of HCl)	solution of HCl)
Height of working sorbent layer $-L_0$,	15.60	14.88	16.56
cm			
Dynamic adsorption activity of sorbent	0.12	0.13	0.10
layer to antibiotic $-a_d$, mg/g			
Equilibrium adsorption activity of	0.09	0.10	0.07
sorbent layer to antibiotic $-a_{equi}$, mg/g			
Degree of utilization of the sorbent $-\eta$,	75.00	76.92	70.00
%			

Experimental data obtained FQ antibiotics adsorption on the studied mordenite samples in dynamic conditions indicates an improvement in the process of adsorption of NOR and MOX by the sample of mordenite modified with 5N hydrochloric acid solution. The efficiency of the equilibrium adsorption capacity of the sorbent layer (η) increases. The height of the working layer (L_o) decreases, which increases the repeatability of sorbent "elementary" volumes in the process of repeated acts of sorption-desorption. The obtained data clearly demonstrates the influence of the pharmaceutical pollutant nature and chemical structure on the process of its extraction from the aqueous solution by zeolite.

Conclusion:-

It has been established that natural and acid-modified (5N HCl) mordenite can be proposed as an eco-friendly, highly efficient adsorbent for the extraction of a fairly wide range of organic substances from aqueous medium, including pharmaceutical pollutants. Most adsorption processes are carried out in equipment with a fixed dense layer. It should be noted that the use of granular zeolites (mordenite) in close-packed adsorbers is very effective for removing ecologically significant concentrations of many pharmaceutical pollutants and many other toxic organic compounds. From the economic point of view, it is very important that it is possible to recycle the used high-silica sorbents after their regeneration by the oxidation method, because such zeolites are resistant to oxidizing agents (such as hydroxyl radicals, ozone, etc.), and can be regenerated without removing them from the adsorber.

Reference:-

- 1. Obuzdina M.V., Rush E.A. Investigation of the regularities of the sorption extraction of organic pollutants from industrial wastewater by zeolites. J. Modern technologies. System analysis. Modeling, 2011, p.117-123.
- 2. Kucherov A.V., Shibileva O.V. The concept of "green" economy: main provisions and development prospects. Young scientist, 2014, #4, p.561-563.
- Torosyan G.O., Simonyan A.A., Petrosyan M.Z., Davtyan V.A., Torosyan N.S. Green adsorbents for wastewater treatment from organic compounds. Water treatment. Water preparation. Water supply, 2018, 6, p.16-21.
- 4. Rubashvili I., Eprikashvili L., Kordzakhia T. Zautashvili M., Pirtskhalava N., Dzagania M. Adsorptive removal study of the frequently used fluoroquinolone antibiotics moxifloxacin and norfloxacin from wastewaters using natural zeolites. Mediterranean Jornal of Chemistry, 2019, 9(2), 142-154.

- Rubashvili I., Zautashvili M., Kordzakhia T., Eprikashvili L. Development and validation of quantitative determination HPLC metods of the fluoroquinolone antibiotics – moxifloxacin hydrochloride and norfloxacine in support of adsorption study on natural zeolites. PERIÓDICO TCHÊ QUÍMICA, 2019, v.16, #33, p.10-20.
- Golet E.M., Alder A.C., Giger W. Environmental exposure and risk assessment of fluoroquinolone antibacterial agents in wastewater and river water of the Glatt Valley Watershed, Switzerland, Environ. Sci. Technol., 2002, 36, 3645–3651.
- 7. Prutthiwanasan B., Phechkrajang C., Suntornsuk L. Fluorescent labeling of ciprofloxacin and norfloxacin and its application for residues analysis in surface water, Talanta, 2016, 159, 74–79.
- 8. Ai Jia, Yi Wan, Yang Xiao, Jianying Hu, Occurrence and fate of quinolone and fluoroquinolone antibiotics in a municipal sewage treatment plant, Water Res., 2012, 46(2), 387-394.
- 9. Nan Jiang, Ran Shang, Sebastiaan G.J. Heijman, Luuk C. Rietveld. High-silica zeolites for adsorption of organic micro-pollutants in water treatment. Water Research, 2018, 144, p.145-161.
- 10. Andronikashvili T., Kordzakhia T., Eprikashvili L., Gamkrelidze E. Zeolite Application for Desiccation of solvents Used in HPLC. Chemical Anal (Warsaw) 1997, 42, p.555-560.
- 11. Eprikashvili L., Kordzakhia T., Andronikashvili T. Zeolites the unique desiccation agent for organic liquids. LAP LAMBERT Academic Publishing, 2015, 91p.
- 12. Andronikashvili T.G., Tsitsishvili G.V., Sabelashvili Sh.D., Chumburidze T.A., Eprikashvili L.G. Chromatographic properties of tuffs containing some Zeolites. Journal of Chromatography, 1978, 148, p.61-68.
- 13. Breck D. Zeolite molecular sieves. M .: Mir, 1976, p.239.
- 14. Keltsev N.V. Basics of adsorption technics. M .: Chemistry, 1984, 592p.
- 15. Tsitsishvili G.V., Tsintskaladze G.P., Charkviani M.K. The effect of heat treatment on the IR spectra of some synthetic and natural zeolites in the frequency range of the framework vibrations. Reports of the USSR Academy of Sciences, 1983, v.273, #6, p.1434-1439.
- 16. Greg S., Sing K. Adsorption, specific surface area, porosity. M., 1984, p.126-300.
- 17. Vyacheslavov A.S., Pomerantseva E.A. Measurement of surface area and porosity by capillary nitrogen condensation. M. 2006, p. 9-23.
- Castillo J.M., Silvestro-Albero J., Rodriguez-Reinoso F., Thijs J.H. Vlugt, Calero S. Water adsorption in hydrophilic zeolites: experiment and simulation. Physical Chemistry Chemical Physics, 2013, Issue 40, 15, p.17374-17382.
- 19. Tsintskaladze G.P., Eprikashvili L.G., Kordzakhia T.N., Nanikashvili P.M., Sharashenidze T.V. Thermal and chemical modification of natural mordenites as a method for obtaining new zeolite materials. Surface, 2012, 4 (19), p.153-159.
- Sakthinathan S., Tamizhdurai P., Ramesh A., Chiu Te-Wei, Mangesh V.L., Veerarajan S., Shanthi K. Platinum incorporated mordenite zeolite modified glassy carbon electrode used for selective electrochemical detection of mercury ions. Microporous and Mesoporous Materials, 2020, 292, 109770.