THE POSSIBILITY OF USING CLINOPTILOLITE FOR WATER PURIFICATION

Dolaberidze N.[1], Tsitsishvili V.[1], Mirdzveli N.[1], Dzhakipbekova N.[2*], Sakibayeva S.[2]

[1]*Tbilisi State University, Tbilisi, Georgia*
[2]*M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan*

[*]**Corresponding author's e-mail:** dzhakipbekova@mail.ru

ABSTRACT

Metal-containing zeolite adsorbents and ion exchangers are promising for environmental protection and medical application. Of this work is described the scientific substantiation of the possibility of using clinoptilolite for water purification and decontamination. The environmental use of zeolites, aluminosilicates is based on the complex of their properties, especially on the ability of zeolites to enter into ion exchange reactions with the participation of Me^{+n} ions compensating the negative charge of the crystal lattice constructed from alternating SiO_4 and AlO_4^- tetrahedrons. Many studies showed that natural and synthetic zeolites exchanged by ions of silver, copper, zinc or some other transition metals (M-Z) exhibit antimicrobial activity toward a broad range of microorganisms. The group of researchers who presented the work from the Petre Melikishvili Institute of Physical and Organic Chemistry at Tbilisi State University (Georgia) and M.Auezov South Kazakhstan State University (Kazakhstan) believes that the development of methods for producing new zeolite filter materials, including bactericidal ones, with desired properties and improved characteristics, is relevant.

Key words: zeolite, clinoptilolite, water purification, ion-exchange, antibacterial activity, zeolite filter.

INTRODUCTION

Zeolites are aluminosilicates of general formula $M_{x/n}[Al_xSi_yO_{2(x+y)}]. mH_2O$, where the metal M (usually Na, K, Ca, Mg) is in a ionic form M^{+n}, compensating the negative charge of the aluminum in crystal lattice. Each silicon and aluminum atom has covalent bonds with four oxygen atom, SiO_4 and AlO_4^- tetrahedrons are linked in their corners forming open, "framework" structure with cages and channels. For example, the most commonly used zeolite of the HEU type (clinoptilolite) forms a monoclinic crystal structure with "wide" channels formed by 10-membered rings with sizes 0.31 x 0.75 nm, and "narrow" channels formed by 8-membered rings (0.28 x 0.47 and 0.36 x 0.47 nm)(Fig.1). Presence of channels and cavities causes molecular-sieve, sorption and other properties of zeolites, they adsorb a variety of heavy metals and ammonia, and remove a wide range of pollutants.

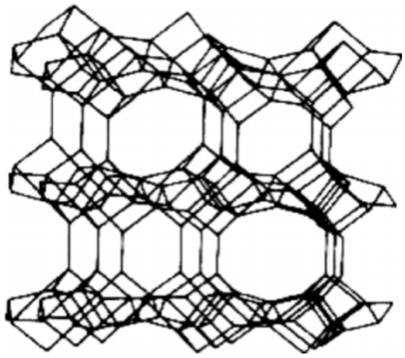

Fig. 1. Framework of Clinoptilolite

The environmental use of zeolites, aluminosilicates is based on the complex of their properties, especially on the ability of zeolites to enter into ion exchange reactions with the participation of Me^{+n} ions compensating the negative charge of the crystal lattice constructed from alternating SiO_4 and AlO_4^- tetrahedrons (Fig. 2).

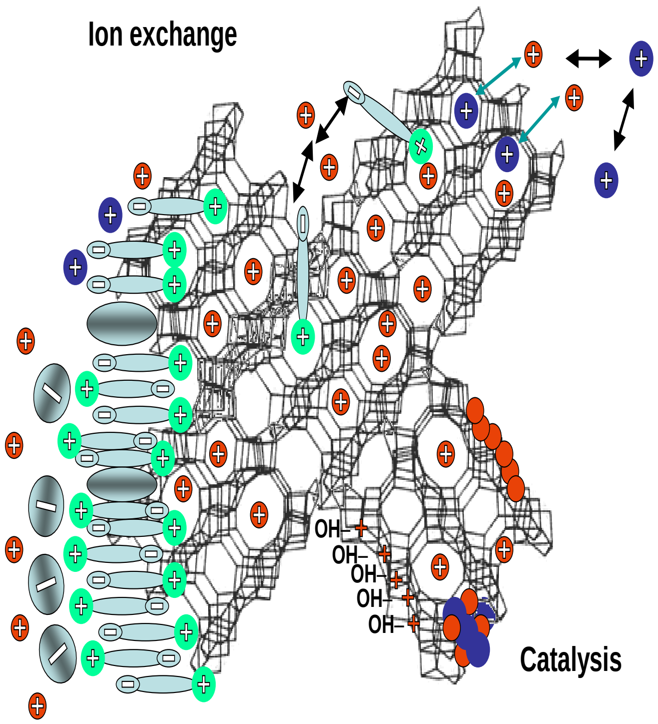

Fig. 2. Ion-exchange and Catalytic Properties of Clinoptilolite

Started at the beginning of the 21stcentury and continuing to this day, studies showed that natural and synthetic zeolites exchanged by ions of silver, copper, zinc or some other transition metals (M-Z) exhibit antimicrobial activity toward a broad range of microorganisms [1-11]. In comparison to other transition metal-containing zeolites, Ag-Z exhibits the most powerful antibacterial activity [3, 8, 10]. In general, silver is considered as antibacterial agent with well-known mode of action, bacterial resistance against silver is well described [12], similarities and differences between silver ions (Ag^+) and silver in nanoforms (Ag^0) as antibacterial agents were discussed recently [13].

Treatment of water used for municipal and industrial purposes refers to the removal of impurities such as dissolved substances, as well as suspended colloids and solids. Among all available water treatment technologies (coagulation, foam flotation, solvent extraction, electrolysis, etc.), adsorption is considered the best option because of convenience, ease of operation, and simplicity of design [14]. Activated carbon [15], clay minerals [16], biopolymers [17], some solid waste materials [14, 18, 19], and zeolites [20-26] have been widely used as adsorbents for adsorption of ions and organics in wastewater treatment.

MATERIALS AND METHODS

At first, most of the studies in the area of utilization of the natural zeolites in water treatment were concentrated on the use of clinoptilolite in the removal of ammonium ions [27- 29] and heavy metals [29-46].The results of the experimental study of adsorption of heavy metal ions by Na-clinoptilolite [45,46] suggest that the selectivity of zeolite is strongly influenced by the pH of the contact solution, as well as dehydration energy and diffusion coefficient of ions, and for the pH>4 can be expressed by the series: $Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+}>Mn^{2+}>Co^{2+}>Ni^{2+}$.In the case of simultaneous contamination of water with iron, copper, manganese, nickel and lead ions, a combined filter consisting of quartz sand, clinoptilolite and laumontite turned out to be effective [47].

From a practical point of view, it was suggested [10] that zeolite formulations containing biologically active metals could be combined with various materials used in manufacturing medical devices, surfaces, textiles, or household items where antimicrobial properties are required. Other problem that can be solved by application of metal-containing zeolites is possible microbiological contamination of zeolite sorbents used in the remediation of hazardous heavy metal-polluted soils [48] or in the purification of industrial wastewater [49]. In such cases it is necessary to provide the sorption materials with bacteriostatic properties in order to prevent the growth of microorganisms on their surface.

RESULTS AND DISCUSSION

Today it is recognized that natural zeolites outperform conventional granular materials in water purification, they are cost-effective, abrasion resistant, non-toxic and environmentally friendly, especially in the treatment of such special wastewater streams as acid mine drainage, landfill leachate, nuclear fallout, and urban runoff [25]. To obtain ion exchangers saturated with biologically active transition metals, either cheap natural clinoptilolite of different origin [28-46,1-4,6, 8, 9,11-13,48,49] or synthetic zeolites of types A, X, and Y with high aluminum content [5, 7,10,50-53] are applied.

However, the content of bioactive metals in synthetic zeolites and in natural clinoptilolites does not exceed 0.3 meq/g, which is much lower than the scientific ion exchange capacity of this zeolite (3.08 meq/g at Si/Al=3.5). Besides, by the method of ion exchange isotherms, it was shown [3] that clinoptilolite can contain up to 1.85 meq/g of silver and up to 1 meq/g of zinc. The adsorption and ion exchange characteristics of any zeolite are defined by its chemical and structural properties (the Si/Al ratio, nature of compensating metal ions, their charge and location, etc.) that can be changed by several chemical treatments to improve efficiency of raw natural zeolite. To obtain materials with a higher content of bioactive metals, it is also possible to use not clinoptilolite, but zeolites with a higher ion-exchange capacity (phillipsite, laumontite, etc.).

The main problem in the use of materials containing bioactive metals is the uncertainty of the mechanism of their action. Several studies showed that zeolites not containing silver, copper, zinc or other transition metals (such as mercury, cadmium, chromium, and lead) are not active toward microorganisms [6,51], but it has recently been established that in some cases the antibacterial activity could be attributed to the metal-containing material M-Z itself [53,54], while the original zeolite remains inert. The introduction of silver, copper and zinc ions into the zeolite lattice has an insignificant, but still an impact on many properties of the zeolite, so only a multilateral thorough study of the composition, structure and properties of the materials obtained will help shed light on this problem.

Currently, filter materials, including zeolite, are widely used in replaceable holders filter cartridges of systems mounted on water taps (faucet mount filters). Drinking water filtration systems are now found in the majority of homes across the world in developed nations', their number is growing rapidly in Georgia and Kazakhstan. Manufacturers have come up with an extremely large variety of different types of filtration systems to meet consumer's pure drinking water needs.

Zeolite filter materials are developed by research laboratories in many countries, including Canada, USA, Australia, China, Romania, Slovakia, Greece, Bulgaria, Turkey and in several other countries.

CONCLUSION

As a result of the study, and also drawing on its scientific experience, a group of Georgian and Kazakh researchers believes that as a result of solid-phase ion-exchange reactions between Georgian and Kazakh natural clinoptilolites and a salt of the corresponding transition metal, followed by washing, zeolite materials will be obtained that will have sorption and bactericidal properties sufficient for their use in the purification and disinfection of water.

REFERENCES

1 Kawahara, K., Tsuruda, K., Morishita, M., Uchida, M. Antibacterial effect of silver-zeolite on oral bacteria under anaerobic conditions. *Dental Materials Journal*, 2000, no. 16, pp.452-455.

2 Rivera-Garza, M., Olguin, M.T., Garcia-Sosa, I., Alcantara, D., Rodriguez-Fuentes, G. Silver supported on natural Mexican zeolite as an antibacterial material. *Microporous and Mesoporous Materials*, 2000, no.39, pp.431-444.

3 Top, A., Ülkü, S. Silver, zinc, and copper exchange in Na-clinoptilolite and resulting effect on antibacterial activity. *Applied Clay Science*, 2004, no. 27, pp.13-19.

4 De la Rosa-Gomez, I., Olguin, M.T., Alcantara, D. Bactericides of coliform microorganisms from wastewater using silver-clinoptilolite rich tuffs. *Applied Clay Science*, 2008, no.40, pp.45-53.

5 Ferreira, L., Fonseca, A.M., Botelho, G., Almeida-Aguiar, C., Neves, I.C. Antimicrobial activity of faujasite zeolites doped with silver. *Microporous and Mesoporous Materials*, 2012, no.160, pp.126-132.

6 Hrenovic, J., Milenkovic, J., Ivankovic, T., Rajic, N. Antibacterial activity of heavy metal-loaded natural zeolite. *Journal of Hazardous Materials*, 2012, pp. 201-202, 260–264.

7 Guerra, R., Lima, E., Viniegra, M., Guzman, A., Lara, V. Growth of Escherichia coli and Salmonella typhi inhibited by fractal silver nanoparticles supported on zeolite. *Microporous and Mesoporous Materials*, 2012, no.147, pp.267-273.
8 Hrenovic, J., Milenkovic, J., Goic-Barisic, I., Rajic, N. Antibacterial activity of modified natural zeolite against clinical isolates of Acinetobacterbaumannii. *Microporous and Mesoporous Materials*, 2013, no.169, pp.148-152.
9 Akhigbe, L., Ouki, S., Saroj, D., Min Lim, X. Silver-modified clinoptilolite for the removal of Escherichia coli and heavy metals from aqueous solutions. *Environmental Science and Pollution Research*, 2014, no.21, pp.10940-10948.
10 Demirci, S., Ustaoğlu, Z., Yılmazer, G.A., Sahin, F., Baç, N. Antimicrobial properties of zeolite-X and zeolite-A ion-exchanged with silver, copper, and zinc against a broad range of microorganisms. *Applied Biochemistry and Biotechnology*, 2014, no. 172(3), pp.1652-1662.
11 Rossainz-Castro, L.G., De la Rosa-Gomez, I., Olguín, M.T., Alcantara-Díaz, D. Comparison between silver- and copper-modified zeolite rich tuffs as microbicidal agents for Escherichia coli and Candida albicans. *Journal of Environmental Management*, 2016, no.183, pp.763-770.
12 Klasen, H.J. Historical review of the use of silver in the treatment of burns. I. Early uses. II. Renewed interest for silver. Burns: journal of International Society for Burn Injuries, 2000, no. 26(2), pp.117-138.
13 Kędziora, A., Speruda, M., Krzyżewska, E., Rybka, J., Łukowiak, A., Bugla-Płoskońska, G. Similarities and differences between silver ions and silver in nanoforms as antibacterial agents. *International Journal of Molecular Sciences*, 2018, no. 19(2), pp.444-461.
14 A. Bhatnagar, and M. Sillanpää, “Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment – A review”, Chem. Eng. J., 2010, vol. 157, pp. 277-296.
15 S. J. T. Pollard, G. D. Fowler, C. J. Sollars, and R. Perry, “Low-cost adsorbents for waste and waste-water treatment – a review”, Sci. Tot. Environ, 1992 vol. 116, pp. 31-52.
16 G. Crini, “Non-conventional low-cost adsorbents for dye removal: a review”, Bioresource Technology, 2006. vol. 97, pp. 1061-1085.
17 G. Crini, “Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment”, Progress in Polymer Science, 2005. vol. 30, pp. 38-70.
18 S. B. Wang, and H. W. Wu, “Environmental-benign utilization of fly ash as low-cost adsorbents”, J. Hazard. Mat., 2006. vol. 136. pp. 482-501.
19 S. Wang, H. M. Ang, and M. O. Tadѐ, “Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes”, Chemosphere, 2008, vol. 72, pp. 1621-1635.
20 A. Hedstrom, “Ion exchange of ammonium in zeolites: a literature review”, J. Env. Eng., 2001, vol. 127, pp. 673-681.
21 Wang, S.B., Boyjoo, Y., Choueib, A., Zhu, Z.H. Removal of dyes from aqueous solution using fly ash and red mud, *Water Research*, 2005, no. 39, pp.129–138.
22 Wang, S.B., Li, H.T., Xie, S.J., Liu, S.L., Xu, L.Y. Physical and chemical regeneration of zeolitic adsorbents for dye removal in wastewater treatment, *Chemosphere*, 2006, no.65, pp.82–87.
23 Wang, S.B., Zhu, Z.H. Characterization and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution, *Journal of Hazardous Materials*, 2006, no.136, pp. 946–952.
24 S. Wang, and Y. Peng, “Natural zeolites as effective adsorbents in water and wastewater treatment”, Chem. Eng. J., 2010. vol. 156, pp. 11-24.

25 Delkash, M., Bakhshayesh, B. E., Kazemian, H. Using zeolitic adsorbents to cleanup special wastewater streams: A review, *Micropor. Mesopor. Mat.*, 2015, no. 214, pp. 224-241.
26 Nakhli, S.A.A., Delkash, M., Bakhshayesh, B.E., Kazemian. H. Application of Zeolites for Sustainable Agriculture: a Review on Water and Nutrient Retention. *Water, Air, & Soil Pollution*, 2017, no. 228(12), pp. 464.
27 Klieve, J.R., Semmens, M.J. An evaluation of pretreated natural zeolites for ammonium removal. *Water Research*, 1980, no. 14, pp. 161-168.
28 Jama, M.A., Yücel, H., Equilibrium studies of sodium-ammonium, potassium-ammonium, and calcium-ammonium exchanges on clinoptilolite zeolite. *Separation Science and Technology*, 1989, no. 24(15), pp.1393-1415.
29 Langella, A., Pansini, M., Cappelletti, P., de Gennaro, B., de Gennaro, M., Colella, C. NH^{4+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} exchange for Na^{+} in a sedimentary clinoptilolite, North Sardinia, Italy. *Microporous and Mesoporous Materials*, 2000, no.37, pp.337-343.
30 Semmens, M.J., Seyfard, M., The selectivity of clinoptilolite for certain heavy metals. In: *Natural Zeolites:Occurrence, Properties and Use*. (Eds. Mumpton, F.A., Sand, L.B.), New York: Pergamon, 1978, pp. 517-526.
31 Semmens, M.J., Martin, W.P., The influence of pretreatment on the capacity and selectivity of clinoptilolite for metal ions. *Water Research*, 1988, no. 22(5), pp.537-542.
32 Zamzow, M.J., Murphy, J.E. Removal of metal cations from water using zeolites. *Separation Science and Technology*, 1992, no. 27(14), pp. 1969-1984.
33 Kesraoui-Ouki, S., Cheeseman, C.R., Perry, R. Effects of conditioning and treatment of chabazite and clinoptilolite prior to lead and cadmium removal. *Environmental Science and Technology*, 1993, no.27, pp.1108-1116.
34 Zamzow, M.J., Schultze, L.E. Treatment of acid mine drainage using natural zeolites. In: *Natural Zeolites 93: Occurrence, Properties, Use*. (Eds. Ming, D.W., Mumpton, F.A.), New York: International Committee on Natural Zeolites, 1995, pp. 405-413.
35 Panayotova, M. Use of zeolite for cadmium removal from wastewater. *Journal of Environmental Science and Health Part A: Toxic/Hazardous Substances & Environmental Engineering*, 2000, no.35, pp.1591–1601.
36 Panayotova, M.I. Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite. *Waste Management*, 2001, no. 21, pp. 671–676.
37 Panayotova, M., Velikov, B. Kinetics of heavy metal ions removal by use of natural zeolite. *Journal of Environmental Science and Health Part A: Toxic/Hazardous Substances & Environmental Engineering*, 2002, no. 37, pp. 139–147.
38 Panayotova, M., Velikov, B. Influence of zeolite transformation in a homoionic form on the removal of some heavy metal ions from wastewater, *Journal of Environmental Science and Health Part A: Toxic/Hazardous Substances & Environmental Engineering*, 2003, no. 38, pp.545–554.
39 Doula. M.K. Removal of Mn2+ions from drinking water by using clinoptilolite and clinoptilolite-Fe oxide system. *Water Research*, 2006, no.40, pp.3167-3176.
40 Dimirkou, A. Uptake of Zn2+ ions by a fully iron-exchanged clinoptilolite. Case study of heavily contaminated drinking water samples. *Water Research*, 2007, no. 41, pp. 2763–2773.
41 Oter, O., Akçay.H. Use of natural clinoptiloliteto improve water quality: sorption and selectivity studies of lead(II), cooper(II), zinc(II), and nicel(II). *Water Environ Res*., 2007, no. 79(3), pp. 329-335.
42 Dimirkou, A., Doula, M.K. Use of clinoptilolite and an Fe-over exchanged clinoptilolite in Zn2+ and Mn2+ removal from drinking water. *Desalination*, 2008, no. 224, pp. 280–292.

43 Barlokova, D. Natural zeolites in the water treatment process. *Slovak Journal of Civil Engineering*, 2008, no.2, pp. 8-12.
44 Barlokova, D., Ilavsky, J. Removal of iron and manganese from water using filtration by natural materials. *Polish Journal of Environmental Studies*, 2010, no. 19(6), pp. 1117-1122.
45 Cozmuta, L.M., Cozmuta, A.M., Peter, A., Nicula, C., Nsimba, E.B., Tutu, H. The influence of pH on the adsorption of lead by Na-clinoptilolite: Kinetic and equilibrium studies. *Water SA*, 2012, no.38 (2), pp.269-278. DOI: http://dx.doi.org/10.4314/wsa.v38i2.13
46 Mihaly-Cozmuta, L., Mihaly-Cozmuta, A., Peter, A., Nicula, C., Tutu, H., Silipas, D., Indrea, E. Adsorption of heavy metal cations by Na-clinoptilolite: Equilibrium and selectivity studies, *Journal of environmental management*, 2014, vol. 137, pp. 69-80.
47 Tsitsishvili V., Osipova N., Kvernadze T., Burkiashvili N. Combined filter for water treatment. *Elixir Organic Chemistry*, 2018, no.117, pp.50342-50345.
48 Shi W.Y., Shao H.B., Li H., Shao M.A., Du S. Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite. *Journal of Hazardous Materials*, 2009, no. 170(1), pp. 1-6.
49 Martemianova I., Nadeina L., Plotnikov E., Martemianov D. Modification of natural sorbent for providing it with bactericidal and bacteriostatic properties. MATEC Web of Conferences, 2016, no. 85, pp. 1-7, doi: 10.1051/matecconf/20168501030.
50 Kwakye-Awuah, B., Williams, C., Kenward, M.A., Radecka, I. Antimicrobial action and efficiency of silver-loaded zeolite X. *Journal of Applied Microbiology*, 2008, no.104, pp.1516-1524.
51 Jiraroj, D., Tungasmita, S., Tungasmita, D.N. Silver ions and silver nanoparticles in zeolite Acomposites for antibacterial activity. *Powder Technology*, 2014, no.264, pp.418-422.
52 Jędrzejczyk, R.J., Turnau, K., Jodłowski, P.J., Chlebda, D.K., Łojewski, T., Łojewska, J. Antimicrobial properties of silver cations substituted to faujasite mineral. *Nanomaterials (Basel)*, 2017, no. 7(9), pp.240-251.
53 Milenkovic, J., Hrenovicm J., Matijasevic, D., Niksic, M., Rajic, N. Bactericidal activity of Cu-, Zn-, and Ag-containing zeolites toward *Escherichia coli* isolates. *Environmental Science and Pollution Research*, 2017, no.24, pp.20273–20281.
54 Dolaberidze N.M., Tsitsishvili V.G., Khutsishvili B.T., Mirdzveli N.A., Nijaradze M.O., Amiridze Z.G., Burjanadze M.N. Silver- and zinc-containing bactericidal phillipsites. *New Materials, Compounds & Applications*, 2018, Vol.2, no. 3, pp.247-260.