HVM BIOFLUX
Human & Veterinary Medicine
International Journal of the Bioflux Society

# Properties of natural zeolites in benefit of nutrition and health

Irina Smical

Faculty of Environmental Science, Babeş-Bolyai University Cluj-Napoca,
30 Fântânele Street, Cluj-Napoca City, Cluj County, Romania, European Union;
e-mail: irinadan2003@yahoo.com

**Abstract**. Due to their remarkable properties, natural zeolites have come to the attention of medicine researchers to find new ways of treating various diseases and ensure an improved supply of minerals in nutrition. The research results have shown the beneficial effects of application of various types of natural zeolites in healing or ameliorating especially gastrointestinal and diarrhea disease and cancer disease, as well. Because natural zeolites have a very good ability as ion exchangers they are largely used in nutrition for supplying the essential minerals in nutrition of animals.
**Key Words**: natural zeolite, ion exchange, adsorption, nutrition, medicine.

**Introduction**. Zeolites are hydrated aluminosilicates especially of calcium and sodium from tectosilicates class. They are characterized by a crystalline structure consisting of three-dimensional networks represented by aluminium tetrahedra, silicon and oxygen, with large channel gaps which are usually filled with water molecules that can be easily removed by heating gradually and which can be again absorbed or replaced by molecules of other substances (Fig. 1) (Coombs et al 1998).

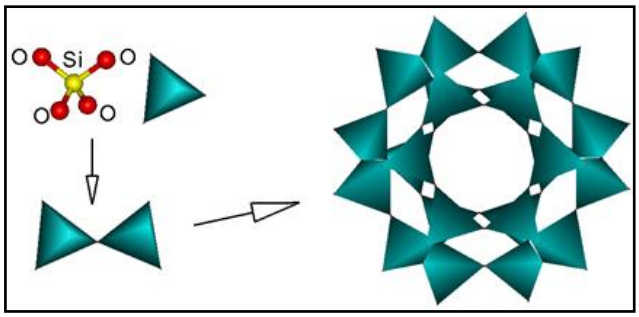


Fig. 1. Tetrahedral structure of a natural zeolite
(http://www.bza.org/zeolites.html)

Natural zeolites are the most important inorganic ion exchangers showing high ion exchange capacity, selectivity and compatibility with the natural environment (Nicula et al 2010; Smical et al 2010ab; Smical 2011). Their applications are based on one or more of the following properties: ion exchange, adsorption and molecular sieve, catalyst, high moisture and easy dehydration, low density and large volume of voids when dehydrated, lattice stability after dehydration, molecular sized channels in the dried crystals (Christie et al 2002; Ackley et al 1991; Pansini 1996; Mumpton 1999; Hugon et al 2000; Woinarski et al 2003).

From these properties, in applying of natural zeolites in medicine, the most important are: molecular adsorption and ion exchange.

**Molecular Adsorption**. Adsorption process carried out by natural zeolites can be both physical and chemical by ion exchange being called in this case chemosorption, as well (Fig. 2). Physical adsorption is achieved when the dissolved contaminants in water

adhere and become immobilized on the surface of zeolite particles without destroying the atomic structure of the zeolite.

Large cavities and channels of input of natural zeolites are generally filled with water molecules forming hydration spheres around changing cations. If the water is removed, the small enough in diameter molecules to pass through the input channels are rapidly adsorbed on the surfaces of dehydrated central cavities rings. The available area for adsorption can be up to several hundred square meters per gram (Mumpton 1983).

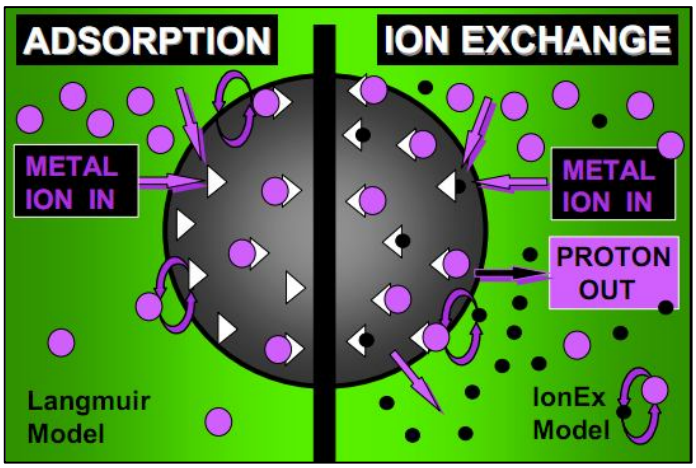


Fig. 2. Adsorption and ion exchange mechanism (Volesky 2003)

**Ion Exchange**. Ion exchange capacity is primarily a function of the degree of substitution of silicon by aluminum in the structure of the network. In zeolite structures, negative charge is given by substitution $Si^{4+}$ by $Al^{3+}$ in tetrahedron, generating a deficit of positive charge on the network. This negative charge is balanced by divalent cations and monovalent ($Na^+$, $K^+$, $Mg^{2+}$, $Sr^{2+}$ and $Ba^{2+}$) that are located in channels. The greater substitution is the more pronounced deficiency of charge is and also the greater number of cations required to electrical neutralize is.

The ion exchange process may be presented by the following equation:

$$z_A B^{Z_B^+}_{(z)} + z_B A^{z_A^+}_{(s)} \Leftrightarrow z_A B^{z_B^+}_{(s)} + z_B A^{z_A^+}_{(z)}$$

Where:

$z_A$ and $z_B$ represent the A şi B exchangeable ion charges and the coefficient z and s reffers to zeolite and to solution, respectively. The reaction runs up to the equilibrium is established.

Exchangeable cations of natural zeolites are usually represented by: $Mg^{2+}$, $Ca^{2+}$ and $Na^+$. Such theoretical cation exchange capacity (TCEC) is the sum of free cations of zeolite (Table 1) (Tsitsishvili et al 1992; Çulfaz & Yağız 2004).

$$TCEC = \sum(Na, K, Mg, Ca)$$

Table 1

Cation exchange capacity of zeolites (Pabalan & Bertetti 2001)

| *Nr. Crt.* | *Zeolite name* | *Formula* | *CEC (meq/g)* |
|---|---|---|---|
| 1 | Analcime | $Na_{16}(Al_{16}Si_{32}O_{96})\ 16H_2O$ | 4.5 |
| 2 | Chabazite | $Ca_2(Al_4Si_8O_{24})\ 12H_2O$ | 3.9 |
| 3 | Clinoptilolite | $(Na,K)_6\ Si_{30}\ Al_6\ O_{72}\ 20H_2O$ | 2.2 |
| 4 | Heulandite | $(Ca)_4\ (Si_{28}\ Al_8\ O_{72})\ 24H_2O$ | 3.2 |
| 5 | Laumontite | $Ca_4(Al_8Si_{16}O_{48})\ 16H_2O$ | 4.3 |
| 6 | Natrolite | $Na_{16}\ (Al_{16}\ Si_{24}\ O_{80})\cdot 16H_2O$ | 5.3 |
| 7 | Mordenite | $Na_2KCa_2(Al_8Si40O_{96})\ 28H_2O$ | 2.2 |
| 8 | Phillipsite | $K_2(Ca_{0.5}\ Na)_4(Al_6Si_{10}O_{32})\ 12H_2O$ | 4.5 |

In the case of a pure zeolite, its chemical formula can be used to determine the ideal cationic exchange capacity. In Table 2 the ideal cationic exchange capacities are presented based on the pure species formula. Ideal exchange capacity, estimated at 100% for clinoptilolite-rich rocks of the chemical formula was reported to be 2.32 ± 0.12 (Cerri et al 2002).

Tabel 2

Ideal cationic exchange capacity of natural zeolites (Mumpton 1999)

| *Nr. crt.* | *Zeolite name* | *Cationic exchange capacity (meq/g)* |
|---|---|---|
| 1 | Chabazite | 3.84 |
| 2 | Clinoptilolite | 2.16 |
| 3 | Erionite | 3.12 |
| 4 | Ferrierite | 2.33 |
| 5 | Heulandite | 2.91 |
| 6 | Laumontite | 4.25 |
| 7 | Mordenite | 2.29 |
| 8 | Phillipsite | 3.31 |
| 9 | Faujasite | 3.39 |

The real exchange capacity is represented by the (negative) charging of the zeolite network, so to determine the real exchange capacity is to estimate all zeolite cations that could be exchanged from solid phase. This means that the zeolite cations should be completely exchanged. In other words, the negative charge of the zeolite should be balanced by an equivalent amount of ions that interacts with zeolite. This total exchange could be achieved by: repeated balancing in batch systems with periodic renewal of the solution (Cerri et al 2002; Nikashina et al 1995; Mier et al 2001).

**Importance of Zeolites in Nutrition**. According to Mumpton & Fishman (1977), since 1965 the Japanese researchers had tried to use zeolites as suppliment in nutrition of animals (poultry, swine and cattle).

The successful results conducted to and encourage zeolite use, especially clinoptilolite and mordenite, in nutrition for a larger scale of animals. This kind of feed not only assures a gain of weight of animals but also improved their health without negative effects.

The research made by Loughbrough (1993) have shown that zeolites can be used as binding agents in animal feeds. They also appear to act as a buffer in the animals digestive system, storing nitrogen in the form of ammonium and releasing it gradually by ion exchange with sodium and potassium. The animal receives greater benefit from the same quantity of feed.

On the other hand, was noticed the ability of natural zeolites, applied to ruminants, to take up the $NH_4^+$ from the rumen and slowly release it which allowed rumen microorganisms to synthesize cellular protein continuously for easy assimilation into the digestive system of animals (Mumpton & Fishman 1977).

Positive effect of combined feed with zeolite on digestibility of nutrients; balance of nitrogen, calcium and phosphorous, and average daily increase of weight of heifers has been noticed (Kirolove et al 1995). Moreover, zeolite is commonly used in dairy cow rations to reduce the impact of mycotoxins in the feed, and it is also effective for ameliorating the negative impact of mold produced toxins in animal feeds.

**Zeolites Application in Medicine**. Physiological effects of zeolites appear to be related to their ion exchange capacity that affects tissue absorption, as well the transfer of $NH_4^+$, $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Cs^+$ and other cations in animals body (Pond 1995).

Experiments have shown that clinoptilolite is stable in the gastrointestinal tract and reduce the toxicity of ammonia in the body of the sheep and pigs, and the pigs, chickens and turkeys which had been fed with natural zeolite were protected by mycotoxins. With the cows diet containing aflatoxin content of milk is reduced if the feed is added clinoptilolite.

Noticeable results were seen at animals in decreasing the number of cases of gastric ulcer, pneumonia, heart dilation and in overall mortality (Mumpton & Fishman 1977).

When the cows diet contains aflatoxin, its amount in milk is reduced whether in the animals diet clinoptilolite is added. Also, tests have shown that in cases of diarrhea and drug intoxication the presence of clinoptilolite in diet is beneficial (Rodriguez-Fuentes et al 1997; Lam et al 1998; Rivera-Garza et al 2000).

The benefits of natural zeolites for health are (Hecht 2010):

- Detoxification by removing the pollutants and stopping the free radicals;
- Developing the immune system;
- Controlling the mineral metabolism, blood circulation, nervous system and digestion;
- Improving the skin aspect by inhibition of the aging process;
- Generate anti-bacterial, anti-viral, anti-fungal effects;
- Assure positive effect on sleep and reduce stress;
- Reduce the effect of drug, medicines, alchool and caffeine.

In case of endotoxicosis of human and animal organisms, the mechanisms of detoxification by natural zeolites act by adsorption the endotoxins and exogenous toxins in the macropores and mesopores of natural zeolites (Hect 2010).

The work made by Russian researchers using a natural zeolite from Kholinskoe deposit (Russia) have conducted to several conclusions regarding the important role of natural zeolite use in different mecial affections. The obtained data from experimental work on rats, have shown that the preparate containing the zeolite from above mentioned deposit, has the capacity to reduce the level of endogenic intoxication in relation to atropine, amitriptyline, digi-toxin and organophosphorus compounds. This zeolite underwent in vivo tests, is effective in relation to alcaloids (atropine), barbiturates (ethaminal-sodium), tricyclic anti-depressants (amitriptyline), in case of poisoning with arsenic, toxic metals (copper, barium, lead). It also allows effective reduction of endogenic intoxication level in case of radiation damage, and as enterosorbent to the standard therapy course contributes to the improvement of functional condition of main barrier and detoxicating organs and systems, correction of basic pathogenic mechanisms of toxicity in industrial poisons (Novosyolova 2010).

As well, other Russian researchers show that natural zeolite can be an excellent enterosorbent, which can be used in intestinal form of anthrax, and possibly with septicemia (Ibragimova 2010).

The experiments made on calves in order to observe the influence of clinoptilolite on resorption of colostrums immunoglobulin, haematology parameters and enzyme activities in blood serum (AST, ALD and LDH), body weight and daily weight gains of calves in first three months of life have shown that increases the resorption rate of colostrum immunoglobulin G in the digestive tract of calves, evidenced by their significantly higher concentration in blood serum and causes no significant functional or morphological changes in the tissue of parenchymatous organs and muscles.

Pavelic et al (2001) reported that clinoptilolite has been successfully used as vaccine adjuvant and for diarrhea treatment for animals. Other data published by them, indicate the role of natural zeolites as potential adjuvant in anticancer therapy according to his research made on mice and dogs which presented tumors. The clinoptilolite application has improved the overall health state and diminished tumor size of the animals.

Pavelic et al (2002) also reported that micronized zeolites administrated in diet of mice injected with melanoma cells, significantly reduced the number of melanoma metastases and the lymphocytes from lymph nodes provoked a noticeable higher allogeneic graft-versus-host reaction than cells of control mice. They also refer to an increased of peritoneal marcrophages and their production of superoxide anion. The researchers concluded that micronized zeolites have antimetastatic and immunostimulatory effect on organisms.

Purified natural zeolite has shown good stability in its passage through the stomach, and pharmacological and clinical studies have established it does not produce

any biological damage to humans. It is also a good gastric alcalinisant and anti-diarrheic adjuvant (Farías et al 2003).

According to Vrzgula & Seidel (1989), clinoptilolite proved his ability as sorbent for arsenic, cadmium, and lead ion from the rumen and abomasums juice. Zeolite was found to sorb 91% of lead and 45% of cadmium from rumen fluid in 24 hours. The sorption effectiveness was even higher from abomasums juice where zeolite sorbed 98% lead in 24 hours.

Natural zeolites, also have a benefic role in healing the dermal affections, and also have a good role in healing quickly the inflicted wounds, scrapes, surgical lesions and other open wounds (Izmirova et al 2002).

**Conclusions**. Natural zeolites due to their remarkable properties as ion exchangers and molecular sieve, have known a significant approach in the last decades especially in nutrition and medicine fields. The results of their usage in feeding animals have shown a significantly success in gaining weight and assuring a better health to the research subjected animals.

Researchers have got encouraging results on animals so that there is a premise to apply the usage of these zeolites in human nutrition with excellent results.

A very important role of natural zeolites was registered in applications against various diseases and other organism affections where they got excellent results even in cancer diminishing effects. This could represent a hope for human medicine that the usage of natural zeolites could come in supporting the incurable diseases healing.

## References


Ackley M. W., Rege U. S., Saxena H., 2003 Application of natural zeolites in the purification and separation of gases. Microporous and Mesoporous Materials **61**:25–42.

Cerri G., Langella A., Pansini M., Cappelletti P., 2002 Methods of determining cation exchange capacities for clinoptilolite rich rocks of the Logudoro region in Northern Sardinia, Italy. Clays and Clay Minerals **50**:127-135.

Christie T., Brathwaite B., Thompson B., 2002 Mineral Commodity Report 23 – Zeolites, New Zealand Mining Volume 31 June 2002.

Coombs D., Alberti A., Armbruster T., Artioli G., Colella C., Galli E., Grice J., Liebau F., Mandarino F., Minato H., Nickel E., Passaglia E., Peacor D., Quartieri S., Rinaldi R., Ross M., Sheppard R., Tillmanns E., Vezzalini G., 1998 American Mineralogist Special Feature, IMA Zeolite Report, p. 1-28.

Çulfaz M., Yağız M., 2004 Ion exchange properties of natural clinoptilolite: Lead-Sodium and Cadmium-Sodium equilibria. Separation and Purification Technology **37**(2):93-105.

Farías T., Ruiz-Salvador A. R., Rivera A., 2003 Interaction studies between drugs and a purified natural clinoptilolite, zeolite. Microporous and Mesoporous Materials **61**(1-3):117-125.

Hecht K., 2010 Clinoptilolite-Zeolite and Montmorillonite Minerals Rich in Sio2: What Are They? What Can They Achieve? Why Are They so Important for Human Health?, Application of natural zeolites in medicine and cosmetology – ZEOMEDCOS. SWB, Baku-London, 2010, pg. 7-45.

Hugon O., Sauvan M., Benech P., Pijolat C., Lefebvre F., 2000 Sensors Actuators B: Chem., 67, p. 235.

Ibragimova S. M., 2010 The Researching Results Of Adsorption Op-Portunities Of Natural Zeolites For The Bacillus Anthracis, Application of natural zeolites in medicine and cosmetology – ZEOMEDCOS. SWB, Baku-London, 2010, pg. 81-85.

Izmirova N., et al., 2002 Diagnostics, Prophylactics and Healing by Clinoptilolite Zeolite, Zeolite '02, 6th International Conference, Occurrence, Properties and Utilisation of Natural Zeolite, P. Misaelides (Ed.), pg. 150 – 151;

Kirilove M. P., Kalinin V. V., Fantin V. M., Sadykov S. M., 1995 Metabolism and reproductive feature of replacement heifers under feeding of combined fodder with

zeolites. Seskokhoziajstrennaya biologiya. Seriya Biologiya Zhivotnykh (Russian Federation) **2**:77-81.
Lam A., Sierra L. R., Rojas G., Rivera A., Rodriquez-Fuentes G., Montero L. A., 1998 Theoretical study of the physical adsorption of aspirin on natural clinoptilolite. Microporous and Mesoporous Materials **23**(5-6):247-252.
Loughbrough R., 1993 Minerals for Animal Feed, in a Stable Market. Industrial Minerals, March 1993, pg. 19 –33.
Mier M. V., Callejas R. L., Gehr R., Cisneros B. E., Alvarez P. J. J., 2001 Heavy metal removal with Mexican clinoptilolite: multi-component ionic exchange. Water Research **35**(2):373–378.
Mumpton F. A., Fishman P. H., 1977 The application of natural zeolites in animal science and aquaculture. J Anim Sci **45**:1188-1203.
Mumpton F. A., 1983 The Role of Natural Zeolites in Agriculture Zeo - Agriculture use of Natural Zeolites in Agriculture (ed. Wilson. 6 Paundand F.A. Mumpton), p. 3-27.
Mumpton F. A., 1999 La roca magica: Uses of natural zeolites in agriculture and industry. Proceedings of National Academy Sciences, USA **96**:3436-3470.
Nicula M., Banatean-Dunea I., Gergen I., Harmanescu M., Simiz E., Patruica S., Polen T., Marcu A., Lunca M., Szucs S., 2010 Effect of natural zeolite on reducing tissue bioaccumulation and cadmium antagonism related to some mineral micro- and macronutrients in Prussian carp (*Carassius gibelio*). AACL Bioflux **3**(3):171-179.
Nikashina V. A., Galkina N. K., Komarova I. V., Anfilov B. G., Argin M. A., 1995 In: D. W. Ming, F. A. Muphton (Eds.), Natural Zeolites 93: Occurrence, Properties, Use, Brockport, NY, 1995, p. 289.
Novosyolova T. I., 2010 Pre-Clinical And Clinical Studies of “Litovit” Biologically Active Food Supplement (BAFS), Application of natural zeolites in medicine and cosmetology – ZEOMEDCOS. SWB, Baku-London, 2010, pg. 58-71.
Pabalan R. T., Bertetti F. P., 2001 Cation exchange capacity of natural zeolites. In: Natural zeolites: occurrence, properties, applications. Reviews in Mineralogy and Geochemistry v. 45, David Bish and Doug Ming (Eds) Mineralogical Society of America, p. 453-518.
Pansini M., 1996 Natural zeolites as cation exchangers for environment protection. Miner Deposita **31**:563–575.
Pavelic K., Colic M., et al., 2001 Natural zeolite clinoptilolite: new adjuvant in anticancer therapy. J Mol Med (Springer-Verlag) **78**:708-720.
Pavelic K., Colic V., et al., 2002 Immunostimulatory effect of natural clinoptilolite as a possible mechanism of its antimetastatic ability. J Cancer Res Clin Oncol (Springer-Verlag) **128**:37-44.
Pond W. G., 1995 Zeolite in animal nutrition and health: A review. In: Natural Zeolite '93: Occurrence, Properties, Use. D. W. Ming and F. A. Mumpton (eds.), Int Comm Nat Zeolite, Brockpot New York, p. 449-457.
Rivera-Garza M., Olguín M. T., García-Sosa I., Alcántara D., Rodríguez-Fuentes G., 2000 Silver supported on natural Mexican zeolite as an antibacterial material. Microporous and Mesoporous Materials **39**:431–444.
Rodriguez-Fuentes G., Ruiz-Salvador A. R., Mir M., Picazo O., Quintana G., Delgado M., 1998 Thermal and cation influence on IR vibrations of modified natural clinoptilolite. Microporous and Mesoporous Materials **20**:269-281.
Smical I., 2011 Sorption kinetics of $Pb^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ ions by natural zeolites from Maramures County (northern Romania): potential application in wastewater reuse. AACL Bioflux **4**(4):481-489.
Smical I., Mihaly-Cozmuta L., Costin D., 2010a Research concerning the influence of several factors on $Pb^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ ions adsorption by natural zeolite tuff from Maramureş county, Northern Romania. AES Bioflux **2**(2):171-180.
Smical I., Mihaly-Cozmuta L., Costin D., 2010b Use of natural zeolites from Maramures county (Romania) in removal of $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$ ions from industrial wastewaters. AES Bioflux **2**(2):181-188.
Tsitsishvili G. V., Andronikashvili T. G., Kirov G. N., Filizova L. D., 1992 Natural Zeolites, Ellis Horwood, New York, 295 pg.

Volesky B., 2003 Sorption and biosorption. BV Sorbex, Inc., Montreal, Canada, ISBN 0-9732983-0-8, 316 p, p. 103.
Vrzgula L., Seidel H., 1989 Sorption characteristics of natural zeolite (Clinoptilolite) in biological material in vitro. Vet Med (Praha) **34**(9):537-544.
Woinarski A. Z., Snape I., Stevens G. W., Stark S. C., 2003 The effects of cold temperature on copper ion exchange by nature zeolite for use in a permeable reactive barrier in Antarctica. Cold Regions Science and Technology **37**:159-168.

Received: 02 October 2010. Accepted: 18 December 2010. Published online: 08 July 2011.
Author:
Irina Smical, Faculty of Environmental Science, Babeş-Bolyai University of Cluj-Napoca, 30 Fântânele Street, Cluj-Napoca City, Cluj County, România, irinadan2003@yahoo.com
New adress: Irina Smical, Environmental Protection Agency of Maramures County, Romania, loc. Baia Mare, str. Iza, nr. 1A, judeţul Maramureş, irinadan2003@yahoo.com
How to cite this article:
Smical I., 2011 Properties of natural zeolites in benefit of nutrition and health. HVM Bioflux **3**(2):51-57.