

Aluminosilicate Mineral Zeolite. Interaction of Water Molecules in Table and Mountain Zeolite Water Sevtopolis from Bulgaria

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Abstract
We studied the mathematical model of interaction of water of with microporous crystalline aluminosilicate mineral natural zeolite (Bulgaria). In this report are submitted data about the interaction of zeolite with water, obtained by non-equilibrium (NES) and differential-equilibrium energy spectrum (DNES) of water. The water is preparing from Company Sevtopolis, Kazanlak, Bulgaria. There are two waters – Table Zeolite Water Sevtopolis and Mountain Zeolite Water Sevtopolis. The average energy ($\Delta E_{H...O}$) of hydrogen H…O-bonds among individual molecules H_2O after treatment of zeolite with water measured by NES-method is -0.1232 eV for Table Zeolite water Sevtopolis. The calculation of $\Delta E_{H...O}$ for Table Zeolite water Sevtopolis with using DNES method compiles -0.0101±0.0011 eV. The average energy ($\Delta E_{H...O}$) of hydrogen H…O-bonds among individual molecules H_2O after treatment of zeolite with water measured by NES-method is -0.1235 eV for Spring Mountain Zeolite water Sevtopolis. The calculation of $\Delta E_{H...O}$ for Spring Mountain Zeolite water Sevtopolis with using DNES method compiles -0.0104±0.0011 eV. These results suggest the restructuring of $\Delta E_{H...O}$ values among H_2O molecules with a statistically reliable increase of local maximums in DNES-spectra.
Keywords: Table Zeolite water Sevtopolis, Spring Mountain Zeolite water Sevtopolis, NES, DNES

1. Introduction

Mineral Zeolite is from new generation of natural mineral sorbents (NMS). Zeolites are the alumosilicate members of the family of microporous solids known as "molecular sieves", named by their ability to selectively sort molecules based primarily on a size exclusion process. Natural zeolites form when volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quarts, or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

Zeolites is widely used in industry as a desiccant of gases and liquids, for treatment of drinking and sewage water from heavy metals, ammonia, phosphorus, as catalyst in petrochemical industry for benzene extraction, for production of detergents and for extracting of radionuclides in nuclear reprocessing. Zeolite is also used in medicine as nutritional supplements having antioxidant properties.

A wide range of properties of zeolite defines the search for new areas of industrial application of these minerals in science and technology that contributes to a deeper study the mechanism of interaction of these minerals with water. This paper deals with evaluating of mathematical model of interaction of zeolite with water.

2. Materials and Methods

2.1. Materials

The study was performed with samples of table and spring mountain Zeolite water Sevtopolis from Bulgaria. Samples were taken from water after the process of purified with zeolite. The water samples are 120 ml for research with methods NES and DNES.

2.2. Analytical Methodss

The analytical methods were accredited by the Institute of Geology of Ore Deposits. Petrography, Mineralogy, and Geochemistry (Russian Academy of Sciences). Samples were treated by various methods as ICP-OES, GC, and SEM.

2.3. Gas-Chromatography

Gas-chromatography (GC) was performed at Main Testing Centre of Drinking Water on Kristall 4000 LUX M using Chromaton AW-DMCS and Inerton-DMCS columns (stationary phases 5% SE-30 and 5% OV-17), equipped with flame ionization detector (FID) and using helium (He) as a carrier gas.

2.4. Transmission Electrom Microscopy (TEM)

The structural studies were carried out with using JSM 35 CF (JEOL Ltd., Korea) device, equiped with X-ray microanalyzer “Tracor Northern TN”, SE detector, thermomolecular pump, and tungsten electron gun (Harpin type W filament, DC heating); working pressure: 10^{-4} Pa (10^{-6} Torr); magnification: 300.000, resolution: 3.0 nm, accelerating voltage: 1–30 kV; sample size: 60–130 mm.

2.5. IR-Spectrospopy

IR-spectra of water samples, obtained after being contacted 3 days with zeolite, were registered on Fourier-IR spectrometer Brucker Vertex ("Brucker", Germany) (a spectral range: average IR – 370–7800 cm^{-1}; visible – 2500–8000 cm^{-1}; the permission – 0.5 cm^{-1}; accuracy of wave number – 0.1 cm^{-1} on 2000 cm^{-1}); Thermo Nicolet Avatar 360 Fourier-transform IR; Non-equilibrium Spectrum (NES) and Differential Non-equilibrium Spectrum (DNES).

3. Results and Discussions

3.1. Chemical composition of zeolite (Bulgaria)

In comparison with zeolite comprises a microporous crystalline aluminosilicate mineral commonly used as commercial adsorbents, three-dimensional framework of which is formed by linking via the vertices the tetrahedra $[AlO_4]^{2-}$ and $[SiO_4]^{2-}$ (Panayotova & Velikov, 2002). Each tetrahedron $[AlO_4]^{2-}$ creates a negative charge of the carcasses compensated by cations (H^+, Na^+, K^+, Ca^{2+}, NH_4^+, etc.), in most cases, capable of cation exchange in solutions. Tetrahedrons formed the secondary structural units, such as six-membered rings, five-membered rings, truncated octahedra, etc. Zeolite framework comprises interacting channels and cavities forming a porous structure with a pore size of 0.3–1.0 nm. Average crystal size of the zeolite may range from 0.5 to 30 μm. The composition of the zeolite from Bulgaria is in the Table 1.

Table 1. The chemical composition of zeolite (Bulgaria), in % (w/w)

№	Chemical component	Content, % (w/w)
1	SiO_2	22.14
2	TiO_2	0.01
3	Al_2O_3	17.98
4	FeO	23.72
5	Fe_2O_3	1.49
6	MgO	14.38
7	MnO	0.61
8	CaO	0.36
9	Na_2O	0.5
10	K_2O	0.4
11	S	0.32
12	P_2O_5	0.06
13	Ba	0.0066
14	V	0.0272
15	Co	0.0045
17	Cu	0.0151
18	Mo	0.0012
19	As	0.0025
20	Ni	0.0079
21	Pb	0.0249
22	Sr	0.0021
23	Cr	0.0048
24	Zn	0.1007
25	H_2O	1.43

By the measurement of IR spectra in the range of vibrations in the crystal mineral framework one can obtain the information: a) on the structure of the framework, particularly type lattice ratio SiO_2/Al_2O_3, nature and location of cations and changes in the structure in the process of the thermal treatment; b) on the nature of the surface of the structural groups, which oftnen serve as adsorption and catalytically active sites.

3.2.Mathematical Models of Spring Mountain and Table Water Sevtopolis

Other method for obtaining information about the average energy of hydrogen bonds in an aqueous sample is measuring of the spectrum of the water state. It was established experimentally that at evaporation of water droplet the contact angle θ decreases discretely to zero, whereas the diameter of the droplet changes insignificantly (Antonov, 2005). By measuring this angle within a regular time intervals a functional dependence f(θ) can be determined, which is designated by the spectrum of the water state (Ignatov, 2005; Ignatov, 2012; Ignatov & Mosin, 2013). For practical purposes by registering the spectrum of water state it is possible to obtain information about the averaged energy of hydrogen bonds in an aqueous sample. For this purpose the model of W. Luck was used, which consider water as an associated liquid, consisted of O–H…O–H groups (Luck *et al.*, 1980). The major part of these groups is designated by the energy of hydrogen bonds (-E), while the others are free (E = 0). The energy distribution function f(E) is measured in electron-volts (eV^{-1}) and may be varied under the influence of various external factors on water as temperature and pressure.

For calculation of the function f(E) experimental dependence between the water surface tension measured by the wetting angle (θ) and the energy of hydrogen bonds (E) is established:

$$f(E) = b\, f(\theta) / 1 - (1 + b\, E)^2)^{1/2},$$

where $b = 14.33\ eV^{-1}$; $\theta = \arccos(-1 - b\, E)$

The energy of hydrogen bonds (E) measured in electron-volts (eV) is designated by the spectrum of energy distribution. This spectrum is characterized by non-equilibrium process of water droplets evaporation, thus the term "non-equilibrium energy spectrum of water" (NES) is applied.

The difference Δf(E) = f (samples of water) – f (control sample of water)

– is designated the "differential non-equilibrium energy spectrum of water" (DNES).

DNES calculalated in milielectron volts (0.001 eV or meV) is a measure of changes in the structure of water as a result of external factors. The cumulative effect of all other factors is the same for the control sample of water and the water sample, which is under the influence of this impact.

The research with the NES method of water drops is received with two water samples from Zeolite water Sevtopolis – table and mountain spring. The mathematical model gives the valuable information for the possible number of hydrogen bonds as percent of H_2O molecules with different values of distribution of energies (Table 2). These distributions are basically connected with the restructuring of H_2O molecules having the same energies.

Table 2: The distribution (%, $(-E_{value})/(-E_{total\ value})$ of H_2O molecules in water samples from Zeolite waters Sevtopolis – table and mountain spring

Table 2. Characteristics of spectra of Zeolite table and mountain water Sevtopolis by NES-method

-E(eV) x-axis	Table Zeolite Water Sevtopolis y-axis (%(($-E_{value}$) */ ($-E_{total\ value}$)**	Mountain Spring Zeolite Water Sevtopolis y-axis (%(($-E_{value}$)*/ ($-E_{total\ value}$)**	-E(eV) x-axis	Table Zeolite Water Sevtopolis y-axis (%(($-E_{value}$) */ ($-E_{total\ value}$)**	Mountain Spring Zeolite Water Sevtopolis y-axis (%(($-E_{value}$)*/ ($-E_{total\ value}$)**
0.0937	0	0	0.1187	0	2.0
0.0962	6.3	2.0	0.1212	**20.8**[2]	**18.5**[2]
0.0987	6.3	3.1	0.1237	4.1	10.2
0.1012	6.3	1.0	0.1262	0	3.1
0.1037	6.3	4.1	0.1287	4.1	3.1
0.1062	4.1	0	0.1312	8.4	14.1
0.1087	2.0	2.0	0.1337	5.2	4.1
0.1112	**8.4**[1]	**12.2**[1]	0.1362	5.2	8.2
0.1137	0	0	0.1387	**8.4**[3]	**8.2**[3]
0.1162	4.1	4.1	–	–	–

E=-0.1212 eV is the local extremum for anti-inflammatory effect

Notes:

* The result ($-E_{value}$) is the result of hydrogen bonds energy for one parameter of (-E)

** The result ($-E_{value}$) is the total result of hydrogen bonds energy

There are two waters – Spring Mountain Zeolite Water Sevtopolis and Table Zeolite Water Sevtopolis. The average energy ($\Delta E_{H...O}$) of hydrogen H…O-bonds among individual molecules H_2O after treatment of zeolite with water measured by NES-method is -0.1232 eV for Table Zeolite water Sevtopolis. The calculation of $\Delta E_{H...O}$ for Table Zeolite water Sevtopolis with using DNES method compiles -0.0101±0.0011 eV. The average energy ($\Delta E_{H...O}$) of hydrogen H…O-bonds among individual molecules H_2O after treatment of zeolite with water measured by NES-method is -0.1235 eV for Spring Mountain Zeolite Sevtopolis. The calculation of $\Delta E_{H...O}$ for Spring Mountain Zeolite Sevtopolis with using DNES method compiles -0.0104±0.0011 eV. These results suggest the restructuring of $\Delta E_{H...O}$ values among H_2O molecules with a statistically reliable increase of local extremums in DNES-spectra. In Mountain Spring and Table Zeolite waters Sevtopolis there is increasing of energy of hydrogen bonds among water molecules with stimulating effect on human body. The results with local extremums at – 0.1212 eV show expressed anti-inflammatory effect.

Owing to the unique porous structure the natural mineral zeolite are ideal absorbents and fillers (Gorshteyn *et al.*, 1979), and as sorbents have a number of positive characteristics:

- High adsorption capacity, characterized by low resistance to water preasure;
- Mechanical strength and low abrasion resistance;
- Corrosion-resistance;
- Absorption capacity felative to many substances, both organic (oil, benzene, phenol, pesticides, etc.) and inorganic (chlorine, ammonia, heavy metals);
- Catalytic activity;
- Relatively low cost;
- Environmental friendliness and ecological safety.

Owing to all these positive properties zeolite may find its application for the preparation of drinking water in flow-through systems of any capacity for industrial and domestic purposes, as well as in the wells in order to improve the quality characteristics of water to return water its beneficial properties.

Especially effective and technologically justified is the use of complex filter systems based of the mixtures of zeolite, with subsequent regeneration of the absorbents. When adding to the treatment scheme to shungite other natural absorbents (zeolite, dolomite, glauconite) purified water is enriched to physiologically optimal levels by calcium, magnesium, silicon and sodium ions.

4. Conclusions

The research shows the result with NES and DNES spectra of table and spring Zeolite waters Sevtopolis. In mountain spring and table Zeolite waters Sevtopolis there is increasing of energy of hydrogen bonds among water molecules with stimulating effect on human body. The results with local extremums show expressed anti-inflammatory effect.

References

Antonov, A. (2005) Research of the nonequilibrium processes in the area in allocated systems. Diss. thesis doctor of physical sciences. Sofia: Blagoevgrad, 1–255.

Ignatov, I. (2005) *Energy Biomedicine*, Gea-Libris, Sofia, 1–88.

Ignatov, I. (2010) Which Water is Optimal for the Origin (Generation) of Life? *Euromedica*, Hanover: 34-35.

Ignatov, I. (2011) Entropy and Time in Living Matter, *Euromedica:* 74.

Ignatov, I. (2012) Origin of Life and Living Matter in Hot Mineral Water, Conference on the Physics, Chemistry and Biology of Water, Vermont Photonics, USA.

Ignatov I., Mosin O.V. (2013) Possible Processes for Origin of Life and Living Matter with Modeling of Physiological Processes of Bacterium *Bacillus Subtilis* in Heavy Water as Model System, *Journal of Natural Sciences Research*, **3** (9): 65-76.

Ignatov, I., Mosin, O. V. (2013) Modeling of Possible Processes for Origin of Life and Living Matter in Hot Mineral and Seawater with Deuterium, *Journal of Environment and Earth Science*, **3**(14): 103-118.

Ignatov, I., Mosin, O. V. (2013) Structural Mathematical Models Describing Water Clusters, *Journal of Mathematical Theory and Modeling*, **3** (11): 72-87.

Ignatov, I., Mosin, O. V. (2014) The Structure and Composition of Carbonaceous Fullerene Containing Mineral Shungite and Microporous Crystalline Aluminosilicate Mineral Zeolite. Mathematical Model of Interaction of Shungite and Zeolite with Water Molecules *Advances in Physics Theories and Applications*, **28**: 10-21.

Ignatov, I.&Mosin,O.V. (2014) The Structure and Composition of Shungite and Zeolite. Mathematical Model of Distribution of Hydrogen Bonds of Water Molecules in Solution of Shungite and Zeolite, *Journal of Medicine, Physiology and Biophysics*, **2**: 20-36.

Ignatov, I.&Mosin,O.V. (2014) Mathematical Models of Distribution of Water Molecules Regarding Energies of Hydrogen Bonds, *Medicine, Physiology and Biophysics*, **2**: 71-94.

Ignatov, I.&Mosin,O.V. (2014) Mathematical Model of Interaction of Carbonaceous Fullerene Containing Mineral Shungite and Aluminosilicate Mineral Zeolite with Water, *Journal of Medicine, Physiology and Biophysics*, **3**: 15-29.

Ignatov, I., Mosin, O. V.&Bauer, E. (2014) Carbonaceous Fullerene Mineral Shungite and Aluminosilicate Mineral Zeolite. Mathematical Model ans Practical Application of Water Solution of Water Shungite and Zeolite, *Journal of Medicine, Physiology and Biophysics*, **4**: 27-44.

Ignatov, I. (2016) Product of LavaVitae BOOST is Increasing of Energy of Hydrogen Bonds among Water Molecules in Human Body, *Journal of Medicine, Physiology and Biophysics*, **27**: 30-42.

Ignatov, I. (2016) VITA intense – Proofs for Anti-inflammatory, Antioxidant and Inhibition Growth of Tumor Cells Effects. Relaxing Effect of Nervous System. Anti Aging Influence, *Journal of Medicine, Physiology and Biophysics*, **27**: 43-61.

Ignatov, I.et al. (2016) Results of Biophysical and Nano Technological Research of ZEOLITH detox of LavaVitae Company, *Journal of Health, Medicine and Nursing*, **30**.: 44-49.

Luck, W., Schiöberg, D. & Ulrich, S. (1980) Infared investigation of water structure in desalination membranes. *J. Chem. Soc. Faraday Trans*., **2**(76), 136–147.

Mosin O.V., Ignatov I. (2013a) Composition and structural properties of fullerene analogous mineral shungite. *Journal of Nano and Microsyctem Technique*, **1**, 32–40 [in Russian].

Mosin, O.V. & Ignatov, I. (2013b) The structure and composition of natural carbonaceous fullerene containing mineral shungite. *International Journal of Advanced Scientific and Technical Research*, **6**(11–12), 9–21.

Mosin, O.V. & Ignatov, I. (2012) The Composition and structural properties of fullerene natural mineral shungite. *Nanoengineering*, **18**(12), 17–24 [in Russian].

Panayotova, M. & Velikov, B. (2002) Kinetics of heavy metal ions removal by use of natural zeolite. *Journal of Environmental Science and Health*, **37**(2), 139–147.