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New Properties and Bio effects of High Quality Bulgarian Zeolite Rhodosorb-H® and Cosmetic Water Rhodosorb-W®

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Abstract

The author studied the mathematical model of interaction with water of natural mineral and microporous crystalline mineral zeolite Rhodosorb-H from Bulgaria. Clinoptilolite is from the groups of minerals with name zeolite. Clinoptilolite is a natural zeolite comprising a microporous arrangement of silica and alumina tetrahedra. It has the complex formula: $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36} \cdot 12H_2O$. The Bulgarian zeolite consists 90-92% clinoptilolite.

In this report are submitted data about the interaction of zeolite Rhodosorb-H with water, obtained by non-equilibrium (NES) and differential-equilibrium energy spectrum (DNES) of water. The average energy ($\Delta E_{H...O}$) of hydrogen H…O-bonds among individual molecules H_2O after treatment of zeolite Rhodosorb-H with water measured by NES- and DNES-methods is ΔE=-0.0077±0.0011 eV for zeolite Rhodosorb-H. This result suggests the restructuring of $\Delta E_{H...O}$ values among H_2O molecules with a statistically reliable increase of local extremums in DNES-spectra. The research is performed for zeolite Rhodosorb-H with study of pH and oxidative reduction potential (ORP).

The author studied the properties of Bulgarian cosmetic water Rhodosorb-W according the cosmetic water as control sample from the market**.** The research is with methods NES and DNES. The average energy ($\Delta E_{H...O}$) of hydrogen H…O-bonds among individual molecules H_2O of cosmetic water Rhodosorb-W measured by NES- and DNES-methods is ΔE=-0.003±0.0011 eV. The research is performed for cosmetic water Rhodosorb-W with study of pH and oxidative reduction potential (ORP).

There is review of the effects of the chemical composition of Rhodosorb-H – anti-inflammatory (Climent, Corma, Iborra; 2005), antioxidant (Montinaro et al.;2013) etc. With methods NES we show the following effects – anti-inflammatory and inhibition of development as size and number of tumor cells, anti toxin. As results of these effects Rhodosorb-W has anti aging influence. The base of this influence is anti-inflammatory effect. This article deals with the review of the basic biophysical-biochemical and biological processes underlying the Rhodosorb-H. The author is studying their physical-chemical properties and biophysical and biological effects on human organism. Additionally, by using IR, NES, and DNES methods are investigated various samples of water from Bulgarian water springs: the melt water from Glacier Rosenlaui, Swiss Alps, as well as the human blood serum of people with excellent health and cancer patients between 50 and 70 years old (Ignatov, Mosin; 2012).

Other experiments were performed on a 1% (v/v) solution of Rhodosorb-H in deionized water. As an estimation factor in NES and DNES was measured the values of the average energy of hydrogen bonds ($\Delta E_{H...O}$) among H_2O molecules in water samples, as well as a local extremums in the NES and DNES-spectra of various samples

of water and the human blood serum at E = -0.1387 eV and λ = 8.95 μm. For a group of people in critical condition of life and patients with malignant tumors the greatest values of local extremums in IR-, DNES-spectra were shifted to lower energies relative to the control healthy group. Further we applied this method for calculation of percent distribution of H_2O molecules in all studied water samples according to energies of hydrogen bonds ranged from (-0.08 to -0.1387 eV). Rhodosorb-H makes increasing of local extremum at E = -0.1387 eV and λ = 8.95 μm as indicator for re structuring of the hydrogen bond toward highest energy level at E = -0.1387 eV and λ = 8.95 μm.
Zeolite Rhodosorb-H and cosmetic water Rhodosorb-W are with registered trade marks®.

Keywords: zeolite Rhodosorb-H, cosmetic water Rhodosorb-W, mathematical model, NES, DNES.

1. Introduction

The zeolite Rhodosorb-H is mineral refers to 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.

As natural mineral zeolite has unusually broad scope of applications in industry - adsorption, catalytic, and reduction-oxidation. 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. It is also used in medicine as nutritional supplements having antioxidant properties. Some authors make qualifications of zeolites as nano materials.

A wide range of properties of zeolite defines the search for new areas of industrial application of these minerals in science and nano 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 Rhodosorb-W with water. There is research of cosmetic water Rhodosorb-W.

There are radioprotective properties of zeolites**.** The most part of effects are with isotopes of Cesium (Cs-134, Cs-137) и and Strontium (Sr-90) . The basic publication for this application is in Nature (Yeritsyan, H. et al., 2013).

2. Materials and Methods

2.1. Materials

The study was performed with samples of 1% water solution of zeolite Rhodosorb-H and cosmetic water Rhodosorb-W.

In the world the companies perform double activization with the following two levels.

First activization – Tribo Mechanical - Fine grinding of the material so that it can raise the absorption area to a maximum.

Second activation - Thermal - in order to extract the molecular moisture, so that zeolite can better absorbs the poisons of our organism. When zeolite is wet there is a poorly effective absorption effect.

The company ECOTECH Ltd, Bulgaria makes third activization with knowhow. The Bulgarian company processes the material with a special high-frequency device by special technology to prevent the formation of colonies of zeolite particles. When colonies form in the body, the cleansing effect is much weaker.
By preventing the formation of these colonies, we allow each particle to move as a "free substance" in our body for cleaning.
For the Rhodosorb zeolite there are valid the following three activizations:
First activization – According to the manufacturer there is grinding of the zeolite from 1 to 5 μm. That means from one gram there are 1200 m^2 absorption area.
Second activation is through a vacuum drier. There is extraction of near to 100% of the molecular moisture in zeolite.
Third method is with special high-frequency electromagnetic device by special technology to prevent the formation of colonies of zeolite particles.

There are valid the following methods for research of zeolite.

2.2. Analytical Methods

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) is performed at Main Testing Centre of Drinking Water (Moscow, the Russian Federation) 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. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The mineral composition is studied by inductively coupled plasma optical emission spectrometry (ICP-OES) on Agilent ICP 710-OES (Agilent Technologies, USA) spectrometer, equipped with plasma atomizer (under argon stream), MegaPixel CCD detector, and 40 MHz free-running, air-cooled RF generator, and Computer-optimized exhale system: the spectral range at 167–785 nm; plasma gas: 0–22.5 l/min in 1.5 l/min; power output: 700–1500 W in 50 W increments.

2.5. 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.

2.6. IR-Spectrospopy

IR-spectra of water samples, obtained after being contacted 3 days with shungite and zeolite, are 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});

For the research of Rhodosorb-W and cosmetic water Rhodosorb-W the methods are:

2.7. Non-equilibrium Spectrum (NES) and Differential Non-equilibrium Spectrum (DNES)

The energy spectrum of water is characterized by a non-equilibrium process of water droplets evaporation, therefore, the term non-equilibrium spectrum (NES) of water is used. The difference $\Delta f(E) = f$ *(samples of water)* – *f (control sample of water)* – is called the "differential non-equilibrium energy spectrum of water" (DNES).

2.8. Studying the Bulgarian Long Living People and Centenarians

Interviews have been conducted with 415 Bulgarian centenarians and long living people and their siblings. Their heredity, body weight, health status, tobacco consumption, physical activity, attitude towards life has been analyzed. With using DNES method was performed a spectral analysis of 15 mountain water springs located in municipalities Teteven and Kuklen (Bulgaria). The composition of water samples was studied in the laboratory of "Eurotest Control" (Bulgaria). Statistics methods were attributed to the National Statistical Institute of Bulgaria.

2.9. Studying the Human Blood Serum

1% (v/v) solution of human blood serum was studied with the methods of IR-spectroscopy, non-equilibrium (NES) and differential non-equilibrium (DNES) spectral analysis. The specimens were provided by Kalinka Naneva (Municipal Hospital, Bulgaria). Two groups of people between the ages of 50 to 70 were tested. The first group (control group) consisted of people in good clinical health. The second group included people in critical health or suffering from malignant diseases.

2.10. Measurement of pH and ORP (oxidative-redox potential)

The research is performed from Georgi Gluhchev with device from Hanna Instruments.

3. Results and Discussion

3.1. Properties of Bulgarian Zeolite. Spectral Methods NES and DNES.

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 tetrahedral $[AlO_4]^{2-}$ 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. Zeolites framework comprise interacting channels and cavities forming a porous structure with a pore size of 0.3–1.0 nm. Average crystal size of the zeolites may range from 0.5 to 30 μm.

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 often serve as adsorption and catalytically active sites.

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 $\Delta f(E)$ = f (samples of water) – f (control sample of water)

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

DNES is calculated in milli-electron 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 NES method of water drops received after 3 days stay with zeolite in deionized water may also give valuable information on the possible number of hydrogen bonds as percent of water molecules with different values of distribution of energies. These distributions are basically connected with restructuring of H_2O molecules with the same energies.

3.2. Results with 1 % solution of zeolite Rhodosorb-H

The average energy ($E_{H...O}$) of hydrogen H…O-bonds among individual H_2O molecules in 1% solution of zeolite Rhodosorb-H is measured at E=-0.1249 eV. The result for the control sample (deionized water) is E=-0.1172 eV. The results obtained with the NES method are recalculated with the DNES method as a difference of the NES (1% solution of zeolite Rhodosorb-H) minus the NES (control sample with deionized water) equaled the DNES spectrum of 1% solution of zeolite Rhodosorb-H. Thus, the result for 1% solution of zeolite Rhodosorb-H recalculated with the DNES method is $\Delta E=-0.0077\pm0.0011$ eV. The result shows the increasing of the values of the energy of hydrogen bonds in 1% solution of zeolite Rhodosorb-H regarding the deionized water. The result is effect of stimulation on human body. This shows restructuring of water molecules in configurations of clusters, which influence usefully on human health on molecular and cellular level. The effects are describing with mathematical model of 1% solution of zeolite Rhodosorb-H. The research with the NES method of water drops is received with 1% solution of zeolite Rhodosorb-H, and deionized water as control sample. The mathematical models of 1% solution zeolite Rhodosorb-H 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 1 and Fig. 1). These distributions are basically connected with the restructuring of H_2O molecules having the same energies.

Table 1: The distribution (%, $(-E_{value})/(-E_{total\ value})$ of H_2O molecules in 1% water solution of zeolite Rhodosorb-H and control deionized water

-E(eV) x-axis	1% water solution zeolite Rhodosorb-H y-axis (%((-E_{value}) */ (-$E_{total\ value}$)**	Control Sample Deionized water y-axis (%((-E_{value})*/ (-$E_{total\ value}$)**	-E(eV) x-axis	1% water solution zeolite Rhodosorb-H y-axis (%((-E_{value}) */ (-$E_{total\ value}$)**	Control Sample Deionized water y-axis (%((-E_{value})*/ (-$E_{total\ value}$)**
0.0937	0	0	0.1187	0	10.1
0.0962	0	0	0.1212	**27.2**[2]	0
0.0987	0	0	0.1237	0	10.1
0.1012	0	10.1	0.1262	0	2.8
0.1037	0	0	0.1287	9.1	6.2
0.1062	0	10.1	0.1312	0	0
0.1087	0	10.1	0.1337	9.1	5.1
0.1112	**9.1**[1]	0	0.1362	9.1	5.1
0.1137	9.1	10.1	0.1387	**18.2**[3]	0
0.1162	9.1	20.2	–	–	–

Notes:

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

E= -0.1387 eV is the local extremum for inhibition of development of tumor cells of molecular level

Notes:

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

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

Figure 1 shows the distribution (%, $(-E_{value})/(-E_{total\ value})$ of H_2O molecules in and 1% of water solution of zeolite Rhodosorb-H (red line) and control sample deionized water (blue line).

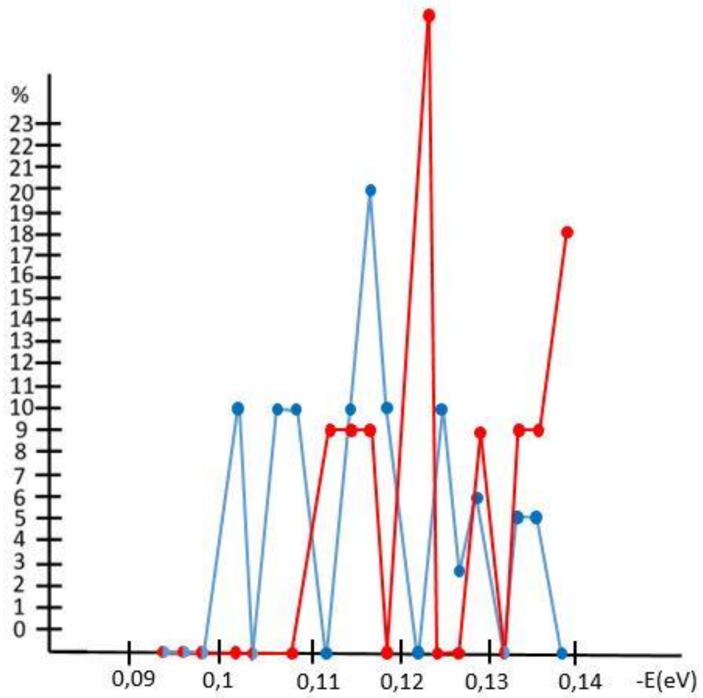

Figure 1: Mathematical model (Ignatov, Mosin, 2013) of 1% water solution of zeolite Rhodosorb-H.

Notes:

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

E= -0.1387 eV is the local extremum for inhibition of development of tumor cells of molecular level

The experimental data obtained testified the following conclusions from the mathematical model of in 1% water solution of zeolite Rhodosorb-H and control deionized water. The distribution (%, $(-E_{value})/(-E_{total\ value})$ of water molecules in mathematical model of in 1% water solution of zeolite Rhodosorb-H and control deionized water. The distribution (%, $(-E_{value})/(-E_{total\ value})$ of water molecules in zeolite Rhodosorb-H according control sample is different. However, for the value E = -0.1387 eV or λ = 8.95 μm there is the bigger local extremum (18.2 (%, $(-E_{value})/(-E_{total\ value})$) corresponding to the re-structuring of hydrogen bonds among H_2O molecules for inhibition of development of tumor cells of molecular level. This difference may indicate on the different number of hydrogen bonds in water samples, as well as their physical parameters (pH, ORP), resulting in different distribution of H_2O molecules and different values of H_2O molecules with ratios of $(-E_{value})/(-E_{total\ value})$. Particularly it was observed the statistical re-structuring of H_2O molecules in water samples according to the energies. The experimental data may prove that stipulates the restructuring of H_2O molecules on molecular level and may be used for the prophylaxis of development of tumor cells. For the value E=-0.1212 eV or λ=10.23 μm there is the biggest local extremum (27.2 (%, $(-E_{value})/(-E_{total\ value})$) corresponding to the re-structuring of hydrogen bonds among H_2O molecules for anti inflammatory effect.. The experimental data for zeolite Rhodosorb-H may prove that stipulates the restructuring of H_2O molecules on molecular level and the biophysical effects are:

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

E= -0.1387 eV is the local extremum for inhibition of development of tumor cells of molecular level

As a result of different energies of hydrogen bonds, the surface tension of 1% solution of water sample with zeolite Rhodosorb-H is increasing. The increasing of surface tension is regarding the control sample. This effect is connected with preservation of the energy in human body as result of biochemical process among water molecules and bio molecules. As effect of big increasing of surface tension and the spectrum is begging from E= -0.1112 eV and this shows effects of detoxification.

3.2. Results with cosmetic water Rhodosorb-W

The average energy ($E_{H...O}$) of hydrogen H…O-bonds among individual H_2O molecules in cosmetic water Rhodosorb-W is measured at E=-0.1240 eV. The result for the control sample (cosmetic water from the market) is E=-0.1210 eV. The results obtained with the NES method are recalculated with the DNES method as a difference of the NES (cosmetic water Rhodosorb-W) minus the NES (control sample with cosmetic water from the market) equaled the DNES spectrum of cosmetic water Rhodosorb-W. Thus, the result for cosmetic water Rhodosorb-W recalculated with the DNES method according the control sample of cosmetic water from the market is $\Delta E=-0.003\pm0.0011$ eV. The result shows the increasing of the values of the energy of hydrogen bonds in cosmetic water Rhodosorb-W regarding the cosmetic water from the market. The result is effect of stimulation on human body. This shows restructuring of water molecules in configurations of clusters, which influence usefully on human health on molecular and cellular level. The effects are describing with mathematical model of cosmetic water Rhodosorb-W. The research with the NES method of water drops is received with of cosmetic water Rhodosorb-W, and cosmetic water from the market as control sample. The mathematical models of cosmetic water Rhodosorb-W 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 and Fig. 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 cosmetic water Rhodosorb-W and control cosmetic water from the market

-E(eV) x-axis	Cosmetic water Rhodosorb-W y-axis (%((-E_{value}) */ (-$E_{total\ value}$)**	Control Sample Cosmetic water from the market y-axis (%((-E_{value})*/ (-$E_{total\ value}$)**	-E(eV) x-axis	Cosmetic water Rhodosorb-W y-axis (%((-E_{value}) */ (-$E_{total\ value}$)**	Control Sample Cosmetic water from the market (%((-E_{value})*/ (-$E_{total\ value}$)**
0.0937	0	0	0.1187	0	6.2
0.0962	0	0	0.1212	**25.2**[2]	6.2
0.0987	0	0	0.1237	0	6.2
0.1012	0	0	0.1262	12.4	6.2
0.1037	0	12.7	0.1287	0	6.2
0.1062	0	12.5	0.1312	0	12.7
0.1087	12.4	0	0.1337	12.4	6.2
0.1112	**0**[1]	6.2	0.1362	0	0
0.1137	0	6.2	0.1387	**25.2**[3]	12.5
0.1162	12.4	0	–	–	–

Notes:

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

E= -0.1387 eV is the local extremum for inhibition of development of tumor cells of molecular level

Notes:

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

Figure 2 shows the distribution (%, ($-E_{value}$)/($-E_{total\ value}$) of H_2O molecules in cosmetic water Rhodosorb-W (red line) and control sample cosmetic water from the market (blue line).

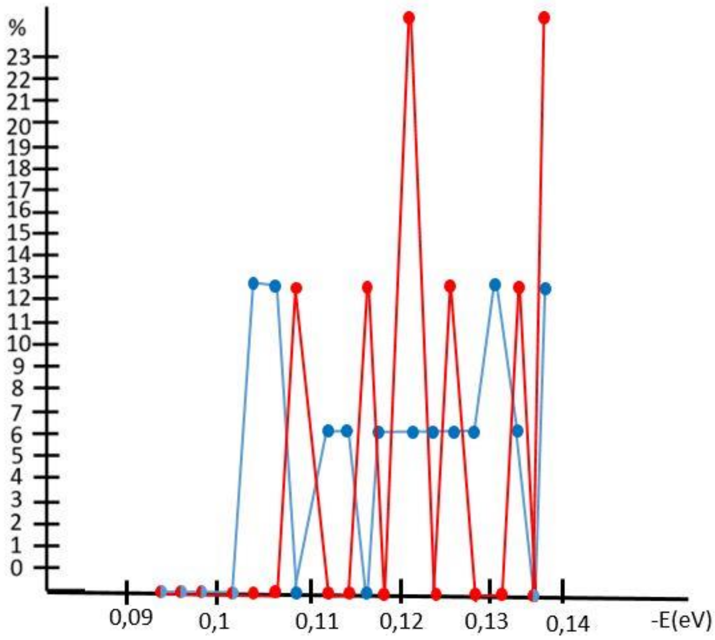

Figure 2: Mathematical model (Ignatov, Mosin, 2013) of cosmetic water Rhodosorb-W

Notes:

E=-0.1212 eV is the local extremum for anti-inflammatory effect
E= -0.1387 eV is the local extremum for inhibitation of development of tumor cells of molecular level

The experimental data obtained testified the following conclusions from the mathematical model of cosmetic water Rhodosorb-W and control cosmetic water from the market. The distribution (%, ($-E_{value}$)/($-E_{total\ value}$) of water molecules in mathematical model of cosmetic water Rhodosorb-W and control cosmetic water from the market. The distribution (%, ($-E_{value}$)/($-E_{total\ value}$) of water molecules in cosmetic water Rhodosorb-W according control sample is different. However, for the value E = -0.1387 eV or λ = 8.95 μm there is the biggest local extremum (25.2 (%, ($-E_{value}$)/($-E_{total\ value}$)) corresponding to the re-structuring of hydrogen bonds among H_2O molecules for inhibition of development of tumor cells of molecular level. This difference may indicate on the different number of hydrogen bonds in water samples, as well as their physical parameters (pH, ORP)**,** resulting in different distribution of H_2O molecules and different values of H_2O molecules with ratios of ($-E_{value}$)/($-E_{total\ value}$). Particularly it was observed the statistical re-structuring of H_2O molecules in water samples according to the energies. The experimental data may prove that stipulates the restructuring of H_2O molecules on molecular level and may be used for the prophylaxis of development of tumor cells. For the value E=-0.1212 eV or λ=10.23 μm there is the bigger local extremum (25.2 (%, ($-E_{value}$)/($-E_{total\ value}$)) corresponding to the re-structuring of hydrogen bonds among H_2O molecules for anti inflammatory effect.. The experimental data for cosmetic water Rhodosorb-W may prove that stipulates the restructuring of H_2O molecules on molecular level and the biophysical effects are:

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

E= -0.1387 eV is the local extremum for inhibition of development of tumor cells of molecular level

As a result of different energies of hydrogen bonds, the surface tension of cosmetic water Rhodosorb-W is increasing. The increasing of surface tension is regarding the control sample. This effect is connected with preservation of the energy in human body as result of biochemical process among water molecules and bio molecules. As effect of big increasing of surface tension and the spectrum is begging from E= -0.1112 eV and this shows cosmetic effects with the skin and detoxification. This effect of cosmetic water Rhodosorb-W is higher than effect of control sample with cosmetic water from the market.

3.3. Clinical studies with human blood serum testing

A convenient method for studying of liquids is non-equilibrium differential spectrum. It was established experimentally that the process of evaporation of water drops, the wetting angle θ decreases discreetly to zero, and the diameter of the water drop basis is only slightly altered, that is a new physical effect (Antonov, 1995; Antonov & Yuskesselieva, 1983). Based on this effect, by means of the measurement of the wetting angle within equal intervals of time is determined the function of distribution of H_2O molecules according to the value of f(θ). The distribution function is denoted as the energy spectrum of the water state. The theoretical research established the dependence between the surface tension of water and the energy of hydrogen bonds among individual H_2O-molecules (Antonov, 1995).

For calculation of the function f(E) represented the energy spectrum of water, the experimental dependence between the wetting angle (θ) and the energy of hydrogen bonds (E) is established:

$$f(E) = \frac{14{,}33 f(\theta)}{[1-(1+bE)^2]^2} \qquad (1)$$

where b = 14.33 eV^{-1}

The relation between the wetting angle (θ) and the energy (E) of the hydrogen bonds between H_2O molecules is calculated by the formula:

$$\theta = arcos\ (-1 - 14.33E) \qquad (2)$$

The energy spectrum of water is characterized by a non-equilibrium process of water droplets evaporation, therefore, the term non-equilibrium spectrum (NES) of water is used.

The difference $\Delta f(E) = f\ (E samples\ of\ water) - f\ (E control\ sample\ of\ water)$ – is called the “differential non-equilibrium energy spectrum of water” (DNES).

Thus, the DNES spectrum is an indicator of structural changes in water, because the energy of hydrogen bonds in water samples differ due to the different number of hydrogen bonds in water samples, which may result from the fact that different waters have different structures and composition and various intermolecular interactions – various associative elements etc (Ignatov et al, 2014; Ignatov et al., 2015). The redistribution of H_2O molecules in water samples according to the energy is a statistical process of dynamics.

Figure 3 shows the average NES-spectrum of deionised water. On the X-axis are depicted three scales. The energies of hydrogen bonds among H_2O molecules are calculated in eV. On the Y-axis is depicted the function of distribution of H_2O molecules according to energies f(E), measured in reciprocal unit eV^{-1}.

Arrow A designates the energy of hydrogen bonds among H_2O molecules, which is accepted as most reliable in spectroscopy.

Arrow B designates the energy of hydrogen bonds among H_2O molecules the value of which is calculated as:

$$\bar{E} = -0.1067 \pm 0.0011 \text{ eV} \quad (3)$$

Arrow C designates the energy at which the thermal radiation of the human body, considered like an absolute black body (ABB) with a temperature +36.6 ^{0}C, is at its maximum.

A horizontal arrow designates the window of transparency of the Earth atmosphere for the electromagnetic radiation in the middle infrared range of the Sun toward the Earth and from the Earth toward the surrounding space. It can be seen that the atmosphere window of transparency almost covers the NES-spectrum of water.

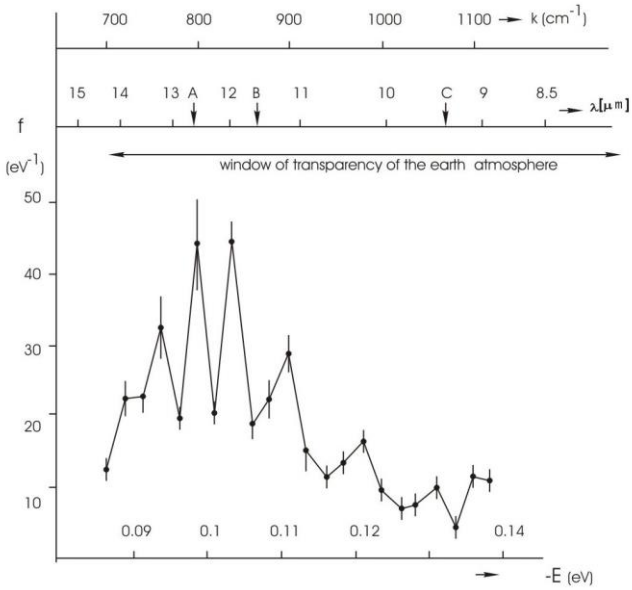

Figure 3: The NES-spectrum of deionized water (chemical purity – 99.99 %; pH – 6,5–7,5; total mineralization – 200 mg/l; electric conductivity – 10 μS/cm): the horizontal axis shows the energy of the H...O hydrogen bonds in the associates – E (eV); the vertical axis – the energy distribution function – f (eV^{-1}); *k* – the vibration frequency of the H–O–H atoms (cm^{-1}); λ – wavelength (μm)

We have conducted studies of 1% (v/v) solution of human blood serum taken from two groups of people between 50 and 70 years of age by IR, NES and DNES spectral analysis. The first group consisted of people in excellent health. The second group consisted of people in a critical state and patients with malignant tumors. The average energy of hydrogen bonds ($\Delta E_{H...O}$) between H_2O molecules in the blood serum was investigated as the main biophysical parameter. The result was registered as a difference between the NES-spectrum of 1% solution of human blood serum and the NES-spectrum of deionized water control sample – DNES-spectrum, measured as the difference Δf(E) = f (samples of water) – f (control sample of water). The DNES-spectrum obtained from the first group has a local extremum energy ($\Delta E_{H...O}$) at E = -9.1±1.1 meV and from the second group at E = -1.6±1.1 meV. The results between the two groups have a statistical difference in Student's criterion at $p < 0.05$.

For the control group of healthy people the value of the largest local extremum in the DNES-spectrum was detected at E = -0.1387 eV, or at a wavelength λ = 8.95 μm. For the group of people in a critical health state and the patients with malignant tumors, the analogous values of the largest local maximums of the DNES-spectrum shifted to lower energies compared with the control group of people. For a group of people in critical health condition and patients with malignant tumors the greatest values of local extremum in the IR-spectrum are shifted to lower energies relative to the control group. In IR-spectrum of human blood serum are detected 8 local maxima at λ = 8.55, 8.58, 8.70, 8.77, 8.85, 9.10, 9.35 and 9.76 μm (Krasnov, Gordetsov, 2009). The resulting peak at λ = 8.95 μm in the IR-spectrum (Ignatov, 2012) approaching the peak at λ = 8.85 μm was monitored by Russian researchers. In the control group of healthy people the average value of the energy distribution function f(E) at λ = 8.95 μm compiles E = 75.3 eV, and in a group of people in critical condition – E = 24.1 eV. The norm has statistically reliable result for human blood serum for the control group of people having cancer at the local extremum of f(E) ~24.1 eV^{-1}. The level of reliability of the results is $p< 0.05$ according to the Student's t-test. In 1995 were performed DNES-experiments with an impact on tumor mice cells in water solutions containing Ca^{2+} (Antonov, 1995). There was a decrease in the DNES-spectrum compared with the control sample of cells from a healthy mouse. The decrease was also observed in the DNES-spectrum of human blood serum of terminally ill people relative to that of healthy people. With increasing of age of long-living blood relatives, the function of distribution of H_2O molecules according to energies at -0.1387 eV decreases. In this group of tested people the result was obtained by the DNES-method at E = -5.5±1.1 meV; the difference in age was of 20–25 years in relation to the control group. It should be noted that many of Bulgarian centenarians inhabit the Rhodopes Mountains areas. Among to the DNES-spectrum of mountain waters the similar to the DNES-spectrum of blood serum of healthy people at λ = 8.95 μm, was the DNES-spectrum of water in the Rhodopes. The mountain water from Teteven, Boyana and other Bulgarian provinces has similar parameters. Tables 1, 2 and 3 show the composition of mountain water springs in Teteven and Kuklen (Bulgaria) and local extremums in NES-spectra of water samples. The local extremums is water samples were detected at E = -0.11 eV and E = -0.1387 eV. The value measured at E = -0.11 eV is characteristic for the presence of Ca^{2+} in water. The value measured at E = -0.1387 eV is characteristic for inhibiting the growth of cancer cells. Experiments conducted by A. Antonov with cancer cells of mice in water with Ca^{2+} demonstrated a reduction of this local extremum to a negative value in spectra. Analysis by the DNES-method of aqueous solutions ofnatural mineral sorbent –zeolite Rodosorb-H (microporous crystalline aluminosilicate mineral from Rhodope mountain, Bulgaria) showed the presence of a local extremum at E = -0.1387 eV and the value is. 72.7 eV^{-1}. This result shows increasing of energy of hydrogen bonds at E = -0.1387 eV for zeolite Rhodosorb as prevention of the development of tumor cells, because the group of people having cancer is with value at at E = -0.1387 eV of the local extremum of f(E) ~24.1 eV^{-1}. This result shows increasing of the energy of hydrogen bonds It should be noted that owing to the unique porous structures both the natural minerals zeolite are ideal natural water absorbers effectively removing from water organochlorine compounds, phenols, dioxins, heavy metals, radionuclides, and color, and gives the water a good organoleptic qualities, additionally saturating water with micro-and macro-elements until the physiological levels (Mosin & Ignatov, 2013). It is worth to note that in Bulgaria the main mineral deposits of Bulgarian zeolites are located in the Rhodope Mountains, whereat has lived the greatest number of Bulgarian centenarians. It is believed that water in these areas is cleared out in a natural way by mineral zeolite.

4. Results with pH and ORP

There are valid the following results of pH as indicator for acid alkaline medium of the products zeolite Rhodosorb-H and cosmetic water Rhodosorb-W. There are the results also for ORP or Oxidation-reduction potential.

The results are for 1% of solutions of zeolite Rhodosorb-H and cosmetic water Rhodosorb-W. This research is performed with Georgi Gluhchev from Bulgarian Academy of Science. Table 4 shows the results of pH and ORP.

Table 3. Results of zeolite Rhodosorb-H and cosmetic water Rhodosorb-W for pH and ORP

Product	pH	ORP (mV)	Coordinates Fig. 3
Zeolite Rhodosorb-H	8.91 ±0.02	±0.20	Point 1 (8.91; ±0.20)
Cosmetic water Rhodosorb-W	7.30 ±0.02	+163.0	Point 2 (7.30;163.0)

Figure 4 shows the dependence between the acidity and basicity (pH) of electrochemically activated solutions and the oxidation-reduction potential (ORP). The pH value within the interval from 3 to 10 units and the ORP within the interval from -400 mV to +900 mV characterize the area of the biosphere of microorganisms. Outside these ranges of pH and ORP the microorganisms will hardly survive.

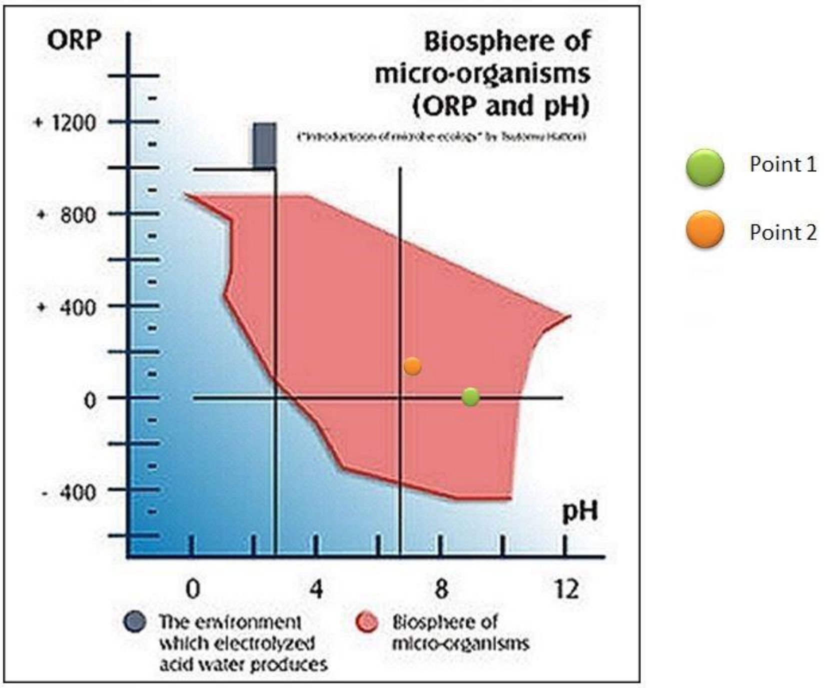

Figure 4. The dependence between acidity and basicity (pH) of solutions and the ORP on the biosphere of micro-organisms (point 1; Zeolite Rhodosorb-H), (point 2; Cosmetic water Rhodosorb-W).

The results from the Figure 4 show that the products zeolite Rhodosorb-H and cosmetic water Rhodosorb-W are useful as medium for microorganisms, which are with positive effects on human health.

Owing to the unique porous structure the mineral Zeolites 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 pressure;
- Mechanical strength and low abrasion resistance;
- Corrosion-resistance;
- Absorption capacity relatives 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.

5. Conclusion

The interaction of Zeolite Rhodosorb-H with water is quiet complex and results the restructuring of energy values among H_2O molecules with a statistically reliable increase of local extremums in DNES-spectra after treatment of Zeolite Rhodosorb-H with water. These values are measured at -0.1249 eV for Zeolite Rhodosorb-H. The result for control sample (deionized water) is -0.1172 eV. The results with NES method were recalculated by the DNES method. The result of Zeolite Rhodosorb-H with DNES method is -0.0077±0.0011 eV. From the NES and DNES spectrum and mathematical model of 1% solution of Zeolite Rhodosorb-H and deionized water as control sample are valid the following conclusions for biophysical effects for Zeolite Rhodosorb-H.

- Anti-inflammatory effect;
- inhibition of development of tumor cells of molecular level;

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. In comparison with zeolite comprises a microporous crystalline aluminosilicate mineral commonly used as adsorbent. Zeolite$^-$ creates a negative charge of the carcasses compensated by cations (H^+, Na^+, K^+, Ca^{2+}, NH_4^+, etc.), in most cases, capable of cations exchange in solutions. Efficiency of using zeolite is stipulated by the high range of valuable properties (absorption, catalytic, antioxidant, regenerative, antibacterial). There is permanent antioxidant activity of zeolite on enzymes (Dogliotti et al., 2012; Ignatov, Mosin, 2015).

As a result of different energies of hydrogen bonds, the surface tension of cosmetic water Rhodosorb-W is increasing. The increasing of surface tension is regarding the control sample. This effect is connected with preservation of the energy in human body as result of biochemical process among water molecules and bio molecules. As effect of big increasing of surface tension and the spectrum is begging from E= -0.1112 eV and this shows cosmetic effects with the skin and detoxification. This effect of cosmetic water Rhodosorb-W is higher than effect of control sample with cosmetic water from the market.

The dependence between acidity and basicity (pH) of solutions and the oxidation-reduction potential (ORP) on the biosphere of micro-organisms (point 1; Zeolite Rhodosorb-H) and (point 2; Cosmetic water Rhodosorb-W) on Figure 4 show the anti inflamatorry effects and that the two products are medium for microorganisms, which are with positive effects on human health.

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