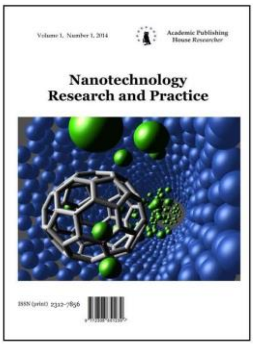

Published in the Slovak Republic
Nanotechnology Research and Practice
Has been issued since 2014.
E-ISSN: 2413-7227
2018, 5(1): 3-13

DOI: 10.13187/nrp.2018.5.3
www.ejournal13.com

Carbonaceous Fullerene Containing Nano Mineral Shungite. Properties for Purification of Water Detoxification of Human Body

Ignat Ignatov [a, *]

[a] Scientific Research Center of Medical Biophysics, Sofia, Bulgaria

Abstract

Shungite is amorphous, uncrystallized, fullerene analogous carbon containing natural mineral. Shungite carbon is a fossilized organic material of sea bottom Precambrian sediments of high level of carbonization containing the fullerene-like regular structures. Shungite got its name after the village of Shunga in Karelia (Russian Federation), located on the shore of Onezhskoe Lake, where is located Zazhoginsky deposit. The total shungite reserves of Zazhoginsky deposit amount to approximately 35 million tons. The plant production capacity for the mining and processing of shungite makes up 200 thousand tons of shungite per year. We study the properties of shungite for purification of water and detoxification of human body. In the report the authors show the properties for purification of water. There are basic data for detoxification of human body with water solution of shungite.

Keywords: shungite, nanostructure, fullerenes, detoxification, water purification, NES, DNES.

1. Introduction

Shungite is mineral refers to new generation of natural mineral sorbents (NMS). Shungite is an intermediate form between the amorphous carbon and the graphite crystal containing carbon (30 %), silica (45 %), and silicate mica (about 20 %). As natural mineral shungite has unusually broad scope of application in industry. Shungite was used initially, mainly as a filler and substitute of the carbon coal coke (fuel) in blast furnace production of high-silicon cast iron, in ferroalloys melting, in the production of non-stick heat-resistant paints and coatings, and as filler in rubber production. Subsequently there were discovered other new valuable properties of shungite – adsorptional, bactericidal, catalytic, reduction-oxidation properties, as well as the ability of sungite minerals to screen off electromagnetic and radio radiations.

These properties have made the use of shungite in various branches of science, industry and technology, for creating on its basis a variety of new nanotechnological materials with nano-molecular structure. On the basis of shuntite have been created new conductive paints, fillers for plastic materials, rubber and carbon black substitutes, composite materials, concrete, bricks, stuccoing plasters, asphalts, as well as materials having bactericidal activity, and materials shilding off the radio and electromagnetic radiation. Adsorptional, catalytic, and reduction-oxydation properties of shungite favored its use in water treatment and water purification technologies, i.g. in treatment of sewage waters from many organic and inorganic substances (heavy metals,

* Corresponding author
E-mail addresses: mbioph@dir.bg (I. Ignatov)

ammonia, organochlorine compounds, petroleum products, pesticides, phenols, surfactants, etc.). Moreover, shungite has a strongly marked biological activity and bactericidal properties.

Shungite 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. They are also used in medicine as nutritional supplements having antioxidant properties.

A wide range of properties of shungite and 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 methods NES and DNES evaluating of mathematical model of interaction of shungite with water (Ignatov, Mosin, 2013).

2. Materials and Methods

2.1. Materials

The study was performed with samples of shungite obtained from Zazhoginsky deposit (Karelia, Russia). Samples were taken and analyzed in solid samples according to National standard of the Russian Federal Agency of Technical Regulation and Metrology. Samples were put into 100 cm^3 hermetically sealed glass tubes after being washed in dist. H_2O and dried in crucible furnace, and homogenized in homogenizer by mechanical grinding. For the decomposition of the shungate samples a system of microwave decomposition was used. Other methods of samples processing were waching with dist. H_2O, drying, and homogenization on cross beater mill Retsch SK100 (“Retsch Co.”, Germany) and Pulverisette 16 (“Fritsch GMBH”, Germany).

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) was 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 of shungite was studied by inductively coupled plasma optical emission spectrometry (ICP-OES) on Agilent ICP 710-OES (Agilent Technologies, USA) spectrometer, equiped witth plasma atomizer (under argon stream), MegaPixel CCD detector, and 40 MHz free-running, air-cooled RF generator, and Computer-optimized echelle 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. Elemental Analysis

The total amount of carbon (C_{total}) in sungtate was measured according to the ISO 29541 standard using elemental analyzer CHS-580 (“Eltra GmbH”, Germany), equipped with electric furnace and IR-detector by combustion of 200 mg of solid homogenized sample in a stream of oxygen at the temperature 1500 ^oC.

2.6. 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.

2.7. IR-Spectrospopy

IR-spectra of water samples, obtained after being contacted 3 days with shungite, 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 (Chakarova); Non-equilibrium Spectrum (NES) and Differential Non-equilibrium Spectrum (DNES) (Antonov, 1995; Ignatov, 1998).

3. Results and Discussion

According to the last structural studies shungite is a metastable allotropic form of carbon with high level of carbonization (carbon metamorhism), being on prior to graphite stage of coalification.

Shungite differs in composition of mineral matrix (aluminosilicate, siliceous, carbonate), and the amount of carbon in shungite samples. Shungite minerals with silicate mineral basis are divided into low-carbon (5 % C), medium-carbon (5–25 % C), and high-carbon shungite (25–80 % C) (Kasatochkin et al., 1978). The sum (C + Si) in shungites of Zazhoginsky deposit (Karelia, Russian Federation) is varied within 83–88 % as shown in Figure 1.

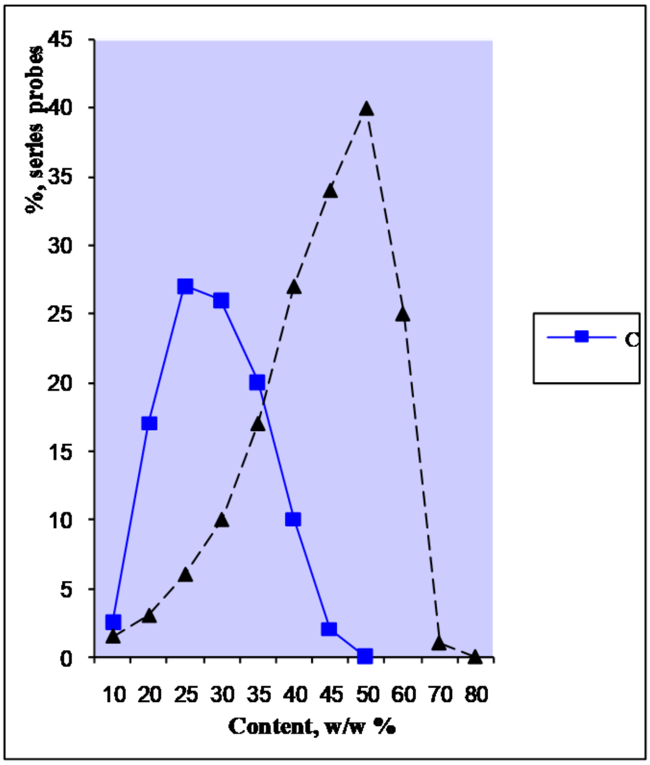

Fig. 1. The distribution (%) of carbon (C) (solid line) and silicon (Si) (dotted line) in shungite samples from Zazhoginsky deposit (Karelia, Russian Federation) according to atomic emission spectrometry (AES) Along with carbon the shungite, obtained from Zazhoginsky deposit in Karelia (Russian Federation) contains C (30.0%), SiO_2 (57.0%), TiO_2 (0.2%), Al_2O_3 (4.0%), FeO (0.6%), Fe_2O_3 (1.49%), MgO (1.2%), MnO (0.15%), K_2O (1.5%), S (1.2%) (Table 1)

Table 1. The chemical composition of shungite, Zazhoginsky deposit (Karelia, Russia), in % (w/w)

№	Chemical component	Content, % (w/w)
1	C	30.0
2	SiO_2	57.0
3	TiO_2	0.2
4	Al_2O_3	4,0
5	FeO	0.6
6	Fe_2O_3	1.49
7	MgO	1.2
8	MnO	0.15
9	K_2O	1.5
10	S	1.2

Physical and chemical properties of shungite have been sufficiently studied (Parfen'eva, 1994). Density of shungite 2.1–2.4 g/cm^3; porosity – up to 5%; the compressive strength – 1000–1200 kgf/cm^2; conductivity coefficient – 1500 SI/m; thermal conductivity coefficient – 3.8 W/m·K, the adsorption capacity up to 20 m^2/g.

The crystals of crushed, fine ground shungite possess strong bipolar properties. This results in a high adhesion, and the ability of shungite to mix with almost all organic and inorganic substances. Besides, shungite has a broad spectrum of bacterecidal properties; the mineral is adsorptive active against some bacterial cells, phages, and pathogenic saprophytes (Khadartsev, Tuktamyshev, 2002).

The unique properties of the mineral are defined by nanostructure and composition of its constituent elements. Schungite carbon is equally distributed in the silicate framework of fine dispersed quartz crystals having the size of 1–10 μm (Kovalevski, 1994; Mosin, Ignatov, 2013), as confirmed by studying of ultra-thin sections of shungite by transmission electron microscopy (TEM) in absorbed and backscattered electrons.

The carbonaceous material of shungite is the product of a high degree of carbonization of hydrocarbons. Its elemental composition (%, w/w): C – 98.6–99.6; H – 0.15–0.5; (H + O) – 0.15–0.9 (Golubev, 2000). With virtually constant elemental composition of shungite carbonaceous matter is observed variability in its structure – both molecular and supramolecular, as well as surface, and porous structure. X-ray studies showed that the molecular structure of schungite carbon is represented by a solid uncristallized carbon, which components may be in a state close as to graphite and carbon black and glassy carbon as well, i.e. the maximally disordered (Kovalevski et al., 2001). Carbonaceous matter of shungite having a strongly marked structural anisotropy shows a significant increase in the diamagnetism at low temperatures that is characteristic for fullerites (Jushkin, 1994).

The basis of shungite carbon compose the hollow carbon fullerene-like multilayer spherical globules with a diameter of 10–30 nm, comprizing inclusive packages of smoothly curved carbon layers covering the nanopores. The globule structure is stable relative to shungite carbon phase transitions into other allotropic carbon forms. Fullerene-like globules (the content of fullerenes makes up 0.001 %) may contain from a few dozen to a several hundred carbon atoms and may vary in shape and size (Reznikov, Polehovsky, 2000).

According to the data on adsorption capacity shungite loses effectiveness before the activated carbon filter in the first stage of filtration, during the first 24 h, further shungite began purifiy water with a high and constant speed. This is explaned by high catalytic properties of shungite and its ability to catalytically oxidize organic substances absorbed on the surface. The mechanism of interaction of shungite with water has not been completely understood. It is assumed that shungite can adsorb oxygen actively interacting with them as a strong reducing agent in water and in air. In this process is produced atomic oxygen, which is a strong oxidizing agent oxidizing adsorbed on shungit organic substanses to CO_2 and H_2O, thus, freeing the surface of shungite for new acts of adsorption. Atomic oxygen is produces in the process of electrolyses of water in anolyte with anti inflammatory and virucidal effects, (Ignatov et al., 2014). Overexposure of shungite in respect to dissolved metal cations in water as Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+} and Fe^{3+} is explaned by the fact that the metals are transferred by the catalytically active shungite into the form of insoluble carbonates due to the oxidation of organic matter to CO_2.

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.

The methods NES and DNES obtaining information about the average energy of hydrogen bonds in an aqueous sample is measuring of the spectrum of the water state (Antonov, 1995; Ignatov, Mosin, 2013).

The research of antioxidant properties of shungite in relation to organochlorine compounds, and free radicals have shown that shungite removes free radicals (Mosin, Ignatov, 2013). This is a very important factor, because the free radicals formed during water treatment with chlorine and its derivatives, have a negative impact on the human health that is the cause of many diseases. The research of with methods NES and DNES shows that water solution of shungite decreases the tumor cells as size and number (Ignatov, Mosin, 2013).

In 2017 from Koreahave performed interesting research that the redox profile of shungite-treated groups showed counterbalance of ROS/RNS and superoxide levels in serum and skin lysates. The team has confirmed the involvement of Nrf2- and MAPK-mediated oxidative stress pathways in the antioxidant mechanism of shungite. Collectively, the results clearly show that shungite has an antioxidant and anti-inflammatory action against UVB-induced skin damage in hairless mice (Ma. Easter Joy V. Sajo et al., 2017).

Our study shows anti inflammatory effect of shungite. For the value E=-0.1212 eV or λ=10.23 μm. there is local extremum corresponding to the re-structuring of hydrogen bonds among H_2O molecules for anti inflammatory effect of shungite. Anti inflammatory effect is part of process of detoxification of shungite with the following effects - absorption, catalytic, antioxidant, regenerative, antibacterial. Shungite$^-$ creates a negative charge by cations (Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, etc.), in most cases, capable of cations exchange in solutions. There is permanent antioxidant activity of shungite on enzymes (Ignatov, Mosin, 2015). Our study shows connection between pH (7.17) and ORP (+175) and that water solution of shungite has positive role for microorganisms. Inhibition of development of tumor cells is influenced from anti inflammatory effects. Our proofs are for the value E = -0.1387 eV or λ = 8.95 μm there is local extremum, corresponding to the re-structuring of hydrogen bonds among H_2O molecules for inhibition of development of tumor cells of molecular level.

These positive qualities allow using shungite as an effective filter material for wastewater treatment and purification from organic and chlorinated organic substances (oil, pesticides, phenols, surfactants, dioxins, etc.). Thus shungite is able to purify wastewater from oil up to threshold limit value (TLV) of water discharge into the water reservoir. Shungit adsorbs on its surface up to 95 % of contaminants, including organochlorine compounds, phenols, dioxins, heavy metals, radionuclides, etc., removes turbidity and color, and gives the water good organoleptic qualities, additionally saturating it with micro-and macro-elements (Table 2). Thus, adsorption activity of shungite relative to phenol makes up 14 mg/g , while for thermolysis resins – 20 mg/g, for oil products – more then 40 mg/g. Model experiments showed that heavy metals (copper, cadmium, mercury, lead), boron, phenol and benzenecontained in water in concentrations being in 10–50 times higher than the TLVs, after the treatment by shungite in stationary or dynamic conditions on the shungite filter units, the content of these pollutants in water is reduced below the established levels of regulatory documents. In this case into the water does not enter any toxic elements from shungite adsorbents.

Table 2. Indicators of performance of filters based of mineral shungite

№	Common water pollutants	The removal degree, %
1	Fe^{2+}/Fe^{3+}	95
2	Zn^{2+}	80
3	Pb^{2+}	85
4	Cu^{2+}	85
5	Cs^{2+}	90
6	St^{2+}	97
7	Radionuclides	90
8	Fluorine	80
9	Ammonia	90
10	Chlorine and organochlorine compounds	85
11	Phenols	90
12	Dioxins	97
13	Helminth's eggs	90
14	Smell	85
15	Turbidity	95

From a practical point of view, carbonate-shale shungite is of interest because it provided the largest decline in chlorides (1.7 %) and the smallest increase in sulphates (13.5 %). Use of all shungite has a beneficial health effect on the process of water purification, as coliform bacteria were not found in experimental samples (Turkaeva et al., 2017).

Owing to the unique porous structure the natural mineral shungite is ideal absorbent and filler (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.

In addition, owing to adsorption activity of shungite against pathogenic microflora shungite has strong bactericidal properties that allow carrying out the efficient disinfection of drinking water by this mineral in water treatment and water purification technologies. It is observed the bactericidal activity of shungite against pathogenic saprophytes and Protozoa. There is evidence that after the passage of water containing bacterium *E. coli*, through shungite filter there is an almost complete removal of this bacterium (the viral titer varries from 2300 cells /l in initial water up to 3 cells/l in treated water) (Mosin, Ignatov, 2013). Of 1785 cells/l of protozoa (ciliates, rotifers and crustaceans) contained in the initial water after the treatment by shungite were observed only a few exemplars (5 cells/l). In addition to these qualities, shungite has biological activity.

Owing to all these positive properties shungite 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 shungite with activated carbon or zeolite, with subsequent regeneration of the absorbents (Podchaynov, 2007). When adding to the treatment scheme to shungite other natural absorbents (zeolite, dolomite, glauconite) purified water is enriched to a physiologically optimal levels by calcium, magnesium, silicon and sodium ions.

4. Conclusion

Shungite can find wide practical applications in many branches of science and industry, and can be used as an alternative to activated carbon the natural mineral absorbent in water treatment. Efficiency of using of shungite is stipulated by the high range of valuable properties (absorption, catalytic, antioxidant, regenerative, antibacterial), high environmental safety and relatively low cost of filters based on shungite.

Our study shows anti inflammatory effect of shungite. For the value E = -0.1212 eV or λ = 10.23 μm. there is local extremum corresponding to the re-structuring of hydrogen bonds among H_2O molecules for anti inflammatory effect of shungite. Anti inflammatory effect is part of process of detoxification of shungite with the following effects - absorption, catalytic, antioxidant, regenerative, antibacterial. Shungite$^-$ creates a negative charge by cations (Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, etc.),, in most cases, capable of cations exchange in solutions. There is permanent antioxidant activity of shungite on enzymes (Ignatov, Mosin, 2015).

Our study shows connection between pH (7.17) and ORP (+175) and that water solution of shungite has positive role for microorganisms. Inhibition of development of tumor cells is influenced from anti inflammatory effects. Our proofs are for the value E = -0.1387 eV or λ = 8.95 μm there is local extremum corresponding to the re-structuring of hydrogen bonds among H_2O molecules for inhibition of development of tumor cells of molecular level.

The research of Mosin and Ignatov show different applications of shungite.

References

Antonov, 1995 – *Antonov, A.* (1995). Research of the Nonequilibrium Processes in the Area in Allocated Systems. Diss. Thesis Doctor of Physical Sciences, Sofia: Blagoevgrad, 1-255.

Cascarini de Torre et al., 2004 – *Cascarini de Torre, L.E., Fertitta, A.E., Flores, E.S., Llanos, J.L., Bottani, E.J.* (2004). Characterization of Shungite by Physical Adsorption of Gases. *J. Argent. Chem. Soc.*, 92(4–6): 51-58.

Gluhchev et al., 2015 – *Gluhchev, G., Ignatov, I., Karadzhov, S., Miloshev, G., Ivanov, I., Mosin, O.V.* (2015). Biocidal Effects of Electrochemically Activated Water. *Journal of Health, Medicine and Nursing*, 11: 67-83.

Gluhchev et al., 2015a – *Gluhchev, G., Ignatov, I., Karadzhov, S., Miloshev, G., Ivanov, I., Mosin, O.V.* (2015). Electrochemically Activated Water. Biophysical and Biological Effects of Anolyte and Catholyte as Types of Water. *Journal of Medicine, Physiology and Biophysics*, 10: 1-17.

Gluhchev et al., 2015b – *Gluhchev, G., Ignatov, I., Karadzhov, S., Miloshev, G., Ivanov, N., Mosin, O.V.* (2015). Electrochemically Activited Water: Biophysical and Biological Effects of Anolyte and Catholyte Types of Water. *European Journal of Molecular Biotechnology*, 1: 12-26.

Gluhchev et al., 2015c – *Gluhchev, G., Ignatov, I., Karadzhov, S., Miloshev, G., Ivanov, N., Mosin, O.V.* (2015). Studying the Antimicrobial and Antiviral Effects of Electrochemically Activated Nacl Solutions of Anolyte and Catholyte on a Strain of E. Coli DH5 and Classical Swine Fever (CSF) Virus. *European Journal of Medicine*, 9 (3): 124-138.

Gluhchev et al., 2018 – *Gluhchev, G., Mehandjiev, D., Ignatov, I,, Karadzhov, S., Pesheva, Y., Atanasov, A.* (2018). Water Electrolysis-Processes in Catholyte and Anolyte Results with Differential Non-Equilibrium Water Spectrum. *European Journal of Medicine*, 6(1): 3-12.

Golubev, 2000 – *Golubev, E.A.* (2000). Local Supramolecular Structures Shungite Carbon, *in Proceedings of the Int. Symp. "Carbon-formation in geological history", Petrozavodsk: Publishing House of the Karelian Research Center, Russian Academy of Sciences:* 106-110.

Gorshteyn et al., 1979 – *Gorshteyn, A.E., Baron, N.Y., Syrkina, M.L.* (1979). Adsorption Properties of Shungites. *Izv. Vysshykh Uchebn. Zaved. Khimia i Khim. Technol.*, 22(6): 711–715.

Ignatov et al., 2014 – *Ignatov, I., Karadzhov, S., Atanasov, A., Ivanova, E., Mosin, O.V.* (2014). Electrochemical Aqueous Sodium Chloride Solution (Anolyte and Catholyte) as Types of Water. Mathematical Models. Study of Effects of Anolyte on the Virus of Classical Swine Fever Virus, *Journal of Health, Medicine and Nursing*, 8: 1-28.

Ignatov et al., 2015 – *Ignatov, I, Gluhchev, G., Karadzhov, S., Ivanov, N., Mosin, O.V.* (2015). Preparation of Electrochemically Activated Water Solutions (Catholyte/Anolyte) and Studying Their Physical-Chemical Properties, *Journal of Medicine, Physiology and Biophysics*, 16: 1-14.

Ignatov et al., 2015a – *Ignatov, I., Gluhchev, G., Karadzhov, S., Miloshev, G., Ivanov, I., Mosin, O.V.* (2015). Preparation of Electrochemically Activated Water Solutions

(Catholyte/Anolyte) and Studying Their Physical-Chemical Properties. *Journal of Medicine, Physiology and Biophysics*, 11: 1-21.

Ignatov et al., 2015b – *Ignatov, I., Gluhchev, G., Karadzhov, S., Miloshev, G., Ivanov, I., Mosin, O.V.* (2015). Preparation of Electrochemically Activated Water Solutions (Catholyte/Anolyte) and Studying of their Physical-Chemical Properties, *Journal of Medicine, Physiology and Biophysics*, 13: 18-38.

Ignatov et al., 2015c – *Ignatov, I., Gluhchev, G., Karadzhov, S., Miloshev, G., Ivanov, I., Mosin, O.V.* (2015) Preparation of Electrochemically Activated Water Solutions (Catholyte/Anolyte) and Studying of their Physical-Chemical Properties. *Journal of Health, Medicine and Nursing*, 13: 64-78.

Ignatov et al., 2015d – *Ignatov, I., Mosin, O. V. , Gluhchev, G., Karadzhov, S., Miloshev, G., Ivanov, I.* (2015). Studying Electrochemically Activated NaCl Solutions of Anolyte and Catholyte by Methods of Non-Equilibrium Energy Spectrum (NES) and Differential Non-Equilibrium Energy Spectrum (DNES). *Journal of Medicine, Physiology and Biophysics*, 14: 6-18.

Ignatov et al., 2015e – *Ignatov, I., Mosin, O.V., Gluhchev, G., Karadzhov, S., Miloshev, G., Ivanov, N.* (2015). The Evaluation of Mathematical Model of Interaction of Electrochemically Activated Water Solutions (Anolyte and Catholyte) with Water. *European Reviews of Chemical Research*, 2 (4|): 72-86.

Ignatov et al., 2016 – *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 et al., 2016a – *Ignatov, I., Mosin, O.V., Gluhchev, G., Karadzhov, S., Miloshev, G., Ivanov, N.* (2016). Studying Electrochemically Activated NaCl Solutions of Anolyte and Catholyte by Methods of Non-Equilibrium Energy Spectrum (NES) and Differential Non-Equilibrium Energy Spectrum (DNES). *Journal of Medicine, Physiology and Biophysics*, 20: 13-23.

Ignatov et al., 2016b – *Ignatov, I., Mosin, O.V., Kirov, P.* (2016). Matematical Model of Kangen Water® Biophysical and Biochemical Effects of Catholyte. *Advances in Physics Theories and Applications*, 51: 33-55.

Ignatov et al., 2016c – *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.

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

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

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

Ignatov, 2012 – *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, 2016 – *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, 2016a – *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, 2017 – *Ignatov, I.* (2017). Aluminosilicate Mineral Zeolite. Interaction of Water Molecules in Zeolite Table and Mountain Water Sevtopolis from Bulgaria. *Journal of Medicine, Physiology and Biophysics*, 31: 41-45.

Ignatov, 2017a– *Ignatov, I.* (2017). Biophysical Research of ZEOLITH detox and ZEOLITH Creme, *European Journal of Medicine*, 5 (2): 31-42.

Ignatov, 2017b – *Ignatov, I.* (2017). Distribution of Molecules of ZEOLITH detox and ZEOLITH Creme in Water as Factor for Health. *European Journal of Molecular Biotechnology*, 5, (1): 11-22.

Ignatov, 2017c – *Ignatov, I.* (2017). VITA intense and BOOST – Products with Natural Vitamins and Minerals for Health. *Journal of Medicine, Physiology and Biophysics*, 31: 58-78.

Ignatov, 2017d – *Ignatov, I.* (2017). VITA intense –Antioxidant and Inhibition Growth of Tumor Cells Effects. Anti Aging Influence. Negative Oxidation-reduction Potential (ORP) Has Important Role in These Effects. *Journal of Medicine, Physiology and Biophysics*, 39: 20-42.

Ignatov, 2017e – *Ignatov, I.* (2017). ZEOLITH detox for Detoxification and ZELOLITH Creme for Skin Effects as Products of LavaVitae Company. *Journal of Medicine, Physiology and Biophysics*, 31: 79-86.

Ignatov, Mosin, 2013 – *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, Mosin, 2013a – *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, Mosin, 2013b – *Ignatov, I., Mosin, O.V.* (2013). Perspective for the Use of Shungite in Water Treatment. *Communal Complex of Russia*, 113 (11): 1-5.

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

Ignatov, Mosin, 2014 – *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, Mosin, 2014a – *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, Mosin, 2014b – *Ignatov, I., Mosin, O.V.* (2014). Composition and Structural properties of Fulleren Analogious Shungite. Mathematical Model of Interaction of Shungite with Water Molecules. *Acknowledge*, 2(21): 1-17.

Ignatov, Mosin, 2014c – *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, Mosin, 2014d – *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, Mosin, 2014e – *Ignatov, I., Mosin, O.V.* (2014). Mathematical Models of Distribution of Water Molecules Regarding Energies of Hydrogen Bonds. *Journal of Medicine, Physiology and Biophysics,* 6: 50-72.

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

Ignatov, Mosin, 2014g – *Ignatov, I., Mosin, O.V.* (2014). Methods for Measurements of Water Spectrum. Differential Non-equilibrium Energy Spectrum Method (DNES). *Journal of Health, Medicine and Nursing,* 6: 50-72.

Ignatov, Mosin, 2014 h– *Ignatov, I., Mosin, O.V.* (2014). Nano Mix of Shungite and Zeolite for Cleaning of Toxins and Increasing of Energy of Hydrogen Bonds among Water Molecules in Human Body. *Journal of Medicine, Physiology and Biophysics,* 27: 1-10.

Ignatov, Mosin, 2014i – *Ignatov, I., Mosin, O.V.* (2014). Structural Models of Water and Ice Regarding the Energy of Hydrogen Bonding. *Nanotechnology Research and Practice*, 7 (3): 96-117.

Ignatov, Mosin, 2014j – *Ignatov, I., Mosin, O.V.* (2014). The Structure and Composition of Carbonaceous Fullerene Containing Mineral Shungite and Microporous Crystalline Aluminosilicate Mineral Zeolite. *Nanotechnology Research and Practice*, 1 (1): 30-42.

Ignatov, Mosin, 2014k – *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, Mosin, 2015 – *Ignatov, I., Mosin, O. V.* (2015). Carbonaceous Fullerene Containing Mineral Shungite. Alunonusilicate Mineral Zeolite. Interaction of Water Molecules with Shungite and Zeolite. *Journal of Health, Medicine and Nursing*, 9: 1-14.

Ignatov, Mosin, 2015a – *Ignatov, I., Mosin, O.V.* (2015). Carbonaceous Fullerene Containing Mineral Shungite. Research of Influence of Shungite on Mountain Water. *Journal of Medicine, Physiology and Biophysics*, 11: 22-38.

Ignatov, Mosin, 2015b – *Ignatov, I., Mosin, O.V.* (2015). Physical-Chemical Properties of Mountain Water From Bulgaria Influenced by a Fullerene Containing Mineral Shungite and Aluminosilicate Mineral Zeolite. *Journal of Medicine, Physiology and Biophysics*, 16: 15-29.

Ignatov, Mosin, 2015c – *Ignatov, I., Mosin, O.V.* (2015). Physical-Chemical Properties of Mountain Water from Bulgaria after Exposure to a Fullerene Containing Mineral Shungite and Aluminosilicate Mineral Zeolite. *European Reviews of Chemical Research*, 5 (3): 166-179.

Ignatov, Mosin, 2015d – *Ignatov, I., Mosin, O.V.* (2015). Physical-Chemical Properties of Mountain Water from Bulgaria after Exposure to a Fullerene Containing Mineral Shungite and Aluminosilicate Mineral Zeolite. *European Reviewed of Chemical Research*, 5(3): 143-172.

Ignatov, Mosin, 2015e – *Ignatov, I., Mosin, O.V.* (2015). Research of Influence of Shungite for Activation of Mountain Water from Different Mountain Sources. *Journal of Health, Medicine and Nursing*, 12: 1-18.

Ignatov, Mosin, 2015f – *Ignatov, I., Mosin, O.V.* (2015). Research of Influence of Shungite on Mountain Water from Bulgaria. Mathematical Models of Water Influenced from Shungite and Zeolite. *Journal of Medicine, Physiology and Biophysics*, 12: 1-18.

Ignatov, Mosin, 2015g – *Ignatov, I., Mosin, O.V.* (2015). Studying Physical-Chemical Properties of Mountain Water from Bulgaria Influenced by a Fullerene Containing Mineral Shungite and Aluminosilicate Mineral Zeolite by IR, NES, and DNES Methods. *Journal of Medicine, Physiology and Biophysics*, 14: 19-34.

Ignatov, Mosin, 2015h – *Ignatov, I., Mosin, O.V.* (2015). The Mathematical Model of Interaction of Carbonaceous Fullerene Containing Mineral Shungite and Microporous Crystalline Aluminosilicate Mineral Zeolite with Water. *Nanotechnology Research and Practice*, 5 (1): 23-36.

Ignatov, Mosin, 2015i – *Ignatov, I., O.V.Mosin.* (2015). Origin of Life and Living Matter in Hot Mineral Water. *Advances in Physics Theories and Applications*, 39: 1-22.

Ignatov, Mosin, 2016 – *Ignatov, I., Mosin, O.V.* (2016). Deuterium, Heavy Water and Origin of Life. LAP LAMBERT Academic Publishing, 1-500.

Ignatov, Mosin, 2016a – *Ignatov, I., Mosin, O.V.* (2016). Nano Mix of Shungite and Zeolite for Cleaning of Toxins and Increasing of Energy of Hydrogen Bonds among Water Molecules in Human Body. *Journal of Medicine, Physiology and Biophysics*, 27: 1-11.

Ignatov, Mosin, 2016b – *Ignatov, I., Mosin, O.V.* (2016). Research of the Structural-Functional Properties of the Fullerene-Like Shungite and Micro-Crystalline Alumosilicate Mineral Zeolite by Elemental Analysis, TEM, IR and DNES Spectroscopy. *Nano- and Microsystem Technique*, 18 (6): 357-372.

Ignatov, Mosin, 2016c – *Ignatov, I., Mosin, O.V.* (2016). Water for Origin of Life. Altaspera Publishing & Literary Agency Inc, 1-616.

Ignatov, Pesheva, 2018 – *Ignatov, I., Pesheva, Y.* (2018). VITA Intense – Product with Negative Oxidation-reduction Potential (ORP) as Important Quality for Antioxidant and Inhibition Growth of Tumor Cells Effects. Anti Aging Effects. *European Journal of Medicine*, 6(1): 20-42.

Ignatov, Pesheva, 2018a – *Ignatov, I., Pesheva, Y.* (2018). ZEOLITH detox for Detoxification of Human Body. Proofs for Anti inflammatory Effects of Zeolite and Detoxification. *European Journal of Molecular Biotechnology*, 6(1): 41-52.

Jushkin, 1994 – *Jushkin, N.P.* (1994). Globular Supramolecular Structure Shungite: Data Scanning Tunneling Microscopy. *Reports. Acad. Science USSR*, 337(6): 800-803.

Kasatochkin et al., 1978 – *Kasatochkin, V.I., Elizen, V.M., Melnichenko, V.M., Yurkovsky, I.M., Samoilov. V.S.* (1978). Submikroporous Structure of Shungites. *Solid Fuel Chemistry*, 3: 17-21.

Khadartsev, Tuktamyshev, 2002 – *Khadartsev, A.A., Tuktamyshev, I.S.* (2002). Shungites in Medical Technologies. *Vestnik Novih Medicinskih Technologii,* 9(2): 83-86.

Khavari-Khorasani, Murchison, 1979 – *Khavari-Khorasani, G., Murchison, D.G.* (1979). The Nature of Carbonaceous Matter in the Karelian Shungite. *Chem. Geol.*, 26: 165-82.

Kovalevski et al., 2001 – *Kovalevski, V.V., Buseckb, P.R., Cowley J.M.* (2001). Comparison of carbon in shungite rocks to other natural carbons: an X-ray and TEM study. *Carbon*, 39: 243–256.

Kovalevski, 1994 – *Kovalevski, V.V.* (1994). Structure of Shungite Carbon. *Natural Graphitization Chemistry*, 39: 28-32.

Krivushina et al., 2015 – *Krivushina, A.A., Polyakova, A.V., Goryashnik, Yu.S., Yakovenko, T.V.* (2015). Biocidal Compositions with Metal Nanoparticles for the Protection of

Non-metallic Materials Against Microbiological Damage. *International Polymer Science and Technology*, 42(12): 63-66.

Ma. Easter Joy V. Sajo et al., 2017 – *Ma. Easter Joy V. Sajo et al.* (2017). Antioxidant and Anti-Inflammatory. Effects of Shungite against Ultraviolet B Irradiation-Induced Skin Damage in Hairless Mice. *Oxidative Medicine and Cellular Longevity*: 1-11.

Mosin, Ignatov, 2011 – *Mosin, O.V., Ignatov, I.* (2011). New Natural Mineral Sorbent–shungite, Sanitary Engineering, 3.

Mosin, Ignatov, 2012 – *Mosin, O. V, Ignatov, I.* (2012). Natural Fulleren Containing Mineral Sorbent Shungite in Water Treatment and Water Partification. *Clean Water: Problems and Decisions*, Moscow, 3-4: 109-115.

Mosin, Ignatov, 2012a – *Mosin, O. V, Ignatov, I.* (2012). Perspectives of Executing of Fulleren Analogious Shungite in Water Preparation. *Energy Saving and Water Preparation*, 5: 13-18.

Mosin, Ignatov, 2012b – *Mosin, O.V, Ignatov, I.* (2012). Application of Fullerene Analogious Mineral Shungite in Construction Industry and Building Technologies. *Nanotechnologies in Construction Industry*, 6: 81-93.

Mosin, Ignatov, 2012c – *Mosin, O.V, Ignatov, I.* (2012). The Composition and structural properties of fullerene natural mineral shungite. *Nanoengineering*, 18(12): 17–24.

Mosin, Ignatov, 2012d – *Mosin, O.V., Ignatov, I.* (2012). Composition and Structural Properties of Fullerene Analogious Mineral Shungite. *Nanomaterials and Nanotechnologies, Science of Education*, 5-36.

Mosin, Ignatov, 2013 - *Mosin O.V., Ignatov I.* (2013). Composition and Structural Properties of Fullerene Analogous Mineral Shungate. *Journal of Nano and Microsyctem Technique*, 1: 32-40.

Mosin, Ignatov, 2013a – *Mosin, O. V., I. Ignatov, I.* (2013). The Composition and Properties of Fullerene Natural Mineral Shungite, Nano and Microsystem Technique, 1: 21-26.

Mosin, Ignatov, 2013b – *Mosin, O.V, Ignatov, I.* (2013). Composition and Structural Properties of Fulleren Analogious Shungite. *Biotechnosphere*, 25(1): 29-33.

Mosin, Ignatov, 2013c – *Mosin, O.V., Ignatov, I.* (2013). Fulleren Analogious Mineral Shungite for Preparation of Buildings Materials, Buildings Materials. *Equipment and Technologies XXI Century*, 179 (12): 28-31.

Mosin, Ignatov, 2013d – *Mosin, O.V., Ignatov, I.* (2013). 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, Ignatov, 2014 – *Mosin, O.V., Ignatov, I.* (2014). Shungite, Structure and Properties of the Mineral, *Nanoindustry*, 3, (41): 32-38.

Parfen'eva, 1994 – *Parfen'eva, L.S.* (1994). Electrical Conductivity of Shungite Carbon. *Solid State Physics*, 36(1): 234-236.

Reznikov, Polehovsky, 2000 – *Reznikov, V.A., Polehovsky, Y.S.* (2000). Shungite Amorphous Carbon – The Natural Environment of Fullerene. *Technical Physics Letters*, 26(15), 689-693.

Rozhkov, Goryunov, 2013 – *Rozhkov, S.P., Goryunov, A.S.* (2013). Interaction of Shungite Carbon Nanoparticles with Blood Protein and Cell Components. *Russian Journal of General Chemistry,* 83(12): 585-2595.

Turkaeva et al., 2017 – *Turkaeva, A. et al.* (2017). Chemical and Microbiological Nature of Produced Water Treatment Biotechnology. *Energy Procidia,* 113: 116-120.

Volkova, Bogdanov, 1986 – *Volkova, I.B, Bogdanov, M.V.* (1986). Petrology and Genesis of the Karelian Shungite-high Rank Coal. *Int. J. Coal Geol.,* 6: 369-79.