EVOdrop Device for Water Filtration. Spectral Analyses, NMR and Physichochemical Composition Investigations

Ignat Ignatov[1*], Nikolai Neshev[2], Fabio Huether[3]

1. Scientific Research Center of Medical Biophysics, Sofia, Bulgaria
2. Faculty of Physics, Sofia University St. Kliment Ohridski
3. Fabio Huether, Evodrop AG, Zurich, Switzerland

* E-mail of the corresponding author: mbioph@abv.bg

ABSTRACT

EVOdrop water treatment device output was tested together with samples of filtered water and compared to control samples of tap water. The device includes an ultra-nano membrane and rotation jet nozzle for water vortexing. Investigations were conducted with Non-equilibrium Energy Spectrum (NES) and Differential Non-equilibrium Energy Spectrum (DNES) analysis of hydrogen bonds energy distribution, mathematical models of water molecules clustering, ^{1}H NMR, hardness and pH. Alteration of hydrogen bonds energy distribution and chemical shifts were measured and subsequently interpreted as restructuring of water molecule clusters in the direction of beneficial health effects. Reduced hardness and unchanged pH levels of treated tap water were additionally observed.

Key words: Evodrop device, NES, DNES, ^{1}H NMR.

1. Introduction

The influence on water of magnetic fields [1, 2, 3] and nano membrans [4, 5] has been clearly demonstrated. It can be interpreted with the following considerations. Hydroxyl groups (-OH) in H_2O molecules are polar. Their covalent bond involves sharing of electron pairs between O and H atoms. In addition, electromagnetic hydrogen bonds (O–H…O) occur between H_2O molecules. Hydrogen bonds are weaker than covalent bonds.

It has been generally accepted that aqueous solutions can undergo autoprotolysis, i.e. H^+ (protons) are released from H_2O molecules and then transferred and accepted by other neighboring H_2O molecule, thus resulting in formation of hydronium ions as H_3O^+, $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$, etc. That is how, water should be considered as an associated liquid composed of individual H_2O molecules, linked together by hydrogen bonds and weak intermolecular van der Waals forces [6]. The simplest example of such associate can be a dimer of water. This approach has been forther extended in the research by Keutsch, Saykally et al. on water clusters with 3 to 50 water molecules [7, 8]. Different models of water clusters have also been described in the work of Fowler et al. [9], Shu et al. [10], Chaplin [11], Sykes [12], Liu, Cruzan, Saykally [6], Choi, Jordan [13], Loboda, Goncharuk [14], Timothy, Zwier [15].

The following methods have generally been used to study water clusters – ^{1}H NMR [16, 17], far-infrared spectroscopy [18], vibration-rotation-tunneling (VRT) spectroscopy [6], neutron diffraction [19], SCC-DFTB method [13, 20]. A cluster model with hydrogen bonds energy equal to -0.1387 eV has been proposed with 20 water molecules in a dodecahedral structure with diameter of the circumscribed sphere equal to 0.822 nm [21, 22, 23].

Along these lines, beneficial effects of drinking water containing different types of molecular clusters on human longevity (Ignatov, 2018) [24] and tumor suppression (Toshkova, Ignatov, Zvetkova, Gluhchev, 2019) [25] have been observed.

The present study of water processed with EVOdrop technology aimed at measurement of changes in molecular clustering due to alterations in hydrogen bonding with Non-equilibrium Energy Spectrum and ^{1}H NMR. In addition, changes in hardness and pH were observed.

2. MATERIALS AND METHODS

2.1. Evodrop turbine water purifier

The investigated device is EVOfilter with ultra-nano membrane [26] and rotation jet nozzle for vortex water [27]. The ultra-nano membrane is a competitor to the Reverse Osmosis Membrane. The rotation jet nozzle for vortex water [28] is equipped with three injection nozzles designed with a golden ratio based algorythm.

The proprietary operating principle and developed geometry of EVOdrop turbine (Figures 1, 2, 3) allow for highly efficient treatment. Incoming water passes through rotating turbine, driving them with its pressure, whereby it passess through the device rotating. Specific outcomes of such treatment are based with and magnetohydrodynamic forces [26, 27]. Figures 1 and 2. show EVOdrop turbine operation principle

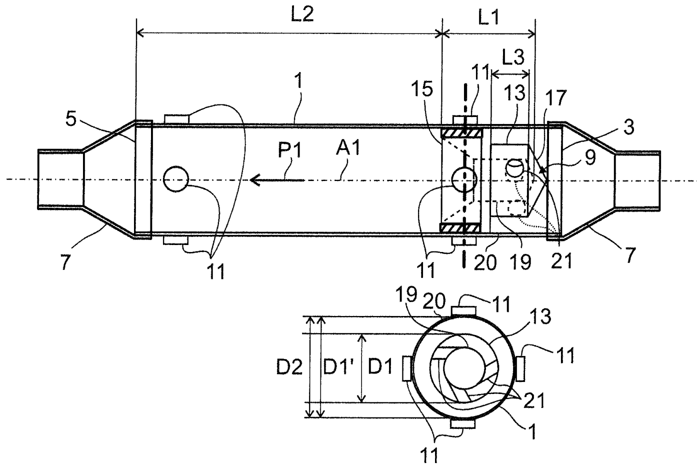

FIG. 1

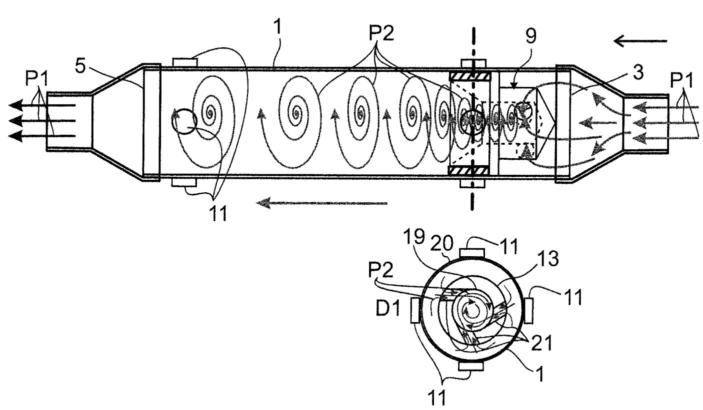

FIG. 2

Fig 1 and 2. EVOdrop turbine operation principle

Figure 3 illustrates EVOdrop fillter

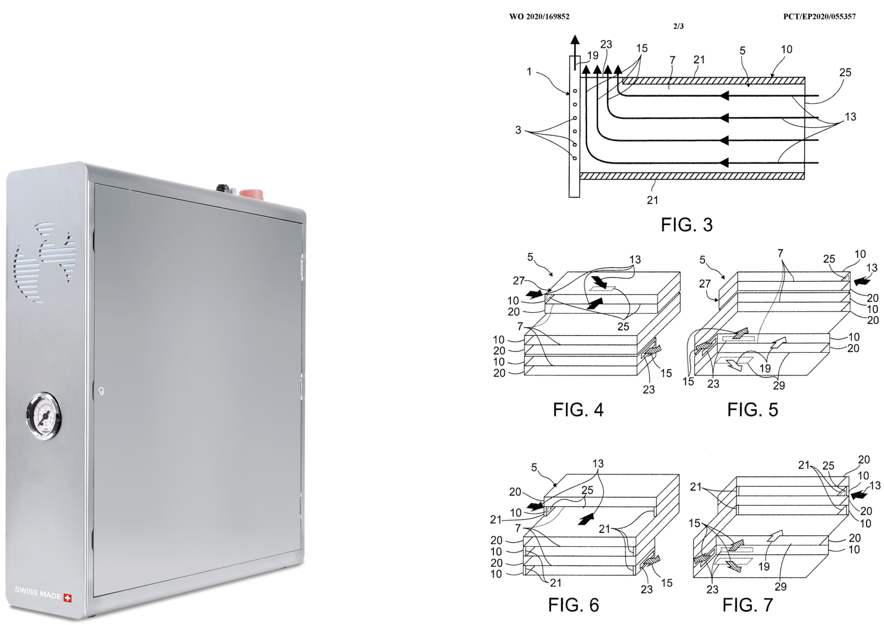

Fig 3. EVOdrop filter

2.2. NES and DNES Spectral Analyses

The methods of Non-equilibrium Energy Spectrum (NES) and Differential Non-equilibrium Energy Spectrum (DNES) for measurement of hydrogen bonds energy distribution were applied for characterization of the effect of EVOfilter technology on processed water.

The device invented by A. Antonov [29, 30, 31] for spectral analysis with NES and DNES methods is based on an optical principle. The evaporation of water drops takes place in a hermetic chamber on a glass plate covered with 350 μm thick BoPET (biaxially-oriented polyethylene terephthalate) foil. The evaporation of water drops was performed at a stable temperature of 20 °C (figure 4).

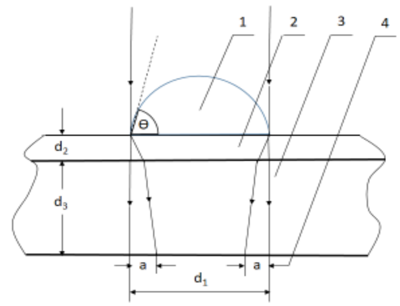

Fig. 4. Operating principle of the method for measurement of wetting angle of liquid drops on a hard surface: 1-drop, 2 – thin maylar foil, 3 –glass plate, 4 – refraction ring width. The wetting angle θ is a function of **a** and **d_1**.

The device has the following technical features:

- Monochromatic filter with wavelength λ = 580±7 nm;
- Angle of evaporation of water varies from 72.3 deg to 0 deg;
- Measured range of energy of hydrogen bonds among water molecules is λ = 8.9–13.8 μm or E=-0.08– -0.1387 eV.

The energy ($E_{H...O}$) of hydrogen O...H-bonds among H_2O molecules in water sample is measured in eV. The function f(E) is called spectrum of distribution according energies. The energy spectrum of water is characterized by a non-equilibrium process of water droplets evaporation and this is non-equilibrium energy spectrum (NES) and is measured in eV^{-1}. DNES is defined as the difference

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

DNES is measured in eV^{-1}

where *f(*)* denotes the evaluated energy [32, 33, 34].

2.2. Bruker Avance II+ 600 NMR spectrometer

Standardized nuclear magnetic resonance (NMR) spectroscopy platform enabling cost-effective, high-performance NMR pre-clinical screening and IVD-by-NMR discovery and validation (on RUO Level) of novel NMR assays. The new AVANCE IVDr system, presently for research use only, is a complete, proven and standardized platform for NMR pre-clinical research and screening, as well as for IVD-by-NMR research. It features high sensitivity and information-rich output at 600 MHz proton-NMR frequency, and incorporates advanced hardware, software, automation, spectral libraries and standard operating procedures (SOPs) for high-performance biofluid assay validation and pre-clinical screening. Customer benefits include higher information content and spectral feature differentiation compared to low-field NMR systems, as well as excellent reproducibility, high throughput and potentially dramatically lower cost per sample for better preparation and support of clinical screening and IVD-by-NMR discovery and validation (on RUO level).

3. RESULTS

The results are average results between results of the application of the device with three different samples of waters after the treatment with EVOdrop devices and control samples with tap waters. For each semple were performed 10 measurments. T-criteria of Student were applied. There was statistical significant difference of the three groups of results with samples and control samples according to the t-criterion of Student at level $p < 0,05$.

3. 1. Mathematical Models of clusters of EVOdrop water

A mathematical model of the number of water molecules [35, 36] according to the energy of hydrogen bonds in EVOdrop water has been developed (Table 1; Figure 5).

Table 1: Distribution of the number of water (H_2O) molecules in EVOdrop water according to the energy of hydrogen bonds

-E(eV) x-axis	EVOdrop Water® (Samples) Number of water molecules	Tap water (Control Samples) Number of water molecules	-E(eV) x-axis	EVOdrop® Water (Samples) Number of water molecules	Tap water (Control Samples) Number of water molecules
0.0912	0	0	0.1162	1	5
0.0937	2	9	0.1187	1	6
0.0962	4	7	0.1212	**8**[2]	**3**[2]
0.0987	5	14	0.1237	2	6
0.1012	0	3	0.1262	3	3
0.1037	4	9	0.1287	4	2
0.1062	6	5	0.1312	5	3
0.1087	1	5	0.1337	6	2
0.1112	**11**[1]	**3**[1]	0.1362	5	6
0.1137	5	6	0.1387	**27**[3]	**3**[3]

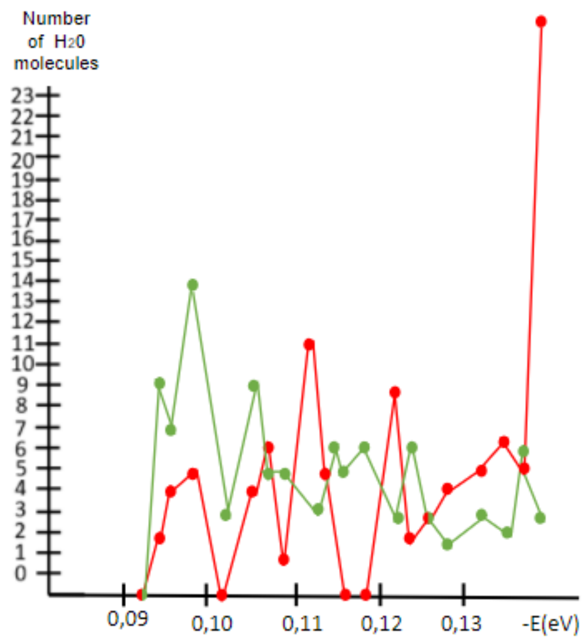

Fig. 5: Distribution of the number of water (H_2O) molecules in EVOdrop water and tap water according to the energy of hydrogen bonds

The model shows the number of water molecules and their structuring in clusters.

Notes:

E=-0.1112 eV; λ=11.15 µm; 897 cm^{-1} is the local extremum for stimulating effect on nervous system and improvement of nervous conductivity

E=-0.1212; λ=10.23 µm; 978 cm^{-1} is the local extremum for anti inflammatory effect

E= -0.1387 eV; λ=8.95 µm; 1117 cm^{-1} is the local extremum for inhibition of development of tumor cells of molecular level

The function f(E) is spectrum of distribution according to energies. The Non-equilibrium energy spectrum (NES) and is measured in eV^{-1}

Table 2 illustrates comparative analyese between EVOdrop water and other waters

Table 2. Comparative analyese between EVOdrop water and other waters

Type of Water	**Value eV $^{-1}$ of Local Extremum at (-0.1362– -0.1387)**
Deionized water	18.2±1.2
Mountain water from Vasiliovska mountain, Bulgaria	44.9±2.2
Northern Rhodope	59.3±3.0
Glasier Rosenlaui, Switzerland	70.1±3.5
Glasier Mappa, Chile	81.3±4.1
Tap water from Zurich before EVODROP device	38.3±1.9
EVODROP drinking water	128.3±6.5

The results of Table 2 are statistically estimated with t-test of Students ($p < 0.05$).

3.2. Results with spectral analyses of EVOdrop water with methods NES and DNES

The measurements with spectral methods NES and DNES show significant difference between EVOdrop water and control sample with tap water. The result for EVOdrop water in the NES-spectrum is -0.1255 eV, while for control sample with tap water it is -0.1130 eV. The value of $\Delta E_{O...H}$ for EVOdrop water measured by the DNES method are in the interval (-0.0115 eV).

The highest local extremum for EVOdrop water is 128.3 eV^{-1} at (-0.1362 eV; 9.10 μm; 1099 cm^{-1}) – (-0.1387 eV; 8.95 μm; 1117 cm^{-1}). This value is responsible for its antitumor effect. The results from NES for $\Delta E_{O...H}$ and DNES for $\Delta E_{O...H}$ show that the wetting angle at the EVOdrop water is larger than the one at tap water (control sample). The present investigation points at the relationship between the number of water molecules and the energy of hydrogen bonds, which may serve as a starting point for future research.

3.3. Research of hardness of EVOdrop water

Table 3 illustrates the results with hardness of water with influence of EVOdrop device [37, 38, 39]

Table 3 shows the results with hardness of water with influence of EVOdrop device

Number of samples*	hardness of water ($mgeqv.L^{-1}$) Tap water	hardness of water ($mgeqv.L^{-1}$) EVOdrop water	hardness of water difference ($mgeqv.L^{-1}$)
6523; 6522	6.65±0.33	4.81±0.24	1.84±0.09
6870; 6869	5.28±0.26	2.74±0.14	2.54±0.13
7064; 7063	2.71±0.14	0.53±0,05	2.18±0.11
average result	4.88±0.24	2.69±0.13	2.19±0.11

Table 4 shows the results with hardness of water with influence of EVOdrop device

Number of samples*	pH of water Tap Water	pH of water EVOdrop water
6523; 6522	7.67±0.11	7.51±0.11
6870; 6869	7.83±0.11	7.80±0.11
7064; 7063	7.64±0.11	7.12±0.11
average result	7.71±0.11	7.48±0.11

The numbers* are from Licenced Laboratory Eurotest Control, Sofia, Bulgaria

The hardness of EVOdrop water is 7.02±0.35 $mgeqv.L^{-1}$. The difference 7.82-7.02=0.8±0.04 shows effect of decreasing of hardness of tap water from the device for EVOdrop water.
This effect is ecential for human health for cardiovascular system.

3.3. Results of EVOdrop water with ^{1}H NMR

The ^{1}H NMR spectra were measured on Bruker Avance II+ 600 NMR spectrometer using 5 mm direct detection dual broadband probe [40, 41]. The experiments were performed at a temperature of 293 K. ^{1}H NMR spectra were acquired with 128K time domain points, spectrum width of 9600 Hz, 16 scans and a relaxation delay of 60 s. The chemical shifts were referenced to the residual dmso-d6 resonance used as an external reference (2.5 ppm). The dmso-d6 was placed in a coaxial capillary in the sample tube and also used as a lock signal.
The results of EVOdrop water and control sample with ^{1}H NMR are of figure 6.

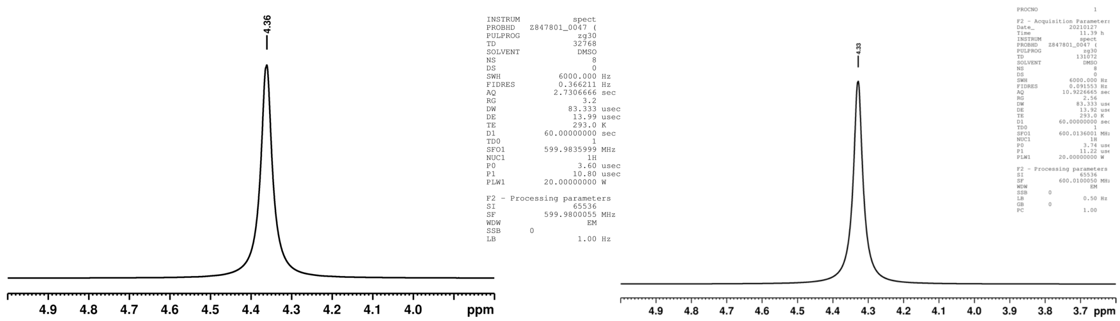

Figure 6. Results of EVOdrop water and control sample with ^{1}H NMR

There are the following parameters:

EVOdrop water Sample – Chemical shifts 4.36 ppm (1308 Hz) line widths $\Delta\nu_{1/2}$ = 17.7 Hz

Control sample – $\Delta\nu_{1/2} = \delta$ = 4.33 ppm (1299 Hz) line widths $\Delta\nu_{1/2}$ =16.9 Hz

Greater chemical shifts correspond to bigger clusters [17].

The results shows that in EVOdrop water there is structuring bigger clusters regarding control samples tap water.

The number of nuclei of hydrogen atoms and ions is determined by the area of the signal [42].

A bigger line width $\Delta\nu_{1/2}$ means faster relaxation hydrogen nucleus. The increase of relaxation rate with NMR is observable in natural water [43]. The increase of relaxation rate is quantitatively interpreted in terms of fast chemical exchange between water molecules and protein protons [44, 45].

4. CONCLUSION

EVO drop drinking water treatment technology, in addition to the reduction of hardness and preservation of the pH level of processed tap water, was shown to significantly rearrange water molecule clustering towards greater similarity to that of high-quality natural waters, even being superior to them. That is why it would be fesible to conduct further investigations in the direction of scaling up the technology for wastewater treatment. Such a development could be expected to provide more effective environmental protection.

DISCLAIMER

The products used for this research are only for scientific purpose and they are not products of companies. There is absolutely no conflict of interests. The research was not funded by the producing company, rather it was funded by the authors themselves.

ETHICAL APPROVAL

1. I, the alone corresponding author, am authorized to submit this manuscript.

2. Submission of the manuscript represent
that the manuscript has not been published previously and is not considered for publication elsewhere.
3. The manuscript, or any part thereof, is in no way a violation of any existing original or derivative copyright.

References:

[1] O. V. Mosin and I. Ignatov, "Basic concept of magnetic water treatment," *European Journal of Molecular Biotechnology*, vol. 4, no. 2, pp. 72-85, 2014.

[2] H. J. Choi et al. "Characteristics and applications of magnetized water as a green technology," *Journal of Cleaner Production,* vol. 161, pp. 908-921, 2017.

[3] P. Puzowski and I. Scocsko, "Investigation on magnetic field usage for urban water treatment," *Proceedings*, vol. 51, no. 1, 2020.

[4] E. A. Anaeva, E. A. Mesiats and V. V. Sergievski, "Crystallization of Calcium carbonate with the filtration of aqueous solutions through a microporous membrane," *Russian Journal of Physical Chemistry A,* vol. 91, pp. 2121–2123, 2017.

[5] Ch. Thamaraiselvan et al., "Characterization of a support-free carbon nanotube-microporous membrane for water and wastewater filtration," Purification Technology, vol. 202, no. 1-8, 2018.

[6] K. Liu, J. D. Cruzan and R. J. Saykally, "Water clasters," *Science Magazine* **271**(5251) 929–933, 1996.

[7] J. P. Smith, R. J. Saykally et al. "Unified description of temperature-dependent hydrogen bond rearrangements in liquid water," *PNAS,* vol. 102, no. 40, pp. 14171–14174, 2005.

[8] F. N. Keutsch and R. J. Saykally, "Water clusters: Untangling the mysteries of the liquid, one molecule at a time," *PNAS,* vol. 98, no. 19, pp. 10533–10540, 2001.

[9] P. W. Fowler, C. M. Quinn and D. B. Redmond, "Decorated fullerenes and model structures for water clusters." *The Journal of Chemical Physics,* vol. 95, no. 10, 7678, 1991.

[10] Y. Gao, H. Fang and K. Ni, "A hierarchical clustering method of hydrogen bond networks in liquid water undergoing shear flow," *Scientific Reports,* 11, 9542, 2021.

[11] M. Chaplin, "The water molecule, Liquid water, Hydrogen bonds and water networks/in: Water The Forgotten Biological Molecule," D.Le Bihan & H.Fukuyama (eds.), *Singapore: Pan Stanford Publishing Pte. Ltd*., 2011.

[12] M. Sykes, "Simulations of RNA base pairs in a nanodroplet reveal solvation-dependent stability," *PNAS,* vol. 104, no. 30, pp. 12336–12340, 2007.

[13] T. N. Choi and K. D. Jordan, “Application of the SCC-DFTB method to $H^+(H_2O)_6$, $H^+(H_2O)_{21}$, and $H^+(H_2O)_{22}$,” *J. Phys. Chem. B,* vol. 114, pp. 6932–6936, 2010.

[14] O. Loboda and V. Goncharuk, “Theoretical study on icosahedral water clusters,” *Chemical Physics Letters,* vol. 484, no. 4–6, pp. 144–147, 2010.

[15] S. Timothy and S. Zweier, “Chemistry: the structure of protonated water clusters,” *Science,* vol. 304, no. 5674, pp. 1119–1120, 2004.

[16] P. D’ Aangelo, A. Zitolo, G. Aquilanti and V. Migliorati, “Using a combined theoretical and experimental approach to understand the structure and dynamics of imidazolium-based ionic liquids/water mixtures. 2. EXAFS Spectroscopy,” *The Journal of Physical Chemistry B,* vol. 117, no. 41, pp. 12516-12524, 2013.

[17] V. Turov, T. Krupskaya, V. Barvinchenko, N. Lipkovska, M. Kartel, L. and Suvorova, “Peculiarities of water cluster formation on the surface of dispersed KCl: The influence of hydrophobic silica and organic media,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* V, 499, pp. 97-102, 2016.

[18] K. Liu, R. Fellers, M. Viant, R. Mclaughlin, M. Brown and R. J. Saykally, “A long path length pulsed slit valve appropriate for high temperature operation: Infrared spectroscopy of jet-cooled large water clusters and nucleotide bases,” *Review of Scientific Instruments,* vol. 67, no. 2, 1998.

[19] K. Yoshida and S. Ishuda, “Hydrogen bonding and clusters in supercritical methanol–water mixture by neutron diffraction with H/D substitution combined with empirical potential structure refinement modeling,” *Molecular Physics,* vol. 117, 22, pp. 3227-3310, 2019.

[20] P. Goyal, M. Elstner and Q. Coi, “Application of the SCC-DFTB method to neutral and protonated water clusters and bulk water,” *J. Phys. Chem.,* vol. 115, no. 20, pp. 6790–6805, 2011.

[21] I. Ignatov and O. V. Mosin, “Structural mathematical models describing water clusters,” *Journal of Mathematical Theory and Modeling*, vol. 3, no. 11, pp. 72-87, 2013.

[22] I. Ignatov, G. Gluhchev, N. Neshev and D. Mehandjiev, “Structuring of water clusters depending on the energy of hydrogen bonds in electrochemically activated waters Anolyte and Catholyte,” *Bulgarian Chemical Communications,* vol. 53, no. 2, pp. 234-239, 2021.

[23] D. Mehandjiev, I. Ignatov, G. Gluhchev, N. Neshev and Ch. Drossinakis, “Hydrogen bond energies in formation of water molecule clusters,” *Physical Science International Journal,* 25, 12, pp. 15-20, 2021.

[24] I. Ignatov, “Research of the factors of health and longevity of for the population in Bulgaria,” *Bulgarian Journal of Public Health,* vol. 10, no. 3, pp. 52-85, 2018.

[25] R. Toshkova, E. Zvetkova, I. Ignatov and G. Gluhchev, "Effects of Catholyte water on the development of experimental *Graffi* tumor on hamsters," *Bulgarian Journal of Public Health*, vol. 11, pp. 3, pp. 60-73, 2019.
[26] F. HUETHER, FILTER SYSTEM. FABIO AND MARKUS MEMBRANE ENG GMBH [CH] WO2020169852A1, 2020.
[27] F. HUETHER, WATER PURIFIER, FABIO AND MARKUS TURBINE ENG GMBH [CH] WO2020178200A1, 2020.
[28] A. B. Timilsina, S. Mulligan and T. R. Bajracharya, "Water vortex hydropower technology: a state-of-the-art review of developmental trends," *Clean Technologies and Environmental Policy,* vol. 20, pp. 1737-1760, 2018.
[29] A. Antonov and L. Yuskesselieva, "Method for determination of structural changes in liquids," *Author's certificate of invention* 43821, 1983.
[30] A. Antonov, "An optical method version for determination of the welling angle of liquids," *Comptes Rendus de l'Académie Bulgare des Sciences* **37** 1199, 1984.
[31] I. Ignatov, G. Gluhchev and F. Huether, "Dynamic nano clusters of water on EVOdrop water," *Physical Science International Journal,* vol. 24**,** no. 7, pp. 47-53, 2020.
[32] A. Antonov, "Research of the Non-equilibrium Processes in the Area in Allocated Systems, *Dissertation thesis for degree "Doctor of physical sciences"*, Blagoevgrad, Sofia, 1-254, 1995.
[33] S. Todorov, A. Damianova, I. Sirviev, A. Antonov and T. Galabova, "Water energy spectrum method and investigation of the variations of the H-bond structure of natural waters," *Comptes Rendus de l'Académie Bulgare des Sciences,* vol. 61, no. 5251, pp. 857-862, 2008.
[34] P. Gramatikov, A. Antonov and M. Gramatikova*,* "A study of the properties and structure variations of water systems under the stimulus of outside influences," *Fresenius' Journal of Analytical Chemistry*, vol. 343, no. 1, pp. 134–135, 1992.
[35] A. Antonov, L. Yuskesselieva and I. TEODOSSIEVA (1989) "Influence of ions on the structure of water under conditions far away from equilibrium," *Physiologie,* vol. 26, no. 4, pp. 255-260.
[36] I. Ignatov, N. Neshev, G. Gluhchev, F. Huether and D. Mehandjiev, "Research of physical alterations of water treated with turbine technology," *Contemporary Engineering Sciences,* vol. 14, no. 1, pp. 51-60, 2021.
[37] Documents No. 6522/ No. 6523 from 20.10.2021 Research of physichochemical indicators of EVOdrop water according to Ordinance No. 9/2001, Official State Gazette, issue 30, and decree No. 178 / 23.07.2004 regarding the quality of water intended for drinking and household purposes, 2021.

[38] Documents No. 6869/ No. 6870 from 12.11.2021 Research of physichochemical indicators of EVOdrop water according to Ordinance No. 9/2001, Official State Gazette, issue 30, and decree No. 178 / 23.07.2004 regarding the quality of water intende for drinking and household purposes, 2021.

[39] Documents No. 7063/ No. 7064 from 23.11.2021 Research of physichochemical indicators of EVOdrop water according to Ordinance No. 9/2001, Official State Gazette, issue 30, and decree No. 178 / 23.07.2004 regarding the quality of water intended for drinking and household purposes, 2021.

[40] N. Bloembergen, E. Purcell and R. Pound, "Relaxation effects in nuclear magnetic resonance absorption," *Phys. Rev,* vol. 73, pp. 679–712, 1948.

[41] A. M. Tsedelin et al., "How sensitive and accurate are routine NMR and MS measurements? *Menedeleev Communications,* vol. 25, no. 6, pp. 454-456, 2015.

[42] K. OKA et al., "Long-lived water clusters in hydrophobic solvents investigated by standard NMR techniques," *Scientific reports,* vol. 223, 2019.

[43] H. Elgarbarty, R. Z. Khaliullin and Th. D. Kuehne,*"*Covalency of hydrogen bonds in liquid water can be probed by proton nuclear magnetic resonance experiments," *Natutre Communicstions,* 6, 8318, 2015.

[44] S. Meiboom, "Nuclear Magnetic Resonance study of the proton transfer in water," *J. Chem. Phys.,* vol. 34, no. 375, 1961.

[45] B. P. Hills, S. F. Takacs and P. S. Belton,*"*The effects of proteins on the proton N.M.R. transverse relaxation times of water," *Molecular Physics* 903-918, 2006.