

The Industrial Production of Water Dedicated to Absorption of Gases

Ihar Yelkin¹, Edward Reszke², Grzegorz Binkiewicz¹, Grzegorz Schroeder^{3*}

¹Research and Development Department, Plasma Investment Ltd., Wrocław, Poland

²Ertec-Poland, Wrocław, Poland

³Faculty of Chemistry, Adam Mickiewicz University in Poznan, Poznan, Poland

Email: *schroede@amu.edu.pl

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Abstract

The paper presents a flow plasma reactor permitting modification of the properties of water/aqueous solutions by stochastic resonance amplification of vibrations of selected chemical species in water with electromagnetic noise generated during a plasma discharge. The main parameters characterizing the quality for super-pure water, tap water and water from the intake in Besko (Poland) before and after the process in the plasma reactor were presented for comparison. In addition, the ¹⁷O NMR (the full width at half maximum) and electrospray ionization mass spectrometry (ESI MS) methods were used to determine differences in physicochemical parameters between the untreated and plasma-treated water. It has been established that the water subjected to plasma treatment shows much different gas absorption properties than the untreated water samples, as a function of temperature and pressure, in this paper we report exemplary data for CO₂, oxygen and acetylene. The improved gas absorption properties of the plasma-treated water make it attractive for the use in industrial processes. It is worth pointing to a great capacity of the new reactor (4000 l/h), and low energy consumption (20 MJ/h) for the treatment of the above mentioned volume flow rate of water.

Keywords

Flow-Through Plasma Reactor for Water Treatment, Modification of the Properties of Water/Aqueous Solutions, Industrial Production of Water, Physicochemical Parameters of Water Solution

1. Introduction

Water is known to be the most abundant chemical compound in the Universe.

Due to its properties, water, at least on the Earth surface, does not exist as a pure hydrogen-oxygen (H₂O) compound. In scientific terms, water is an aqueous solution with a complex molecular structure and a system containing various inorganic, organic or gas substances. Recently, the structure and properties of water at the molecular level have become again a subject of discussions thanks to the availability of new measurement techniques and advanced computational methods [1] [2] [3] [4] [5].

Knowledge of the properties of water (water solution) at the molecular level controlled and forced by external factors allows not only better understanding of the impact of water on living organisms at the cellular level, but also permits deeper insight into the processes in living organisms. These two factors: the cluster structure of water forced by the formation of hydrogen bonds between H₂O molecules and the solubility of chemical compounds and gases in water, modify the water properties in response to physical and chemical external factors [6] [7] [8]. Recently, thanks to the progress in plasma technology, changes in the properties of water (aqueous solutions) induced by external factors are mainly studied by the use of plasma [9] [10] [11]. Non-thermal plasma (NTP) is used to induce complex oxidation processes in water solutions and has been increasingly often used to change the properties of water and for wastewater treatment [12] [13] [14] [15] [16]. The impact of plasma on the properties of water is realized through the induced electrical discharges in water, in air above the water level or simultaneously in water and in gas [17] [18] [19]. Lacke *et al.* [20] have shown the effect of interaction of non-thermal plasma with water as direct in situ generation of many types of highly reactive chemical species (radicals), quenching in the gas phase and liquid phase radical reaction products, generation of UV light and shock waves. Chwastowski *et al.* [21] have presented methods of water treatment with low-temperature, low-pressure glow discharge plasma. The same authors have described the glow discharge plasma treated water under anaerobic nitrogen. This operation produced nitrogen in the water in different excited states depending on the treatment time. The excited nitrogen molecules built up water clathrates around them. The number and structures of these clathrates depended on the duration of treatment with the glow discharge plasma. Ciesielska *et al.* [22] have reported the treatment of CO₂-saturated water using low-temperature, low-pressure, low-frequency glow plasma. The macrostructure of the water treated with this method consisted mainly of tetrahedral and deformed stabilized tetrahedral structural units with long-lived free radicals. Hiratsuka *et al.* [23] have presented application of sound waves for the improvement of water treatment process. In that study, various sound waves such as: ultrasonic wave, music box, and wind-bell were used to water and wastewater for removing contaminants. As a result, a possibility of improvement of water and wastewater treatment process using sound waves with various frequencies was proposed. Implementation of a similar approach by Acoustic Wave Separation, led to industrial water cleaning process using a pattern of ultrasonic waves to exert acoustic forces on hydrocarbons and other water contaminants [24]

[25].

In a previous paper, we presented the apparatus for inducing changes in water properties in closed vessels as a result of treatment with plasma generated by pulsed direct current glow discharges, hypothesizing that the action of plasma on the structure of water consists in resonant excitation of water aggregates [26]. The method presented in the above mentioned paper is characterized by the transmission of electromagnetic radiation generated by plasma maintained by pulsed direct current glow discharge formed in special conditions. The impact of plasma is exerted through a dielectric and not necessary transparent shield and results in changes in the composition of aqueous solutions in closed vessels induced in a contactless manner. Previous methods of modifying the properties of water solutions with low-temperature plasma have been focused on the treatment of a certain amount of water in vessels of volumes not exceeding a few liters.

In this work, we present for the first time an efficient flow-through method that allows changes in water properties in flow as a result of treatment with plasma generated by pulsed direct current glow discharges which can efficiently produce a wideband electromagnetic noise. In order to assess the influence of the process on the physicochemical parameters of the solutions, different methods of analysis were applied. The method described above can be used to improve water solution and wastewater physicochemical parameters on an industrial scale, and in particular, to enhance absorption of different gases for example carbon dioxide, oxygen and acetylene.

2. Experimental

2.1. Materials

The following types of water were used in the study: for small-scale experiments—Ultra Clean Water—produced in accordance with ISO 13,485 for use in production of pharmaceutical products (Nano-Tech, Warsaw, Poland), while for industrial scale experiments—tap water from the city of Wrocław and also water from the intake in Besko, Poland. Water analysis was performed in an accredited laboratory (Oikos, Święta Katarzyna, Poland) in accordance with the applicable standards for water analysis. ORP-200: Waterproof Professional Series ORP/Temp Meter and RP-969 ORP Test Pen Oxidation Reduction Potential Tester were used to test the redox potential of liquids, with resolution of 1 mV, and with a standard measuring range of 0 ± 1999 mV. The meters were calibrated to +92 mV. TDS-3Water Quality Tester TDS Meter was used for measurements of the Total Dissolved Solids (TDS) which are the total amount of mobile charged ions, including minerals, salts or metals dissolved in a given volume of water. TDS principle is based on conductivity and the results of measurements by this method are expressed in parts per million (ppm). TDS-3Water Quality Tester has been calibrated to a NaCl 342 ppm solution. The pH measurement was performed using a pH meter CP-505 with an EPS-1 measuring electrode (Elmetron,

Poland). The electrode was calibrated in two buffer solutions (pH = 4.00 and 10.00). The full width at half maximum (FWHM) of the ^{17}O NMR signal of water was measured using a Bruker 500 spectrometer at 25 °C (Polish Academy of Science Poznan, Poland). The ^{17}O NMR spectra were recorded as an average of 1600 scans. The full width at half maximum (FWHM) of the ^{17}O NMR signal was measured independently for two samples prepared from the supplied water. The Raman spectra of the water from Besko were obtained on a Ramana DXR, Thermo Scientific, (USA) system equipped with a frequency doubled Nd: YAG laser (532 nm) as the excitation source whose output laser power is 8 mW, 50 μm slit, Number of exposures: 100, Exposure time: 1 sec, Spectral range: 3500 - 50 L/cm, Objective lens: Olympus MPlan 4x. Spectrum Correction: No Correction.

The electrospray ionization (ESI) mass spectra were recorded on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump. The ESI spectra of water solutions of salts at the concentration of 10^{-5} M were recorded. The samples were infused into the ESI source using a Harvard pump at the flow rate of 20 $\mu\text{dm}^3/\text{min}$. The ESI source potentials were: capillary 3 kV, lens 0.5 kV, extractor 4 V. The spectra were taken at different cone voltages (cv = 5, 10, 15, 20, 25 and 30 V). The source temperature was 120 °C and the desolvation temperature was 250 °C. Nitrogen was used as the nebulizing and desolvation gas at the flow-rate of 150 dm^3/h .

The contents of dissolved gases in the tested water samples were determined by the gravimetric method at atmospheric pressure (993 hPa). CO_2 was introduced into 500 mL of water via an atomizer, at different temperatures. Solubility of gases in g/500g water was studied after decompression at a pressure of 993 hPa, having gas fed into given water sample at a pressure of 7 bar for CO_2 and O_2 and 2.2 bar for acetylene, respectively. Water temperature was determined with the accuracy to 0.1 °C. The amount of dissolved gas is given in g/100 mL of water at various temperatures.

2.2. Construction of an Industrial System for Water Treatment with Stochastic Noise

The plasma water treatment system (**Figure 1**) named stochastic water softener consists of: a tank (5 m^3) filled with 4 m^3 of water, a module of noise lamps (diodes) connected by pipes to the tank, a control module containing a vacuum preparation system for noise generating lamps, pumping systems, a computer control and monitoring panel capable of transmitting data from/to the stochastic water softener system with the possibility of on-line communication via GSM network. Please do not revise any of the current designations.

The lamp module consists of 2×5 noise generating glow discharge lamps with a dynamic vacuum seeded with a stream of moist air, all built into two metal bodies. The arrangement of the lamps in the metal body is shown in **Figure 2**. The lamps are powered from an electronic power supply with a 3.5 kHz sinus generator feeding a D class power amplifier and output transformer connected

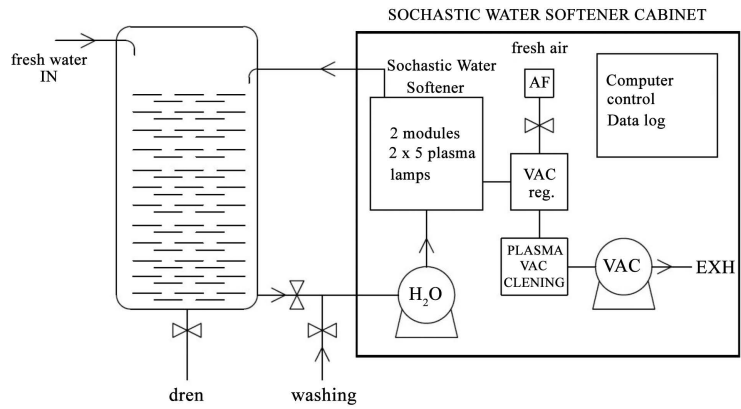


Figure 1. Industrial system for an incorporating stochastic noise water softener.

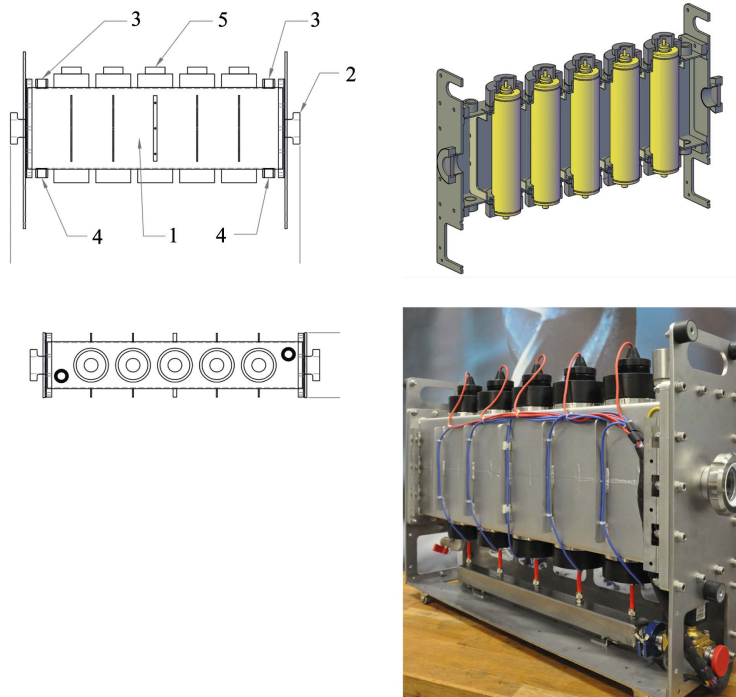


Figure 2. The lamp module. Arrangement of noise tubes in a flow-through stochastic noise softener. Metal body (1), Spectacle glass (2), Water inlet/outlet (3), Water drain plug (4), plasma discharge noise lamps (5).

to a full wave diode rectifier. The electronic regulator stabilizes the module current level at approx. 5 mA DC at an average voltage of approx. 450 V DC [27] [28]. Each noise generating lamp is a diode having a cylindrical metal anode of 15 mm in diameter, 20 mm in length and a flat cathode of 70 mm in diameter placed in a borosilicate tube with a diameter of 80 mm and a length of 380 mm. Vacuum within the lamps of approx. 1 mbar is maintained dynamically by a rotary oil pump with air flow regulation by means of an electromechanically-controlled needle valve. An important element of the vacuum installation is the plasma system for cleaning the working gas for noise generating lamps, which also makes use of glow discharge to carry out in situ cleaning of the gas under reduced pressure, especially to remove contamination with lubricants from the oil pump. In the process of lamp cleaning certain amounts of gas hydrogen are added to the gases [29].

The cleaning processes increase the service life of the noise tubes by more than 100 times, the noise tubes do not have to be replaced more often than once a year in continuous operation. The entire process is controlled by a computer program with a data-logging function and automatic data transmission via the GSM network. The system provides full process control and monitoring. The water flow between the tank and the plasma reactors is forced by an impeller pump and its rate is 4 m³/h. The time needed to process 4 m³ is 1 hour. The energy efficiency of the process is very high; the total energy expenditure for the preparation of 1 m³ is only 5 MJ.

3. Results and Discussion

A highly efficient stochastic-resonance system to change the parameters of water or water solutions was built. The systems permitted the treatment of 4000 l of water per hour. The construction of the flow system, plasma noise-generating lamps and the control system has been presented in the details in the experimental part. The flow stochastic-resonant system for changing the parameters of water or aqueous solutions is based on the use of broadband electric noise generated in the plasma and transmitted in the contactless manner through the dielectric wall to the flowing water. Stochastic resonance is the phenomenon that occurs in dynamical systems whose response to an external signal reaches the optimal value in the presence of noise of certain intensity [30].

Stochastic resonance refers to the enhancement of a weak periodic signal by addition of an external white noise representing a wide range of frequencies. When the sum of the subthreshold periodic signal and the noise amplitude crosses the threshold, the excitable system responds with a burst signal [31] [32]. The stochastic system uses a plasma discharge noise-generating and noise transmitting ability in a wide frequency range. In the stochastic system, the energies corresponding to the frequencies of the generated noise are in resonance with those of vibrations of different water structures, different chemical species and molecules contained in water.

Plasma noise can be easily modified by adding components present in the

treated water as seeds to the plasma gas and thus obtaining a coherent resonant energy coupling. Such a system in terms of energy is optimal from the point of view of resonant energy transfer to water. An important benefit is that very significant changes to the structure of the water can be made as a result of exposition to noisy plasma, while the energy consumption by the entire treatment process may be really low. The questions that arise at this point are what kind of water/aqueous solution is the most susceptible to the stochastic resonance interaction and which analytical methods should be used to permit experimental observation of the changes that occur in the solution under the influence of the plasma discharge.

Three types of water were tested in the constructed system: super-clean water, tap water and spring water from the intake in Besko. The water before and after treatment in the flow-through apparatus was analyzed in accordance with the applicable standards for the contents of basic components (Table 1).

Table 1. The values of physicochemical parameters of water prior to and after treatment with plasma.

	Concentration result \pm standard deviation					
	super-clean water		tap water		water from Besko intake	
	Prior to	After processing	Prior to	After processing	Prior to	After processing
pH	6.4 \pm 0.2	6.6 \pm 0.2	7.5 \pm 0.2	7.6 \pm 0.2	7.1 \pm 0.2	7.2 \pm 0.2
The specific electric conductivity (μ S/cm)	<0.1	<0.1	570 \pm 63	521 \pm 45	830 \pm 91	679 \pm 75
The permanganate index (mg O ₂ /dm ³)	<0.5	<0.5	<0.5	0.9 \pm 0.1	<0.5	1.6 \pm 0.1
The content of magnesium—EDTA titrimetric method (mg Mg/dm ³)	<5.0	<5.0	10 \pm 1	11 \pm 1	7 \pm 1	7 \pm 1
The calcium content—EDTA titrimetric method (mg Ca/dm ³)	<1.0	<1.0	200 \pm 10	203 \pm 11	172 \pm 10	176 \pm 10
The content dissolved oxygen—Electrochemical probe method (mg O ₂ /dm ³)	<0.2	<0.2	<0.2	<0.2	8.8 \pm 0.7	8.6 \pm 0.7
The ammonium content (mg NH ₄ /dm ³)	<0.03	<0.03	<0.129	<0.129	<0.129	<0.129
The content of dissolved anions—nitrates (mgNO ₃ /dm ³)	<0.2	<0.2	1.92 \pm 0.71	2.23 \pm 0.85	7.46 \pm 0.97	8.62 \pm 1.12
The content of dissolved anions—chloride (mg Cl/dm ³)	<5	<5	40 \pm 3	35 \pm 3	33 \pm 3	31 \pm 3
The concept of dissolved anions - sulfates (mg SO ₄ /dm ³)	<5	<5	66 \pm 7	66 \pm 7	32 \pm 5	43 \pm 7
The content of dissolved anions—Fluoride (mg F/dm ³)	<0.12	<0.12	0.222 \pm 0.046	0.226 \pm 0.045	0.251 \pm 0.045	0.228 \pm 0.041
Oxidation Reduction Potential (ORP) (mV)	170 \pm 3	179 \pm 3	142 \pm 3	161 \pm 4	135 \pm 3	158 \pm 4
Total Dissolved Solids (TDS) (ppm)	7 \pm 3	9 \pm 3	261 \pm 5	257 \pm 5	204 \pm 5	195 \pm 5

Analyzes performed in accordance with the procedures specified in the reference document: PN-EN ISO 10523:2012, PN-EN-27888:1999, PN-EN ISO 8467:2001, PN-C-04554-4:1999, PN-ISO 6058:1999, PN-ISO 5814:2013-04, PN-ISO 7150-1:2002, PN-EN ISO 10304-1:2009, Ac2012, and PN-EN ISO 10304-1:2009, Ac2012.

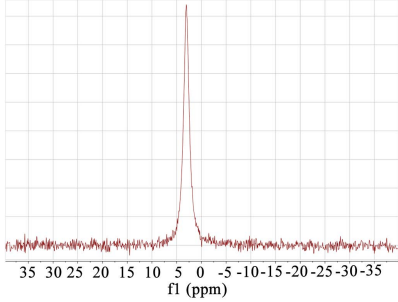
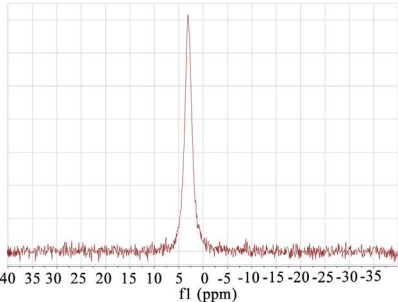
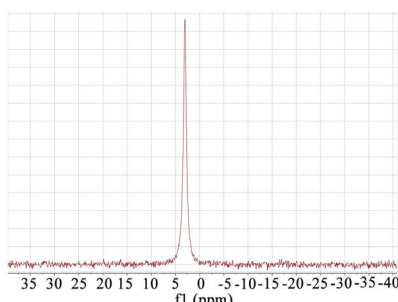
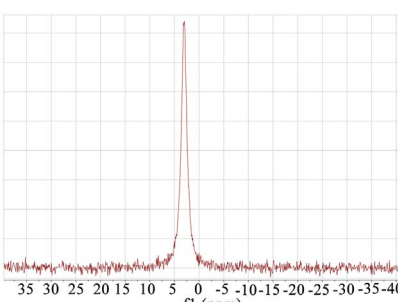
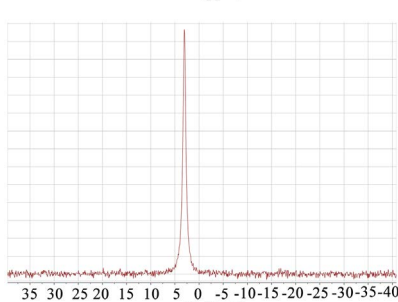
Table 2 shows the values of FWHM of the signal of water were determined by ^{17}O NMR measurements. The basic physicochemical tests of water before and after plasma treatment revealed that in the case of super-clean water, apart from a slight but measurable increase in the pH of the solution, no significant changes in the other water parameters were observed.

For the samples of tap water and the water from the Besko intake, containing of calcium and magnesium compounds, an increase in the value of pH was observed. The value of the permanganate index and the content of dissolved anions-nitrates, used as a parameter in assessment of water quality, also increased for both types of examined water. Moreover, a significant decrease, by about 10%, in the value of electric conductivity and an ascending trend in the value of oxidation-reduction potential (ORP) were detected. A slight increase in the ORP value of water after the water treatment process proves an increase in the oxidizing properties of the water solution. The increase in ORP value, depending on the type of water, varied in the range 5% - 17% confirmed the results of our previous studies, proving the lack of free radicals generated in the process of stochastic resonance water treatment. The FWHM of the ^{17}O NMR signal in the spectra of the tested water samples increased from 76 - 86 Hz to 109 - 114 Hz after the plasma treatment. On the other hand, after saturation of water treated with plasma with CO_2 the FWHM of the ^{17}O NMR signal decreased to the value of 48 - 52 Hz. The water molecules in aqueous solution formed aggregates/clusters thanks to the connecting ability of hydrogen bonds. The sizes of the H_2O molecular clusters are continually changing and strongly depend on the presence of ions (H^+ and M^{n+}) or neutral particles in the solution [33] [34]. Li *et al.* [35] have reported a decrease in the FWHM values of ^{17}O -NMR spectral line of pure water from 123.94 Hz to 65.13 Hz, and correlated these values with the strength of water molecular hydrogen bond. Lei *et al.* [36] have studied the influence of nanoparticles on the FWHM of the ^{17}O NMR signal, showing that the added nanoparticles can effectively weaken the hydrogen bonding between water molecules, changing the network structure.

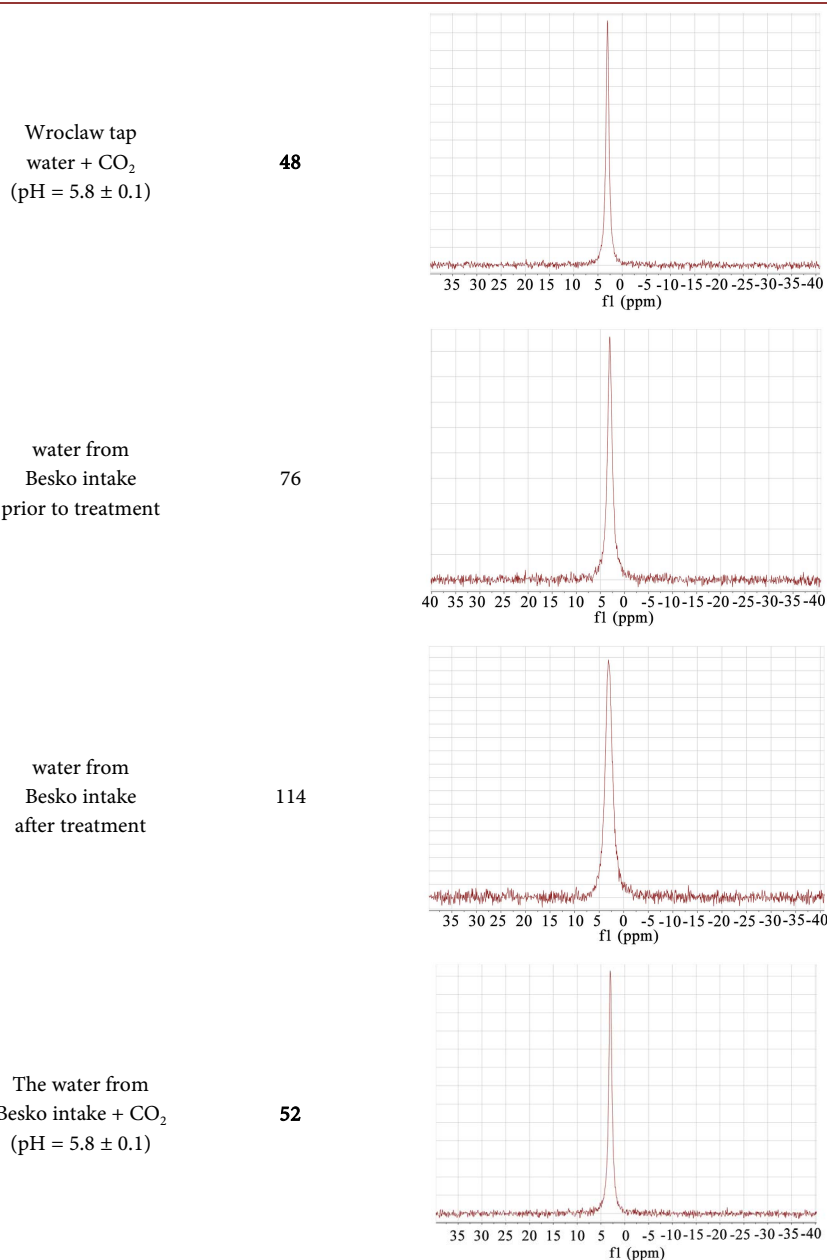
The nanoparticles ability to weaken the association of molecules (atoms) via hydrogen bonds formation is manifested by a reduction in the FWHM of the ^{17}O NMR signal. The FWHM values of the H_2O peak in the ^{17}O -NMR spectra reflect the velocity of molecular movement, which is directly related to the degree of association of the molecules.

As mentioned by Hiraoka *et al.* [37], it has been generally accepted that the sizes of H_2O molecules clusters cannot be evaluated on the basis of the ^{17}O NMR spectra as the correlation between the H_2O cluster sizes and the spectral data also depends on other factors. The width of the bands depends on the pH, the degree of association of molecules, ions, neutral molecules and nanoparticles added to water solution. The results obtained in our study refer to a situation in which, as a result of the interaction of water with plasma radiation, an increase in the pH value of the solution and changes in some basic physicochemical parameters of water are observed, **Table 1**.

Table 2. The values of parameters of water and FWHM of the ^{17}O NMR signal (Hz).

	The full width at half maximum of ^{17}O NMR signal (Hz)	^{17}O NMR signal
super clean water prior to treatment	85	
super clean water after treatment	110	
super clean water + CO ₂ (pH = 5.6 ± 0.1)	49	
Wroclaw tap water prior to treatment	86	
Wroclaw tap water after treatment	109	

Continued



Raman spectroscopy (RS) is widely applied for qualitative and quantitative analysis of solid, liquid and gas samples. This method is based on the phenomenon of electromagnetic radiation scattering associated with the change in energy of scattered photons. The mentioned change in energy of the scattered photons provides information about the oscillating energy levels of the test substance. Raman spectra contain vibrational bands corresponding to the normal vibrations of molecules. In this study, Raman spectroscopy was used to analyze changes in the water from the Besko intake appearing as a result of flow through the plasma reactor. **Figure 3** shows the Raman spectra of the water sample from the Besko intake before and after treatment in the reactor. The spectra of this

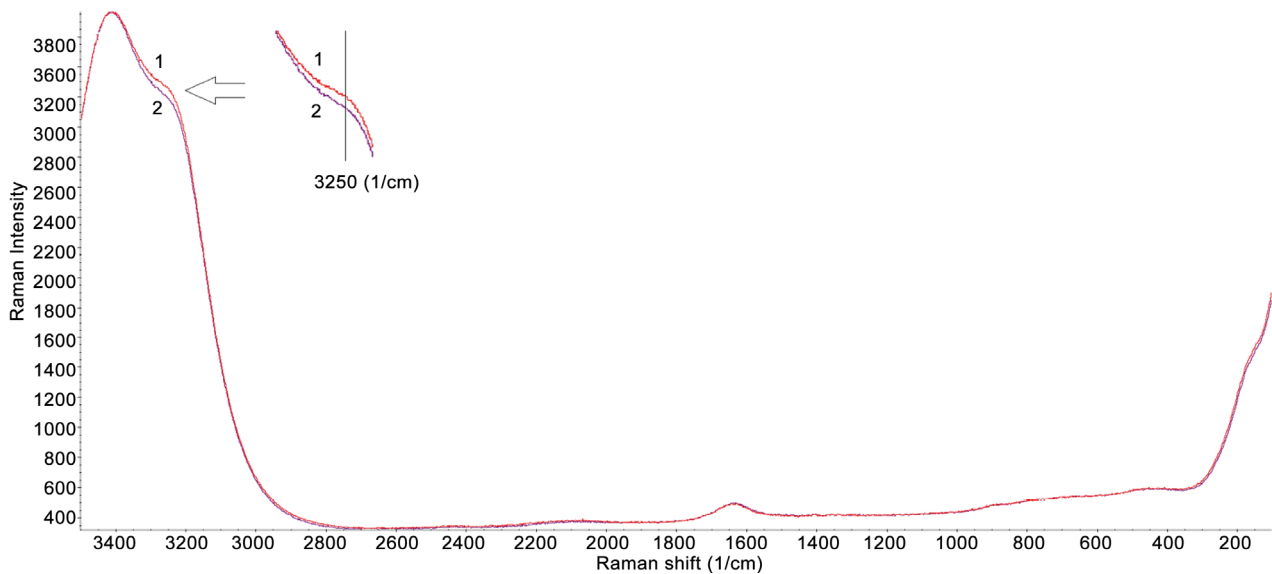


Figure 3. The raman spectroscopy spectra of waters before (1) and after (2) treatment in the reactor.

sample of water recorded before and after the treatment differed only in the region of 3150 - 3350 cm^{-1} .

In the Raman spectrum, the peaks at 3250 cm^{-1} unambiguously indicate the presence of the stretching vibrations of the O-H bands in the fully hydrogen-bonded water molecule that forms tetrahedron-like structure by connecting other four water molecules through hydrogen bonds.

The Raman peaks between 3300 cm^{-1} and 3630 cm^{-1} are ascribed to Raman scattering of partly hydrogen bonded water [38] [39] [40]. In the water after treatment in the flow reactor, the number of water molecules with tetrahedron-like structure formed by connecting other four water molecules through hydrogen bonds decreases.

The Electrospray Ionization Mass Spectrometry (ESI MS) method was used to study the water samples before and after exposure to radiation produced by the plasma discharge. ESI mass spectra at various cone voltages recorded in positive mode (m/z 2 - 300) of super-clean water, tap water and the water from Besko intake before (a) and after (b) plasma treatment are shown in **Figures 4-6**.

The ESI mass spectra at various cone voltages recorded in positive mode (m/z 2 - 300) of super-clean water, tap water and the water from Besko intake before (a) and after (b) plasma treatment with formic acid (1:1) are presented in **Figures 7-9**.

The ESI MS spectra of water samples before and after the plasma treatment, depending on the degree of water purity, show signals from the protonated forms of water aggregates $[\text{H}_2\text{O} + \text{H}]^+$, calcium and magnesium compounds and their hydrated forms. In the case of pure water, an increase in the intensity of signals $[\text{H}_2\text{O} + \text{H}]^+$ m/z 19 and 37 at $cv = 5 - 15$ V is observed, while for the remaining water samples with a high concentration of calcium and magnesium salts, an increase in the intensity of the signals of non-solvated compounds is observed (m/z 41 and 85).

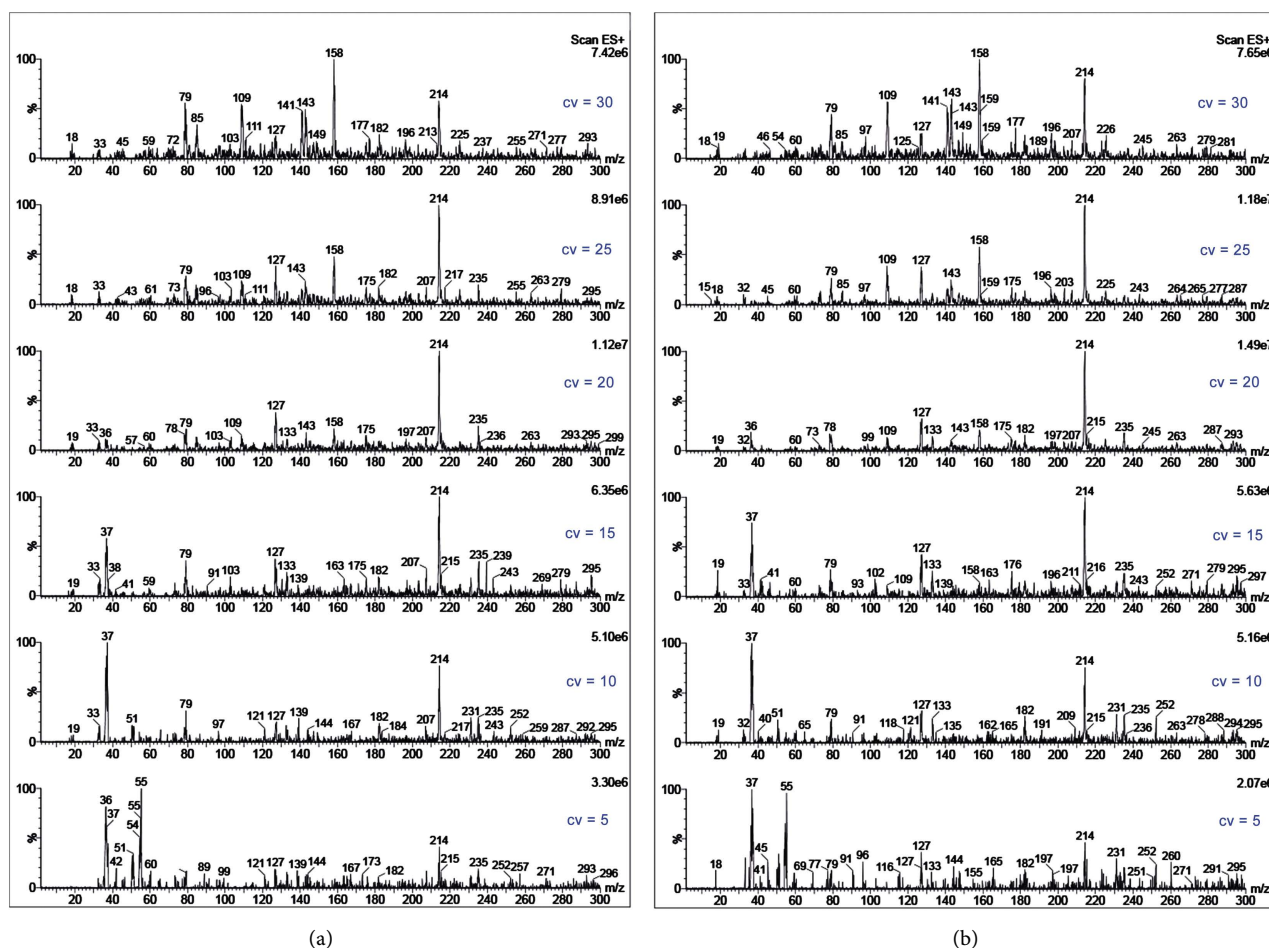


Figure 4. ESI mass spectra at various cone voltages of super-clean water before (a) and after (b) treatment with plasma. m/z $[\text{H}_2\text{O} + \text{H}]^+$ 19, $[2\text{H}_2\text{O} + \text{H}]^+$ 37, $[3\text{H}_2\text{O} + \text{H}]^+$ 55, $[6\text{H}_2\text{O} + \text{H}]^+$ 109, $[7\text{H}_2\text{O} + \text{H}]^+$ 127, $[\text{MgHCO}_3]^+$ 85, $[\text{N-butyl benzenesulfonamide} + \text{H}]^+$ 214, $[\text{N-butyl benzenesulfonamide} + \text{Na}]^+$ 236, $[\text{N-butyl benzenesulfonamide} - 56]^+$ 158 and $[\text{N-butyl benzenesulfonamide} - 71]^+$ 143, $[\text{C}_6\text{H}_7]^+$ 79 (The water supplied and stored in plastic bottles, N-butyl benzenesulfonamide—a plasticizer [41]).

In the previous paper [26], on the basis of ESI MS study of water samples before and after plasma treatment, we showed that this process significantly affects the solvation of ions in a solution. In this paper we examined the following aqueous solutions: super clean water: formic acid (1:1), tap water intake: formic acid (1:1) and water Besko intake: formic acid (1:1) before and after plasma treatment in a batch reactor, using the ESI MS method.

For super-pure water after the treatment with plasma in the technological process studied, with the addition of formic acid, the ESI MS spectrum showed only a slight increase in the intensity of the m/z $[\text{HCOOH} + \text{H}]^+$ 47 and $[2\text{xHCOOH} + \text{H}]^+$ 93 signals with respect to those of untreated water.

However, in the spectra of the tap water and the water from the Besko intake, a significant increase in intensity of the signal assigned to low-molecular solvated metal ions is observed, with a simultaneous decrease in intensity of the signals corresponding to better solvated species.

Water subjected to the treatment with plasma is characterized by a different

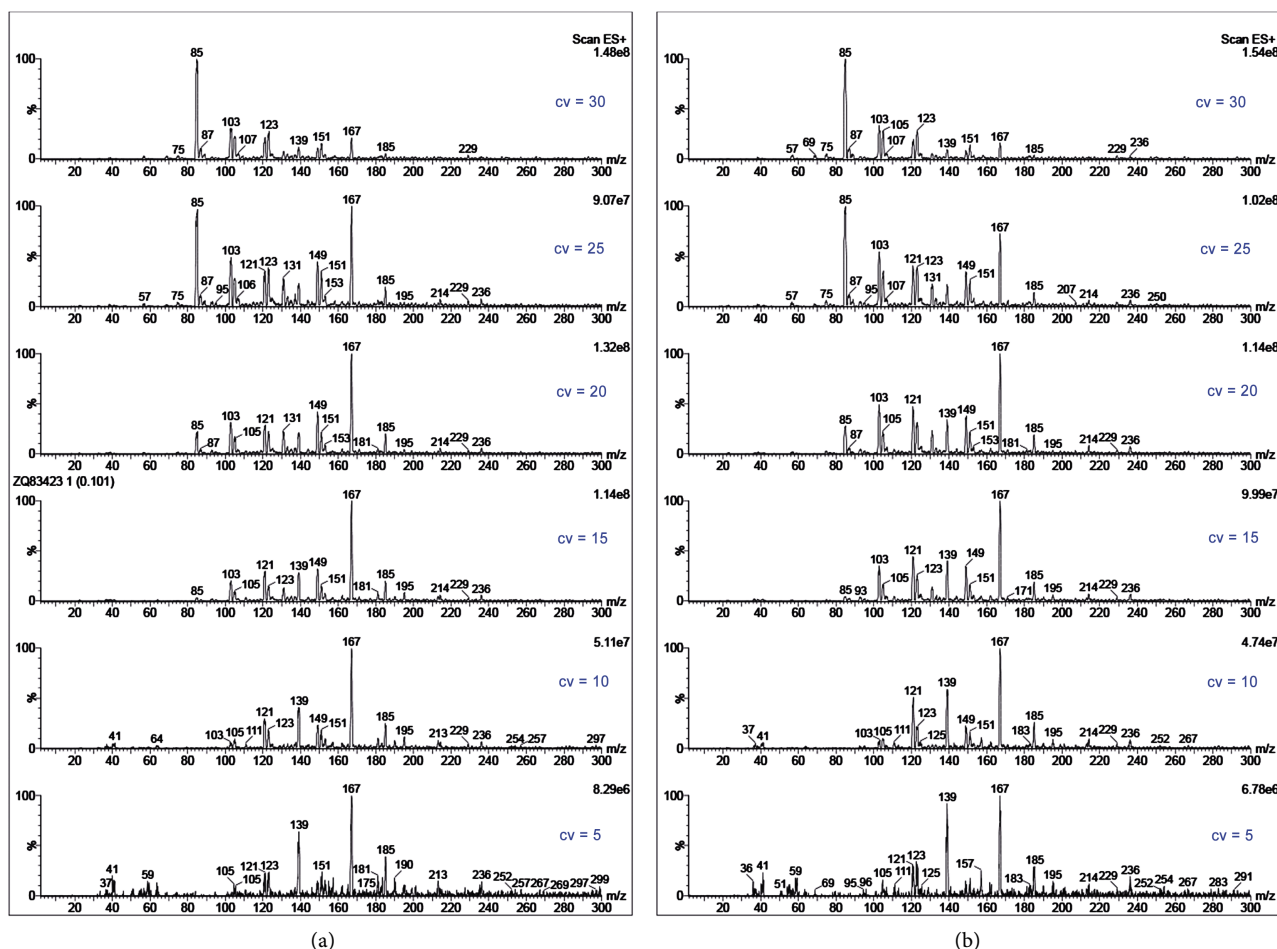


Figure 5. ESI mass spectra at various cone voltages of tap water before (a) and after (b) plasma treatment. m/z $[2\text{H}_2\text{O} + \text{H}]^+$ 37, $[\text{Na} + \text{H}_2\text{O}]^+$ 41, $[\text{MgOH}]^+$ 41, $[\text{MgOH} + \text{H}_2\text{O}]^+$ 59, $[\text{MgHCO}_3]^+$ 85, $[\text{MgHCO}_3 + \text{H}_2\text{O}]^+$ 103, $[\text{CaHCOO} + \text{H}_2\text{O}]^+$ 103, $[\text{MgHSO}_4]^+$ 121, $[\text{MgHSO}_4 + \text{H}_2\text{O}]^+$ 139, $[\text{CaHCOO} + \text{HCOOH} + 2\text{H}_2\text{O}]^+$ 167.

way of ion solvation with a smaller number of water molecules in the aqua complexes than in those made with the untreated water. The process of treatment with plasma changes the ability of water to solvation of ions present in the treated water samples, which is manifested by the m/z signals in the recorded ESI MS spectra. The water samples after the treatment in the flow-through reactor show a specific ability to dissolve gases, which is different from that of the water before the treatment. The fractions of dissolved carbon dioxide, carbonic acid and carbonate in the water samples as a function pH are shown in **Figure 10** [42] [43].

The pH of the solutions after CO_2 saturation was 5.6 - 5.8, at this pH, CO_2 is present in water mainly in the form of gas. The solubility of CO_2 gas in water was measured as a function of temperature at atmospheric pressure (**Table 3** and **Figure 11**).

The solubility of CO_2 in the water treated with the plasma compared to the starting water differs at higher temperatures, the effect increases with temperature, e.g., the solubility of CO_2 is lower by 30% - 40% at 25 °C.

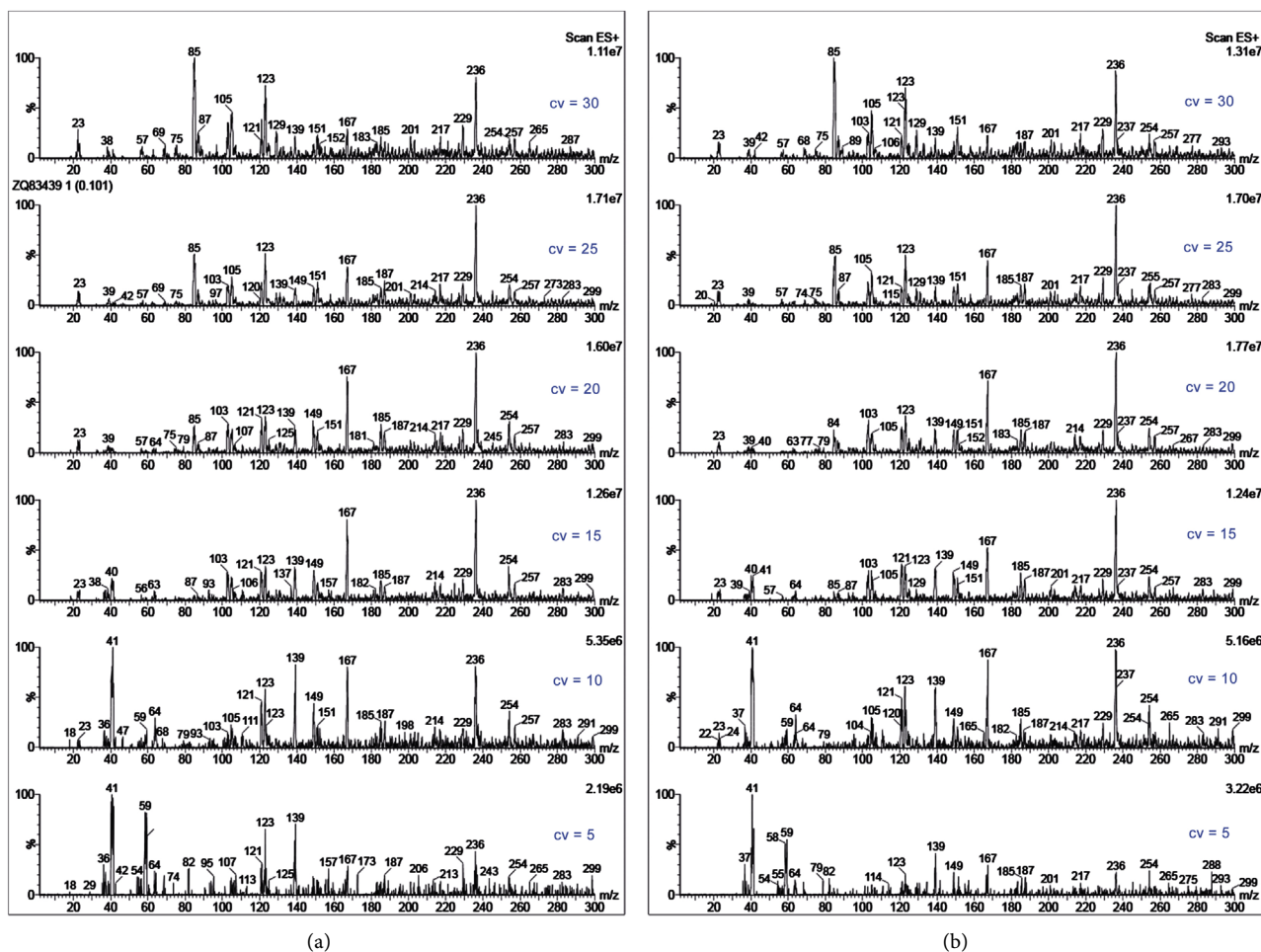


Figure 6. ESI mass spectra of water from Besko intake at various cone voltages before (a) and after (b) plasma treatment. m/z [Na]⁺ 23, [Na + H₂O]⁺ 41, [MgOH]⁺ 41, [MgOH + H₂O]⁺ 59, [MgHCO₃]⁺ 85, [CaHCOO + H₂O]⁺ 103, [MgHSO₄]⁺ 121, [MgHSO₄ + H₂O]⁺ 139, [CaHCOO + HCOOH + 2H₂O]⁺ 167, [N-butyl benzenesulfonamide + Na]⁺ 236.

Table 3. The mass solubility of CO₂ in water after processing (g gas/100g water).

Temperature [°C]	Literature data [43] [44]	The super clean water	The tap water	The water from Besko intake
1	0.3213	0.324	0.324	0.312
5	0.2774	0.276	0.269	0.274
10	0.2318	0.220	0.218	0.222
15	0.197	0.178	0.178	0.178
20	0.1688	0.143	0.124	0.132
25	0.1449	0.102	0.094	0.092
30	0.1257	0.071	0.062	0.070
35	0.1105	0.050	0.034	0.036
40	0.0973	0.020	0.020	0.020
45	0.0860	0.006	0.001	0.001
50	0.0761			
60	0.0576			

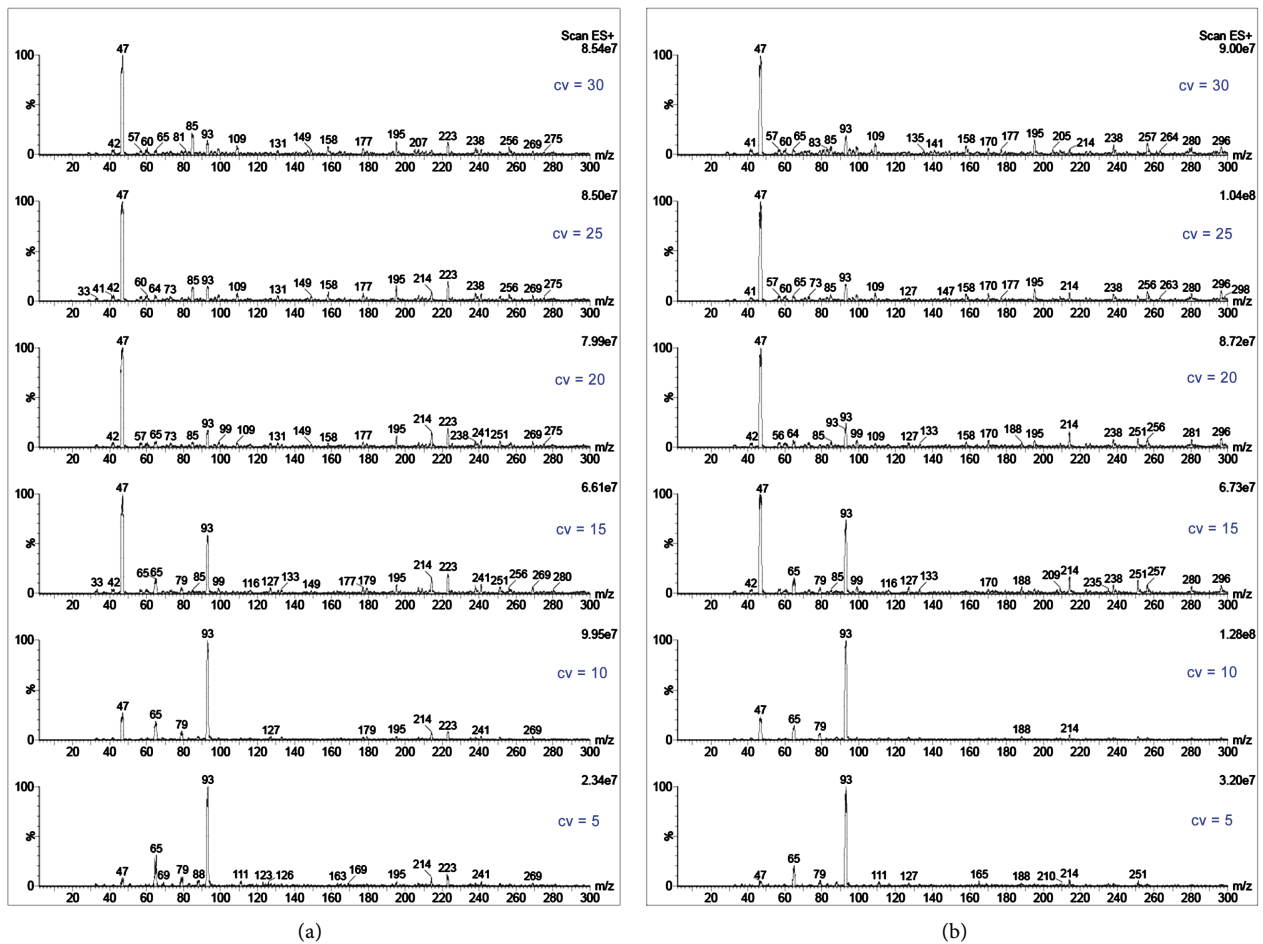


Figure 7. ESI mass spectra at various cone voltages of super clean water: formic acid (1:1) before (a) and after (b) plasma treatment. m/z $[\text{HCOOH} + \text{H}]^+$ 47, $[\text{2xHCOOH} + \text{H}]^+$ 93.

Gas oxygen dissolves in water. This process is of fundamental importance for biological life in the aquatic environment. Oxygen dissolves in water because the polar charges in the water molecule induce a dipole in the oxygen molecule. When water and oxygen molecules meet, the negative dipole of water repels electrons around the oxygen molecule, creating a temporary dipole in the oxygen molecule. Solubility of different gases in water was studied when gas was fed into water at 4°C, at a pressure of 7 bar for CO_2 and O_2 and 2.2 bar for acetylene, respectively, followed by decompression at a pressure of 993 hPa (Table 4).

The solubility of CO_2 is 0.2871 g/100g in water [43] [44]. Under conditions of elevated pressure, the solubility of CO_2 in the water treated with the plasma increases sharply compared to the starting water (e.g., 3.6 times at 5°C). Under these conditions, water can be used to absorb CO_2 .

Gas oxygen molecule O_2 is symmetrical and non-polar, but it can be the recipient of several intermolecular attractions: hydrogen bonding, Debye forces and London dispersion forces. The solubility of oxygen thus depends on the interaction of gas oxygen with water dipoles. An important role in the increased solubility of gas oxygen under increased pressure in the water samples after the

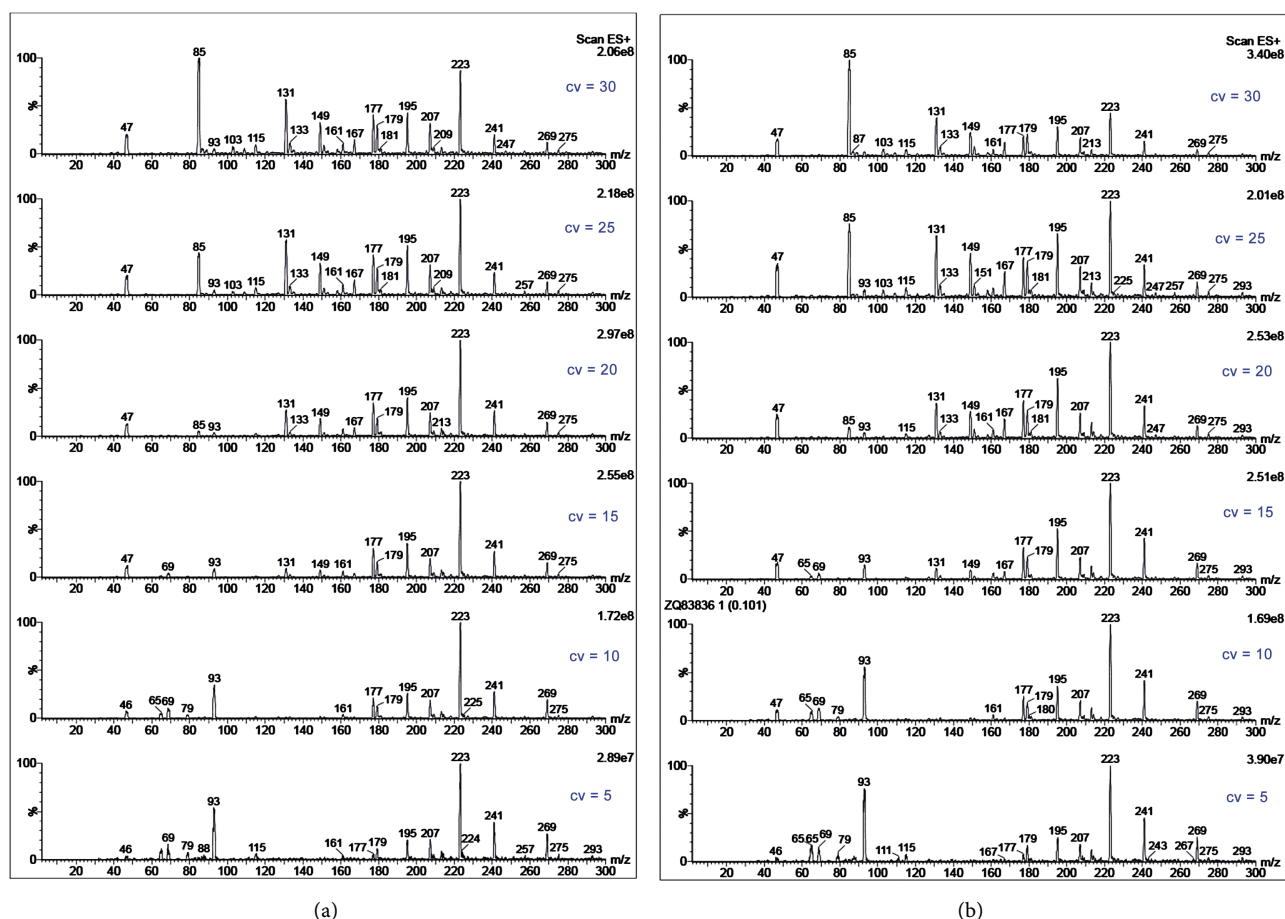


Figure 8. ESI mass spectra of tap water intake: formic acid (1:1) before (a) and after (b) plasma treatment. m/z [HCOOH + H] + 47, [2xHCOOH + H] + 93, [Ca + HCOO] + 85, [Ca + HCOO + HCOOH] + 131, [Ca + HCOO + HCOOH + H₂O] + 149, [Ca + HCOO + HCOOH + 2xH₂O] + 167, [Ca + HCOO + 2xHCOOH] + 177, [Ca + HCOO + 2xHCOOH + H₂O] + 195, [Ca + HCOO + 2xHCOOH + 2xH₂O] + 213, [Ca + HCOO + 3xHCOOH] + 223, [Ca + HCOO + 3xHCOOH + H₂O] + 241, [Mg + HCOO + HCOOH] + 115, [Mg + HCOO + HCOOH + H₂O] + 133, [Mg + HCOO + HCOOH + 2H₂O] + 151, [Mg + HCOO + 2xHCOOH] + 161, [Mg + HCOO + 2xHCOOH + H₂O] + 179, [Mg + HCOO + 3xHCOOH] + 207.

Table 4. Solubility of gases in g/100g water from Besko intake after decompression at a pressure of 993 hPa, when gas was fed into water at 4°C, at a pressure of 7 bar for CO₂ and O₂ and 2.2 bar for acetylene, respectively.

Temp (°C)	Solubility of gases (g/100g water)		
	CO ₂	O ₂	Acetylen
1	1.248	0.644	0.562
5	1.042	0.601	0.522
10	0.724	0.592	0.260
20	0.264	0.508	0.204
30	0.012	0.482	0.166
40		0.438	0.121
50		0.418	0.042
60		0.386	

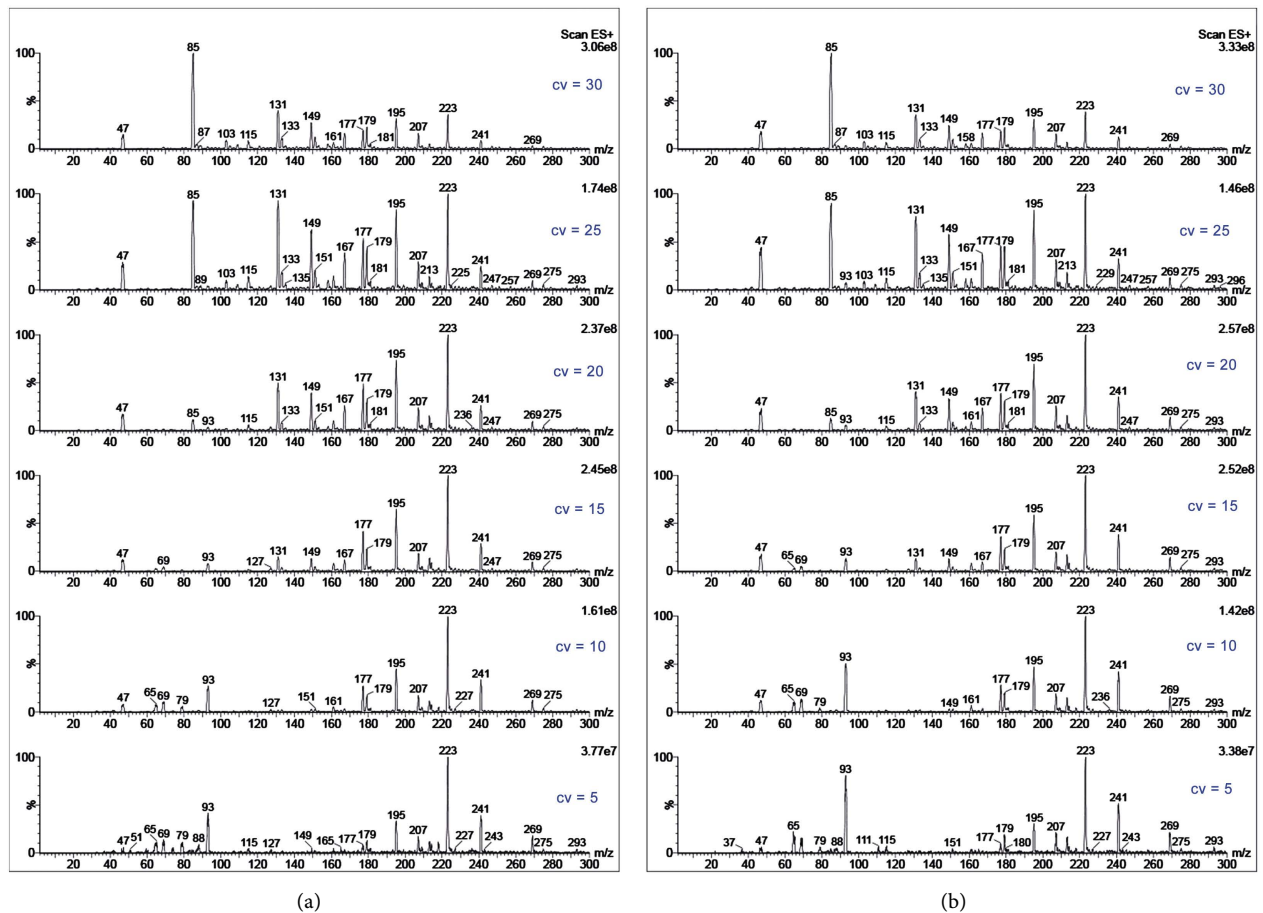


Figure 9. ESI mass spectra of water at various cone voltages from Besko intake: formic acid (1:1) before (a) and after (b) plasma treatment. m/z $[\text{HCOOH} + \text{H}] + 47$, $[2\text{xHCOOH} + \text{H}] + 93$, $[\text{Ca} + \text{COO}] + 85$, $[\text{Ca} + \text{HCOO} + \text{HCOOH}] + 131$, $[\text{Ca} + \text{HCOO} + \text{HCOOH} + \text{H}_2\text{O}] + 149$, $[\text{Ca} + \text{HCOO} + \text{HCOOH} + 2\text{xH}_2\text{O}] + 167$, $[\text{Ca} + \text{HCOO} + 2\text{xHCOOH}] + 177$, $[\text{Ca} + \text{HCOO} + 2\text{xHCOOH} + \text{H}_2\text{O}] + 195$, $[\text{Ca} + \text{HCOO} + 2\text{xHCOOH} + 2\text{xH}_2\text{O}] + 213$, $[\text{Ca} + \text{HCOO} + 3\text{xHCOOH}] + 223$, $[\text{Ca} + \text{HCOO} + 3\text{xHCOOH} + \text{H}_2\text{O}] + 241$, $[\text{Mg} + \text{HCOO} + \text{HCOOH}] + 115$, $[\text{Mg} + \text{HCOO} + \text{HCOOH} + \text{H}_2\text{O}] + 133$, $[\text{Mg} + \text{HCOO} + \text{HCOOH} + 2\text{H}_2\text{O}] + 151$, $[\text{Mg} + \text{HCOO} + 2\text{xHCOOH}] + 161$, $[\text{Mg} + \text{HCOO} + 2\text{xHCOOH} + \text{H}_2\text{O}] + 179$, $[\text{Mg} + \text{HCOO} + 3\text{xHCOOH}] + 207$.

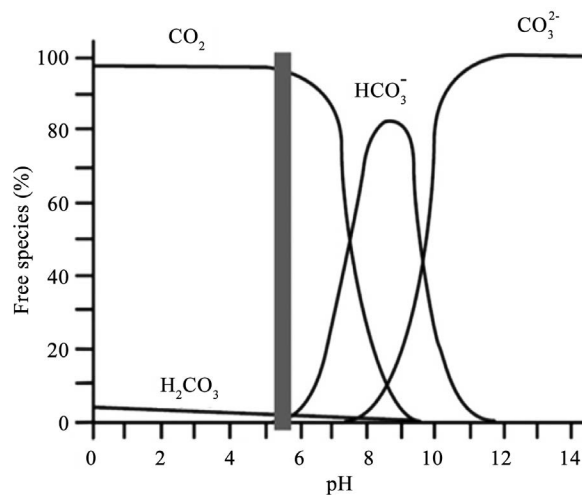


Figure 10. Fraction of dissolved carbon dioxide, carbonic acid and carbonate in water as a function of pH. The gray marking—pH water after saturation with CO_2 [42] [43].

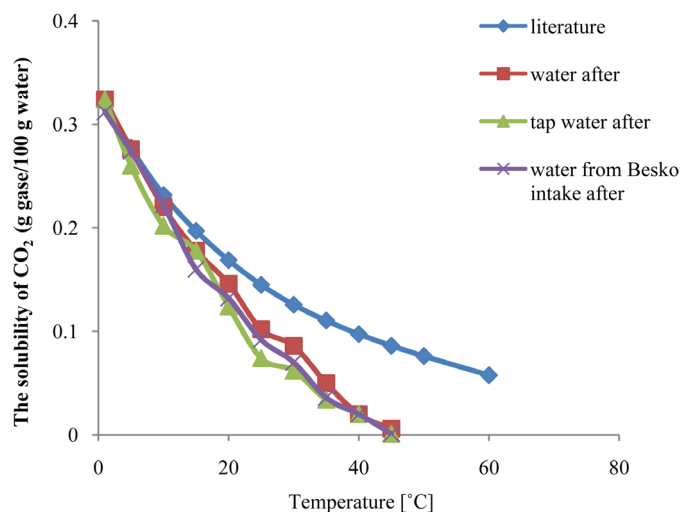


Figure 11. The mass solubility of CO₂ in water as a function of temperature at atmospheric pressure.

treatment with plasma play the voids in the water structure that can be filled with oxygen.

Molecular oxygen in liquid water becomes a dipole upon interaction with water molecules. The presented technological process significantly increases the interaction of gas oxygen with water, making it possible to obtain highly oxygenated water without the presence of reactive oxygen species. The solubility of oxygen at 4°C is 0.006232 g/100g in water [44]. The solubility of oxygen in water after the action of white plasma noise is unexpectedly very high (100 times high) and surprising.

The water solubility of acetylene (gas) was also tested. Acetylene is only slightly soluble in water, 0.120 g/100g at 25°C [44] [45]. Tzeli *et al.* [46] have presented a theoretical study of the interaction between acetylene and water molecules, which is very weak.

Acetylene in water dissolves under high pressure by being trapped in the liquid structure.

Using this precondition of introducing gas under increased pressure, higher amounts of gas have been dissolved in water. We hypothesize that at high gas pressures the introduction of gas to water after plasma treatment is readily enhanced as gas molecules can be deposited in the spaces of the altered water structure.

The ORP values of water before and after gas absorption were measured. These values change after CO₂ absorption from 135 to 140, after oxygen saturation from 135 to 170, while for acetylene from 135 to 115. This parameter may be a marker of the process of water saturation with gases.

4. Conclusion

We present a flow plasma reactor permitting modification of the physicochemical properties of water/aqueous solutions by stochastic resonance amplification

of vibrations of selected chemical species in water with electromagnetic noise generated during plasma discharge. The impact of the treatment on the properties of water was characterized by a number of methods. The basic parameters of water quality for the samples of super-pure water, tap water and the water from the intake in Besko before and after the process in the plasma reactor were measured and compared. In addition, ^{17}O NMR (FWHM), Raman spectroscopy (RS) and electrospray ionization mass spectrometry (ESI MS) methods were used to determine differences between the raw water samples and plasma-treated ones. The water samples after the treatment in the apparatus proposed were characterized by much different gas absorption properties (examples provided for CO_2 , oxygen and acetylene) as a function of temperature and pressure, which allows the use of the water after treatment in industrial processes. Worth stressing are both, the great capacity of the new reactor (4000 L/h) and the appreciably low energy consumption (20 MJ) spent for the treatment of that amount of solution. Further research on gas absorption will be carried out with other gases important from the point of view of industrial and laboratory applications.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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