Process Technology for Production of Hydrogen-Rich Water and Water Characterizing by Highly Negative Oxidation Reduction Potential

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Authors’ contributions

This work was carried out in collaboration among all authors. Authors ER, GB designed the study, wrote the protocol and author GS wrote the first draft of the manuscript. The technological line was created on the basis of scientific research at Plasma Investment. Authors GB and GS managed the literature searches. All authors read and approved the final manuscript

ABSTRACT

The construction of plasma reactors and the technological process of obtaining water rich in hydrogen and characterized by a negative oxidation potential are presented in the publication. Hydrogen-rich water was obtained based on non-plasma technology and water saturation with hydrogen gas in a reactor vessel or in glass bottles. We have developed a plasma flow reactor that allows for contactless microstructuring and modifying the properties of water / aqueous solutions by resonant stochastic vibration amplification of selected chemical compounds in water with broadband electromagnetic noise with frequencies ranging from 100 Hz to 50 MHz generated during plasma discharge. This water is then saturated with hydrogen gas in the reactor or in glass bottles. The water obtained in the reactor is characterized by a high concentration of hydrogen (8 mg/L) and a negative oxidation-reduction potential (ORP) value (−450 mV). In this technology, the process of saturating water with hydrogen in a 1 m³ tank at a temperature of 20°C takes about 30 minutes. In the technology of obtaining water with negative ORP potential in the bottles, the process of saturating the water with hydrogen lasts only 5-10 seconds. Water obtained with such technology in
the glass bottles does not contain much hydrogen gas after 24 hours, while it is characterized by a
negative ORP value of about −380 mV even for a period of three months. Obtaining water with
presented parameters is possible only in the case of water subjected to the influence of broadband
electromagnetic noise with frequencies ranging from 100 Hz to 50 MHz generated during plasma
discharge.

Keywords: Hydrogen-rich water (HRW); stochastic liquid softener system for water; hydrogen
concentration in water; oxidation reduction potential (ORP).

1. INTRODUCTION

Hydrogen water is water with dissolved hydrogen
gas (H₂). Hydrogen water is made by dissolving
gaseous molecular hydrogen into water under
pressure or by the electrolysis process of water
[1]. Interest in hydrogen-rich water (HRW) has
grown rapidly in the last decade [2-6]. This
interest is dictated, on the one hand, by the
possibility of industrial production of simple
alcohols in the reaction of hydrogen gas and CO₂
in water with the use of catalysts [7-11]. It is also
worth mentioning the use of hydrogen water in
the alternative medicine as a pro-health factor
[12-14]. The concentration of hydrogen gas (H₂)
in pure water is usually low, about 8.65 × 10⁻⁷
mg/L, and such water has limited industrial use
and no therapeutic value, and therefore, methods
are being sought to increase hydrogen concentration in water. Testing the concentration of
hydrogen gas in water is analytically difficult.
The hydrogen gas in water easily penetrates
plastic vessel walls and thus it is released
leaking into the atmosphere [15]. Better, although
more expensive choice is glass or metal bottles.
Hydrogen does not react with water. It does,
however, dissolve to the extent of about 0.00160
g kg⁻¹ at 20°C (297 K) and 1 atmosphere
pressure [16]. It is therefore advantageous to use
water with free spaces enveloped by one of the
known treatment technologies, and therefore
capable of dissolving more gases. Experimental
data for the phase behavior of (H₂O + H₂) have
been reported by several authors. Wiebe et al.
[17,18] studied the solubility of H₂ in H₂O by
means of a degassing technique whereby H₂
saturated H₂O samples were expanded to low
pressure and the amount of gas evolved could
have been measured in a gas burette. Kling [19]
studied the (H₂O + H₂) system temperatures
between 323.15 K and 423.15 K using a
synthetic variable-volume bubble-point method at
pressures between 3 MPa and 15 MPa.
Additional data were reported by Gillespie [20]
and Rahbari [21]. Sabo [22] calculated that the
most probable water cluster formed around the
hydrogen molecule within the first hydration shell
contains 16 water molecules, and the
coordination number of H₂ in liquid water is 16.
H₂-H₂O mixtures have revealed the formation of
the hydrogen clathrate hydrates. A rhombohedral
hydrate with a H₂O sublattice like ice II is stable
between 0.75 and 3.1 GPa (295 K). Above 2.3
GPa, a novel hydrate forms with the H₂O
molecules in a cubic diamond structure and with
a very high H₂:H₂O stoichiometry of 1:1. The H₂
molecules occupy voids in the H₂O framework,
thus improving the packing efficiency and
stabilizing this hydrate to very high pressures of
at least 30 GPa [23]. At low temperature (T) and
high pressure (P), gas molecules can be held in
ice cages to form crystalline molecular
compounds that may have application for energy
storage. We synthesized a hydrogen clathrate
hydrate, H₃(H₂O)₂, that holds 50 g/L hydrogen by
volume or 5.3 wt %. The clathrate, synthesized at
200-300 MPa and 240-249 K, can be preserved
to ambient P at 77 K. The stored hydrogen is
released when the clathrate is warmed to 140 K
at ambient P [24]. The H₂ gas in water solution
forms clusters. The water-water hydrogen bond
is reinforced when its proton donor moiety acts
as the hydrogen bond acceptor with respect to
the H₂ molecule and when the acceptor moiety
acts as a hydrogen bond donor. On the other
hand, the water-water hydrogen bond is
weakened when the donor water molecule
behaves as a double donor, or the acceptor
water molecule as a double acceptor [25].
Clathrate hydrates belong to a group of inclusion
solid state compounds in which the hydrophobic
guest molecule occupies the host polyhedra
cages that are formed by hydrogen bonded water
molecules. One can imagine clathrate hydrates
as solid solutions of water trapping hydrophobic
molecules. The local structure of water around
the hydrogen solute is only weakly perturbed
from its bulk structure and thermodynamically
resembles bulk water. In order to be of practical
utility for hydrogen storage, hydrogen clathrates
need to satisfy two criteria: first, they need to be
synthesized under more moderate temperature
and pressure; second, at the same
time they should maximize hydrogen occupancy [26]. Many scientists, especially those elaborating therapeutic purposes, link the oxidation-reduction potential (ORP) with concentration H₂ in water [27,28]. The oxidation-reduction potential (ORP) is used to determine the oxidation-reduction potential of water but such an approach needs more detailed explanation. The value of ORP is usually expressed in positive or negative millivolts as a measure of water’s tendency to act either as a reducing agent (electron donor) or oxidizing agent (electron acceptor). A positive ORP indicates the presence of potential oxidizers, while a negative ORP indicates the presence of potential reducers. In case of hydrogen-rich water, the negative values of ORP are an indication of the presence of a reducing agent in form of hydrogen gas (H₂). However, a value of ORP is not a real measure of concentration of hydrogen gas in the water but it only represents redox potential from two species of hydrogen in the water: hydrogen gas (H₂) and hydrogen ions (H⁺). Therefore, the pH of the solution must play a key role in this type of measurement. The values of ORP measurement are sensitive to changes in the water’s pH but also insensitive to changes in dissolved hydrogen gas, especially at high concentrations of gaseous hydrogen in the water [29,30,31,32]. H₂ is an inert molecule which can scavenge the highly active oxidants as hydroxyl radical (-OH) and peroxynitrite (ONOO−) [33].

In our previous paper [34,35] we presented an industrial method of obtaining water capable of dissolving different gasses such as CO₂ and O₂, but soon after and quite unexpectedly very good results have been recorded for hydrogen gas. Its solubility in water which passed the treatment with the use of radio noise enabled a high concentration of hydrogen to become a real admixture.

In this paper we describe a stable formation of hydrogen-rich water and water a high negative ORP potential. Changes in time between the concentration of gaseous hydrogen dissolved in water and the values of oxidation reduction potential water will be discussed and the physicochemical parameters of water at various stages of production of water rich in dissolved hydrogen and water characterized by negative ORP will be presented. The uniqueness of this method is the pretreatment of the raw water with broadband electromagnetic noise with frequencies ranging from 100 Hz to 50 MHz generated by plasma.

2. EXPERIMENTAL METHODS

For industrial scale, the water was used from our own intake (Besko, Poland) using several processes to obtain HRW. Water analysis was performed in an accredited laboratory (Oikos, Swieta 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 oxidation-reduction potential of liquids, with resolution of 1 mV, and with a standard measuring range of 0 to ±1999 mV. Meters were calibrated to +92 mV.

TDS-3 Water Quality Tester TDS Meter was used to 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 is expressed in parts per million (ppm). TDS-3 Water Quality Tester has been calibrated with 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 using two buffer solutions (pH = 4.00 and 10.00). Calibration of the pH meter was performed at the temperature at 25°C, while the measurement of pH of water in the technological process was performed at the temperature of the process.

2.1 Determination of Hydrogen Concentrations

Oxidimetry determination of the hydrogen concentration was performed by a redox titration [36]. The methylene blue-platinum colloid reagent H2Blue (Aquacentrum Munich) is effective in determining the concentration of hydrogen gas in an aqueous solution. H2Blue formula is a reagent which can be used to measure the concentration of dissolved H₂ gas in hydrogen-rich water. The H2Blue reagent was added dropwise to 20 mL samples of hydrogen-rich water until the solution changed from blue to colorless. 20 mL of hydrogen water reduces one drop of the methylene blue-platinum colloidal reagent, the concentration of dissolved hydrogen (DH) is 14.5 μmol/L or 0.03 ppm or each drop represents 0.10 ppm of hydrogen gas dissolved under pressure into a water state using a 6 mL sample of water.
3. RESULTS AND DISCUSSION

The demand for hydrogen-rich water increases annually. This is mainly due to the search for industrial methods of obtaining organic compounds in water rich in hydrogen and carbon dioxide [37] and the increasing use of hydrogen-rich water as an antioxidant for industrial and medical purposes [38,39,40]. The methods of obtaining hydrogen-rich water can be divided into two groups. The first consists in desolvation process of hydrogen gas in water at reduced temperature and often under elevated pressure, and the second is to use procedures in which the water is enriched with hydrogen using electrolysis process.

The method and device to produce antioxidant drinking water enriched with active hydrogen are known from the Polish patent application No. PL 406260 [41]. The method consists in the fact that the water taken from the source, ground by a water nozzle, is subjected to demineralization in order to achieve a uniform structure and chemical composition, and then cooled to a temperature of 2-3°C and poured into a saturation buffer tank. Hydrogen is fed to the tank through a valve, and then, through a mixing device and a dosing pump, water with hydrogen is transported to the expansion tank. A method for producing hydrogen-rich water is described in US Patent No. US10953041 [42]. The method of producing hydrogen-containing water includes the steps of: pumping water into at least one process vessel; degassing of liquids with a vacuum pump; mixing the liquid; lowering the temperature of the liquid; pumping chilled, agitated, degassed carrier liquid into a hydrogen reactor containing hydrogen gas. The concentration of hydrogen gas in the water in the hydrogen reactor vessel ranges from 3 ppm to 10 ppm.

The device for producing hydrogen-rich water with an ejector is also known from Chinese utility model No. CN209348450 [43]; it comprises a series of interconnected water tanks in which the hydrogen is dissolved in water by a series of ejectors. The method of producing hydrogen-rich water by physical method and the device for its production are known from the Chinese patent applications No. CN110482667 [44] and CN107021556 [45]. The method is carried out in a closed environment. High purity hydrogen under high pressure is fed into the water either directly or through molecular sieves.

Another method of obtaining hydrogen-rich water is method based on electrolysis [46], in which a high concentration of hydrogen in water is obtained by changing the cross-linking structure of water and creating stable hydrogen hydrates. In HRW-such water, in which the structural network of hydrogen bonds loosens, water molecules acquire additional degrees of freedom. The essence of water activation is the destruction of cluster structures to saturate water with monomolecules. The cluster of activated water contains 5-6 molecules (ordinary water: 13-16 molecules). Such water is considered more active in terms of biophysical and biological indicators. Water, activated in any way, has a high fluidity (low surface tension) and a dissolving power. The content of dissolved hydrogen in water can be from 1.6 to 10 mg/L and depends on the pressure. The ORP of water in this case is from −600 to −50 mV, but the total mineralization of water and pH do not change. The solution does not lose substantially its properties for 30 days, which allows it to be transported and stored. When the solution is sealed in glass containers, the storage life is up to one year [47,48].

In this publication, based on previous experience, we present a new technology for obtaining water rich in hydrogen. We have developed a plasma flow reactor that allows for contactless microstructuring and modifying the properties of water / aqueous solutions by resonant stochastic vibration amplification of selected chemical compounds in water with broadband electromagnetic noise with frequencies ranging from 100 Hz to 50 MHz generated during plasma discharge [49]. Plasma treated water shows different gas absorption properties than pre-process water samples [34,35,36].

We present two installations for water saturation with hydrogen gas (Figs. 1 and 2). Both installations consist of three modules. The first module (UW) for obtaining water from the natural water reservoir is equipped with a set of pumps enabling water transport to the second module (MS). The tank (ZM) of the second module with a capacity of 2 m³ connected by pipes to the plasma flow devices (RS) makes it possible to obtain, after 30 minutes, 2 m³ of water with changed physicochemical parameters as a result of plasma treatment. The third module of the system is presented in two technical solutions; the first solution is intended for obtaining water saturated with hydrogen at a temperature of
20°C in a 1 m³ tank equipped with a diffuser through which hydrogen gas is introduced under the pressure of 6 hPa. The process of water saturation with hydrogen is carried out for 30 minutes. After this time, the water from the reservoir is used technologically. The second presented technological solution is intended for the preparation of water with a stable, negative potential of ORP of water rich in hydrogen in 250 ml glass bottles (PD) (Fig. 3). At each station, water is automatically poured into the bottles after plasma treatment, and a small diffuser is introduced through which hydrogen gas is dosed for only 5-10 sec. The system enables a simultaneous process on 10 workstations.

Characteristics of the system in terms of hydrogen-rich water quality

The method of obtaining HRW is based on water taken from Besko, our own intake, which is then subjected to a unique process changing the properties of the water in a flow plasma reactor with DS1 - DSn plasma-filled noise diodes, which have A cavity anodes and cold K cathodes supplied with pulsating DC voltage. Inside the glass bodies of the DS1 - DSn noise diodes, a vacuum is maintained which is necessary to generate glow discharge plasma in air of natural or increased humidity. As a result of such a process, the physicochemical parameters of the water and the mineral composition in relation to the initial water do not change significantly, while the size of the dominant water clusters does change. This reduction in the size of the dominant water clusters enables a better placement of inert gases, e.g. hydrogen, in the spaces between the water structures and the formation of low-volume hydrogen hydrates. The water from the ZM tank is fed with hydrogen gas saturation in the ZN module. The physicochemical parameters of water, the mineral composition of hydrogen-rich water after saturation with hydrogen are retained; the dissolved oxygen concentration undergoes a significant change and oxidation-reduction potential (ORP). HRW is characterized by the content of hydrogen gas at the level of 10 ppm, approx. –400 eV ORP at pH = 7.22. The advantages of this technology in relation to those used so far include the possibility of obtaining the level of water saturation with hydrogen to the level of approx. 10 ppm without the need for additional water cooling and degassing before soaking. With the temperature of the water taken from the deep source of 13-15°C, the duration of the soaking process does not exceed 60 seconds. The physicochemical parameters of water during the process are presented in Table 1.

Fig. 1. The scheme of the installation for the production of HRW in the plasma reactor
Fig. 2. The scheme of the installation for the production of HRW in glass bottles

List of symbols in the drawing:
A - cavity anode
BP<sub>1</sub> - first back pressure regulator
BP<sub>2</sub> - second back pressure regulator
BT - bottle
CP<sub>1</sub> - first water level sensor
CP<sub>2</sub> - second water level sensor
DF - diffuser
DS<sub>1</sub>, ..., DS<sub>n</sub> - glass noise diode
FI - air filter
H<sub>2</sub> - hydrogen cylinder
K - flat cold cathode
KN - hydrogen saturation chamber
KS - mineral composition corrector
MS - noise-operated microcluster
PD - dosing pump
PG - submersible pump
PM - microcluster water pump
PP - vacuum pump
RD - regulator - pressure reducer
RS - plasma reactor
SU - water treatment plant
UW - water source
VT<sub>1</sub> - VT<sub>n</sub> - ventilation exhaust
WP - humid ambient air inlet
ZM - microcluster tank
ZN - hydrogen infiltration unit
ZG - main gas valve
ZL - linear water flow valve
ZR - vacuum regulating valve
ZW - hydrogenated water outlet valve
ZT - three-way hydrogen valve
Table 1. The values ± standard deviation of physicochemical parameters of water prior (from the source) and after processing

| No. | Reference document | Unit | Water taken from the source | Water at the output of the module MS | HRW Method 1 In the tank | HRW Method 2 In glass bottles |
|-----|-------------------|------|-----------------------------|-------------------------------------|--------------------------|-------------------------------|
| 1.  | pH                | [pH] | 7.1 ± 0.2                   | 7.2 ± 0.2                           | 7.8± 0.4                 | 7.9 ± 0.4                     |
| 2.  | Determination of specific electrical conductivity | [μS/cm] | 830 ± 91                    | 679± 75                             | 754 ± 89                 | 764 ± 90                     |
| 3.  | Determination of permanganate index | [mg O2/dm3] | <0.5                        | 1.6± 0.1                           | <0.5                     | <0.5                         |
| 4.  | Determination of the magnesium – EDTA titrimetric method | [mg Mg/dm3] | 7±1                        | 7±1                                  | 6±1                      | 6±1                          |
| 5.  | Determination of calcium | [mg Ca/dm3] | <5.0                        | <5.0                                | <5.0                    | <5.0                         |
| No. | Reference document | Unit | Water taken from the source | Water at the output of the module MS | HRW Method 1 In the tank | HRW Method 2 In glass bottles |
|-----|-------------------|------|----------------------------|-------------------------------------|--------------------------|-----------------------------|
| 6.  | Determination of Iron | PN-EN ISO 17294-2:2016-11 | [mg Fe/dm³] | 0.045± 0.012 | 0.100± 0.012 | 0.100± 0.012 | 0.100± 0.012 |
| 7.  | Determination of Manganese | PN-EN ISO 17294-2:2016-11 | [mg Mn/dm³] | 0.007± 0.001 | 0.003± 0.004 | <0.003 | <0.003 |
| 8.  | Determination of dissolved oxygen - Electrochemical probe method | PN-ISO 5814:2013-04 | [mg O₂/dm³] | 8.8± 0.7 | 8.6± 0.7 | <0.1 | <0.1 |
| 9.  | Determination of ammonium | PN-ISO 7150-1:2002 | [mg NH₄/dm³] | <0.129 | <0.129 | <0.129 | <0.129 |
| 10. | Determination of dissolved anions - nitrates | PN-EN ISO 10304-1:2009, Ac2012 | [mg NO₃/dm³] | 7.46 ± 0.97 | 8.62 ± 1.12 | 7.11 ± 0.85 | 7.09 ± 0.67 |
| 11. | Determination of dissolved anions - chloride | PN-EN ISO 10304-1:2009, Ac2012 | [mg Cl/dm³] | 33 ± 3 | 31 ± 3 | 32 ± 3 | 32 ± 3 |
| 12. | Determination of dissolved anions - sulfates | PN-EN ISO 10304-1:2009, Ac:2012 | [mg SO₄/dm³] | 32 ± 5 | 43 ± 7 | 42 ± 5 | 43 ± 7 |
| 13. | Determination of dissolved anions - Fluoride | PN-EN ISO 10304-1:2009, Ac:2012 | [mg F/dm³] | 0.251 ± 0.045 | 0.228 ± 0.041 | 0.231 ± 0.044 | 0.232 ± 0.042 |
| 14. | Total Dissolved Solids (TDS) [ppm] | | | 204±5 | 195±5 | 208±5 | 198±5 |
| 15. | Determination of hydrogen concentrations, H2Blue method | ppm | | 12±1 | 10±1 | | |
| 16. | Oxidation Reduction Potential (ORP) [mV] | | | 135±3 | 158±4 | -480±8 | -502±8 |
| 17. | Temperature | | | 13°C | 15°C | 20°C | 20°C |
Table 2. The values ± standard deviation of physicochemical parameters of water in time, characterized product durability

| Parameter Description | Reference document | Unit | Water at the output of the module MS | Water from module MS after 7 days in glass bottles | HRW after 7 days in tank reactor | Water after 7 days in glass bottles |
|-----------------------|--------------------|------|--------------------------------------|--------------------------------------------------|---------------------------------|-----------------------------------|
| pH                   | PN-EN ISO 10523:2012 | [pH] | 7.2 ± 0.2                            | 7.9 ± 0.4                                        | 8.1 ± 0.4                       | 8.1 ± 0.4                          |
| Determination of specific electrical conductivity | PN-EN-27888:1999 | [μS/cm] | 679± 75                              | 717 ± 78                                        | 720 ± 70                        | 714 ± 78                           |
| Determination of permanganate index | PN-EN ISO 8467:2001 | [mg O₂/dm³] | 1.6± 0.1                            | <0.5                                            | <0.5                            | <0.5                               |
| Determination of the magnesium – EDTA titrimetric method | PN-C-04554-4:1999 | [mg Mg/dm³] | <5.0                              | <0.5                                            | <0.5                            | <0.5                               |
| Determination of calcium content — EDTA titrimetric method | PN-ISO 6058:1999 | [mg Ca/dm³] | <5.0                             | <5.0                                            | <5.0                            | <5.0                               |
| Determination of dissolved oxygen - Electrochemical probe method | PN-ISO 5814:2013-04 | [mg O³/dm³] | 8.6± 0.7                         | 5.2± 0.7                                         | <0.5                            | <0.5                               |
| Determination of ammonium | PN-ISO 7150-1:2002 | [mg NH₄/dm³] | <0.129                             | 0.46±0.05                                       | <0.1                            | <0.1                               |
| Determination of dissolved anions - nitrates | PN-EN ISO 10304-1:2009, Ac2012 | [mgNO₃/dm³] | 8.62 ± 1.12                        | 2.4± 0.4                                        | 2.1 ± 0.4                       | 2.1 ± 0.4                          |
| Determination of dissolved anions - chloride | PN-EN ISO 10304-1:2009, Ac2012 | [mg Cl/dm³] | 31 ± 3                           | 32 ± 3                                          | 35 ±3                           | 36 ±3                              |
| Determination of dissolved anions - sulfates | PN-EN ISO 10304-1:2009, Ac2012 | [mg SO₄/dm³] | 43 ± 7                           | 55 ± 5                                          | 54 ± 5                          | 54 ± 5                             |
| Determination of dissolved anions- Fluoride | PN-EN ISO 17294-2:2016-11 | [mg F/dm³] | 0.22 ± 0.04                        | 0.26 ± 0.05                                     | 0.25 ± 0.05                    | 0.26 ± 0.05                        |
| Determination of Iron | PN-EN ISO 17294-2:2016-11 | [mg Fe/dm³] | 0.100± 0.012                      | <0.10                                          | <0.10                           | <0.10                             |
| Determination of Manganese | PN-EN ISO 17294-2:2016-11 | [mg Mn/dm³] | 0.003± ± 0.0004                  | <0.003                                         | <0.003                          | <0.003                            |
| Reference document                                      | Unit | Water at the output of the module MS | Water from module MS after 7 days in glass bottles | HRW after 7 days in tank reactor | Water after 7 days in glass bottles |
|---------------------------------------------------------|------|--------------------------------------|---------------------------------------------------|----------------------------------|-----------------------------------|
| Determination of hydrogen concentrations, H2Blue method | ppm  | 0                                    | 0                                                 | 8                                | 0                                 |
| Oxidation Reduction Potential (ORP) [mV]                |      | 158±4                                | 123±4                                             | -450±8                           | -379±8                            |
| Temperature                                             |      | 15°C                                 | 25°C                                              | 25°C                             | 25°C                              |
Characteristics and durability of the final HRW water product with negative values of ORP

In this paper, we also undertook research on the durability of the water ORP potential and concentration of hydrogen. The values of physicochemical parameters of water in time characterized product durability shown in Table 2.

Detailed studies of changes in the ORP value (Fig. 4) and the concentration of hydrogen (Fig. 5) in water in tank reactor and in glass bottles over time were carried out, focusing on changes occurring up to 60 minutes and up to 7 days, also analyzing the ORP value of water after 90 days.

As a result of hydrogen saturation into water in a steel tank (Method 1) and glass bottles (Method 2), water with dissolved hydrogen is obtained with an ORP value of -480 and -502 mV, respectively. After about 5 minutes, the ORP value of the water decreases to obtain stability after about 20 minutes. After seven days, the water in both the tank and glass bottles is characterized by high negative ORP values of -450 mV in the tank and -380 mV in glass bottles, respectively. Simultaneously with the water ORP measurements, the content of hydrogen gas in the water was determined.

As a result of hydrogen saturation into water in a steel tank (Method 1) and glass bottles (Method 2), a system with hydrogen concentration of 12 and 10 mg/L (ppm) is obtained, respectively. The concentration of hydrogen both in the tank (Method 1) and in closed glass bottles (Method 2) systematically decreases during the first hour. On the other hand, significant differences in the concentration of hydrogen in water are observed over a longer period of time. In the tank, the concentration of hydrogen in the water dropped to 9 mg/L within 7 days, i.e. by 35%, while in closed glass bottles after two days the concentration of hydrogen in water was undetectable.
The molecular hydrogen (H₂) is a neutral molecule which, when dissolved in water, has no influence on the water's pH. Negative ORP values of water -380 +/- 20 in closed glass bottles are maintained for 90 days. On the other hand, in PET bottles of water, after two days, the ORP values of water take positive values, while the concentration of hydrogen dissolved in water is immeasurable after 6 hours.

The influence of water temperature on the ORP value was investigated. For this purpose, water from the reactor at a temperature of 20°C containing 8 ppm of hydrogen and characterized by an ORP value of -450 mV was poured into an open bottle and heated to a temperature of 90-95°C. After 20 min, the water was cooled to 25°C and the water was found to be free of dissolved hydrogen (H2Blue method) and the ORP value decreased by 6-10 mV from the initial value. The pH value of the water did not change. The measurements were repeated three times. The presence of gaseous hydrogen dissolved in water has a slight effect on the ORP value of the water. The big influence on the ORP of water has of pH and the content of chemical compounds in the water [50].

4. CONCLUSION

A method of obtaining water rich in dissolved hydrogen and water characterized by negative ORP is presented. The uniqueness of this method is the interaction of the raw water with broadband electromagnetic noise with frequencies ranging from 100 Hz to 50 MHz generated by plasma. Hydrogen-rich water was obtained based on plasma technology and water saturation with hydrogen gas in a reactor vessel or in the glass bottles. The water obtained in the reactor in process of saturating water with hydrogen in a 1 m³ tank takes about 30 minutes at a temperature of 20°C is characterized by a high concentration of hydrogen (8 ppm) and a negative oxidation-reduction potential (ORP) value (-450 mV). In the technology of obtaining water with negative ORP potential in the bottles, the process of saturating the water with hydrogen lasts only 5-10 seconds. Water obtained with this technology in bottles does not contain hydrogen gas after 24 hours, while it is characterized by a negative ORP value of about -380 mV even for a period of 3 months. The physicochemical parameters and concentration of ions present in the water during the hydrogenation process practically does not change, which allows applying this method to waters with different ion content in the solution.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Kim JJ, Yu AR, Park, GS, Park SK, Jang HD, Yang HJ, Lee MY. Development of hybrid-reduced water and its antioxidative effects. Toxicol Environ Health Sci. 2011;3:227–231. DOI: 10.1007/s13530-011-0104-3
2. Sim M, Kim CS, Shon WJ, Lee YK, Choi EY, Shin DM. Hydrogen-rich water reduces inflammatory responses and prevents apoptosis of peripheral blood cells in healthy adults: A randomized, double-blind, controlled trial. Sci Rep. 2020;10:12130. DOI: 10.1038/s41598-020-68930-2
3. Ostojic SM. Hydrogen-rich water as a modulator of gut microbiota? J Functional Foods. 2021;78:104360. Available:https://doi.org/10.1016/j.jff.2021.104360
4. An R, Luo S, Zhou H, Zhang Y, Zhang L, Hu H, Li P. Effects of hydrogen-rich water combined with vacuum precooling on the senescence and antioxidant capacity of pakchoi (Brassica rapa subsp. Chinensis). Scientia Horticulturae. 2021;289:110469. DOI: 10.1016/j.scienta.2021.110469
5. Vazquez D, Guillen-Gosalbez G. Process design within planetary boundaries: Application to CO₂ based methanol production. Engineering Science 2021;246; 116891. DOI: 10.1016/j.ces.2021.116891
6. Khunathorncharoenwong N, Charoensuppenimit P, Assabumrungrat S, Kim-Lohsoontorn P. Techno-economic analysis of alternative processes for alcohol-assisted methanol synthesis from...
7. Lu C, Zhang Z, Zhou X, Hu J, Ge X, Xia C, et al. Effect of substrate concentration on hydrogen production by photo-fermentation in the pilot-scale baffled bioreactor. Bioresearch Technology 2018;247:1173–1176. DOI: 10.1016/j.bioresearch.2017.07.122

8. Liu Y, Zhang Y, Wang T, Tsubaki N. Efficient conversion of carbon dioxide to methanol using copper catalyst by a new low-temperature hydrogenation process. Chem Lett. 2007;36:1182–1183. DOI: 10.1246/cl.2007.1182

9. Jadhav SG, Vaidya PD, Bhanage BM, Joshi JB. Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies. Chem Eng Res Des. 2014;92:2557–2567. DOI: 10.1016/j.cherd.2014.03.005

10. Boretti A. Renewable hydrogen to recycle CO2 to methanol, Int. J. Hydrogen Energy. 2013;38:1806 -1812. DOI: 10.1016/j.ijhydene.2012.11.097

11. Mao WL, Mao HK. Hydrogen storage in molecular compounds., PNAS. 2004;101:708–710. DOI: 10.1073/pnas.0307449100

12. Timon R, Olcina G, Gonzalez-Custodio A, Camacho-Cardenosa M, Camacho-Cardenosa A, Guardado IM. Effects of 7-day intake of hydrogen-rich water on physical performance of trained and untrained subjects. Biol Sport. 2021;38:269–275. DOI: 10.5114/biolspor.2020.9862

13. Lapin AA, Kalayda AA, Filippov SD, Zelenkov VN. Biochemical effects of molecular hydrogen in aqueous systems International Scientific and Practical Conference: Water Power Energy Forum 2019IOP Conf. Series: Earth and Environmental Science. 2019;288:0120541OP.

14. Shen M, Zhang H, Yu C, Wang F, Sun X. A review of experimental studies of hydrogen asa new therapeutic agent in emergency and critical care medicine, Med Gas Res. 2014;4:17. DOI: 10.1186/2045-9912-4-17

15. Tanaka Y, Teraoka F, Nakagawa M, Miwa N. Dependencies of hydrogen-water on mineral-based hardness, temperatures and the container materials, and effects of the oral washing and drinking. Med Gas Res. 2020;10:67-74. DOI: 10.4103/2045-9912.285559

16. Engineering Tool Box, Solubility of Gases in Water vs. Temperature. Available:https://www.engineeringtoolbox.com/gases-solubility-water-d_1148.html

17. Wiebe R, Gaddy VL. The Solubility of Hydrogen in Water at 0, 50, 75 and 100° from 25 to 1000 Atmospheres. J Am Chem Soc. 1934;56:76–79. Available:https://doi.org/10.1021/ja01316a022

18. Wiebe R, Gaddy VL, Heins JC. Solubility of hydrogen in sodium chloride brine at high pressures. Ind Eng Chem. 1932;24:823-825. DOI: 10.1016/j.fluid.2021.113025

19. Kling G, Maurer G. The solubility of hydrogen in water and in 2-aminoethanol at temperatures between 323 K and 423 K and pressures up to 16 MPa. J Chem Thermodyn. 1991;23:531-541. DOI: 10.1016/S0009-2541(05)80095-3

20. Gillespie PRC, Wilson GM. Vapor-liquid equilibrium data on water-substitute gas components: N2 - H2O, H2 - H2O, CO - H2O, H2 - CO - H2O, and H2S - H2O. GPA Research Report. 1980;1-34.

21. Rahbari A, Brenkman J, Hens R, Ramdin M, van den Broeke LJ, Schoon R, et al. Solubility of water in hydrogen at high pressures: A molecular simulation study. J Chem Eng Data. 2019;64:4103–4115. DOI: 10.1021/acs.jced.9b00513

22. Sabo D, Rempe SB, Greathouse JA, Martin MG. Molecular studies of the structural properties of hydrogen gas in bulk water, Molecular studies of the structural properties of hydrogen gas in bulk water. Molecular Simulation. 2006;32:269–278. DOI: 10.1080/08980260600728621

23. Vos WL, Finger LW, Hemley RJ, Mao HK. Novel H2-H2O clathrates at high pressures. Phys Rev Lett. 1993;71:3150-3153. DOI:10.1103/PhysRevLett.71.3150.

24. Mao WL, Mao HK, Hydrogen storage in molecular compounds. PNAS. 2004;101:708–710. Available:doi:10.1073/pnas.0307449100

25. Sadlej J, Cybulski SM, Szczeńiak MM. Ab initio study of nonadditive effects in the (H2O)2·H2. Cluster, Phys. Chem. 1996;100:10875–10881. Available:https://doi.org/10.1021/jp952781 +
26. Sabo D, Varma S, Martin MG, Rempe SB. Studies of the thermodynamic properties of hydrogen gas in bulk water. J Phys Chem B. 2008;112:867-876. DOI: 10.1021/jp075459v

27. Kampbell DH, Wilson JT, McInnes DM. Determining dissolved hydrogen, methane, and vinyl chloride concentrations in aqueous solution on a nanomolar scale with the bubble strip method. Proceedings of the 1998 Conference on Hazardous Waste Research. Available:https://engg.ksu.edu/HSRC/98Proceed/15Kampbell/15kampbell.pdf

28. Goncharuk VV, Bagrii VA, Melnik LA, Chebotareva RD, Bashtan SY. The Use of Redox Potential in Water Treatment Processes. J Water Chem Technol. 2010;32;1–9. DOI:10.3103/S1063455X10010017

29. Oxidation Reduction Potential (ORP) International Hydrogen Standards Association. Available:https://www.intlhsa.org/oxidation-reduction-potential/orp/

30. Sharpe R. Analysis of the relationship between dissolved molecular hydrogen gas, pH and ORP using the nernst equation. Available:https://nebula.wsimg.com/e00f13c6a421e24d28be6558ff968736?AccessKeyId=781CCBA394A3C0D544A&disposition=0&alloworigin=1

31. Miyahara T, Öizumi M, Nakatani T, Sato T. Effect of voltage polarity on oxidation-reduction potential by plasma in water. AIP Advances. 2014;4;047115. Available:https://doi.org/10.1063/1.4871475

32. Chang CN, Ma YS, Lo CW. Application of oxidation-reduction potential as a controlling parameter in waste activated sludge hydrolysis. Chemical Engineering Journal 2002;90:273–281. DOI: 10.1016/S1385-8947(02)00015-3

33. Ohsawa I, Ishikawa M, Takahashi K, Watanabe M, Nishimaki K, Yamagata K, et al. Hydrogen acts as a therapeutic antioxidant by selectively reducing cytotoxic oxygen radicals. Nat Med. 2007;13:688–694. DOI: 10.1038/nm1577

34. Yelkin I, Reszke E, Schroeder G. Glow discharge plasma as a cause of changes in aqueous solutions: The mass spectrometry study of solvation processes of ions. Asian J Chem. 2021;33;220-230. DOI:10.14233/ajchem.2021.2301

35. Yelkin I, Reszke E, Binkiewicz G, Schroeder G. The industrial production of water dedicated to absorption of gases. Journal of Water Resource and Protection. 2021;13:632-653. DOI: 10.4236/jwarp.2021.138034

36. Seo T, Kurokawa R, Sato B. A convenient method for determining the concentration of hydrogen in water: use of methylene blue with colloidal platinum. Medical Gas Research 2012;2:1. Available: http://www.medicalgasresearch.com/content/2/1/1

37. Hadjadi R, Csizmadia IG, Mizsey P, Jensen SK, Viskolcz B, Fiser B. Water enhanced mechanism for CO2 – Methanol conversion. Chem Phys Letters. 2020;746:137298. DOI:10.1016/j.cplett.2020.137298

38. Davoodabadl A, Mahmoudi A, Ghasemi H. The potential of hydrogen hydrate as a future hydrogen storage medium. Science. 2021;24;101907. DOI: 10.1016/j.scitalk.2020.101907

39. Tanaka Y, Teraoka F, Nakagawa M, Miwa N. Dependencies of hydrogen-water on mineral-basedhardness, temperatures and the container materials, and effects of the oral washing and drinking. Med Gas Res. 2020;10:67-74. DOI: 10.4103/2045-9912.285559.

40. Russell G, Nenov A, Kisher H, Hancock JT. Molecular Hydrogen as Medicine: An Assessment of Administration Methods. Hydrogen. 2021;2:444–460. Available:https://doi.org/10.3390/hydrogen2040025

41. Patent PL 405260. Method and device for antioxidant production drinking water enriched with active hydrogen.

42. Patent US10953041. Hydrogen-containing composition.

43. Patent CN209348450. A device for producing hydrogen-rich water with an ejector.

44. Patent CN110482667. A method of producing hydrogen-rich water by physical method and a device for it production.

45. Patent CN107021556. Apparatus and method of automatic production of high concentration water rich in hydrogen.

46. Kim JJ, Yu AR, Park GS, Park SK, Jang HD, Yang HJ, Lee MY. Development of hybrid-reduced water and its antioxidative
effects. Toxicol Environ Health Sci. 2011;3:327–231.
DOI: 10.1007/s13530-011-0104-3
47. Lapin AA, Kalayda AA, Filippov SD, Zelenkov VN. 2019 IOP Conf. Ser.: Earth Environ Sci. 288 012054.
48. Patent RF2557974. A61P43, A61K33 Hydrogen cocktail - a means to stimulate lymphatic drainage, the way it is produced.
49. Patent PL 238174. Method and device for microstructuring of liquids, including body fluids.
50. Tanaka Y, Teraoka F, Nakagawa M, Miwa N. Dependencies of hydrogen-water on mineral-based hardness, temperatures and the container materials, and effects of the oral washing and drinking. Med Gas Res. 2020;10;67–74.
DOI: 10.4103/2045-9912.285559

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