

CONTINUOUS PRODUCTION OF LARGE VOLUMES OF PLASMA ACTIVATED WATER FOR AGRICULTURE

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ABSTRACT

This article is devoted to the issues of using plasma technology to produce plasma-activated water, which serves as liquid nitrogen fertilizers. The use of plasma-activated water in crop production is associated with seed treatment, subsequent stimulation of seed germination, and the stimulation of agricultural crop growth. The study proposes a new plasma system for the direct production of activated water based on a hybrid electric discharge, which combines equilibrium and non-equilibrium plasma. This system operates in a mixture of air and water. The process of plasma-chemical treatment is implemented in a plasma module with a pulsation mode of electric discharge combustion in an aqueous solution. This system is environmentally friendly, as it does not use additional chemicals (since air and water plus electricity are used as raw materials) and does not produce waste. Using the developed plasma system, plasma-activated water with a high content of stable active forms of oxygen and nitrogen (NO_3^- , NO_2^- , H_2O_2 , O_3 , etc) was obtained. Such plasma-activated water has high potential for effective use, as the long-lived active compounds contained in the activated water can participate in plant metabolism and serve as nutrients for them. The small size and weight of the plasma unit, along with its sufficiently high productivity, allow its use in small and medium-sized farms. This ensures environmentally friendly fertilizer production on-site, provides flexibility to meet changing demand, significantly reduces transportation costs, and minimizes losses. The substantial energy consumption required for the production of plasma-activated water can be offset by integration with renewable energy sources.

KEYWORDS: plasma agriculture, hybrid plasma, nitrogen fixation, plasma/liquid interfacial, plasma chemical reactor, plasma fertilizer production, plant growth

INTRODUCTION

Nitrogen fertilizers are essential for the growth of agricultural crops and, consequently, for feeding the growing population. Modern fertilizer production has supported the growth of industrial societies for more than a century. Approximately 40–60 % of global food production is related to the use of commercial fertilizers. According to statistical data, the global production volume of ammonia (NH_3) in 2019 was 235 mln t, making it the second most produced chemical commodity after sulfuric acid (H_2SO_4) [1]. Ammonia plays an important role in the agricultural industry for the production of fertilizers. The primary raw material for the production of nitrogen fertilizers is fossil fuel, and their production is significantly dependent on the extraction of coal and natural gas. The most commonly used method for ammonia production is the Haber-Bosch process. The drawbacks of this technology include high levels of greenhouse gas emissions, exceeding 2.16 kg CO_2 -equivalent per kg of NH_3 , as well as a large amount of energy consumption — more than 30 GJ per ton of NH_3 [2].

As a result, the cost of produced fertilizers depends on market conditions and tends to be high, while greenhouse gas emissions during their production are very significant. In this context, farmers often find themselves making decisions based on prices rather than plant needs, leading to inefficient nitrogen use and low application efficiency. Moreover, entrenched supply chains often overlook the nuances of developing economies, making nitrogen unavailable where it is most needed. Over the past few decades, the world has dramatically changed due to a sharp increase in population. The consequence of this population growth is high demand for food, water, and energy resources. The application of nitrogen fertilizers is one solution to the food security issue that has arisen globally. However, it should be noted that environmental sustainability is at risk due to excessive use of chemical nitrogen fertilizers, which negatively impact all segments of the environment, namely soil, water, and air, and also affects the health of humans and animals. Several strategies are employed to cushion the harmful impact of nitrogen fertilizers. In particular, the use of compost and organic manure, slow-release and controlled-release fertilizers, as well as nano-fertilizers is encouraged. Another widely accepted solution for reducing the excessive use of chemical fertilizers is

to improve the nitrogen uptake efficiency of agricultural crops. Thus, the issue of the form and role of nitrogen fertilizers requires rethinking [3]. The current challenge is to shift the paradigm in the field of nitrogen fertilizers in agriculture towards environmentally friendly production, borrowed from nature, obtaining them solely from nitrogen and oxygen in the air with minimal energy consumption at the point of application. The specific rate of fixed nitrogen should be close to 200 grams per 1 kWh of consumed electricity.

It is expected that new plasma technologies, which provide maximum efficiency with minimal costs, will contribute to the sustainable development of various sectors of the economy. In this regard, a unique method of transferring chemical reactivity and energy from plasma to water without the presence of any chemical substances is currently being actively researched. The interaction of plasma with water results in the creation of a new product with noticeable and diverse activity, referred to as plasma-activated water (PAW) [4]. PAW is environmentally friendly and promising solution for a wide range of applications: from water treatment and biomedicine to agriculture. The application of PAW minimizes the stages of the production process and either eliminates or significantly reduces the use of expensive and/or hazardous reagents. PAW is also used for the inactivation of microorganisms (bacteria, fungi, viruses, algae, pests, etc.), preservation of food products (fruits, vegetables, dairy and meat products, including seafood, etc.), disinfection of dental and medical equipment surfaces, removal of pesticides, selective destruction of cancer cells, preparation of viral vaccines, seed germination, plant growth, as a source of nitrogen fertilizers, and more. It follows that the application of PAW allows for the avoidance of disinfectants (chemicals), preservatives, fertilizers,

pharmaceutical ingredients, and other substances that cause various environmental and health issues. Despite the promising developments in this field, there are currently only a few examples of the practical application of plasma water activation [5–7]. The presented study focuses on the production of PAW. It analyzes issues related to the plasma-chemical synthesis of reactive particles present in the water, as well as various mechanisms that regulate the activity of PAW in agricultural applications, the problems of PAW efficiency and selectivity, and the possibilities for scaling the process. The aim is to advance the understanding of the fundamental aspects of PAW chemistry necessary for optimizing biochemical activity and transitioning this environmentally and human health-safe technology into an energy-efficient strategy for practical application.

The interaction of plasma with water alters its physicochemical properties, which is associated with the formation of reactive oxygen-nitrogen species (RONS). Figure 1 shows the formation of RONS [8, 9].

In the initial stage, dissociation of oxygen, nitrogen, water molecules, and others occurs in the presence of high-energy electrons. These dissociated particles combine to form various compounds, such as NO_x , O_3 and H_2O_2 . Due to the airflow, these particles (via diffusion or convection) enter the liquid-gas interphase boundary, where all short-lived particles disappear, while long-lived ones survive. Subsequently, these “surviving” particles, upon dissolving in water, react with each other and with water molecules, leading to the formation of stable RONS (NO_3^- , NO_2^- , H_2O_2 , O_3 , etc.).

Furthermore, if certain readily accessible metals such as Mg, Al, Zn, and Cu are separately immersed in water activated by plasma, they undergo oxidation

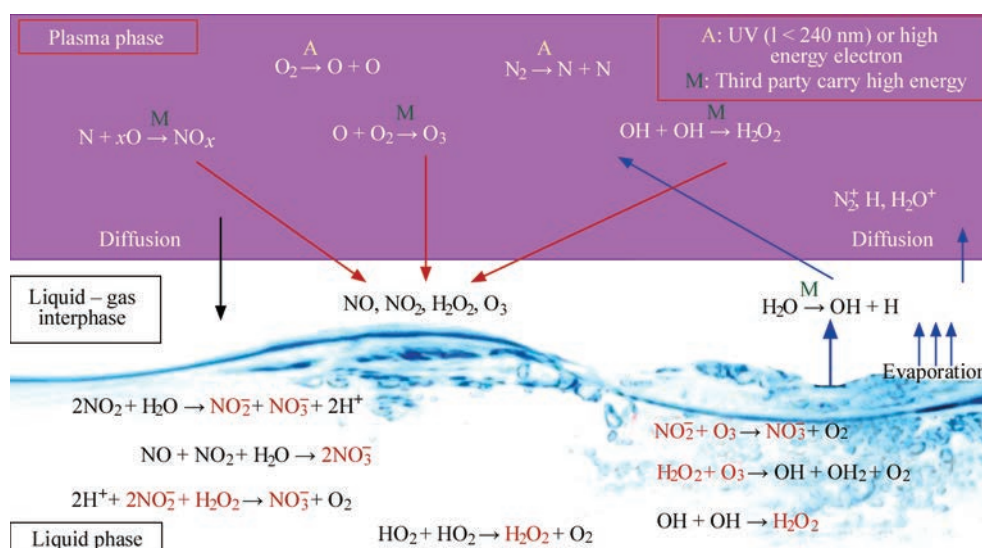


Figure 1. Scheme explaining the physicochemical changes occurring in water (the formation of RONS) as a result of the interaction of plasma with water [8]

in the water, releasing electrons that reduce hydrogen ions to hydrogen atoms. The liberated hydrogen atoms then reduce plasma-excited nitrogen back to ammonia. The reduction of hydrogen ions by metals not only regulates pH but also enhances the rate of ammonia synthesis by providing additional hydrogen donors. This process opens up new avenues for further research in sustainable nitrogen fixation [10].

In the study [11], hydroxyl radicals were apparently introduced for the first time into the electrocatalytic nitrogen oxidation reaction (NOR) to produce nitrates. Here, cobalt tetraoxide (Co_3O_4 , Figure 2, *a*) serves not only as an electrocatalyst but also as a nanozyme (in conjunction with hydrogen peroxide, producing OH), thereby making this compound suitable as a highly efficient electrocatalyst for NOR to synthesize nitrates. $\text{Co}_3\text{O}_4 + \text{OH}$ demonstrates excellent performance in NOR, employing an environmentally friendly approach. This compound is the most active catalyst among non-precious metals reported for the NOR process to date. Additionally, this catalyst exhibits long-term electrochemical and structural stability. Energy barriers for the conversion of N_2 to N_2OH^* (the rate-determining step) were determined from Figure 2, *b*. It was found that the introduction of the hydroxyl radical OH ($\text{Co}_3\text{O}_4/\text{H}_2\text{O}_2$ system) significantly reduces the energy barrier and accelerates the reaction. Figure 2, *c* illustrates the entire scheme of the electrocatalytic NOR process.

Below, we will discuss the application of PAW for seed germination, plant growth, as well as its use as a nitrogen source for various agricultural and aquaculture purposes. PAW can be utilized to enhance seed germination rates. Setting aside the methods of producing PAW, we will focus on the influence of

concentrations of major components NO_3^- , NO_2^- can also be oxidized to NO_3^- or it can interact with H_2O_2 , resulting in the formation of peroxynitrous acid (ON-OOH). The presence of nitrogen in the soil is a primary factor influencing plant growth and determining crop yield. From this perspective, increasing nitrate concentrations through plasma processing potentially serves as a crucial nitrogen source for plant growth and development.

In study [12], PAW was obtained by surface treatment of water using gliding arc discharge with a power of 4.96 W for up to 20 min, resulting in an average nitrate and nitrite concentration of 6 mg/L. Water absorption capacity is crucial for seed germination as it induces swelling and softening of seed coats. PAW significantly improves the water uptake rate by radish, alfalfa, and pea seeds [12]. The water uptake rates for PAW-irrigated seeds (radish, alfalfa, and pea) were $59.94 \pm 0.2\%$, $147 \pm 1.0\%$, and $147.70 \pm 1.3\%$ after 10 hours of irrigation, respectively, which was higher compared to seeds treated with non-ionized water (58.49 ± 0.3 , $120 \pm 0.9\%$, $120.59 \pm 1.2\%$, respectively). Overall, using PAW for seedling irrigation led to favorable physical and chemical changes in them, resulting in significantly higher yields over a shorter period.

PAW can serve as an alternative to chemical fertilizers in agriculture. The effect of PAW treatment at two concentrations (1.5 or 3.0 mg/L NO_3^-) on various morphological, physiological, biochemical parameters, and yield of *Lactuca Sativa* L., cultivated in pots of two different volumes (400 or 3200 cm^3), was studied in research [13]. The study results indicated that both PAW concentrations did not affect germination at the beginning of the process. A positive effect of treat-

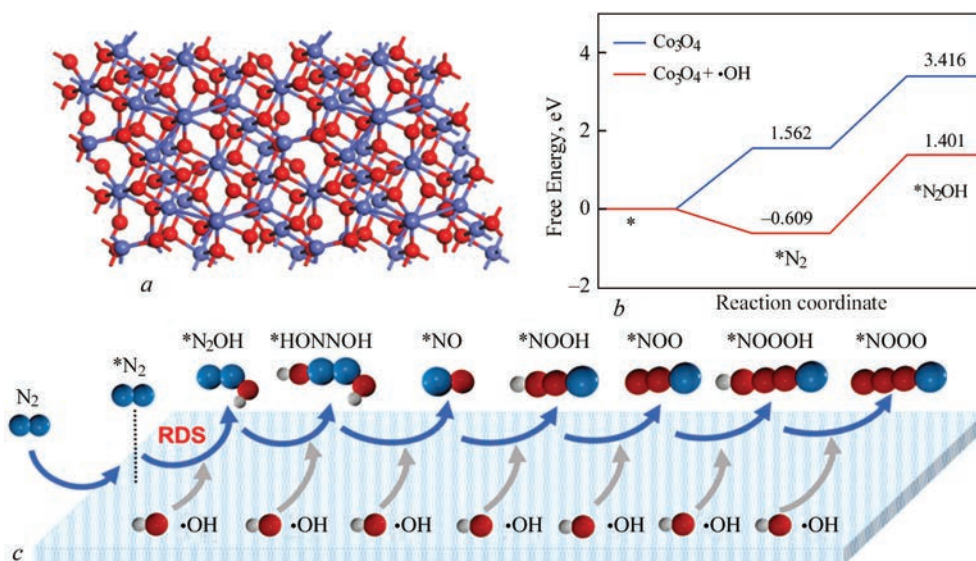


Figure 2. To the use of a Co_3O_4 catalyst: *a* — crystal structure of Co_3O_4 ; *b* — free energy diagram of the electrooxidation reaction N_2 on Co_3O_4 and $\text{Co}_3\text{O}_4 + \text{OH}^-$; *c* — simplified mechanism of NO_3 production on the surface of catalysts [11]

Table 1. Physicochemical properties of the PAW

Water samples	pH	Nitrite NO ₂ ⁻ , mg/L	H ₂ O ₂ , mg/L	Nitrate NO ₃ ⁻ , mg/L	Conductivity, us/cm
Deionized water (DW)	5.74±0.06	0.00	0.00	0.00	1.53±0.13
PAW5 min (PAW5)	3.62±0.02	1.09±0.11	0.09±0.01	25.29±2.88	118.10±2.26
PAW7 min (PAW7)	3.34±0.03	1.24±0.12	0.14±0.01	49.05±2.61	218.50±9.64
PAW12 min (PAW12)	2.94±0.08	1.85±0.07	0.27±0.02	102.67±6.30	460.33±15.25
PAW19 min (PAW19)	2.62±0.07	3.68±0.12	0.88±0.04	202.87±8.74	972.93±32.41
PAW40 min (PAW40)	2.37±0.04	5.17±0.16	1.31±0.04	389.08±12.24	1847.00±79.19

ment was observed in the increase of lettuce length at the 1.5 mg/L NO₃⁻ concentration, while chlorophyll content significantly increased at the 3.0 mg/L NO₃⁻ concentration. Dry weight was notably higher in lettuce treated with PAW grown in larger pots after 57 days. Nitrite content in lettuce grown in larger pots was lower compared to lettuce grown in smaller pots, regardless of PAW concentration.

PAW samples in [14] were obtained using five different treatment durations and utilized in the experiment. The samples are denoted as PAWi (i — plasma treatment time in minutes): PAW5, PAW7, PAW12, PAW19 и PAW40 (see Table 1).

The use of PAW increases the total root length and the number of root hairs in *Arabidopsis* roots, which serves as a typical model for studying plant genetics and developmental biology (Figure 3).

In [15], the foliar application of PAW was evaluated on plant growth during the vegetative period. Periodic application of PAW positively influenced the chlorophyll content in maize leaves. Chlorophyll content decreased over time with maximum application of distilled water by 34.6 and by 24.7 % with PAW at the same doses. Foliar application of PAW significantly increased the electrical capacity of roots, aboveground biomass, and nutrient content in dry matter, except for nitrogen. Periodic application of PAW increased nitrogen content in aboveground dry matter by 13.3 %. The chemical activity of PAW was assessed based on hydrogen peroxide, nitrite, and nitrate formation. The

average concentration of hydrogen peroxide in PAW was (0.7±0.2) mg/L (0.022±0.004 mmol/L), nitrite concentration was (1.071±0.005) mg/L, and nitrate concentration was (24.7±2.3) mg/L.

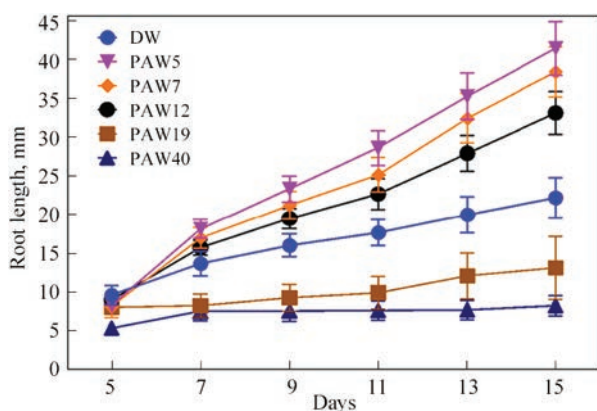
The results obtained by the authors [16] indicate that PAW can effectively stimulate the growth of wheat seedlings and positively influence their metabolism, particularly in nutrient-deficient soil.

The enhanced response to the use of PAW is likely associated with increased water absorption, which leads to accelerated utilization of seed nutrient reserves and nitrogen metabolism during the vegetative growth of wheat. Seeds grown in PAW interact with H₂O₂ primarily in the early stages of growth during imbibition and germination, while NO₂⁻ and NO₃⁻ are metabolized after the seeds begin to grow.

At Kwangwoon University, Seoul, South Korea, physiological, biochemical, and molecular changes were observed in tomato seedlings treated with PAW compared to the control seedlings [17]. The altered chemical properties of water under the influence of cold plasma are shown in Figure 4, *a–c*.

The effects of PAW treatment at different time intervals are presented in Figure 5, *a–c*. Pre-germinated lettuce plants were grown in pots with soil and irrigated with PAW or solutions of H₂O₂ and/or NO₃⁻. After 5 weeks, growth parameters, leaf quantity and quality, fresh and dry plant mass, chlorophyll content of photosynthetic pigments, photosynthesis rate, and the activity of antioxidants and superoxide dismutase (SOD) enzymes were determined. Lettuce plants irrigated with PAW, compared to the chemically equivalent solution of H₂O₂ and NO₃⁻, had the same dry mass, but PAW induced higher content of photosynthetic pigments, higher photosynthesis rate, and lower SOD activity. NO₃⁻ primarily contributed to an increase in dry weight, content of photosynthetic pigments, photosynthesis rate, and better plant appearance. H₂O₂ contributed to an increase in dry weight and induced SOD activity. Overall, H₂O₂ and NO₃⁻ at appropriate concentrations can stimulate plant growth and influence their physiological properties.

In the study [18], the role of PAW was evaluated by examining its effects on lettuce plants and compar-

**Figure 3.** Effect of PAW on root length at the developmental stage of *Arabidopsis* [14]

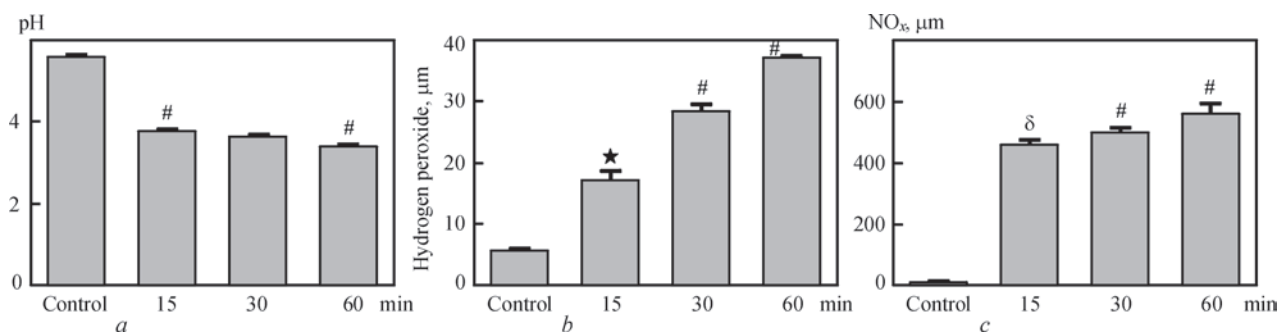


Figure 4. Biochemical properties of PAW: *a* — pH; *b* — H_2O_2 ; *c* — NO_x before and after different times of water exposure to plasma. Mean $\pm$ SE ($n=3$) of each experiment represented in terms of error bars. The SE between the mean of the control and the treatment group was analyzed by student t-test. p-value denoted by * ($p < 0.05$), δ ($p < 0.01$), # ($p < 0.001$) [17]

ing the influence of PAW with the effects of H_2O_2 and/or NO_3^- (considering solutions of various concentrations). chemical composition and pH of plasma activated water (PAW) and various $\text{H}_2\text{O}_2/\text{NO}_3^-$ solutions are shown in Table 2.

The Company VitalFluid B.V. from Eindhoven University positions itself as global leader in PAW application [19]. The synthesized in plasma liquid nitrogen fertilizer is referred to as “Organic nitrogen VitalFluid”. In organic plant cultivation, the USDA (U.S. Department of Agriculture) does not permit the use of nitrogen fertilizers in a form directly available

for crop uptake. Typically, nitrogen is applied in an organic form, which must be processed by microorganisms before becoming available to the crop. Nitrogen fertilizers in the form of PAW are readily accessible for assimilation, providing a clear advantage over organic fertilizers.

The VitalFluid B.V. company developed an organic nutrient solution in accordance with USDA standards using PAW and tested it in a pilot production system. A greenhouse experiment (crop cultivation area of 120 m^2) was conducted with tomato crops grown in a hydroponic system on a peat substrate, fol-

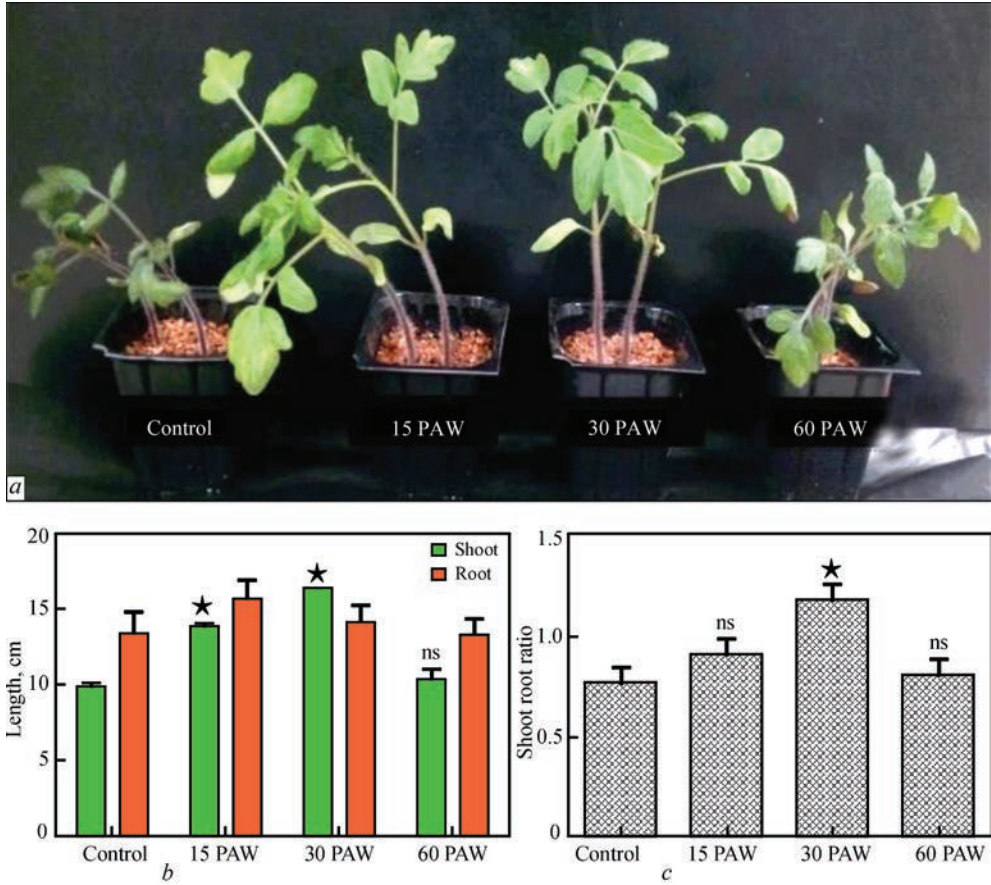


Figure 5. Effect of PAW treatment at different time intervals: *a* — on the physiological state of tomato seedlings (28 days) grown in vermiculite; *b* — shoot and root length (cm); *c* — shoot and root length ratio; $\pm$ SE of mean ($n = 3$) of each experiment represented in terms of error bar. Significant difference between the mean of control and treatment group was analyzed by student t-test. p-value denoted by * ($p < 0.05$), δ ($p < 0.01$), and # ($p < 0.001$) [17]

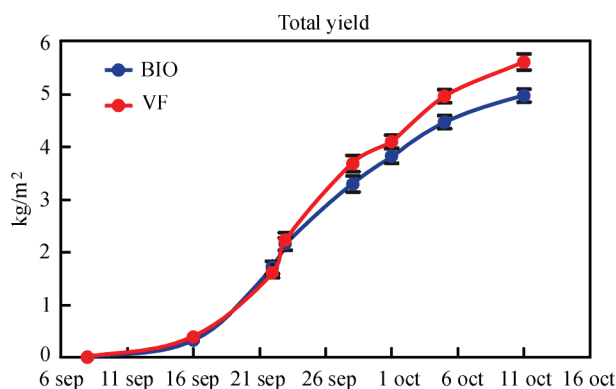
Table 2. Chemical composition and pH of PAW and various $\text{H}_2\text{O}_2/\text{NO}_3^-$ solutions

Solution/variant (abbrev.)	H_2O_2 , mM	NO_3^- , mM	pH
Control (tap water)	—	~0.02	~7.5
PAW	~0.42	~0.85	~7.5
H_2O_2 (4)	0.4	—	~7.6
H_2O_2 (1)	1.0	—	~7.7
H_2O_2 (10)	10.0	—	~7.8
NO_3^- (85)	—	0.85	~7.9
NO_3^- (2)	—	2.0	~7.9
NO_3^- (20)	—	20.0	~7.9
H_2O_2 (4) + NO_3^- (85)	0.4	0.85	~7.9
H_2O_2 (10) + NO_3^- (20)	10.0	20.0	~7.4

lowing USDA organic cultivation principles. Half of the greenhouse section served as the control (following USDA principles). In the other half of the greenhouse, nitrogen fertilizers in the form of PAW were provided by VitalFluid. On average, 10 mmol/L of NO_3^- of natural (plasma) nitrogen was applied. At the beginning of the experiment, the yield was the same for both treatments, but crop development was entirely different. The crop grown with VitalFluid clearly had sufficient nitrates for growth, while the reference crop suffered from nitrogen deficiency, leading to reduced productivity (Figure 6) [20].

Using natural PAW nitrogen as the primary nitrogen source in USDA organic tomato production has been shown to provide opportunities for water and nutrient savings through drainage water reuse. This can improve resource efficiency in USDA organic tomato production.

The literature on plasma agriculture has described in detail the effectiveness of various approaches to using PAW, from seed to field. It can be concluded that, in general, plasma-treated water has a significant effect on seed germination and seedling growth. Plants irrigated with plasma-treated water have increased yields. The studies conducted show that PAW can act as both a plant growth stimulator and an immune inducer. Thus, special attention should be paid to better

**Figure 6.** Cumulative yield of tomatoes (kg/m^2) for VitalFluid (VF) and for reference sample (BIO) [20]

understanding the potential of cold plasma in plant growth, development and protection. Numerous laboratory tests have been performed that demonstrate clear benefits of using PAW and the feasibility of moving to large-scale field practice. The solution to this problem is related to the development of affordable and reliable high-performance plasma equipment.

AIMS OF RESEARCH

The aim of the study is to investigate the potential for high-performance activation of water or aqueous solutions using a hybrid electrical discharge in bubble water for the efficient production of PAW — liquid nitrogen fertilizers.

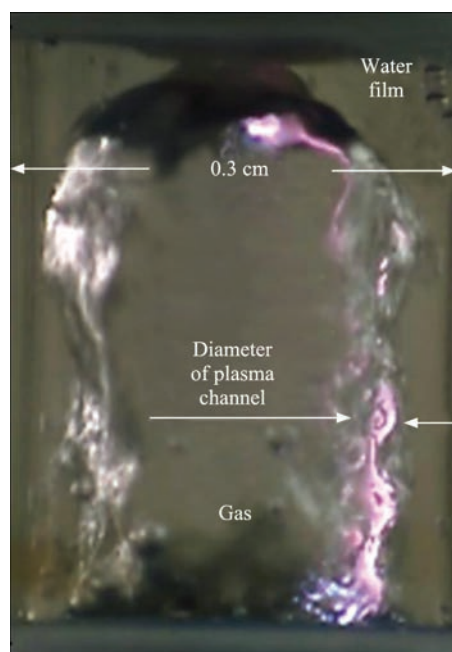
To achieve this goal, the following objectives must be accomplished:

- develop and implement a plasma system operating with a hybrid electrical discharge (with both equilibrium and non-equilibrium zones) in a water-bubble medium.
- determine the operating parameters of the system that ensure direct fixation of NO_x in the plasma flow reactor with a hybrid mode of electrical discharge operation.

MATERIALS AND METHODS

To accomplish the objectives, a plasma system utilizing a flow-type plasma-jet plasma-chemical reactor has been developed.

The developed reactor system for NO_x synthesis includes a plasma-jet reactor equipped with a recuperative cooling-heating system, a power supply, water

**Figure 7.** Zoomed in photo of the discharge region and filamentary plasma channel formed along the surface of the water film for the argon carrier gas [21]

and air supply systems, and monitoring and measurement equipment.

The electrical discharge in the plasma-chemical reactor occurs on the surface of air bubbles in water (Figure 7) [21]. This phenomenon underpins the technology for direct nitrogen fixation in water.

The power supply system for the electrical discharge is built using resonant inverters with a capacity of up to 20 kW. Experiments were conducted by varying the frequency of the applied voltage from 5 to 100 kHz. Bipolar pulses with a voltage amplitude of 4000 V are applied to the reactor electrodes. Air flow rates during the experiments did not exceed 2 m³/hour. Tap water was used in the experimental studies, with a maximum flow rate of 2 tons per hour.

A critical aspect in developing the technological equipment is determining the energy consumption during the discharge process. This determination was carried out by analyzing current and voltage oscillograms during discharge (Figure 8).

To obtain oscillograms, a dual-channel DSO3202A Digital Storage Oscilloscope with a bandwidth of 200 MHz and high sampling rate was used. Digitalization of the oscillograms was performed using the OriginPro 2017 software. Following digitalization, the acquired data facilitated the necessary calculations in the Mathcad mathematical software. Specifically, power calculations were conducted for all phases of discharge combustion.

The parameters of PAW were monitored using ion chromatography on a compact IC-flexometer 930 (manufactured by Thermo Scientific) with a Dionex

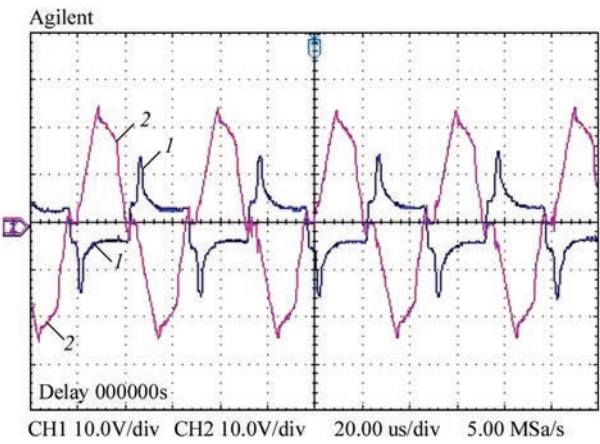


Figure 8. Typical oscillogram of voltage (1) and current (2) for an optimal discharge shape (breakdown voltage 3000 V and current amplitude 14 A)

IonPac AG9-HC guard column and an analytical column Dionex IonPac AS9-HC. The Horiba NO₃ analyzer was used as the measuring instrument. For rapid analyses, QUANTOFIX® indicator test strips were employed. pH values of the solution were measured using a D-51 HORIBA pH meter, and conductivity was assessed with a COND5021ST device from Sato Shouji Inc. The analysis of NO and NO₂ content in exhaust gases was performed using a Testo 340 gas analyzer. Conductivity of both tap water and PAW was monitored using a COND5021ST device from Sato Shouji Inc.

RESULTS

In order to address the research objectives, ERA LLC, in collaboration with GEFEST PE, has developed a new plasma system for direct high-throughput pro-

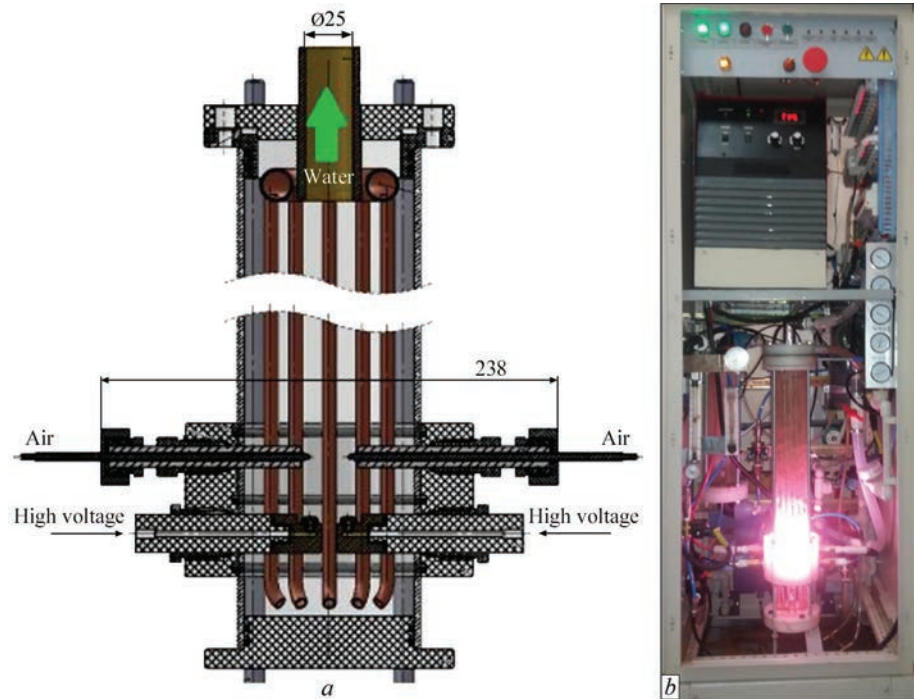


Figure 9. Plasma system for high-performance production of PAW: *a* — plasma module; *b* — system in operation

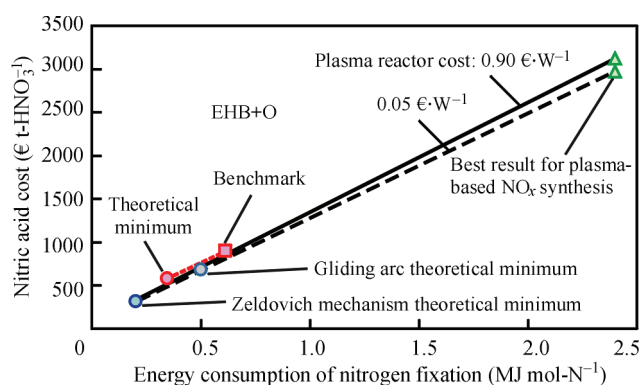


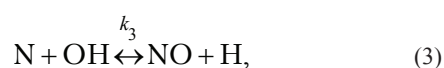
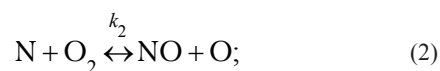
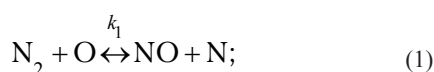
Figure 10. Impact of energy consumption of the plasma NO_x synthesis process on the total cost of nitric acid production [22]

duction of PAW. This system integrates both equilibrium and non-equilibrium plasma states and operates in an air-water mixture. The process is implemented within a plasma module utilizing a pulsating mode of electrical discharge combustion in a flowing bubble stream of water (Figure 9, *a*, *b*).

When conducting the research, it was taken into account that a very important indicator characterizing operating costs is energy consumption. It is obvious that energy consumption has a great impact on the overall cost of RONS production (NO_3^- , NO_2^- , H_2O_2 , O_3 , etc.), while increasing capital costs has little impact on the overall economics of the process. The assessment of energy consumption's impact on the cost of nitric acid in the plasma synthesis of NO_x is depicted by solid and dashed lines in Figure 10 [22]. Analysis of Figure 10 demonstrates that the plasma NO_x synthesis process becomes competitive compared to the Haber–Bosch process based on electrolysis combined with the Ostwald process at an energy consumption of $0.7 \text{ MJ mole-N}^{-1}$.

Among the various nitrogen fixation processes, one of the most promising methods is low-temperature non-equilibrium plasma [23–25]. Compared to the Haber–Bosch process and the early Birkeland–Eyde process, non-equilibrium plasma allows for a larger portion of the supplied energy to activate N_2 at room temperature and atmospheric pressure. The energy consumption for nitrogen fixation with non-equilibrium plasma can be lower than in standard ammonia synthesis, determined by thermodynamics.

The development by the authors is based on two principles. Firstly, extended Zeldovich mechanism was taken as a basis. The extended Zeldovich mechanism [26] is a chemical mechanism describing the oxidation of nitrogen and the formation of NO_x , according to reactions:



where: k_1 and k_2 are reaction rate constants according to Arrhenius law.

Secondly, non-equilibrium plasma affects electrochemical processes influencing chemical bonding of molecules within the plasma and/or on the surfaces of processed materials. Conversely, equilibrium plasma, characterized by high energy density, ensures efficient performance. However, achieving non-equilibrium states with high energy densities is challenging. Therefore, the authors have developed a hybrid plasma processing method that combines both equilibrium and non-equilibrium plasma, leveraging the advantages of each. The electrical discharge in the reactor (Figure 9, *a*) ignites around air bubbles in water (Figure 7). The power supply system for the electrical discharge is based on a resonant inverter with a capacity of up to 20 kW at a frequency of 20 kHz. Bipolar pulses with a voltage amplitude of 4000 V are applied to the electrodes. The formed sheath around the discharge occupies a volume hundreds of times larger than the discharge channel itself, creating a non-equilibrium plasma environment where all plasma-chemical reactions occur.

The radical termolecular reaction (3) between OH and N is still poorly understood, but under conditions of a water plasma discharge, it has a significant influence on the formation of NO in the presence of nitrogen. cobalt tetraoxide (Co_3O_4) can act as an electrocatalyst (in combination with hydrogen peroxide, producing OH), and can be used as a highly efficient electrocatalyst for nitrate synthesis.

In the exhaust gases at the outlet of the plasma module (Figure 9, *a*), NO remains which is not soluble in water. The final stage of the process involves the absorption of NO_2 by water. During the oxidation of NO to NO_2 , several side reactions occur, resulting in the formation of a mixture of nitrogen oxides: NO, N_2O_3 , NO_2 , N_2O_4 , N_2O . The composition of the mixture can vary significantly, but NO_2 is always the predominant component. To enhance the absorption of NO_2 by water, it is necessary to increase pressure and decrease temperature, while maintaining elevated water temperature in the discharge zone. To meet these conflicting conditions, the plasma module design includes an internal heat exchanger, and a separator with gas-water separation is installed in the pneumatic line. Subsequently, this gas containing NO is mixed with ozone for complete oxidation to NO_2 , followed by dissolution in water in a bubbling reactor (Figure 11).

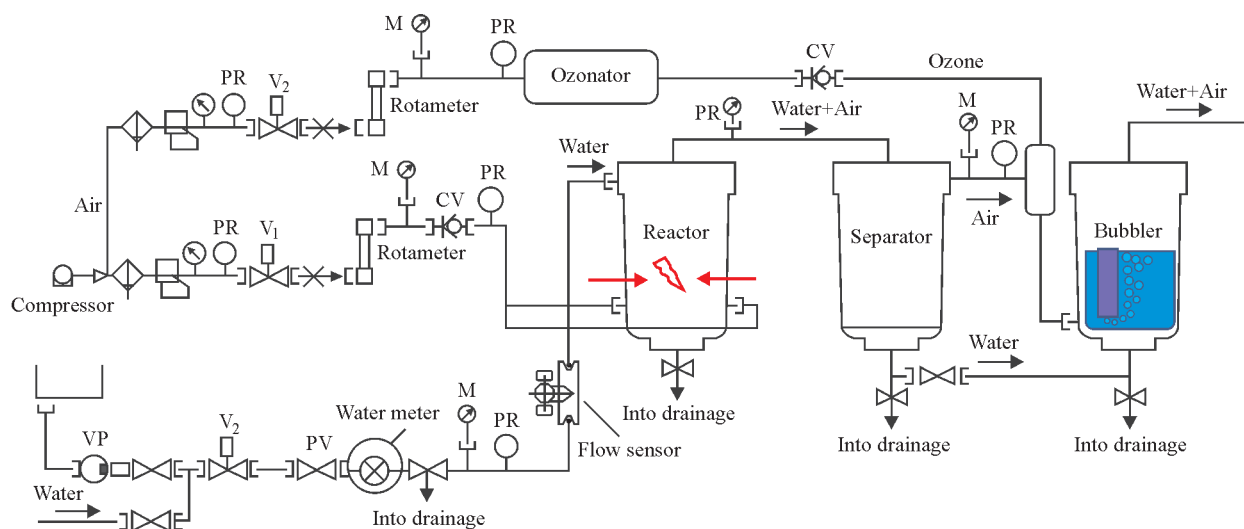


Figure11. Pneumatic hydraulic diagram of the plasma system

Table 3. Parameters of the plasma system for the production of PAW and liquid nitrogen fertilizers

Parameter	Magnitude
Power	10 kW
Water consumption	up to 2 t/h
Air consumption	up to 5 m³/h
NO ₃	up to 6 mol NO ₃ ⁻ per hour (0.4 kg)
Concentration NO ₃ ⁻	up to 500 mg NO ₃ ⁻ per liter
Installation dimensions	0.7×0.7×1.5 m
Installation weight	150 kg

The parameters of the plasma system for the production of PAW and liquid nitrogen fertilizers are presented in Table 3.

The system is scalable up to 100 kW with a capacity of up to 20 t/h. Typical research results are presented in Table 4.

In this series of experiments, air was introduced into the system.

DISCUSSION

The authors, along with several other researchers, are developing a process that simulates lightning flashes in nature. Understanding the chemical processes occurring during induced plasma discharge in water will lead to an understanding of the impact of PAW on seed germination and plant growth.

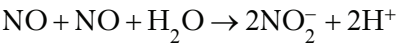
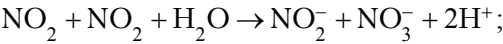
Table 4. Research results

Power, kW	Gas	Gas consumption, m³/hour	Water consumption, L/hour	Ozone, g/hour	Water conductivity, µS/cm	NO, ppm	NO ₃ ⁻ , mg/L	NO ₂ ⁻ , mg/L	O ₂ , mg/L
4.3	Air	0.8	240	–	240/500	2200	150	30	7
4.3	Air	0.8	240	10	240/530	330	180	40	7
–	Air	0.8	240	–	240	–	–	–	0

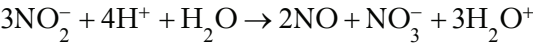
The electric discharge in the surrounding air primarily produces NO and NO₂. During lightning flashes, the air transitions from the gaseous phase to the plasma phase, splitting N₂ and O₂ molecules into active radicals. As demonstrated in [16], upon contact with water, hydroxyl radicals (OH*) are formed, which quickly recombine into hydrogen peroxide (H₂O₂):



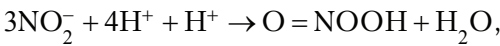
gaseous NO₂ dissolves in water, forming nitrites NO₂⁻ and nitrates NO₃⁻:



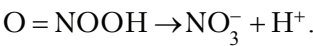
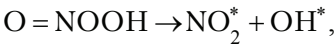
in an acidic environment NO₂⁻ can be oxidized to NO₃⁻



or NO₂⁻ reacts with H₂O₂ to form an intermediate compound, peroxynitrous acid:



which is an unstable product and over time decomposes either into NO₃⁻ or into the radicals NO₂* and OH*:



Thus, the resulting reactive particles dissolve in water and produce PAW. In this form, a mixture of long-lived active oxygen and nitrogen species (H_2O_2 , NO_2^- , NO_3^- , and others) is considered a clean and stable alternative to chemical fertilizers. Such PAW can be effectively utilized for various agricultural purposes [27–29].

The new plasma process, based on phenomena borrowed from nature, is currently in the developmental and testing stage. Plasma sources used in plasma agriculture may vary in design and operating principle. However, their primary goal is to generate plasma and deliver RONS to seeds, plants, soil, or water. Plasma generation devices can range from portable units to larger systems, depending on the scale of agricultural operations and their requirements. The choice of device for plasma generation in water plasma treatment plays a crucial role in obtaining a variety of RONS. In several studies [30–33], a comprehensive analysis was conducted on the efficiency of RONS generation from different types of plasma sources. Various plasma reactors were investigated, including spark discharges, glow discharges, corona discharges, laser discharges, radiofrequency cross discharges, dielectric barrier discharges, arc discharges, microwave discharges, and plasma jets in contact with water.

In the plasma system developed by the authors, a hybrid plasma is utilized, combining equilibrium and non-equilibrium plasmas. The plasma module operates in a pulsating mode of electric discharge combustion (transitioning from arc to diffuse discharge, accompanied by a significant increase in plasma volume by orders of magnitude) within a flowing bubble stream of water. The conductivity of the liquid plays a crucial role in plasma formation and electrical breakdown. Electrical breakdown is a pivotal phase for generating plasma discharge. Analysis of oscillograms (Figure 8) revealed that a system with rapid voltage rise time exhibits much higher tolerance to liquid conductivity and can sustain a stable discharge. Highly reactive particles are produced specifically in the electric discharge in the presence of water and air, dissolving into water to form PAW. Some authors also note that using air as the feed gas in the plasma setup leads to a greater variety of RONS compared to using other gases such as argon, N_2 , and O_2 . The plasma system (Figure 11) includes ozone injection for oxidizing residual NO.

As indicated by the research results presented in Table 4, the system with a hybrid plasma discharge ensures sufficiently high levels of RONS concentration in PAW. The results obtained during the study suggest that the developed plasma system can be used for the direct high-yield production of PAW.

The increase in the amount of air passed through the discharge zone enhances the content of RONS in PAW. Similar results have been obtained in studies [14, 17].

It should be noted, however, that as demonstrated by a series of practical studies, different concentrations of RONS in PAW have varying effects on the development of different agricultural crops and seed germination. For instance, in study [30], correlations between the characteristics of PAW and their impact on various crops were analyzed. Such data allow for the adjustment of RONS content in activated water to target specific agricultural crops. High-concentration solutions can be diluted with water if necessary. Plasma-treated solutions remain stable for several days of storage [13], allowing for the transportation of PAW and its prolonged use over time. PAW has significant potential for effective use in various agricultural applications, as long-lived liquid RONS (H_2O_2 , NO_2^- , NO_3^-) can participate in plant metabolism or serve as nutrients [16].

Nitrites and nitrates in PAW act as nitrogen fertilizers and contribute to enhanced seedling growth. As noted in [16], NO_3^- primarily enhances dry biomass, photosynthetic pigment content, photosynthesis rate, and overall plant appearance; and H_2O_2 contributes to increased dry biomass. Additionally, PAW improves seed germination and early seedling development [16].

It should also be noted that agricultural plants are highly susceptible to pathogen attacks. However, PAW contains various RONS in concentrations that can help activate plant defense systems [17].

The small size of the developed plasma system for PAW and liquid nitrogen fertilizer production, and also its lightweight and sufficiently high productivity in generating RONS (Table 3) enable developed plasma system's use in small and medium-sized farms, as well as its shared use among multiple farms.

CONCLUSION

The analysis of the current state of PAW application in agriculture has shown its potential to enhance many key crop production indicators. A primary challenge lies in transitioning from laboratory conditions to industrial-scale applications. High-throughput production of PAW holds promise through the use of hybrid plasma discharge, combining non-equilibrium and equilibrium (arc) discharges with water plasma. Experimental research results on PAW production have demonstrated the effectiveness of hybrid plasma generation technologies in producing water enriched with active substances. Such PAW can be effectively used for seed germination, plant growth, and development. PAW presents an alternative to chemical nitrogen fer-

tilizers in agriculture. Plasma technology for atmospheric nitrogen fixation enables the production of liquid nitrogen fertilizers directly at agricultural sites, eliminating issues related to transportation, product loss, and environmental protection. The advancement of plasma agricultural technologies can be further facilitated by integrating plasma systems with inexpensive renewable electricity sources. The potential of PAW lies in its relative simplicity and convenience of production, although standards development is needed for widespread adoption in crop cultivation.

REFERENCES

1. Soloveichik, G. (2017) NH_3 Energy future of ammonia production: Improvement of Haber–Bosch process or electrochemical synthesis? In: *Topical Conf.: AIChE Annual Meeting, October 29–November 3, 2017, Minneapolis*. <https://nh3fuelassociation.org/wp-content/uploads/2017/11/NH3-Energy-2017-Grigorii-Soloveichik.pdf>
2. Ghavam, S., Vahdati, M., Wilson, I.A.G., Styring, P. (2021) Sustainable ammonia production processes. *Frontiers in Energy Research*, **9**, 580808. DOI: <https://doi.org/10.3389/fenrg.2021.580808>
3. Tyagi, J., Ahmad, S., Malik, M. (2022) Nitrogenous fertilizers: impact on environment sustainability, mitigation strategies, and challenges. *Inter. J. of Environmental Sci. and Technology*, **19**, 11649–11672. DOI: <https://doi.org/10.1007/s13762-022-04027-9>
4. Zhou, R., Zhou, R., Wang, P. et al. (2020) Plasma-activated water: Generation, origin of reactive species and biological applications. *J. of Physics D: Applied Physics*, **53**, 30. DOI: <https://doi.org/10.1088/1361-6463/ab81cf>
5. Petrov, S.V. (2021) *Innovatsionnye plazmenno-struinye tekhnologii*. LAMBERT Academic Publ. [in Russian].
6. Bogaerts, A., Neyts, E.C. (2018) Plasma technology: An emerging technology for energy storage. *ACS Energy Letters*, **3**(4), 1013–1027. DOI: <https://doi.org/10.1021/acsenrgylett.8b00184>
7. Anastasopoulou, A. (2018) *Conceptual process design of plasma-assisted nitrogen fixation through energy, environmental and economic assessment*. Technische Universiteit Eindhoven. https://pure.tue.nl/ws/portalfiles/portal/105883898/20180919_CO_Anastasopoulou.pdf
8. Rathore, V., Nema, S.K. (2021) Optimization of process parameters to generate plasma activated water and study of physicochemical properties of plasma activated solutions at optimum condition. *J. of Applied Physics*, **129**(8). DOI: <https://doi.org/10.1063/5.0033848>
9. Kaushik, N.K., Ghimire, B., Li, Y. et al. (2018). Biological and medical applications of plasmaactivated media, water and solutions. *Biological Chemistry*. **400**(1), 39–62. DOI: <https://doi.org/10.1515/hsz-2018-0226>
10. Lamichhane, P., Paneru, R., Nguyen, L.N. et al. (2020) Plasma-assisted nitrogen fixation in water with various metals. *Reaction Chemistry & Eng.*, **5**, 2053–2057. DOI: <https://doi.org/10.1039/d0re00248h>
11. Wang, Z., Liu, J., Zhao, H. et al. (2023) Free radicals promote electrocatalytic nitrogen oxidation. *Chemical Sci.*, **14**, 1878–1884. DOI: <https://doi.org/10.1039/D2SC06599A>
12. Guragain, R.P., Baniya, H.B., Pradhan, S.P. et al. (2021). Influence of plasma-activated water (PAW) on the germination of radish, fenugreek, and pea seeds. *AIP Advances*, **11**, 125304. DOI: <https://doi.org/10.1063/5.0070800>
13. Stoleru, V., Burlica, R., Mihalache, G. et al. (2020) Plant growth promotion effect of plasma activated water on *Lactuca sativa* L. cultivated in two different volumes of substrate. *Scientific Reports*. **10**, 20920. DOI: <https://doi.org/10.1038/s41598-020-77355-w>
14. Ka, D.H., Priatama, R.A., Park, J.Y. et al. (2021) Plasma-activated water modulates root hair cell density via root developmental genes in *Arabidopsis thaliana* L. *Applied Sci.*, **11**(5), 2240. DOI: <https://doi.org/10.3390/app11052240>
15. Škarpa, P., Klofáč, D., Krěma, F. et al. (2020) Effect of plasma activated water foliar application on selected growth parameters of maize. *Water*, **12**(12), 3545. DOI: <https://doi.org/10.3390/w12123545>
16. Kučerová, K., Henselová, M., Slováková, L., Hensel, K. (2019) Effects of plasma activated water on wheat: Germination, growth parameters, photosynthetic pigments, soluble protein content, and antioxidant enzymes activity. *Plasma Process and Polymers*, **16**(3), 1800131. DOI: <https://doi.org/10.1002/ppap.201800131>
17. Adhikari, B., Adhikari, M., Ghimire, B. et al. (2019) Cold atmospheric plasmaactivated water irrigation induces defense hormone and gene expression in tomato seedlings. *Scientific Reports*, **9**, 16080, 1–15. DOI: <https://doi.org/10.1038/s41598-019-52646-z>
18. Kučerová, K., Henselová, M., Slováková, L. et al. (2021) Effect of plasma activated water, hydrogen peroxide, and nitrates on lettuce growth and its physiological parameters. *Applied Sci.*, **11**(5), 1985. DOI: <https://doi.org/10.3390/app11051985>
19. VitalFluid (2024) *Plasma activated water*. <https://vitalfluid.com/plasma-activated-water/>
20. (2021) *Plasma activated water in USDA-organic fertilization*. <https://vitalfluid.com/wp-content/uploads/2022/03/Newsletter-2-VitalFluid-in-USDA-organic-tomato-cultivation.pdf>
21. Wang, H., Wandel, R.J., Tachibana, K. et al. (2018) The influence of liquid conductivity on electrical breakdown and hydrogen peroxide production in a nanosecond pulsed plasma discharge generated in a water-film plasma reactor. *J. of Physics D: Applied Physics*, **52**(7). DOI: <https://doi.org/10.1088/1361-6463/aaf132>
22. Rouwenhorst, K.H.R., Jardali, F., Bogaerts, A., Lefferts, L. (2021) From the Birkeland–Eyde process towards energy-efficient plasma-based NO_x synthesis: A techno-economic analysis. *Energy & Environmental Sci.*, **14**, 2520–2534. DOI: <https://doi.org/10.1039/d0ee03763j>
23. Muzammil, I., Lee, D.H., Dinh, D.K. et al. (2021) A novel energy efficient path for nitrogen fixation using a non-thermal arc. *RSC Advances*, **11**(21), 12729–12738. DOI: <https://doi.org/10.1039/d1ra01357b>
24. Winter, L.R., Chen, J.G. (2020) N_2 fixation by plasma-activated processes. *Joule*, **5**(2), 300–315. DOI: <https://doi.org/10.1016/j.joule.2020.11.009>
25. Vervloessem, E., Gorbanev, Y., Nikiforov, A. et al. (2022) Sustainable NO_x production from air in pulsed plasma: Elucidating the chemistry behind the low energy consumption. *Green Chemistry*, **24**, 916–929. DOI: <https://doi.org/10.1039/D1GC02762J>
26. Ganz, S.N., Parkhomenko, V.D. (1976). *Obtaining fixed nitrogen in plasma*. Kyiv, Vishcha Shkola [in Russian].
27. Judée, F., Simon, S., Baillyb, C., Dufour, T. (2018) Plasma-activation of tap water using DBD for agronomy applications: Identification and quantification of long lifetime chemical species and production/consumption mechanisms. *Water Research*, **133**, 47–59. DOI: <https://doi.org/10.1016/j.watres.2017.12.035>
28. Sharma, H.P., Patel, A.H., Pal, M. (2021) Effect of plasma activated water (PAW) on fruits and vegetables. *Ameri-*

can J. of Food and Nutrition, 9(2), 60–68. DOI: <https://doi.org/10.12691/ajfn-9-2-1>

29. Rahman, M., Hasan, M.S., Islam, R. et al. (2022) Plasma-activated water for food safety and quality: A review of recent developments. *Inter. J. of Environmental Research and Public Health*, 19(11), 6630. DOI: <https://doi.org/10.3390/ijerph19116630>
30. Konchekov, E.M., Gusein-zade, N., Burmistrov, D.E. et al. (2023) Advancements in plasma agriculture: A review of recent studies. *Inter. J. of Molecular Sci.*, 24(20), 15093. DOI: <https://doi.org/10.3390/ijms242015093>
31. Gao, Y., Francis, K., Zhang, X. (2022) Review on formation of cold plasma activated water (PAW) and the applications in food and agriculture. *Food Research Inter.*, 157, 111246. DOI: <https://doi.org/10.1016/j.foodres.2022.111246>
32. Bruggeman, P.J., Kushner, M.J., Locke, B.R. et al. (2016) Plasma-liquid interactions: a review and roadmap. *Plasma Sources Sci. and Technology*, 25, 053002. DOI: <https://doi.org/10.1088/0963-0252/25/5/053002>
33. Zjup, W., Chen, H., Yuan, D. et al. (2021) Review of low-temperature plasma nitrogen fixation technology. *Waste Disposal & Sustainable Energy*, 3, 201–217. DOI: <https://doi.org/10.1007/s42768-021-00074-z>

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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