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(54) Titre : METHODE ET APPAREIL DE FIXATION D'AZOTE
(54) Title: METHOD AND APPARATUS FOR NITROGEN FIXATION

(57) Abrégé/Abstract:
The present invention relates to methods and systems to be used in precision agriculture, hydroponics, aquaponics and greenhouse cultivation. The invention has useful properties due to the apparatus design allowing a direct single stage nitrogen fixation via plasma discharge in a multiphase aqueous solution. Claimed invention increases efficiency and utility of plasma-assisted nitrogen fixation due to the scalable and modular design suitable for stationary and mobile agricultural applications.

ABSTRACT

METHOD AND APPARATUS FOR NITROGEN FIXATION

The present invention relates to methods and systems to be used in precision agriculture, hydroponics, aquaponics and greenhouse cultivation. The invention has useful properties due to the apparatus design allowing a direct single stage nitrogen fixation via plasma discharge in a multiphase aqueous solution. Claimed invention increases efficiency and utility of plasma-assisted nitrogen fixation due to the scalable and modular design suitable for stationary and mobile agricultural applications.

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International Patent Classification IPC[7]

C05C 5/00 Fertilisers containing other nitrates
C05C 11/100 Other nitrogenous fertilisers
A01C 21/00 Methods of fertilising
H05H 1/24 Generating plasma

METHOD AND APPARATUS FOR NITROGEN FIXATION

Field of invention

The present invention relates to materials, methods and systems that can be used in precision agriculture, hydroponics, aquaponics and greenhouse cultivation for fixation of gaseous nitrogen into water-soluble nitrogen oxides via direct plasma treatment of a multiphase aqueous solution. Since gaseous nitrogen in the atmosphere can not be used directly by either plants or animals, it should be converted to water-soluble forms acceptable for microorganisms, plants and animals. The present invention is related to the nitrogen fixation, i.e. conversion of gaseous nitrogen into nitrogen compounds that can be assimilated by living things.

Background of invention

Nitrogen (N) is the main constituent of proteins, essential for plant growth and development. Agricultural crops are unable to directly assimilate atmospheric nitrogen but accept it only in the form of nitrates/nitrites/ammonium, which are delivered through nitrogenous fertilizers. Nitrogen fixation is the conversion of gaseous nitrogen into nitrogen compounds that can be assimilated by living organisms (microorganisms, plants and animals). Nitrogen fixation is commonly achieved through biological process (rhizobia bacteria), natural process of atmospheric discharge (lightning) and industrial Haber-Bosch (HB) process. Annual uptake of soil nitrogen should be replenished by chemical fertilizers, so intensive agriculture relies on industrial HB process of nitrogen fixation. The problem is that HB process is energy demanding, exploiting non-renewable resources and significantly contributing to GHG emissions.

The preparation of nitrogen oxides by reaction of gaseous nitrogen with oxygen under plasma condition is already known. The reaction conditions described in the state of art can be divided into high-temperature plasma reactions and low-temperature plasma

reactions. For the application of high-temperature plasma reactions, the rapid cooling of the reaction products is of particular importance, because the thermal synthesis of NO from N_2 and O_2 requires very high temperatures (above 700 K), while on the other hand the reaction product decomposes rapidly at high temperatures. For low-temperature plasma the decomposition problem is smaller, because the gas temperature remains comparatively low in plasma zone, but the yield of nitrogen monoxide is also smaller. Both reactions require the reactant molecules to exist in gaseous phase.

In the prior art, the mode of delivery nitrogen oxides generated by plasma into water has been well-described. The main purpose of the processes and devices described in the prior art involve two-stage processes of (1) generation of nitrogen oxides NO/NO_2 in gaseous phase, (2) diffusion of gaseous nitrogen oxides into the liquid phase, and (3) reaction of the nitrogen oxides with the constituents of the liquid medium.

For example, **JP2017228423A** described an underwater point to point arc plasma discharge apparatus based on partially insulated Tungsten electrodes. The electrical discharge results in forming ammonia and nitrate ions, which is circulated through a hydroponic growth system.

US4141715 employed a combustion chamber with spark plug to ionize pressurized air using electric arc discharge with the subsequent injection of gaseous nitrogen oxide into a liquid to obtain dilute nitric acid, that can be used as a fertilizer.

US4297123 employed the arc discharge combustion chambers developed in US4141715, connected in parallel to produce dilute nitric acid, followed by further increasing the concentration via recirculation. The process relies on controlled flows of compressed oxygen and nitrogen to increase the overall nitric acid production.

US4505795 claimed a method and a turbine apparatus for production of gaseous nitric oxides through a hot arc discharge in gases flowing through an annulus at supersonic speeds, and subsequent use of the exiting energized gas for production of electrical energy.

The patent **US7828061B2** described a process using plasma arc in ambient air for creation of nitrogen compounds, that are then brought into contact with water to form nitrate, which helps in preventing formation of hydrogen sulphide in oil-field applications.

All above mentioned art explores point-to-point arc plasma discharge either in gas phase or in liquid phase. The under-water plasma discharges usually lead to electrolysis and subsequent corrosion of electrodes, making the discharge unstable.

US4451436 claimed a method and reactor for low-pressure ionization of gaseous nitrogen and gaseous oxygen using radio-frequency waves to form nitrogen oxide on a catalyst, followed by reaction with hydrogen to form gaseous ammonia that is removed via water.

In **US9475710B2**, a high-frequency voltage driven plasma discharge creates nitrogen oxides which is delivered by airflow to the surface of water. However, no specific applications were claimed or described.

US20120297673A1 describes a system to produce nitric oxide NO and then nitric dioxide NO_2 in gaseous phase in the presence of N_2, O_2 and electric field. This invention, however, requires an injector for combining nitrogen dioxide NO_2 with a liquid to generate nitric acid HNO_3, so essentially it is two-stage process.

WO2009025835A1 describes a method and device of nitrogen fixation, combining N_2 and H_2 in ammonia in the presence of catalyst and non-thermal plasma. To decrease reaction temperature, the invention uses Ruthenium catalyst on the MgO support, while plasma is used to decompose molecular nitrogen and hydrogen in gaseous phase. In the essence, this invention presents modified HB process.

WO2016063302A2 discloses the process of cold plasma-assisted nitrogen fixation from N_2 and O_2 through the combustion of nitrogen and/or nitrogen-containing mixtures in gaseous phase.

WO2018151739A1 describe a method and apparatus for in-situ nitrogen fixation in gaseous form, using catalytic methods, which take the nitrogen, oxygen and water in the air, as well as other trace gases such as CO_2 to convert them into gaseous plant nutrients

such as NO, NO_2, N_2O, ammonia, ethylene and carbonates. This method, however, fix nitrogen only in gaseous phase for further delivery to plants or microorganisms.

The closest analogue of the present invention is **WO2019040775A1** (US patent **US20180062231A1**), describing a method and apparatus for converting atmospheric nitrogen gas into gaseous nitrogen oxides via so called "splitter". Splitter is using controlled plasma field to split molecular nitrogen N_2 into atomic nitrogen, which then react with molecular oxygen O_2, resulting in generation of nitrogen oxides. Optimal temperature for splitting nitrogen was found 60-70 °C. The amount of energy required to power splitting in this invention is lower than in industrial HB process. When operating at room temperature, splitter does not require additional cooling due to the cooling from the water in the collection vessel. Although cooling arrangement was proposed, the method is not efficient due to the spatial separation of two processes (1) splitting of atmospheric nitrogen in gaseous phase and (2) diffusion of metastable products into the liquid phase (water). Two-stage process is not efficient because of possible recombination of metastable nitrogenous compounds.

The invention disclosed herein is unique and novel in several ways-

(1) Plasma-induced nitrogen fixation is more efficient and uniform due to the bubble column design, allowing distributed exposure of the entire volume of gas-liquid mixture.

(2) The system provides very large surface area for diffusion and reaction of the ionized gaseous species through bubbles.

(3) The method does not require any catalysts for the chemical transformation.

(4) The system uses non-contact electrode configuration for plasma generation

(5) Unlike the methods and apparatus described in prior art involving the contact of electrodes with the aqueous medium or water, the non-contact nature of the plasma discharge electrodes in the present invention allows for their long usage life, improved wear characteristics through prevention of electrolysis and mass transfer

from the electrodes. The non-contact nature of the electrodes renders a higher stability of the electrical discharge plasma.

(6) Unlike the methods and apparatus described in prior art involving multi-stage processes of ionization of a gas followed by pumping of the ionized gas into a liquid, followed by diffusion and chemical reactions, the present invention is a single-step process resulting in direct fixation of nitrate, nitrite, and ammonium in the liquid.

(7) Unlike the methods and apparatus described in prior art involving point to point electrodes and discharges between such electrodes, the present invention employs planar to planar type of electrodes with various curvatures that allows to obtain uniform electrical discharges.

Summary of Invention

The primary object of this invention is to eliminate inefficiency of the prior art by single-stage gaseous nitrogen fixation into nitrogen ions via direct plasma treatment of a multiphase aqueous solution with bubbles containing nitrogen and oxygen.

A further object of this invention is to provide a new simple and efficient design of nitrogen fixation system, which could be used for both stationary and mobile applications.

A further object of this invention is to provide solution for controlled nitrogen fixation through detection of nitrogen demand and automated manipulation of control variables, such as electric field strength, temperature and flow rate, to increase or decrease the rate of nitrogen fixation and the concentration of the nitrogenous ions.

A further object of this invention is the scalability of the principal design due to the parallel or series combination of basic chemical reactor units.

A further object of this invention is to extend the functionality of the principal design, allowing to produce reactive chemical species other than nitrogenous chemical species in aqueous solution, by manipulation of process variables.

Detailed description of preferred embodiments

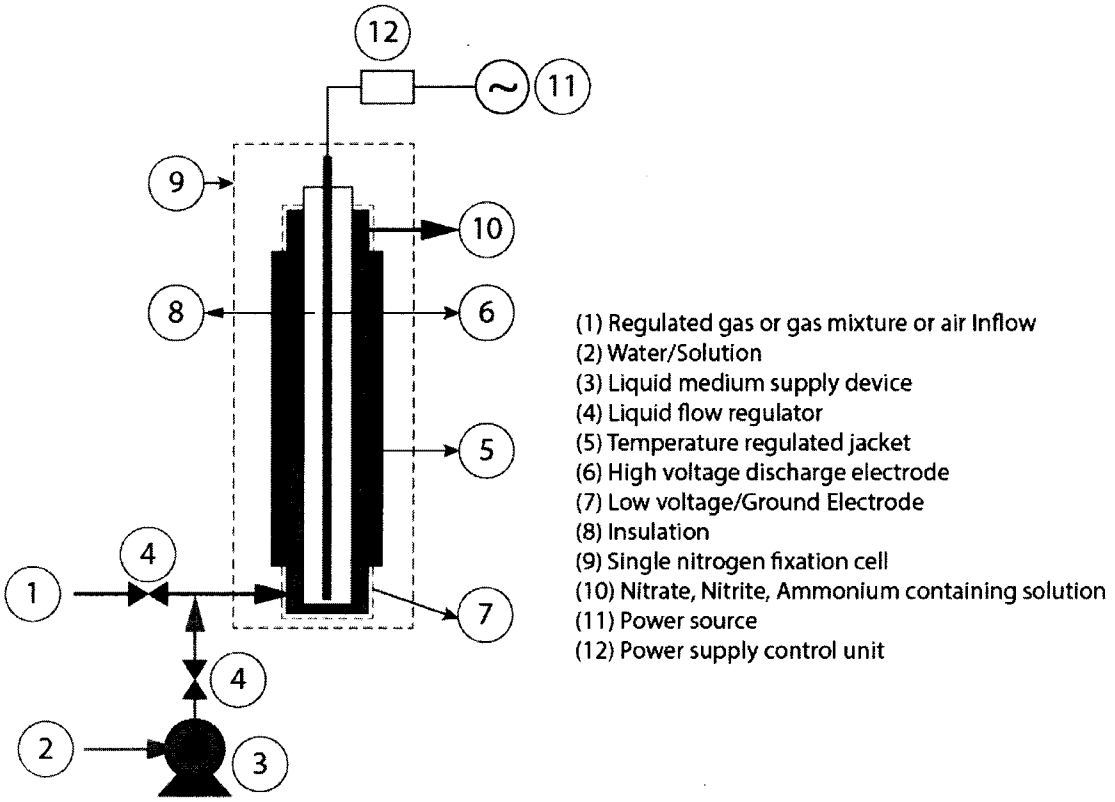

FIG. 1. A single nitrogen fixation cell

[SINGLE NITROGEN FIXATION CELL] With reference to FIG 1, a plasma discharge cell in accordance with embodiments of the technology is presented. FIG 1 illustrates environment 9 which shows an embodiment of a bubble-column type nitrogen fixation cell connected to a controlled power supply 11, controlled through the control unit 12. The high voltage source powers a metallic electrode 6, referred to as the high voltage discharge electrode. The electrode 6 is insulated using an electrical insulator or electrically semi-insulator or dielectric material 8 to prevent formation of an electrical arc with the ground electrode 7. The ground electrode is separated from the insulator 8 with a mixture of water or aqueous solution and gas bubbles. The gaseous medium supply 1 is controlled by a flow regulator 4, that may be manually controlled or actuated through an electronic signal. The flow of liquid medium 2 is regulated by a flow supply device 3, which is controlled by a flow regulator 4, that may be manually controlled or actuated through an electronic signal. The temperature of the solution and air mixture is regulated via a heating element 5, which may be manually controlled or actuated through an electronic signal. In another

embodiment, the heating could optionally be established through an inductive means using the ground electrode 5, rather than a separate standalone heating element. The electrical discharge results in a transformed product 10 containing nitrate, nitrite, and ammonium ions. Depending on the operational conditions of applied voltage, reactor dimensions, flow rate of gas mixture and liquid, the transformed products could also include ozone, peroxide, and hydroxyl radicals. The present technology may be practiced with nitrogen fixation cells of different shapes and sizes that may or may not include the components shown in FIG 1.

[POWER SUPPLY] In one embodiment alternating current or AC power is used to create the electrical plasma discharge in the nitrogen fixation cell. In one embodiment direct current or DC power is used to create the plasma discharge in the nitrogen fixation cell. In another embodiment, the DC voltage is applied at varying pulse widths and pulse frequencies. In one embodiment the shape of the voltage pulses could be square or triangular or sawtooth or a mixture of these. In one embodiment the power source may derive power from the electric grid or solar cell or battery or wind turbine to power the nitrogen fixation cell. In one embodiment, the voltage from the power source to the nitrogen fixation cell is controlled using a control unit. In one embodiment, the electrical current from the power source to nitrogen fixation cell is controlled using the control unit.

[CONTROLS] In one embodiment, the flow of the aqueous solution into the nitrogen fixation cell is controlled using a flow control device. In one embodiment, the flow of the gas into the aqueous solution is controlled using a flow control device. In one embodiment, the flow control devices can be dynamically actuated through electronic means. In one embodiment, the temperature of the nitrogen fixation cell can be monitored using a temperature sensing device. In one embodiment, the temperature of the nitrogen fixation cell can be controlled using a heating device to a pre-set temperature. In one embodiment, the temperature of the nitrogen fixation cell can be dynamically controlled using a heating device based on feedback received from the temperature sensing device. In one embodiment, the concentration of nitrates, nitrites and ammonia in the product 10 is measured by sensors and used for adaptive self-tuning of process variables.

[APPLICATIONS] In one embodiment, the nitrate, nitrite, and ammonium ions rich solution is applied as a nitrogen fertilizer for plant growth applications, including for algal culture. In one embodiment, the nitrate, nitrite, and ammonium ions rich solution is applied as a nitrogen source for microbial growth applications. In particular, the applications are useful in the field of agriculture, horticulture, greenhouses, hydroponics and algal culture.

[SCALABILITY] The nitrogen concentration or nitrogen flow rate can be increased through a series and/or parallel combination of the basic bubble column chemical reactor cells.

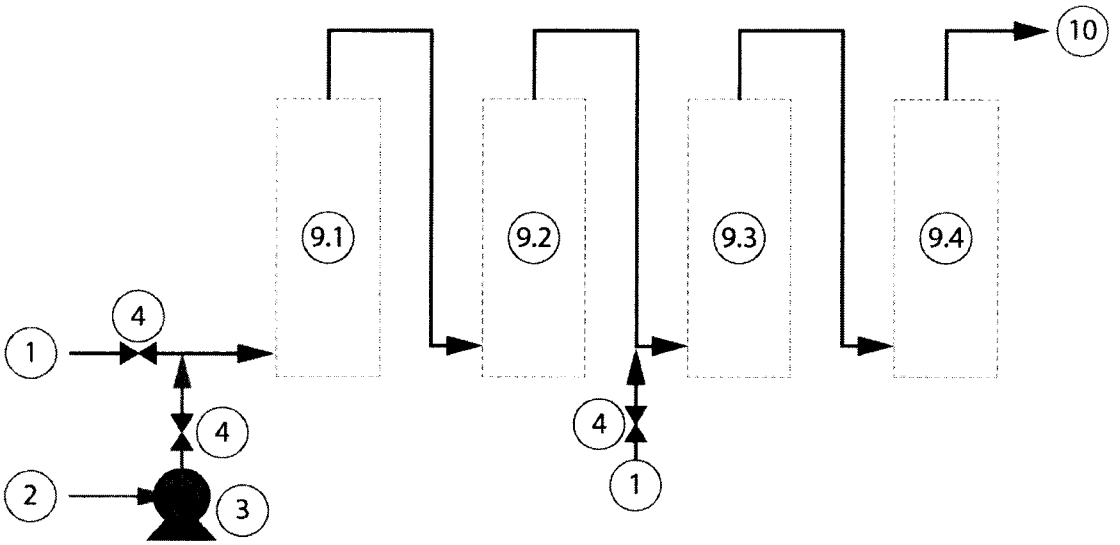

FIG 2. Nitrogen fixation module with cells connected in series configuration

[SERIES OPERATION] With respect to FIG 2, a plurality of nitrogen fixation cells connected in series is described. In one embodiment, the nitrate, nitrite and ammonium ions rich solution from one nitrogen fixation cell is fed as the initial material to the next nitrogen fixation cell. In one embodiment, the sequential feeding of nitrogen rich output from nitrogen fixation cells can be fed as starting material to another cell several times until a desired concentration is achieved. In one embodiment air or a gas mixture can be introduced into a plurality of nitrogen fixation cells. In one embodiment, the air or gas mixture flow and the liquid flow can occur in the same direction, referred to as co-current flow. In one embodiment, the air or gas mixture flow and the liquid flow can occur in the opposite directions, referred to as counter-current flow.

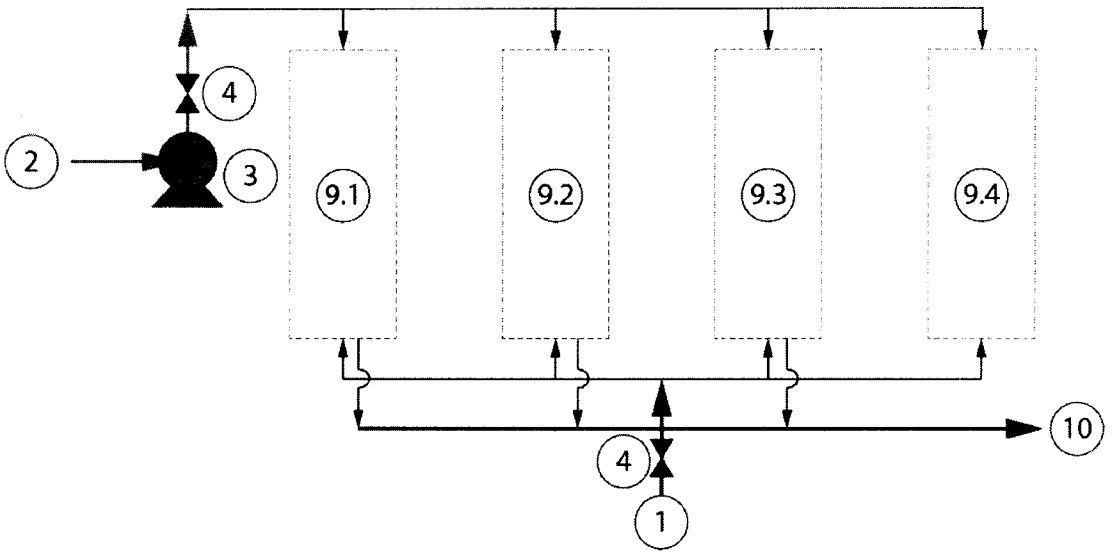

FIG 3. Nitrogen fixation module with cells connected in parallel configuration

[PARALLEL OPERATION] With respect to FIG 3, a plurality of nitrogen fixation cells connected in parallel is described. In one embodiment, the aqueous solution or water is fed simultaneously to all the nitrogen fixation cells using a liquid feeding device. In one embodiment air or a gas mixture is simultaneously introduced into the plurality of nitrogen fixation cells. In one embodiment, the air or gas mixture flow and the liquid flow can occur in the same direction, referred to as co-current flow. In one embodiment, the air or gas mixture flow and the liquid flow can occur in the opposite directions, referred to as counter-current flow. In one embodiment, the number of nitrogen fixation cells connected in parallel can be varied to achieve a desired concentration of the nitrate, nitrite and ammonium in the solution.

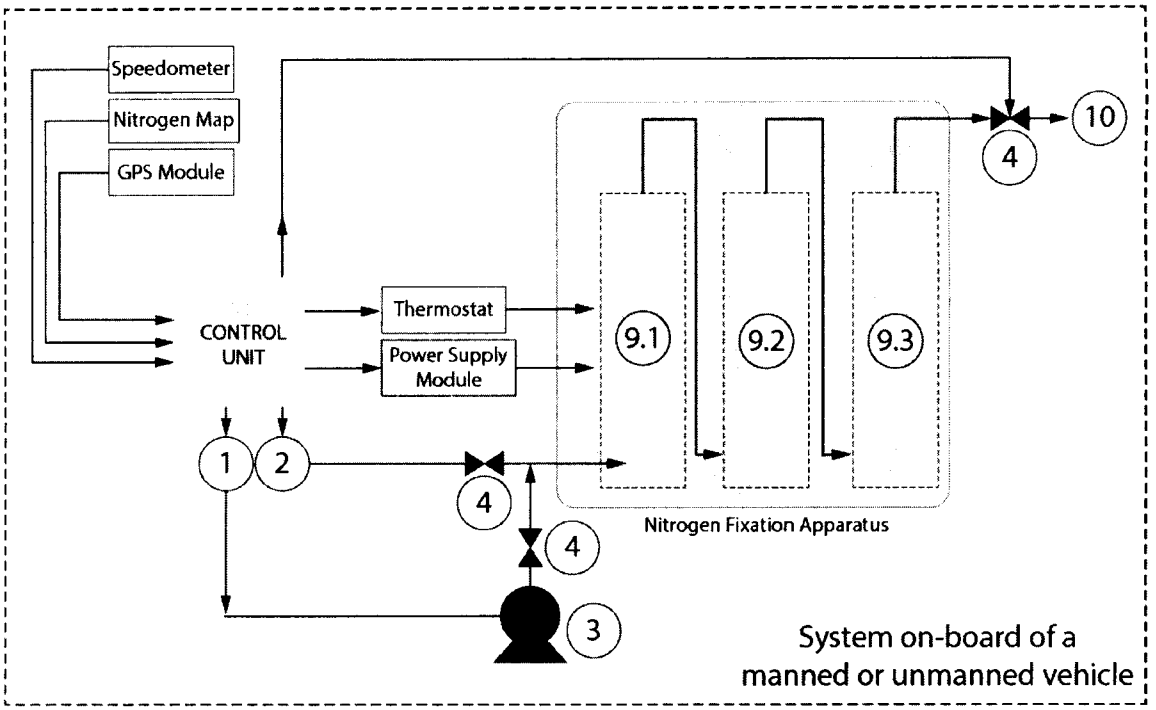

FIG 4. Controlled nitrogen fixation system through detection of nitrogen demand and automated manipulation of control variables, such as electric field strength, temperature and flow rate.

[MOBILE APPLICATION] With respect to FIG 4, a particular configuration of a system for application of the nitrogen fixation modules in mobile vehicles is described. In one embodiment the nitrogen fixation module can be placed on a mobile vehicle such as a manned or an unmanned vehicle for in-situ nitrogen fertilizer production. In one embodiment, the vehicle can be a tractor with a spraying device. In one embodiment, the module used can be comprised of nitrogen fixation cells in series. In another embodiment, the module used can be comprised of nitrogen fixation cells in parallel. In yet another embodiment, the system could comprise of modules connected in series or parallel or both. In one embodiment, the desired quantity of the nitrogen ions rich solution to be produced is decided by nitrogen maps of the field. The location of the system in an agricultural field can be determined from a GPS sensor integrated into the system. In one embodiment of the technology, the rate of application of the nitrogen rich solution to plants or crops is controlled by controlling the rate of spraying using an appropriate device, such as a solenoid valve.

[CONTROL METHODS] In one embodiment, the rate of nitrogen rich solution produced by the system is controlled by the speed of the mobile vehicle as sensed using a speedometer. In one embodiment, the rate of nitrogen rich solution produced by the system is controlled by controlling the temperature of the module(s) using a thermostat, the temperature being sensed using a temperature sensing element. In one embodiment, the rate of nitrogen rich solution produced by the system is controlled by controlling the electrical power applied to the module(s). In one embodiment, the rate of nitrogen rich solution produced by the system is controlled by controlling the electric field applied across the electrodes of the nitrogen fixation cells contained in the module(s). In one embodiment, the rate of nitrogen rich solution produced by the system is controlled by controlling the flow rate of the aqueous solution or water fed to the module. In another embodiment, the rate of nitrogen rich solution produced by the system is controlled by controlling the flow rate of the gas mixture or air fed to the aqueous solution or water stream.

Examples

EXAMPLE 1. Continuous in-situ nitrogen fixation system for farming systems including, but not limited to hydroponics, vertical farms, urban agriculture, and home gardens (FIG. 5) is able to generate plant accessible nitrogen in highly controllable manner, either by maintaining constant N-concentration in the nutrient solution or by sensing the plant nitrogen demand and actuating the N-fixation. The system can regulate the optimal concentration of nitrogen with respect to established agrochemical requirements. In a specific use case, the system can maintain a constant nitrate nitrogen concentration up to 140 ± 10 ppm in the aqueous medium during the fruiting phase for tomato and cucumber in a hydroponic system. In another specific use case, the system can maintain a constant nitrate nitrogen concentration up to 190 ± 10 ppm in the aqueous medium during the fruiting phase for bell peppers in a hydroponic system.

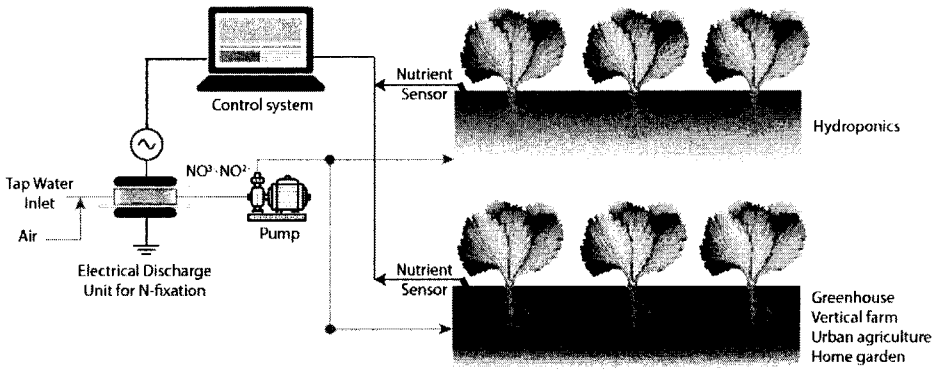

FIG. 5. Continuous nitrogen fixation for hydroponics, greenhouse, home gardens, vertical and urban agriculture.

EXAMPLE 2. Continuous nitrogen fixation for precision agriculture. With respect to FIG 6, the nitrogen fixation cells in parallel or series are powered from the battery of a tractor and use a nutrient solution or water contained in a tank to produce nitrate, nitrite, and ammonium rich fertilizer. The system sprays the required amount of nitrogen solution from sprayer nozzles, such that the information regarding the amount of nitrogen required is obtained from nitrogen map of the field and the present location of the tractor. The geospatial location is obtained using an on-board GPS sensor. The rate of nitrogen rich fertilizer solution production is varied depending on the speed of the tractor.

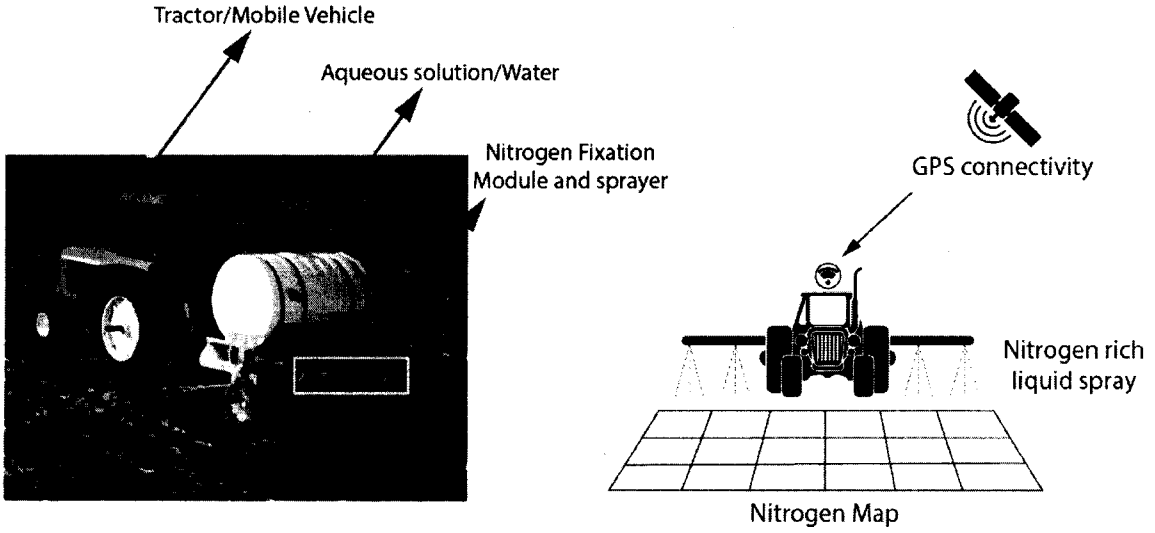

FIG 6. Application of the nitrogen fixation module in soil-based precision agriculture.

EXAMPLE 3. Continuous system for water treatment. The functionality of the principal design of the cell, module and the system could be extended beyond nitrogen fixation applications. For example, the components of the invention in FIG 1 can be configured to produce ozone (O_3), peroxide, and hydroxyl radical directly in the aqueous solution. Direct application of plasma to multiphase aqueous solution efficiently splits molecular oxygen O_2 from the gas mixture into oxygen ions, which then recombine to produce ozone. Likewise, through a cascade of reactions, peroxide and hydroxyl radicals are also formed. These oxidising chemical species formed in water or aqueous solution can effectively inactivate micro-organisms and breakdown recalcitrant chemical contaminants, such as pesticides, endocrine disrupting chemicals, and microbial toxins.

Although the present invention has been described in terms of specific embodiments, it is anticipated that alterations and modifications thereof will no doubt become apparent to those skilled in the art. It is therefore intended that the following claims be interpreted as covering all alterations and modifications that fall within the true spirit and scope of the invention.

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Redundant file. Drawings are provided along with the description.

METHOD AND APPARATUS FOR NITROGEN FIXATION

CLAIMS

What is claimed is:

1. A method for in-situ fixation of gaseous nitrogen into water-soluble nitrogen oxides via direct plasma treatment of a multiphase aqueous solution or water containing finely dispersed bubbles of a gas mixture with at least nitrogen and oxygen as its constituents. The multiphase aqueous solution is uniformly exposed to the high voltage electric discharge over the entire volume of the bubble column.
2. The method in claim 1, where the gas mixture contains at least oxygen and nitrogen and in varying ratios.
3. The method in claim 1, where the gas mixture is atmospheric air.
4. The method in claim 1, where the plasma is created by any means applicable for ionization of the gas, including electromagnetic field and/or ultraviolet light.
5. The method in claim 1, wherein
    - 5.1. The voltage for plasma discharge is at least 0.5 kV and below 220 kV
    - 5.2. The method in claim 1, wherein the frequency of the voltage applied is 0 Hz and up to 3000 MHz
    - 5.3. The applied voltage for plasma treatment has varying rise and fall times, including sinusoidal or square or triangular or saw-tooth pulses, or a mixture thereof.
    - 5.4. The power source supplying the voltage is from electricity distribution lines or solar panels or wind turbine or battery or power generator operated by fuel.
    - 5.5. The gas mixture is dispersed in the liquid media in form of bubbles with the diameters not exceeding 12 mm and preferably below 100 nm.
    - 5.6. The controlled diffusion and reaction of the intermediate ionized gaseous species is optionally achieved by means of distributed infusion of the gas mixture over the length of the column.
    - 5.7. the aqueous solution or water flows at a varying flow rate of at least 0.1 mL/min and up to 10,000 L/min.

5.8. the aqueous solution or water flowing is at a temperature varying between at least 4.1 °C and up to 95 °C.

5.9. other conditions, evident to anyone skilled in the art, for increasing the total surface area of the bubbles leading to rapid diffusion of metastable species into the aqueous medium and reaction with water molecules to stabilize the desired chemical products and prevent recombination of the species

6. An apparatus for direct nitrogen fixation into aqueous solution or water using the method described in claim 1, comprising of two metal electrodes separated by a distance with a dielectric material.

7. The apparatus in claim 6, wherein two electrodes are not in direct contact with the aqueous solution or water.

8. The apparatus in claim 6, wherein two electrodes are made of a single metal or an alloy with a cylindrical shape or spherical shape or spiral shape or a combination thereof.

9. The apparatus in claim 6, wherein dielectric material is a gas or gas mixture.

10. The apparatus in claim 6, wherein dielectric material is a liquid.

11. The apparatus in claim 6, wherein dielectric material is a solid.

12. The apparatus in claim 6, wherein the continuous aqueous solution or water supply is controlled to regulate the mass flow rate and/or volume flow rate.

13. The apparatus in claim 6, wherein the gas mixture or air flow supply rate is controlled to regulate the mass flow rate and/or volume flow rate.

14. The apparatus in claim 6, wherein the temperature of the liquid is controlled using a heating and/or cooling device, the said device optionally being an inductive heating element that also serves as the ground electrode.

15. The apparatus in claim 6, wherein the heat generated in the gas bubbles due to electric field is instantly dissipated by the flowing aqueous solution or water.

16. The apparatus in claim 6, wherein the voltage is supplied using a high voltage, high power source of electromagnetic energy.

17. The apparatus in claim 6, wherein the rate of nitrogen fixation is controlled by

17.1. the flow rate of the aqueous solution or water

17.2. the flow rate of the gas mixture or air

17.3. the electromagnetic field applied across the electrodes

17.4. the temperature of the aqueous solution or water containing the gas mixture or air

18. The apparatus in claim 6, which is designed as a bubble column reactor unit for direct conversion of air or gas mixture containing nitrogen and oxygen in air bubbles into nitrate, nitrite, or ammonium ions.

19. The apparatus in claim 6 and 18, where the units could be connected in series with co-flow or counter-flow of the gas mixture and the aqueous solution.

20. The apparatus in claim 6 and 18, where the units could be connected in parallel with co-flow or counter-flow of the gas mixture and the aqueous solution.

21. The apparatus in claim 6 and claim 18, wherein the modules are placed on a manned or unmanned vehicle and controlled using a programmed and/or adaptive control system to produce the desired concentration and desired rate of nitrates, nitrites, and ammonium ions in solution.

22. The apparatus in claim 21, wherein the desired concentration is determined from nitrogen requirement maps or determined in real-time using sensors together with the geographical location of the module as determined using appropriate sensors, such as a GPS sensor.

23. The apparatus in claim 21, wherein the desired rate of production of nitrates, nitrites, and ammonium ions is calculated in real-time according to the speed of the vehicle and the geographical location of the module.

24. The method of claim 1 and the apparatus of claim 6, claim 18 and claim 21 applied to soil based agriculture, including greenhouse cultivation.

25. The method of claim 1 and the apparatus of claim 6 and claim 18 applied to hydroponic growing system.

26. The method of claim 1 and the apparatus of claim 6 and claim 18 applied to algal cultures.

27. The method of claim 1 and the apparatus of claim 6 and claim 18 applied to microbial cultures.

28. The apparatus of claim 6 and claim 18, wherein the configuration and controlled discharge conditions, including the combination of temperature, flow rate of the

aqueous solution or water and flow rate of gaseous mixture, prevent the formation of hydroxyl radicals.

29. The apparatus in claim 6 and claim 18, wherein the configuration and controlled discharge conditions, including the combination of temperature, flow rate of the aqueous solution or water and flow rate of gaseous mixture, increase the formation of ozone, hydroxyl radicals, and peroxide in the aqueous solution or water.

30. The apparatus in claim 6, claim 18 and claim 29 applied to water treatment for microbial inactivation and/or sterilization and/or breakdown of chemical contaminants.

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