

PLASMA GENERATING METHOD AND DEVICE

Technical Field

【0001】

This invention relates to a plasma generating method and generating device that cause an electric discharge to occur between a fluid and a dielectric tube.

Background of the Invention

【0002】

In recent years, ozone generating devices have been used in the sterilization of bacteria, fungi and yeast, deodorizing of odorants such as aldehydes, sulfur compounds and nitrogen compounds, bleaching of dye effluents and human waste and detoxification of harmful substances such as organic solvents in water and sewage treatment facilities, chemical plants, pharmaceutical plants, food factories and the like.

【0003】

In general, this technique generates ozone using an electric discharge-type ozonizer, which mixes with the water necessary for the process at the gas-liquid mixing section such as the bubbler, ejector, static mixer and the like, causing the gas-liquid contact.

【0004】

However, ozone is an allotrope of oxygen and decomposes to oxygen at room temperature since ozone is a very unstable gas. Storing of ozone is therefore difficult, necessitating the on-site generation of ozone. At the same time, the high processing cost compared to the treatment that utilizes chlorine is also a problem.

【0005】

For this problem, an ozone water treatment device has been proposed wherein a gas passage is formed between a porous ceramic pipe and high voltage electrode by placing a high voltage electrode inside the center of the porous ceramic pipe, and a passage for the water to be treated is formed by placing a grounding electrode on the outside of the porous ceramic pipe as well as

directly connecting it to the outer surface of the porous ceramic pipe and then connecting a high voltage, high frequency power supply or a high-voltage pulse power supply between a high-voltage electrode and grounding electrode (for example, see Patent Document 1).

【0006】

However, in the case of the ozone water treatment device described above, high voltage electrodes are placed inside the center of the porous ceramic pipe, and high voltage or a pulse high voltage is applied using a high voltage, highfrequency power supply or a high-voltage pulse power supply. Precise positioning of the high voltage electrode has to be determined to cause a stable electric discharge, and a dense dielectric coating treatment of the electrode surface and an expensive pulse power supply are necessary.

【0007】

In contrast, a device has been proposed which has a nozzle with a scaled-down inner diameter for the water pipe line provided at the latter portion of the pressure part which pressure feeds the water undergoing treatment; which carries out treatment processes such as degradation or synthesis of substances undergoing treatment such as organic matter contained in water to be treated by generating an electric discharge plasma by applying a high voltage on the cavitation generator for generating cavitation bubbles, on the counter electrodes consisting of the ground side electrode and the high voltage side electrode provided to face the vicinity of the latter portion of the cavitation generator, and between counter electrodes; and wherein the counter electrodes are arranged along the inner surface of the water pipe line inside the cavitation generator so as to form a creeping electric discharge on the surface of the pipe line (for example, see Patent Document 2).

【0008】

However, in the case of the plasma generating device described above, the gas to be dissolved in advance to the water undergoing treatment will generate bubbles via cavitation performing electric discharge at the gas-liquid interface. Arbitrarily adjusting the amount of gas is difficult and cavitation bubbles are not

generated if the liquid to be treated is degassed. Further, since electric discharge does not occur in areas other than where cavitation bubbles are generated, it is difficult for the device to be enlarged.

Prior Art Documents

Patent Documents

【0009】

【Patent Document 1】 JP Patent Publication No. 2002-126769

【Patent Document 2】 JP Patent Publication No. 2009-119347

Summary of Invention

Problems to be Solved by the Invention

【0010】

The results of the intensive research done by the inventors to solve the problems described above showed that by causing an electric discharge to occur while passing the fluid through the dielectric tube, any fluid and any gas can be controlled at any flow rate, which further led to the provision of a plasma generating method and generating device that can generate plasma in the gas phase and the liquid phase while dissolving the gas in the fluid with high efficiency by forming an aspirator structure.

Means of Solving the Problem

【0011】

The plasma generating method and generating device of this invention is a method of generating plasma with an electric discharge within a dielectric tube by applying a voltage to a supplied gas, wherein its first characteristic is: a high voltage electrode is arranged on the outer side of the dielectric tube, a grounding electrode is arranged in a fluid that is discharged into the dielectric tube while remaining at a distance from the inner perimeter of the dielectric tube

and by applying a voltage to the grounding electrode and high voltage electrode connected to the power supply, an electric discharge occurs between the inner wall of the dielectric tube and the fluid.

【0012】

The second characteristic of the device involves the positioning of a water passage pipe, which is used for discharging fluid to the dielectric tube, within or above the dielectric tube.

【0013】

The third characteristic of the method of generating plasma with an electric discharge within a dielectric tube by applying a voltage to a supplied gas involves the following: a high voltage electrode is arranged on the outer side of the dielectric tube, a water passage pipe is arranged through which the fluid passes through the interior of the dielectric tube, a grounding electrode is arranged in a fluid that is discharged through the water passage pipe into the interior of the dielectric tube while remaining at a distance from the inner perimeter of the dielectric tube, and by applying a voltage to the grounding electrode and high voltage electrode connected to the power supply, an electric discharge is caused to occur between the inner wall of the dielectric tube and the water passage pipe.

【0014】

Furthermore, the fourth characteristic of the method and device is that the volume of the above-mentioned supplied gas and the volume of the fluid will have a gas-liquid ratio of 0.5 or less, and the fifth characteristic of the device is that the above-mentioned supplied gas can be either a gas containing at least oxygen or an inert gas.

【0015】

The sixth characteristic of the method and device is that fluid that passes through the portion where the electric discharge occurs is again used as the fluid that is discharged into the interior of the dielectric tube, or it is returned to the upstream side of the water passage pipe again, thus circulating the fluid. Further, the seventh characteristic of the method and device is that the

connections of the dielectric tube, water passage pipe and an inlet which introduces the supplied gas are formed to have the structure of an aspirator, a strong negative pressure is produced in the gap between the fluid that is discharged from the discharge port of the water passage pipe and the interior of the dielectric tube, which causes dissolution of the gas generated by the electric discharge into the fluid by cavitation. In addition, the eighth characteristic is that the generating device consists of a dielectric tube with a high voltage electrode placed outside, a water passage pipe that is positioned within or above the dielectric tube, a grounding electrode arranged so as to be in contact with a fluid that is discharged into the interior of the dielectric tube while remaining at a distance from the inner perimeter of the dielectric tube, and a power supply to which the high voltage electrode and grounding electrode are connected.

【0016】

The ninth characteristic is that the high voltage electrode is arranged outside the dielectric tube at the portion where the dielectric tube and the water passage pipe overlaps. The tenth characteristic is that the grounding electrode is positioned in the fluid that is excreted from the interior of the dielectric tube or from the dielectric tube.

【0017】

In addition, the eleventh characteristic is that the grounding electrode is coated with an insulating compound, and the twelfth characteristic is that the insulating compound is glass.

【0018】

Further, the thirteenth characteristic is that the dielectric tube is at least made of either ceramic or glass.

【0019】

In addition, the fourteenth characteristic is that the water passage pipe is made from one of the following materials: ceramics, glass, resin or metal. The fifteenth characteristic is that the aforesaid resin is a fluorine-based resin.

【0020】

Further, the sixteenth characteristic is that the portion where the electric

discharge occurs has a structure that returns the fluid that has passed through to the upstream side of the water passage pipe again to circulate the fluid. The seventeenth characteristic is that the dielectric tube, water passage pipe and the gas inlet provided on the dielectric tube is formed to have the structure of an aspirator.

Effects of the Invention

【0021】

The following superior effects are obtained from the plasma generating method and generating device of this invention.

【0022】

- (1) By using the plasma generating method and plasma generating device of the present invention, it is possible for the plasma to be irradiated directly or in the vicinity of the fluid to be treated.
- (2) If the supplied gas contains oxygen, it is possible to generate a large amount of ozone. Thus, it is not only possible to supply a large amount of ozone directly to the fluid, but also possible to generate active species such as OH radicals.
- (3) By controlling the gas-liquid ratio of the gas and fluid to be introduced into the dielectric tube, it is possible to dissolve the ozone generated by the electric discharge into the fluid with high efficiency.
- (4) By forming the aspirator structure, a strong negative pressure is produced in the gap between the fluid that is discharged from the discharge port of the water passage pipe and the interior of the dielectric tube, which further dissolves the ozone gas into the fluid with high efficiency by cavitation.

Brief Description of the Drawings

【0023】

Figure 1. A flow diagram of the experimental set-up of the first embodiment of the invention.

Figure 2. A diagram showing the plasma generating device of the first embodiment of the invention.

Figure 3A. A photograph showing the experimental results in the first embodiment of the invention.

Figure 4..A schematic view of the plasma generating device of the second embodiment of the invention.

Figure 5. A graph showing the changes in the generated ozone concentration and dissolved ozone concentration with electric discharge time in Example 1.

Figure 6. A flow diagram of the experimental set-up in Example 1.

Figure 7. A graph showing the relationship between the gas-liquid ratio and the dissolution efficiency from Example 2 through Example 5 and Comparative Example 1.

Figure 8. A diagram showing the plasma generating device in Example 6.

Figure 9. A graph showing the changes in the generated ozone concentration and dissolved ozone concentration with electric discharge time in Example 6.

Figure 10. A graph showing the changes in the generated ozone concentration and dissolved ozone concentration with electric discharge time in Example 7.

Figure 11. A photograph showing the experimental results in Example 8.

Figure 12. A graph showing the changes in the generated ozone concentration with electric discharge time in Example 9.

Figure 13. A diagram showing the plasma generating device in Example 10.

Figure 14. A photograph showing the experimental results in Example 10.

Figure 15. A schematic diagram of the generating device in Example 10.

Figure 16. A graph showing the changes in the generated ozone

concentration with electric discharge time in Example 11 and Comparative Example 2 through Comparative Example 4.

Figure 17. A graph showing the changes in the amount of methylene blue decolorization with electric discharge time in Example 11 and Comparative Example 2 through Comparative Example 4.

Figure 18. A diagram showing the plasma generating device in Example 12.

Figure 19. A photograph showing the experimental results in Example 12.

Figure 20. A schematic diagram of the plasma generating device in Example 12.

Figure 21. A graph showing the changes in the generated ozone concentration and dissolved ozone concentration with electric discharge time in Example 12.

Figure 22. A graph showing the relationship between the gas-liquid ratio and the dissolution efficiency from Example 13 through Example 16 and Comparative Example 5 of the invention.

Figure 23. A diagram showing the plasma generating device in Example 17.

Figure 24. A graph showing the changes in the generated ozone concentration and dissolved ozone concentration with electric discharge time in Example 17.

Figure 25. A graph showing the changes in the generated ozone concentration and dissolved ozone concentration with electric discharge time in Example 18.

Figure 26. A photograph showing the experimental results in Example 19.

Figure 27. A graph showing the changes in the generated ozone concentration with electric discharge time in Example 20.

Mode For Carrying Out the Invention

【0024】

Embodiment 1

The first embodiment of the invention will be explained below based on Figure 2 and Figure 8, although it is to be understood that the invention is not limited to

this embodiment.

【0025】

The plasma generating device of this invention in Figure 2 consists of the dielectric tube 1, water passage 2, high voltage electrode 3, grounding electrode 4, power supply 5 and gas inlet tube 6 and is formed to have the structure of an aspirator.

【0026】

The dielectric tube 1 is made of glass and is substantially cylindrical-shaped. Although the cross section of the dielectric tube 1 may be square, diamond-shaped, or even polygonal, it is preferable for the high voltage electrode 3 to be circular for ease of placement.

【0027】

The water passage pipe 2 is located with its center of circle being identical to that of the dielectric tube 1, and the discharge port of the water passage pipe 2 is arranged at the upstream side of the high voltage electrode 3 portion that is positioned on the dielectric tube 1. Although the cross section of the water passage pipe 2 may be square, diamond-shaped, or even polygonal, since the water passage pipe 2 will function as a dielectric, it is preferable for the water passage pipe 2 to have the same shape as the dielectric tube 1 so that its gap with the dielectric tube 1 will be uniform.

【0028】

The fluid introduced into the water passage pipe 2 should be supplied under pressure by a difference in elevation or by pump, wherein the fluid is a liquid or a gas containing a liquid as exemplified by steam. The introduced fluid goes through the water passage pipe 2, passing through the interior of the dielectric tube 1. However in order to cause the generation of the electric discharge plasma between the fluid and the inner wall of the dielectric tube 1 at the portion where the high voltage electrode 3 is positioned, it is preferable that the fluid does not adhere to the inner wall of the dielectric tube 1 at the portion where the high voltage electrode 3 was positioned. However, even if the fluid adheres to the inner wall of the dielectric wall 1, the electric discharge plasma will still be

generated since gas spaces are formed in the fluid due to the introduction of the gas.

【0029】

The velocity of the fluid can be set arbitrarily, but it is preferable to choose a flow rate that corresponds to the purpose of the fluid to be treated via electric discharge frequency which is calculated from the frequency of the power supply 5 being used. To dissolve gas generated by electric discharge such as ozone into the fluid, it is preferable for the amount of fluid and gas to have a gas-liquid ratio of 0.5 or less. Further, as shown in Figure 2, by forming the aspirator structure, a strong negative pressure is produced in the gap between the fluid that is discharged from the discharge port of the water passage pipe 2 and the interior of the dielectric tube 1, which increases the dissolution efficiency due to resultant cavitation that occurs at the discharge port.

【0030】

The high voltage electrode 3 is wrapped around the outside of the dielectric tube 1 while the grounding electrode 4 is positioned at the center of the interior of dielectric tube 1, and each is connected to the power source 5. When the gas is introduced from the gas inlet tube 6 while voltage is being applied to the fluid, an electric discharge is generated circumferentially between the fluid and the inner wall of the dielectric tube 1 at the portion where the high voltage electrode 3 is positioned.

【0031】

The grounding electrode 4 can be positioned in the interior of the dielectric tube 1 as shown in Figure 2 or in the fluid that is discharged from the dielectric tube 1 as shown in Figure 8. If the grounding electrode 4 is positioned in the interior of the dielectric tube 1, the gap between the high voltage electrode 3 and the grounding electrode 4 decreases, inducing a strong electric field that makes electric discharge easy. However, if the electric conductivity of the fluid is high, for example in the case of seawater, a strong electric field is generated and electric discharge will be easy, even if the grounding electrode 4 is positioned in the fluid that is discharged from the dielectric tube 1. Therefore,

the position of the grounding electrode 4 may be set based on the nature of the fluid.

【0032】

Moreover, metals such as copper or stainless steel should be chosen for the grounding electrode 4, depending on the nature of the fluid. However, if issues arise due to the elution of metal components such as when washing the electronic parts, the grounding electrode 4 should be coated with an insulating compound, preferably glass which has a small dielectric constant and less elution into the fluid.

【0033】

The material of the dielectric tube 1 may be ceramics or glass which are plasma-resistant, heat-resistant and ozone-resistant, while glass having a small dielectric constant is preferable.

【0034】

Any material can be chosen for the water passage tube 2. Because a material serves as a dielectric as long as it is highly insulating, any material may be selected based on its dielectric constant. Ceramics, glass and resins are good for their excellent plasma-resistance, ozone-resistance and durability, with glass and fluorine-based resins being particularly preferable. In addition, highly conductive metallic materials can also be used. In the case of a metallic material, a strong electric field is generated at the dielectric tube 1, making electric discharge easy. Moreover, if a metallic material is chosen for the water passage pipe 2, the installation electrode 4 may be arranged on the water passage pipe 2 itself, which would save time and effort in the production.

【0035】

The gas to be introduced can either be supplied under pressure by a blower, compressed gas cylinder and the like, or it can enter by itself using the negative pressure generated when the fluid passes through. In either case, the gas is introduced into the interior of the dielectric tube 1 through the gas inlet tube 6. The gas to be utilized can be determined arbitrarily according to the purpose of the fluid that is to be treated, however, in order to generate active species such

as ozone or OH radicals, gas containing oxygen 7 should at least be used. Moreover, if the gas containing oxygen 7 will be dissolved in the fluid beforehand, an inert gas may be used.

【0036】

Embodiment 2

Next, second embodiment of the invention will be explained below based on Figure 4, Figure 13 and Figure 15, however the invention is not limited to this embodiment.

【0037】

The description of the plasma generating device will be omitted because it is the same as that of the first embodiment.

【0038】

As shown in Figure 13, the water passage pipe 2 is located on the center of the same circle as the dielectric tube 1, and the discharge port of the water passage pipe 2 is arranged at the downstream side of the high voltage electrode 3 portion that is positioned on the dielectric tube 1.

【0039】

In the plasma generating device, the electric discharge basically occurs between the fluid and the inner wall of the dielectric tube 1 at the portion where the high voltage electrode 3 was positioned, but it is not necessary for the fluid to be present at the inner wall of the dielectric tube 1 at the portion where the high voltage electrode 3 was positioned. Since an electric discharge is generated in a region where the electric field becomes strong, by placing the discharge port of the water passage pipe 2 at the vicinity downstream of the inner wall of the dielectric tube 1 where the high voltage electrode 3 is positioned as shown in Figure 13, a strong electric field is generated between the fluid and the inner wall of the dielectric tube 1 as shown in Figure 15, causing the electric discharge to occur.

【0040】

As shown in Figure 4, if the electric discharge is generated in the fluid and the inner wall of the dielectric tube 1 at the portion where the high voltage electrode 3 is positioned, it is necessary to maintain a constant distance between the fluid and the dielectric tube 1 for a stable electric discharge to rigorously continue, so a flow rectifier should be mounted in the interior of the water passage pipe 2 or a constant pressure valve or the like should be provided at the water passage pipe 2. On the other hand, if the discharge port of the water passage pipe 2 is placed at the vicinity downstream of the inner wall of the dielectric tube 1 where the high voltage electrode 3 is positioned to generate an electric discharge as shown in Figure 15, the distance between the fluid and the inner wall of the dielectric tube 1 at the portion where the high voltage electrode 3 is positioned would be fixed since the discharge port of the water passage pipe 2 is fixed. Hence, even without a flow rectifier, constant pressure valve or the like in the water passage pipe 2, a stable electric discharge can continue between the fluid and the inner wall of the dielectric tube 1. Further, upon the application of a sufficient voltage to the dielectric tube 1, a strong electric field is also generated at the interior of the water passage 2, so a gas-liquid interface electric discharge is generated between the gas and the liquid in the fluid.

【0041】

In this case, the distance of the discharge port of the water passage pipe 2 and the inner wall of the dielectric tube 1 at the portion where the high voltage electrode 3 is positioned must be the length in which the electric discharge is extended. This length can be determined by the interval of the inner diameter of the dielectric pipe 1 and the outer diameter of the water passage pipe 2. For example, if the interval of the inner diameter of the dielectric pipe 1 and the outer diameter of the water passage pipe 2 is 0.5 mm, and the distance between the discharge port of the water passage pipe 2 and the inner wall of the dielectric tube 1 wherein the high voltage electrode 3 is positioned is 20 mm or less, then the electric discharge will be generated between the inner wall of the dielectric tube 1 and the fluid that was discharged from the discharge port of

the water passage pipe 2. Further, if a porous ceramic is used for the water passage pipe 2, the fluid will effuse from the porous holes, and since the electric discharge is generated between the fluid effusing from the pores and the inner wall of the dielectric tube 1 at the portion where the high voltage electrode 3 is positioned, the effort to rectify the fluid is eliminated. Any material can be chosen for the water passage tube 2. A material also serves as a dielectric as long as it is highly insulating, so any material may be selected based on its dielectric constant. However, ceramics, glass and resins are good for their excellent plasma-resistance, ozone-resistance and durability, with glass and fluorine-based resins being preferable. In addition, highly conductive metallic materials can also be used. In case a metallic material is used, a strong electric field is generated at the dielectric tube 1, making electric discharge easy. Moreover, if a metallic material is chosen for the water passage pipe 2, the grounding electrode 4 may be arranged on the water passage pipe 2 itself, which would save time and effort in the production.

Example

【0042】

Photographs were taken during the electric discharge, and exhaust ozone concentration and dissolved ozone concentration tests were performed using the above-mentioned embodiment of the invention. The measurement methods for the test are shown below.

【0043】

(1) Measurement of the Generated Ozone Concentration

Gas-phase ozone concentration meter: OZ-30 manufactured by DKK-TOA Corporation

The ozone concentration sensor is inserted to the top of the water receiving tank, and the generated ozone concentration was measured using a gas-phase ozone concentration meter.

(2) Measurement of the Dissolved Ozone Concentration

Dissolved ozone concentration meter: OZ-20 manufactured by DKK-TOA Corporation

The dissolved ozone concentration is measured by placing the dissolved ozone concentration sensor in the circulation tank.

【0044】

Example 1

Figure 1 shows the flow diagram of the experimental set-up. The experimental set-up consists of the plasma generation device, a water receiving tank (6 L volume of water) that receives the treated water discharged from the plasma generating device and which is equipped with an ozone concentration sensor in the upper surface of the water, and a circulation tank (2 L volume of water) that circulates the tap water, which is equipped with a dissolved ozone concentration sensor at the lower surface of the water and is connected to the water receiving tank by a pipe. The experimental set-up is connected from the circulation tank to the plasma generating device using a magnetic drive pump and silicon rubber tubing, while the gas inlet of the plasma generating device and the oxygen tank are connected by flexible nylon tubing. As shown in Figure 2, the main body of the plasma generating device is made of glass and is formed to have the structure of an aspirator. The water passage pipe 2 (7 mm outer diameter, 5 mm inner diameter) is positioned with its center of circle identical to that of the dielectric tube 1 (10 mm outer diameter, 8 mm inner diameter) and a high voltage electrode 3 made of a 10 mm width copper tape is wrapped around the outside of the dielectric tube 1 so that the 10 mm point at the downstream side from the discharge port of the water passage pipe 2 becomes the center. The stainless steel grounding electrode 4 with a diameter of 1mm is inserted from the vicinity of the gas inlet to the water passage pipe 2 and the dielectric tube 1, and the high voltage electrode 3 and grounding electrode 4 are connected to the power supply 5. The magnetic drive pump is activated to circulate the tap water at a flow rate of 8 L/min. At the other side, voltage is applied (9 kV, 6 kHz) to carry out the electric discharge while oxygen

7 is being introduced from the oxygen tank at an air flow rate of 3 L/min, during which time the electric discharge was observed and the ozone concentration and dissolved ozone concentration were measured. As shown in Figure 3 (photograph) and Figure 4 (schematic diagram), the results indicated that a purple electric discharge was observed between the inner wall of the dielectric tube 1 and the tap water. Further, it is known that ozone is generated if the electric discharge occurs in the presence of oxygen. As proof that electric discharge has occurred, Figure 5 shows that the generated ozone concentration became 1000 ppm, while the dissolved ozone concentration became 0.47 ppm 30 minutes from the start of the electric discharge.

【0045】

Example 2

As shown in Figure 6, a continuous flow of water was maintained without circulating the tap water, and the same experiment as Example 1 was carried out, except that the flow rate of oxygen 7 was 4 L/min (gas-liquid ratio of 0.5), and then the dissolved ozone concentration was measured. The results, as shown in Figure 7, indicated that the ozone dissolution efficiency became 21%.

【0046】

Example 3

The same experiment as Example 2 was carried out except that the flow rate of oxygen 7 was 2.4 L/min, and then the dissolved ozone concentration was measured. The results, as shown in Figure 7, indicated that the ozone dissolution efficiency became 27%.

【0047】

Example 4

The same experiment as Example 2 was carried out except that the flow rate of oxygen 7 was 0.8 L/min, and then the dissolved ozone concentration was

measured. The results, as shown in Figure 7, indicated that the ozone dissolution efficiency became 48%.

【0048】

Example 5

The same experiment as Example 2 was carried out except that the flow rate of oxygen 7 was 0.4 L/min, and then the dissolved ozone concentration was measured. The results, as shown in Figure 7, indicated that the ozone dissolution efficiency became 67%.

【0049】

Example 6

As shown in Figure 8, the same experiment as Example 1 was carried out except that the grounding electrode 4 which is made of stainless steel wire (1 mm diameter) was placed in the water receiving tank, and then the ozone concentration and dissolved ozone concentration were measured. The results, as shown in Figure 9, indicated that the generated ozone concentration became 527 ppm, while the dissolved ozone concentration became 0.18 ppm 30 minutes from the start of the electric discharge.

【0050】

Example 7

The same experiment as Example 1 was carried out except that the size of the water passage pipe 2 was set to 7 mm in outer diameter and 6 mm in inner diameter and the installation electrode was coated with a glass of 0.5 mm in thickness, and then the ozone concentration and dissolved ozone concentration were measured. The results, as shown in Figure 10, indicated that the generated ozone concentration became 700 ppm, while the dissolved ozone concentration became 0.38 ppm 30 minutes from the start of the electric discharge.

【0051】

Example 8

The same experiment as Example 1 was carried out except that the gas

introduced to the plasma generating device was argon gas. The results, as shown in Figure 11 (photograph) and Figure 4 (schematic diagram) indicated that a purple electric discharge was observed between the inner wall of the dielectric tube 1 and the tap water.

【0052】

Example 9

The same experiment as Example 1 was carried out except that the material used for the water passage pipe 2 of the plasma generating device was either PFA (tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer) resin or stainless steel metal, and then the generated ozone concentrations were measured as proof of the occurrence of the electric discharge. The results, as shown in Figure 12, indicated that the generated ozone concentration became 956 ppm and 1043 ppm, respectively, 30 minutes from the start of the electric discharge.

【0053】

Example 10

As shown in Figure 13, an electric discharge was carried out in the same manner as Example 1 except that the discharge port of the water passage pipe 2 was arranged 15 mm at the downstream side from the center of the high voltage electrode 3, which was positioned on the dielectric tube 1, and the gas introduced was argon, and then the electric charge was observed and the ozone concentration and dissolved ozone concentration were measured. The results, as shown in Figure 14 (photograph) and Figure 15 (schematic diagram), indicated that a purple electric discharge was observed between the inner wall of the dielectric tube 1 and the outer wall of the water passage pipe 2 and between the inner wall of the dielectric tube 1 and the tap water.

【0054】

Example 11

The same experiment as Example 10 was carried out except that the introduced gas was oxygen 7, and methylene blue was added to tap water to achieve a concentration of 5 mg/L. The changes in the integrated amount of generated ozone with time are shown in Figure 16 while the changes in the

amount of methylene blue decolorization with time are shown in Figure 17.

【0055】

Comparative Example 1

The same experiment as Example 1 was carried out except that the air flow rate of oxygen 7 was 4.8 L/min, and then the dissolved ozone concentration was measured. The results, as shown in Figure 7 indicated that the ozone dissolution efficiency became 18%.

【0056】

Comparative Example 2

The same experiment as Example 11 was carried out except that t-BuOH, which is an OH radical supplemental agent, was added to achieve a concentration of 0.1 mM. The changes in the integrated amount of generated ozone with time are shown in Figure 16 while the changes in the amount of methylene blue decolorization with time are shown in Figure 17. The results show that the decolorization rate decreased by the addition of t-BuOH even though the generated ozone remained the same, which suggests the generation of OH radicals by the plasma generating device.

【0057】

Comparative Example 3

The same experiment as Example 11 was carried out except that t-BuOH, which is an OH radical supplemental agent, was added to achieve a concentration of 1 mM. The changes in the integrated amount of generated ozone with time are shown in Figure 16 while the changes in the amount of methylene blue decolorization with time are shown in Figure 17. The results show that the decolorization rate decreased by the addition of t-BuOH even though the generated ozone remained the same, which suggests the generation of OH radicals by the plasma generating device.

【0058】

Comparative Example 4

The same experiment as Example 11 was carried out except that t-BuOH, which is an OH radical supplemental agent, was added to achieve a

concentration of 10 mM. The changes in the integrated amount of generated ozone with time are shown in Figure 16 while the changes in the amount of methylene blue decolorization with time are shown in Figure 17. The results show that the decolorization rate decreased by the addition of t-BuOH even though the generated ozone remained the same, which suggests the generation of OH radicals by the plasma generating device.

【0059】

Example 12

As shown in Figure 18, the main body of the plasma generating device is made of glass and is formed to have the structure of an aspirator. The water passage pipe 2 (7 mm outer diameter, 5 mm inner diameter) is positioned with its center of circle being identical to that of the dielectric tube 1 (10 mm outer diameter, 8 mm inner diameter) and a high voltage electrode 3 made of a 10 mm width copper tape is wrapped around the outside of the dielectric tube 1 so that the 25 mm point at the upstream side from the discharge port of the water passage pipe 2 becomes the center. The stainless steel grounding electrode 4 with a diameter of 1 mm is inserted from the vicinity of the gas inlet to the water passage pipe 2 and the dielectric tube 1, and the high voltage electrode 3 and grounding electrode 4 are connected to the power supply 5. The magnetic drive pump is activated to circulate the tap water at a flow rate of 8 L/min. At the other side, voltage is applied (9 kV, 6 kHz) to carry out the electric discharge while oxygen 7 is being introduced from the oxygen tank at an air flow rate of 3 L/min, during which time the electric discharge was observed and the ozone concentration and dissolved ozone concentration were measured. As shown in Figure 19 (photograph) and Figure 20 (schematic diagram), the results indicated that a purple electric discharge was observed between the inner wall of the dielectric tube 1 and the tap water. Further, it is known that ozone is generated if the electric discharge occurs in the presence of oxygen. As proof that electric discharge has occurred, Figure 21 shows that the generated ozone concentration became 990 ppm, while the dissolved ozone concentration became 0.45 ppm 30 minutes from the start of the electric discharge.

【0060】

Example 13

As shown in Figure 6, a continuous flow of water was maintained even without circulating the tap water and the same experiment as Example 1 was carried out, except that the flow rate of oxygen 7 was 4 L/min (gas-liquid ratio of 0.5), and then the dissolved ozone concentration was measured. The results, as shown in Figure 22, indicated that the ozone dissolution efficiency became 21%.

【0061】

Example 14

The same experiment as Example 13 was carried out except that the flow rate of oxygen 7 was 2.4 L/min, and then the dissolved ozone concentration was measured. The results, as shown in Figure 22, indicated that the ozone dissolution efficiency became 26%.

【0062】

Example 15

The same experiment as Example 13 was carried out except that the flow rate of oxygen 7 was 0.8 L/min, and then the dissolved ozone concentration was measured. The results, as shown in Figure 22, indicated that the ozone dissolution efficiency became 50%.

【0063】

Example 16

The same experiment as Example 13 was carried out except that the flow rate of oxygen 7 was 0.4 L/min, and then the dissolved ozone concentration was measured. The results, as shown in Figure 22, indicated that the ozone dissolution efficiency became 73%.

【0064】

Example 17

As shown in Figure 23, the same experiment as Example 12 was carried out except that the grounding electrode 4 which is made of stainless steel wire (1 mm diameter) was placed in the water receiving tank, and then the ozone

concentration and dissolved ozone concentration were measured. The results, as shown in Figure 24, indicated that the generated ozone concentration became 534 ppm, while the dissolved ozone concentration became 0.19 ppm 30 minutes from the start of the electric discharge.

【0065】

Example 18

The same experiment as Example 12 was carried out except that the size of the water passage pipe 2 was set to 7 mm in outer diameter and 6 mm in inner diameter and the installation electrode was coated with a glass of 0.5 mm in thickness, and then the ozone concentration and dissolved ozone concentration were measured. The results, as shown in Figure 25, indicated that the generated ozone concentration became 685 ppm, while the dissolved ozone concentration became 0.37 ppm 30 minutes from the start of the electric discharge.

【0066】

Example 19

The same experiment as Example 12 was carried out except that the gas introduced to the plasma generating device was argon gas. The results, as shown in Figure 26 (photograph) and Figure 20 (schematic diagram), indicated that a purple electric discharge was observed between the inner wall of the dielectric tube 1 and the outer wall of the water passage pipe 2.

【0067】

Example 20

The same experiment as Example 12 was carried out except that the material used for the water passage pipe 2 of the plasma generating device was either PFA (tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer) resin or stainless steel metal, and then the generated ozone concentrations were measured as proof of the occurrence of the electric discharge. The results, as shown in Figure 27, indicated that the generated ozone concentration became 281 ppm and 348 ppm, respectively, 30 minutes from the start of the electric discharge.

【0068】

Comparative Example 5

The same experiment as Example 1 was carried out except that the flow rate of oxygen 7 was 4.8 L/min, and then the dissolved ozone concentration was measured. The results, as shown in Figure 22, indicated that the ozone dissolution efficiency became 17%.

【Description of the Reference Numerals】

【0069】

- 1... Dielectric tube
- 2... Water passage pipe
- 3... High voltage electrode
- 4... Grounding electrode
- 5... Power Supply
- 6... Gas inlet tube
- 7... Oxygen

CLAIMS

1. A plasma generating method characterized by a method for generating plasma with an electric discharge within a dielectric tube by applying a voltage to a supplied gas, wherein a high voltage electrode is arranged on the outer side of the dielectric tube and a grounding electrode is arranged in a fluid that is discharged into the dielectric tube while remaining at a distance from the inner perimeter of the dielectric tube, and an electric discharge is caused to occur between the inner wall of the dielectric tube and the fluid by applying a voltage to the high voltage electrode and the grounding electrode connected to a power source device.

2. A plasma generating method described in Claim 1 wherein a water passage pipe that discharges the fluid to the dielectric tube is positioned within or above the dielectric tube.

3. A plasma generating method characterized by a method for generating plasma with an electric discharge within a dielectric tube by applying a voltage to a supplied gas, wherein a high voltage electrode is arranged on the outer side of the dielectric tube, a water passage pipe is arranged through which the fluid passes through the interior of the dielectric tube and a grounding electrode is arranged in a fluid that is discharged through the water passage pipe into the dielectric tube while remaining at a distance from the inner perimeter of the dielectric tube, and an electric discharge is caused to occur between the inner wall of the dielectric tube and the water passage pipe by applying a voltage to the high voltage electrode and the grounding electrode connected to a power source device.

4. A plasma generating method described in Claims 1 to 3 wherein the volume of the above-mentioned supplied gas and the volume of the fluid will have a gas-liquid ratio of 0.5 or less.

5. A plasma generating method described in any of Claims 1 to 4 wherein the above-mentioned supplied gas is either a gas containing at least oxygen or an inert gas.

6. A plasma generating method described in any of Claims 1 to 4 wherein the fluid that passes through the portion where the electric discharge occurs is again used as the fluid that is discharged into the interior of the dielectric tube, or it is returned to the upstream side of the water passage pipe again, thus circulating the fluid.

7. A plasma generating method described in any of Claims 1 to 6 wherein the connections of the dielectric tube, water passage pipe and an inlet which introduces the supplied gas are formed to have the structure of an aspirator, a strong negative pressure is produced in the gap between the fluid that is discharged from the discharge port of the water passage pipe and the interior of the dielectric tube, which causes dissolution of the gas generated by the electric discharge into the fluid by cavitation.

8. A plasma generating device that consists of a dielectric tube with a high voltage electrode placed outside, a water passage pipe that is positioned within or above the dielectric tube, a grounding electrode arranged so as to be in contact with a fluid that is discharged into the interior of the dielectric tube while remaining at a distance from the inner perimeter of the dielectric tube, and a power supply to which the high voltage electrode and grounding electrode are connected.

9. A plasma generating device described in Claim 8 wherein the high voltage electrode is arranged outside the dielectric tube at the portion where the dielectric tube and the water passage pipe overlaps.

10. A plasma generating device described in Claim 8 or 9 wherein the grounding electrode is positioned in the fluid that is excreted from the interior of

the dielectric tube or from the dielectric tube.

11. A plasma generating device described in any of Claims 8 to 10 wherein the grounding electrode is coated with an insulating compound.

12. A plasma generating device described in Claim 11 wherein the insulating compound is glass.

13. A plasma generating device described in any of Claims 8 to 12 wherein the dielectric tube is at least made of either ceramic or glass.

14. A plasma generating device described in any of Claims 8 to 13 wherein the water passage pipe is made from one of the following materials: ceramics, glass, resin or metal.

15. A plasma generating device described in Claim 14 wherein the aforesaid resin is a fluorine-based resin.

16. A plasma generating device described in any of Claims 8 to 15 wherein the portion where the electric discharge occurs has a structure that returns the fluid that has passed through to the upstream side of the water passage pipe again to circulate the fluid.

17. A plasma generating device described in any of Claims 8 to 16 wherein the dielectric tube, the water passage pipe and the gas inlet provided on the dielectric tube are formed to have the structure of an aspirator.