Advanced Oxidation of Organic and Inorganic Pollutants with Free Radical Generator

TECHNICAL FIELD

[001] The present disclosure relates to device and methods for advanced generation of free radicals that may be used as reactants in various processes.

BACKGROUND

[002] Advanced oxidation processes (AOPs) utilize powerful hydroxyl radical (OH*) as a major oxidizing agent. OH* radical is very nonselective in its behavior and rapidly reacts with numerous species. Their reactions with organic compounds produce carbon-centered radicals (R* or R*–OH). With O_2, these carbon-center radicals may be transformed to organic peroxyl radicals (ROO*). Because hydroxyl radicals have a very short lifetime, they are produced *in-situ* through different methods, including a combination of oxidizing agents (such as H_2O_2 and O_3), and/or irradiation (such as ultraviolet light or cold plasma) of water, or catalysts (such as titanium dioxide).

[003] It is well known that Ozone (O_3) itself is a strong oxidant, however, direct O_3 oxidation is a selective reaction in which O_3 preferentially reacts with the ionized and dissociated form of organic compounds, rather than the neutral form, although under certain conditions, OH* is produced from O_3 to initiate the indiscriminate oxidation. Different mechanisms have been proposed to describe the generation of OH* as below:

$$3O_3 + H_2O \rightarrow 2OH^* + 4O_2 \qquad (1)$$

[004] In the presence of other oxidants or irradiation, the OH* yield can be significantly improved. For example, in the peroxone (O_3/H_2O_2) system, the O_3 decomposition and OH* production are enhanced by hydroperoxide (HO_2^-) produced from H_2O_2 decomposition.

$$H_2O_2 \rightarrow HO_2^- + H^+ \qquad (2)$$

$$HO_2^- + O_3 \rightarrow OH^* + O_2^- + O_2 \qquad (3)$$

[005] Further, with O_3/ultraviolet (UV) irradiation, H_2O_2 is generated as an additional oxidant primarily through O_3 photolysis.

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + h\nu \rightarrow 2OH^* \quad (5)$$

[006] Efficient generation of OH* radicals with a high density and reliability via streamer discharge to achieve practical AOP is desirable. However, prior systems and methods for achieving this are lacking and necessitate further improvement. Hence, new methods and devices are provided for effective AOP.

SUMMARY

[007] The following summary is provided to facilitate an understanding of some of the innovative features unique to the present disclosure and is not intended to be a full description. A full appreciation of the various aspects of the disclosure can be gained by taking the entire specification, claims, drawings, and abstract as a whole.

[008] It is desirable that a streamer discharge device be capable of utilizing gases with high moisture content (for useful OH^* radicals) to generate copious OH* radicals at high efficiency required for advanced oxidation process. However, in the presence of suspended water droplets in the feed gas, the discharge device may malfunction causing unwanted arcing, especially when the feed gas velocity at the discharge tips falls below 2 m/sec. Alternatively, when water itself is used as a counter electrode, surface undulations and discharge gap variation can lead to inhomogeneous AOP treatment and device malfunction.

[009] Provided are methods and devices that solve one or more of these problems optionally by providing in at least one aspect a method for enhancing the moisture content of the feed gas without suspended droplets, and thereby improving the concentration as well as the efficiency of OH* radical generation. This includes providing a feed gas with high dissolved moisture content but maintaining the conditions (pressure and temperature) so that droplet formation is prevented in the discharge space. The device further includes a steam generator as well as a gas heater enabling high dissolved moisture content in the feed gas.

[010] In yet other aspects, method for removing moisture from the feed gas to selectively generate ozone is provided. This optionally includes a regenerative desiccation wheel in the feed gas path which continuously supplies dry air to the discharge space and thereby primarily produces ozone.

[011] In yet other aspects, a method for continuous supply of OH* radicals along with ozone gas to achieve advanced oxidation process of organic and inorganic pollutants is provided. This optionally includes either streamer discharge device that generates both OH* radicals and ozone at a desired ratio or at least two streamer devices, one primarily providing OH* radicals and the other primarily providing ozone to enable advanced oxidation process.

[012] In other aspects, methods for directing the radicals from the discharge devices to the application site and distributing them to react with organic and inorganic pollutants are provided. This optionally includes a method for creating a suction through the discharge device and mixing the radical gas with a target fluid.

[013] Accordingly, it becomes possible to solve the above aforementioned problems and to generate OH* radicals or O_3 or their combination (OH*/O_3) selectively, which can either be utilized in the discharge space or supplied to an application site for advanced oxidation.

BRIEF DESCRIPTION OF THE DRAWINGS

[014] The drawings are not necessarily to scale; some features may be exaggerated or minimized to show details of particular components. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a representative basis for teaching one skilled in the art to variously employ the present invention. Exemplary aspects will become more fully understood from the detailed description and the accompanying drawings, wherein:

[015] FIG. 1 is a schematic illustrating electrode tips with four streamer ignition points to generate four repelling streamers according to at least one teaching of this disclosure;

[016] FIG. 2 is a perspective view of assembled discharge electrode inside the ground electrode according to one of the embodiments of the current disclosure;

[017] FIG. 3 presents the change in specific output ozone concentration with respect to discharge gap pressure and moisture level in a streamer device of the present disclosure;

[018] FIG. 4 presents the relative output concentration of ozone and OH* molecules with humid feed air to the streamer device of the present disclosure;

[019] FIG. 5 is a schematic arrangement for a regenerative desiccator wheel for removing moisture from the feed gas to the discharge gap according to the teachings of the present disclosure;

[020] FIG. 6 is a schematic arrangement for device adding dissolved moisture to the feed gas for generating OH* radicals according to the teachings of the present disclosure**;**

[021] FIG. 7 is a schematic arrangement for a mixing nozzle simultaneously drawing OH* radicals and ozone from respective generators through suction ports and mixing them to a fluid passing through main convergent/divergent passage according to the teachings of the present disclosure**;**

[022] FIG. 8 is a schematic arrangement for a turbine mixer simultaneously drawing OH* radicals and ozone from respective generators through suction ports and mixing them to a fluid according to the teachings of the present disclosure**;**

[023] FIG. 9 is a schematic arrangement for a turbine mixing system according to the teachings of the present disclosure**;**

[024] FIG. 10 is a schematic arrangement for the blades of the turbine according to the teachings of the present disclosure**;**

[025] FIG. 11 is a schematic side view of turbine according to the teachings of the present disclosure**;**

[026] FIG. 12 are the perspective views of the turbine according to the teachings of the present disclosure**;**

[027] FIG. 13 is a schematic arrangement for a recirculation system for providing high flow rate through the discharge device while having low throughput discharge gas from the device according to the teachings of the present disclosure**;**

[028] FIG. 14 presents the simulated flow field for a recirculation system demonstrating high flow rate through the discharge device while having low throughput discharge gas from the device according to the teachings of the present disclosure; and

[029] FIG. 15 presents the reduction in moisture content through the desiccator wheel of disclosed device according to the teachings of this disclosure.

DETAILED DESCRIPTION

[030] Detailed aspects are disclosed herein; however, it is to be understood that the disclosed aspects are merely exemplary in nature and may be embodied in various and alternative forms. The figures are not necessarily to scale. Therefore, specific details disclosed herein are not to be interpreted as limiting, but merely as a representative basis for any aspect of the invention and/or as a representative basis for teaching one skilled in the art to variously employ the present invention.

[031] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting. As used herein, the singular forms “a,” “an,” and “the” are intended to include the plural forms, including “at least one,” unless the content clearly indicates otherwise. “Or” means “and/or.” As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items. It will be further understood that the terms “comprises” and/or “comprising,” or “includes” and/or “including” when used in this specification, specify the presence of stated features, regions, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, regions, integers, steps, operations, elements, components, and/or groups thereof. The term “or a combination thereof” means a combination including at least one of the foregoing elements.

[032] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. It will be further understood that terms such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and the present disclosure, and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[033] Throughout this specification, where publications are referenced the disclosures of these publications in their entireties are hereby incorporated by reference into this application to more fully describe the state of the art to which this invention pertains.

[034] The following terms or phrases used herein have the exemplary meanings listed below in connection with at least one aspect:

[035] A “dielectric” material as used herein is a medium or material that transmits electrical force without conduction and as such has low electrical conductivity. An illustrative example of a dielectric material is glass.

[036] “Discharge space” as used herein means the gap between the active electrode and the ground electrode.

[037] “FRG” as used herein means “Free Radical Generator” operating according to the teachings of this disclosure.

[038] “Carbonaceous material” as used herein includes graphite, woven carbon or graphite fiber filled with binders, graphitized carbon materials, and compacted carbon materials, among others.

[039] “Mist” as used herein includes a cloud of tiny droplets of a liquid suspended in a gas wherein droplet weight is lower than the drag force exerted by the gas.

[040] “Fumigation” as used herein includes applying a gaseous fume of certain radicals to disinfect or to rid of biological organisms or toxins.

[041] “Superbugs” as used herein includes a strain of bacteria that has become resistant to one or more antibiotic drugs.

[042] “Toxins” as used herein includes an antigenic poison or venom of plant or animal origin, optionally one produced by or derived from microorganisms and causing disease when present at low concentration in the body.

[043] “Streamer” means a self-sustained ionization wave having substantial field enhancement in the range of 100-250 kV.cm^{-1} compared to the applied voltage which is in the range of 20-30 kV.cm^{-1} and propagating in neutral gas which is converted into low-temperature plasma behind the wave front, resulting in a channel like appearance. The interior of the streamer channel consists of a conducting plasma with roughly the same electron and ion densities.

[044] “Free radical” means an atom or group of atoms that has an unpaired electron and is therefore unstable and highly reactive as those terms are recognized in the art.

[045] “Field” means the electric field, which can be positive or negative in nature. Similar fields repel each other and opposite fields attract each other.

[046] As a way of background, when multiple streamers are generated from streamer ignition points in close proximity, their own electrical fields would influence the characteristics of each other. Streamers originating from same polarity electrodes diverge away from each other in the absence of any restrictive fields around them. If constrained uniformly from all sides by the fields of neighboring streamers, radius thinning as well as field enhancement would occur, thereby enhancing the product of the electron energy and the probability density distribution, and hence the free radical generation efficiency. The proximity field influence and its resulting streamer tip field enhancement depends on several factors such as the gap and distribution of the ignition points, the distance from the counter electrode, the discharge gas as well as the applied voltage.

[047] FIG. 1 illustrates an optional embodiment of the discharge electrode according to the teachings provided in this disclosure. The discharge electrode **18** comprises of square tips **12** arranged along the circumference of a disc. Aligned with the teachings of the disclosure, the square tip is designed to generate four streamers when brought to the proximity of a counter electrode **16** and a suitable voltage is applied across them. For illustration purpose only, assembly **10** shows a single discharge electrode and four streamers **14** emerging from one of the tips towards the counter electrode **16**. However, in an actual device many discharge electrodes will be assembled together and each pin would generate identical streamers to achieve the field proximity constraints. The important objective here is to position the discharge pins such that the distance between the streamers is kept uniform and they are uniformly distributed on the circumference of the discharge electrode assembly. An exemplary assembly of the device is shown in FIG. 2, where the electrode assembly **22** is deposed inside a cylindrical counter electrode **26** and the spacing between the tips is equal both in radial as well as in axial direction. This ensures uniform interaction of the feed gas **24** with the streamers as the gas passes through the discharge gap. These electrodes can be conveniently precision cut by a laser beam or electron beam or stamped for mass manufacturing. When an appropriate voltage is applied, a multitude of self-constrained streamers would emerge from the discharge electrode assembly **22** and propagate towards the counter electrode **26** presenting a uniform ionization front which generates copious free radicals in the feed gas. For reference, dissociation and ionization of H_2O can be achieved with electron energies in the order of 5 eV, whereas ionization of oxygen requires electron energies in the order of 7 eV. In summary, the streamer head is an effective radical generator. A pulsed electrical voltage is applied to the device and the pulse width depends on several factors including the discharge gap. If the time required for the streamer to cross the discharge gap is Ts and Tp is the full width at half maximum (FWHM) of the current pulse, then their ratio R=Ts/Tp plays an important role on the discharge gap as well as the power supply design. When R=1, the voltage pulse ends at the moment the streamers reach the counter electrode and this presents the best situation.

[048] It will be appreciated that when the streamers traverse through the discharge space both electrons and ions will accumulate in the discharge space. The conductivity of the discharge space plays an important role on the application of successive voltage pulses for successive streamer generation. Therefore, the gas flow in the discharge space plays an important role. Higher the gas flow the more effective is the sweeping of the ions from the discharge space, which prevents arcing. However, higher gas flow reduces the concentration of the radicals, i.e., the number of radicals per unit volume of gas. On the other hand low gas flow results in higher radical concentration, but runs the risk of arcing due to insufficient removal of ions between successive pulses. One of the design goals for a practical device is that the generator should have the ability to run at different gas flow rates to enable generation of radicals at a desired concentration.

[049] The ability to modify the streamers tip by the repulsive fields of surrounding streamers without changing the applied voltage, enables one to modify the probability energy density distribution function of electrons with selective mean energy levels. Consequently, one can selectively generate abundant OH^* radicals by adjusting the mean of the probability energy density distribution to the vicinity of 5 eV, whereas the O^* radicals can be effectively generated by shifting the mean to the vicinity of 7 eV or higher. In a gas mixture, while OH^* radicals can be preferentially generated, it is not possible to avoid O^* radicals completely. However, in a dry gas one can selectively generate O^* radicals leading to ozone production. Generally, for selectively generating OH* radicals (requires low dissociation energy ~5 eV), larger discharge gaps may be preferred, whereas, radicals requiring higher electron energy a smaller discharge gap may be selected. Nevertheless, there are many other parameters such as discharge tip geometry and inter pin distance, which may be tailored to achieve similar outcomes for a given discharge gap and electrical parameter.

[050] As noted above the presence of humidity in the feed gas as well as the probability energy density distribution function play an important role on the selectivity of the radicals to be generated by the radical generator as well as the subsequent reactions involving those radicals. If the mean of the probability energy density distribution function is around 5 eV, there still will be a significant number of electrons with energies higher than 7 eV and they can potentially ionize oxygen. However, if there are abundant water molecules in the feed gas, these high energetic electrons will preferentially ionize H_2O resulting in OH^*. In reality, the dissociation process is complex when multiple species are present. For example, the $O^*$and OH^* radicals may react rapidly with other molecules to form secondary radicals such as HO_2^* or O_3^*. Incidentally, ethylene C_2H_4 also has a dissociation energy in the same range (~4.5 eV) of water. If present in the feed gas (for example in a produce storage environment), it will dissociate along with H_2O forming complex compounds. Now, Referring to Fig. 3, it can be seen, with dry air the ozone production **32** is significantly higher compared to the ozone production **34** in moist air. Further, it is also observed that the ozone production rate decreases with increasing reactor pressure. Higher reactor pressure increases streamer ignition voltage and hence decreases the ionization rate. Similarly, the molecular concentration ozone **42** and OH^* **44** molecules in humid air (99% relative humidity) is shown in Fig. 4. As seen, a considerable amount of OH* radicals is generated along with ozone molecules in humid air. Notably, if contaminations such as CO_2 SO_2 or NO are present in the feed gas, O^*, OH^*, HO_2^* and O_2^* may react with their radicals or directly with them leading to other byproducts.

[051] As the moisture content in the feed gas increases, more and more energy is utilized in generating OH^* radicals. At a given temperature and pressure, there is a limit on how much moisture can be fed to the discharge space without precipitating water droplet. For example, at one atmospheric pressure and 25^0C, only 20 g of water can be added to 1 kg of air (20 g/kg) without precipitating water droplets. As such, the relative humidity at standard temperature an pressure is optionally above 95% (18.97 g/kg), optionally at or above 96% (19.17 g/kg), optionally at or above 97% (19.37 g/kg), optionally at or above 98% (19.56 g/kg), optionally at or above 99% (19.76 g/kg), optionally at or above 99.5% (19.86 g/kg), optionally at or above 99.9% (19.94 g/kg), optionally at or above 99.99% (19.96 g/kg) where amounts are grams water per kilograms air. Optionally, the amount of water per kg air does not exceed 20 g/kg, optionally does not exceed 19.76 g/kg. The forgoing numbers are measured at standard temperature and pressure and will vary at different temperatures and pressures, but the degree of saturation will be constant relative to the above. Addition of moisture beyond the saturation point (dependent on temperature and pressure) or in other words feeding a mist to the discharge space can lead to innovative applications. Now attention is drawn to the streamer interaction with the droplets and the associated chemical reactions and species generation. Depending on the type of discharge (positive and negative), its energy, and the chemical composition of the surrounding environment (of both gas and liquid phases), various types of chemical reactions can be initiated and a number of primary and secondary species can be formed by the streamers in the gas and at the gas–liquid (water) interface, which can dissolve into the liquid droplet and thus provide the chemical and biocidal characteristics to the mist. Among various chemical species produced by the streamer at the oxygen gas–liquid (water) environment, OH* radical, atomic oxygen, ozone and hydrogen peroxide are the main reactive oxygen species (ROS) generally accepted to play the dominant role in the chemical and bio-inactivation process, and the discharge device can be utilized to provide advanced oxidation treatment as will be discussed below.

[052] However, feeding a two phase fluid or in other words air with suspended water droplets, introduces several practical difficulties to efficiently operate the discharge device. First, the suspended water droplets accumulate charge on their surface while traveling through the discharge gap and get attracted to the counter electrode. Accumulation of liquid at the electrodes leads to arcing and hinders reliable and continuous operation of the discharge device. As mentioned above, the primary and secondary radical species that dissolve into the water droplets cannot be utilized if they condense on the electrodes. It has been observed that gas velocity in excess of 5 m/s at the discharge tip can prevent droplet precipitation in 100% humidity air. Higher velocities are preferred for saturated air with suspended droplets, however, the overall concentration of the radicals also reduce with high airflow lending the device unsuitable for applications that require high radical concentrations. The gas velocity at the discharge tip for saturated air is optionally between 5 m/s and 100 m/s. Furthermore, as indicated above the ideal conditions (dissociation voltage and discharge gap etc.) for OH* radical generation are different from that of oxygen and hence ozone production. Therefore, coproduction of OH* radicals and ozone with the same discharge device is not optimal. Alternatively, the discharge device for ozone production should primarily run with dry air and the discharge device for OH* radical generation should deploy air with high moisture content but without suspended water droplets.

[053] Now, referring to Fig. 5, an exemplary discharge device for optionally operating at low moisture content feed gas is disclosed. It comprises of a regenerative desiccant wheel **55** to remove moisture from the feed gas, providing dry gas **54** to the device. The details of the discharge electrode **52** and counter electrode **53** are provided in Appendix A. The regenerative desiccant wheel **55**, is rotated continuously by a motor **59**. The inlet air **57** passes through a larger section **55'** of the desiccant wheel, where the moisture from the feed air is removed. Further, a heater **56'** is provided on the opposite side of the inlet of the desiccant wheel, through which a recovery air stream is provided to regenerate the wheel. The recovery air **58'** removes the moisture from the desiccant wheel and the regenerative section **56'** is substantially smaller than that of the inlet section **55'**. The area ratio between regenerative **56'** to the dehumidification section **55'** on the wheel optionally varies between 1/9 and ½, optionally a ratio is between 1/4 and 1/3. There are many ways to fabricate the desiccant wheel such as packed bed of moisture absorbing material such as silica gel or molecular sieves or coating the moisture absorbing material onto a woven scaffold which allows high air flow rates. The rotation speed of the wheel, air flow, thickness of the wheel and the heater temperature are suitably adjusted to achieve the desired level of moisture in the feed air. The dew point of the feed air may optionally vary between -60^{0}C to 25^{0}C, and optionally a range is between -4^{0}C to 4^{0}C.

[054] Fig. 6 illustrates an exemplary streamer discharge device optionally operating at high dissolved moisture content. As discussed above suspended water droplets in feed air may result in arcing and device malfunction. However, having high amount moisture in the feed air is a pre-requisite to generate high amount of OH* radicals. In other words, the feed air may have moisture content 0.01 g/kg or higher below the saturation point, which is a function of the temperature of the feed air as well as the pressure inside the discharge device. It is well known that as temperature increases the amount of water required to saturate a specific volume of air also increases. For example, at one atmospheric pressure, the specific humidity for saturation is 10 g(w)/Kg(air) at 15^{0}C, whereas it increases to 49.8 g(w)/Kg(air) at 40^{0}C. Now referring to Fig. 6, a steam nozzle **65** is provided at the inlet air channel of the discharge device and the steam nozzle **65** is operably connected with water inlet **67**. Heating coil **69** heats the nozzle assembly ensuring generation of superheated steam (T>100^{0}C) which is ejected to the inlet air channel of the discharge device and carried into the discharge gap by inlet air **66** which is preheated by heating coil **68**. Preheating the air prior to steam injection ensures dissolution of the steam into dissolved moisture and prevents any precipitation of water droplets. The amount of moisture intake will depend on the flow rate, air temperature and the steam temperature. The water feed rate may optionally vary between 1 g/hour and 1 kg/hour, optionally the feed rate may optionally vary between 100 g/hour to 500 g/hour. It is understood that the air flow inside the discharge devices operating at high moisture content be kept high. The air flow may optionally vary between 1 m^3/hour and 200 m^3/hour, optionally the air flow may vary between 20 m^3/hour and 100 m^3/hour. The steam temperature may optionally vary between 100^0C and 1000^0C, optionally the steam temperature may optionally vary between 200^0C and 500^0C. Physiochemical events involving reactions (1) through (5) may optionally occur inside the discharge device providing OH* radicals which can be used for many practical applications. The discharge gas carrying various radicals may optionally precipitate water droplets forming a wet fume as it emerges from the reactor exit **61**. This wet fume can easily attach to surfaces providing biocidal disinfection including breakdown of biofilms. Due to boundary layer phenomenon dry gases such as ozone cannot penetrate through biofilms which provide fertile ground for pathogen proliferation and contamination.

[055] As discussed above, advanced oxidation of organic and some inorganic pollutants can effectively be achieved through in-situ generation OH^* radicals. Different mechanisms for in-situ generation of OH^* radicals were described by Eq. (1) through Eq. (5) which either involve ozonation of water, or H_2O_2 dissociation or a combination thereof known as peroxone (O_3/H_2O_2) system. The critical requirement for advanced oxidation process however, is in situ generation of OH^* radical due to its short life span. According to the teachings of this disclosure, the ability to selectively generate large amount of OH^* radicals as well as ozone through the streamer discharge device lends to beneficial advanced oxidation applications, independent of a H_2O_2 supply chain. In other words, both ozone and OH^* radicals can be generated by supplying oxygen and moisture into the discharge device. Now referring to Fig. 7, an advanced oxidation set up comprising a convergent/divergent flow system **75** is illustrated. This includes a discharge device **76** operating in ozone generation mode and another discharge device **78** operating in OH* generation mode, and are operably joined adjacent to the divergent section **73** of the flow system **75**. When a fluid passes through the flow system **75**, it generates a suction drawing the ozone from device **76** as well as OH* from device **78** and mixes them with the fluid. The fluid optionally can be contaminated water or contaminated air or can be clean water/air which are directed towards disinfecting another object. The convergent/divergent flow system mixes the OH^* radicals/ozone intimately with the fluid leading to advanced oxidation of the pollutants if present in the fluid. The oxidation reaction may proceed beyond the mixing zone of the flow system and an optional contact chamber may be provided to store the mixed fluid to complete the reactions. It is to be noted that the ratio of gas volume supplied through the discharge devices to the flow volume of main fluid through the convergent/divergent flow system **75** impacts the mixing efficiency; lower is the ratio, more suction is created leading to better mixing. Especially, when the main fluid is water, with small air flow through the discharge devices leads to micro bubble formation which leads to better mixing. The air to water volume ratio is optionally between 0.05 and 0.5. Although, the flow system **75** is very simple from operation stand point, it limits the air intake into the discharge device for a given volume of main fluid flow. In other words, the recommended intake air flow may not provide the best operation condition for the discharge device.

[056] It has been discussed earlier that there are certain advantages in having higher gas flow through the discharge device, notably it prevents arcing and enables the use of high moisture content feed gas for effective generation of OH* radicals. Therefore, it is desirable to deploy a mixing system that can utilize high airflow through the discharge device while providing better mixing. Now referring to Fig. 8, a mixing system to handle high air flows is disclosed. The exemplary embodiment **80**, includes a turbine **85** immersed in a liquid **87** and is operably coupled with a motor **81** through a hollow shaft **86** and a coupling **83**. The coupling **83** provides fluid communication to the discharge devices **82** and **84**, thereby enabling suction of radical laden gas into the turbine. Further details of the turbine system is illustrated in Fig. 9. The turbine system **90** is comprised of a hollow shaft that is closed at one end **93** and opens to the suction chamber **95** of the turbine. The suction chamber **95** is provided with a top cover **97** and a bottom cover **96** and is operably in communication with the liquid through the side channels **98**. Further, suction ports **92** are provided through a shaft seal **91** which establishes fluid communication with the discharge devices. The internal blade arrangement for the turbine is illustrated in Fig. 10. Each blade **102** progressively bends towards the suction chamber and provides a progressively narrowing channel **104** between adjacent blades. The side view of the turbine is shown in Fig. 11. Further the perspective views of the turbine are shown in Fig. 12. When the turbine rotates, a suction force is generated which draws radical gas and breaks it into micro bubbles and disperses them into the liquid. The fine bubbles enhance the mixing process significantly. The suction pressure depends on the size and rotation speed of the turbine which is optionally set between 600-2000 rpm. The diameter of the turbine is optionally kept between 2 inches and 50 inches. The suction pressure increases with increasing diameter and rpm which can be beneficially adjusted to draw a desirable amount of radical containing fluid (gas) while forming micro bubble to enhance mass transfer of the radicals.

[057] Since high air flow or in other word high gas velocity at the discharge tip improve the functioning of the discharge device, it is desirable to maintain such flows. However, higher flow reduces the radical concentration in the gas and may not be suitable for applications requiring higher radical concentrations. Now referring to Fig. 13, an exemplary flow system for providing high gas flow as well as high radical concentration is provided. The discharge device **134** is operably coupled to a recirculation system comprising of a turbo fan **133** which draws air from a diffuser **136** and feeds into a condenser **135**. This recirculation system passes the radical gas over and over at high flow rates through the discharge device which enhances the radical concentration. The concentrated radical gas is drawn through an outlet **132** optionally through devices **75** or **90** disclosed herein and utilized for advanced oxidation process. To conserve the air mass inside the recirculation system, an equivalent amount of fresh air is provided through an inlet **131**. Thus the inlet and outlet gas volumes can be maintained at a desired level while maintaining very high flows inside the device. This is particularly beneficial to the venturi type mixing system where low gas flows and high radical concentrations provide the best mixing outcome. Flow simulations for an exemplary recirculation system is presented in Fig. 14. In this example, the discharge device diameter was kept at 80 mm with a discharge gap of 4.5mm. The inlet and outlet air volume was set at 2 m^3/hour. As can be seen the gas flow velocity inside the discharge device is in the order of 10 m/s, whereas the net input and out from the system is at 2 m^3/hour.

EXPERIMENTAL

1. Effect of Moisture

It is believed that ozone forms via $O(^3P) + O_2 + M \rightarrow O_3 + M$ ($M = N_2, O_2, O_3$) and that the streamer dissociated high energy atomic oxygen $O(^1D)$ loses its excessive energy due to relaxation collision with gas molecules via $O(^1D) + M \rightarrow O(^3P) + M$. If dry gas is fed to the discharge space, then OH^* generation as by Eq. (1) through Eq. (5) will be suppressed leading to primarily O_3 formation. To study the effect of moisture content, a device was assembled according to the teachings illustrated in Fig. 5. The device parameters were kept as follows: 3875 discharge tips with square size = 0.25x0.25 mm^2, inter pin distance = 2.5mm and discharge tip to counter electrode distance = 4.25mm, arranged on a discharge electrode assembly having diameter of 30 mm and 430 mm height. The discharge electrode was connected to negative polarity with the following voltage parameters: $V_{applied}$ = -9.5- 10.5kV, Pulse width =600ns-1µs, f = 15kHz. The discharge electrode was made from stainless steel and the ground electrode was made from graphite. A 12" diameter with 1 " width desiccator wheel comprising of woven plastic coated with silica gel was utilized to remove the moisture from the feed air. The regeneration to dehumidification area ratio was kept at 1/3. Fig. 15 presents an exemplary performance data of the desiccator wheel for 3 m^3/hr feed air with due point of 8^0C, which is dried to due point of -4^0C continuously. Discharge experiments were conducted with two different air streams, one with due point of -35^0C and the other with 15^0C, respectively. An ozone monitor (Teledyne API 454 Process Ozone Analyzer) was employed to measure the ozone concentration at the exit and the specific energy consumption was calculated. As shown in Fig. 3, a significant drop in ozone production occurred with moist air.

2: OH* Radical Generation

This example demonstrates OH* radical production from the discharge device. A device was assembled according to the descriptions provided in FIG. 6. The device parameters were kept as follows: 4800 discharge tips, square size = 0.25x0.25 mm^2, with inter pin distance = 2mm and discharge tip to counter electrode distance = 5mm. The discharge electrodes were connected to negative polarity power supply with the following voltage parameters: $V_{applied}$ = -9.5-10.5 kV, Pulse width =600ns-1μs, f = 15kHz, with an average power of 280 Wh. The discharge electrode was made from stainless steel and the ground electrode was made from graphite. Air with 99% relative humidity at a rate of 30 m^3/h was supplied to the discharge device. The device was placed in a 6.4 m^3 semi-airtight chamber and the ozone concentration was measured by an ozone monitor. From the volume of the chamber and ozone concentration, the number of moles of O^3 in the room was calculated. For the OH* concentration measurement, 4 samples of 2 mM disodium terephthalate were left in the test chamber. One sample was removed at each time interval and its fluorescence intensity was measured (fluorescence is seen if disodium terephthalate converts to 2-hydroxyterephthalic acid in the presence of OH*). Using standards for 2-hydroxyterephthalic acid, the concentration of OH* formed is calculated in mM. From this, the number of molecules of OH* is calculated. Fig. 4 presents the concentration of ozone and OH* molecules in the chamber with respect to time. As noticed these concentrations reach a plateau after the initial period indicating conversion of the radicals into some other forms. It is well known that OH* radicals are short lived and would combine with other species. At the end of the test, a de-humidifier was used to condense the moisture in the room. The condensate from the de-humidifier was used for peroxide measurement. The text kit showed 90 ppm of peroxide concentration in the 1800 ml of condensate collected. The observed H_2O_2 in the condensed moisture is a clear indicator of abundant OH^* radical formation in the generator. It is possible that H_2O_2 may form inside the discharge space, however, the dissociation energy for H_2O_2 is in the order of 2.21 eV and will preferably again dissociate to OH^* as almost all the gas gaseous stream is directed to interact with the streamers until they exit the discharge space according to the teachings of this invention.

To demonstrate the advanced oxidation capability of the radicals, three types of bacteria spore strips containing 1 million spores per strip were placed at different locations in the test chamber. The included bacteria spores were; *Bacillus atrophaeus, Bacillus pumilus and Geobacillus stearothermophilus.* The treatment time was set at 6 hours. It is to be noted that this time is not optimized. The observations and inferences are tabulated in Table 1 below. As can be seen, all the three bacteria spores were completely annihilated demonstrating the sterilization capability of the process that only utilizes water and electricity.

Table 1:

S No	Treatment Time (Hrs)	Mist Rate (g/hr)	Reactor Power (W)	Organism	Organism Carrier	Kill success
1	6	500	300	*Bacillus pumilus*	Spore strip – Soft surface	Yes
2	6	500	300	*Geobacillus stearothermophilus*	Spore strip – Soft surface	Yes
3	6	500	300	*Bacillus subtilis*	Spore strip – Soft surface	Yes

3: Mixing Methods

This example demonstrates the efficacy of venturi type as well as turbine type mixing systems. To demonstrate the mixing efficacy of the systems, the discharge device described in example 1 was utilized, which primarily generated ozone. For venturi type mixing system, two nozzles were used, one for flows up to 5 m^3/hr and the other for flows up to 10 m^3/hr. A Pentair Inteliflo variable speed pump (3 hp) was utilized to pump the water through the nozzle. Pump was set to deliver required flows through the nozzle and after ozone injection a residence time was provided in a 120 gallon contact tank with a degasser and destruct unit for undissolved ozone. After the residence tank, water flowed through pH (Coleparmer pH sensor and monitor), ORP (Coleparmer ORP sensor and monitor) and dissolved ozone sensors (Calibrated Emmerson dissolved ozone sensor and analyzer) to monitor the water quality. For the turbine mixer, a Baldor SuperE motor (5 hp) and an 8" turbine was deployed in a 300 gallon retention tank. Water from a reservoir was passed through the retention tank while the turbine mixed ozonated air drawn from the discharge device continuously. Then the water flowed through the same sensors described above.

The results from the mixing experiments are presented in Table 2. As noted, the mass transfer efficiency in the venturi type mixing system increased considerably (67%) with decreasing air/water flow (0.85/9.99) while the mixing performance was a dismal 26% at higher air/water flow (1.42/3.3). On the other hand, at very high air/water flow (3.4/3.3), the turbine system demonstrated high mass transfer efficiency ~83%. As mentioned earlier, the discharge devices of this disclosure operate efficiently at high air flows and the turbine mixing system is appropriate for water treatment. Alternatively, the device illustrated in Fig. 13 can be utilized with the venturi type mixing system. Further, most industrial dielectric barrier type ozone generators utilize purified oxygen as the feed and hence have low flow. However, the generator of this disclosure utilizes air and for a given quantity of ozone, the flow volume will be substantially higher. Attention is drawn to the O_3 dosage in water (g/m^3). While low air flow in venturi system gives better mass transfer efficiency the overall dosage is low. For reference, there are recommended dosages for specific type of water treatment such as drinking water or recreational water etc. On the other hand, the turbine system can provide higher mass transfer efficiency at higher dosage.

Table 2:

Mixing method	Water Flow (m3/hr)	Air Flow(m3/hr)	Air O3 Conc (g/m3)	O3 Productivity (g/hr)	O3 Dosage in water (g/m3)	Mas Transfer Efficiency(%)
Venturi Injector	3.3	1.42	4.5	6.39	1.936364	26
	9.57	1.89	5.4	10.206	1.066458	45
	10.15	1.98	2.5	4.95	0.487685	51
	9.99	0.85	7.7	6.545	0.655155	67
Turbine Aerator	3.3	3.4	2.4	8.16	2.472727	83.3
	3.3	1.7	4.5	7.65	2.318182	78.4
	5.4	3.4	2.4	8.16	1.511111	80.13
	5.4	1.7	4.5	7.65	1.416667	78.72

[058] While aspects of the invention have been illustrated and described, it is not intended that these aspects illustrate and describe all possible forms of the invention. Rather, the words used in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention.

[059] Various modifications of the present invention, in addition to those shown and described herein, will be apparent to those skilled in the art of the above description. Such modifications are also intended to fall within the scope of the appended claims.

[060] It is appreciated that all reagents are obtainable by sources known in the art unless otherwise specified.

[061] The present invention is further detailed with respect to the following appendix: Appendix A – totaling 110 pages. Appendix A and all publications listed therein are hereby incorporated by reference to the same extent as if each appendix was specifically and individually incorporated into and present within the body of this patent specification.

REFERENCE LIST

US PATENT DOCUMENTS

62383046 9/2016 Mohanty, P.

[062] Patents, publications, and applications mentioned in the specification are indicative of the levels of those skilled in the art to which the invention pertains. These patents, publications, and applications are incorporated herein by reference to the same extent as if each individual patent, publication, or application was specifically and individually incorporated herein by reference.

[063] The foregoing description is illustrative of particular embodiments of the invention, but is not meant to be a limitation upon the practice thereof.

EXEMPLARY CLAIMS

1. A method in accordance with one or more aspects of this disclosure in any combination.

2. A discharge device substantially as provided in accordance with one or more aspects of this disclosure in any combination.

3. A method for cleansing chemical and biological contaminants from a gaseous environment in accordance with one or more aspects of this disclosure in any combination.

4. A method for disinfecting superbugs and their spores in accordance with one or more aspects of this disclosure in any combination.

5. A method for disinfecting water in accordance with one or more aspects of this disclosure in any combination.

ABSTRACT

An advanced oxidation method for organic and inorganic pollutants deploying OH* radicals and ozone generated by streamer discharge device is disclosed. Optionally, a first discharge device, providing OH* radicals and second discharge device providing ozone, are combined to provide the chemical and biocidal characteristics. Further, efficient mixing systems for transferring the radicals to the target fluid is disclosed.